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Canada

GEOCHEMISTRY OF APHEBIAN CARBONATES:
ALBANEL FORMATIONS, NORTH CENTRAL QUÉBEC.

A Dissertation Presented to
the School of Graduate Studies
University of Ottawa

In Partial Fulfillment of
the Requirements for the
Master's Degree in Geology

by

Michel D. Mirota

1989

Dr. Jan Veizer

Supervisor



Michel D. Mirota, Ottawa, Canada, 1989.

ABSTRACT

The Aphebian Mistassini Basin is composed of a 2.5 kilometer generally undeformed and unmetamorphosed sedimentary sequence characterized by shallow southeast dipping carbonates, located approximately 80 kilometers northeast of Chibougamau, Québec.

The pink and beige dolostones of the Upper Albanel Formation are divided into an upper stromatolitic, finely to coarsely crystalline dolostone and a lower sandy, commonly cross-bedded, mature quartz dolostone unit. The former is characterized by numerous shallowing upward stromatolitic cycles. In contrast, the grey to black dolostones, limestones and shales of the Lower Albanel Formation are distinguished by varying proportions of fine-grained, immature clastics and are commonly cross-laminated. Depositional environments range from peritidal-shallow subtidal to deep water euxinic conditions. Normal marine to locally elevated salinities are suggested.

Evidence of early cementation and meteoric phreatic diagenesis is presented for the Upper Albanel dolostones, whereas the more continually submerged portion of the Lower Albanel carbonates exhibits evidence of burial diagenetic fabrics. Petrographic evidence for aragonite and high magnesium calcite in the Upper Albanel dolostones contrasts with its absence in the Lower Albanel carbonates. Textural evidence suggests that dolomitizat-

ion in both formations was early, although burial and fault-related varieties are also present.

High and low strontium dolostones, and limestones can be identified on chemical and isotopic grounds. Extrapolation to least altered strontium concentrations suggests the presence of precursor aragonite for the high strontium dolostones. A portion of the low strontium dolostone group may, in contrast to the theoretical considerations, actually be less altered than the strontium-rich group; a proposition supported by oxygen and strontium isotopes. The discrepancy can be a consequence of the difference in the precursor mineralogy of the carbonate (aragonite for strontium-rich group, high magnesium calcite for strontium-poor one). The stratigraphically superior low Sr dolostones (enriched in ^{18}O) appear to have been affected by diagenesis in a near surface, meteoric environment characterized by high water/rock ratios. In contrast, the underlying high Sr dolostones (^{18}O depleted) may have been subjected to post depositional alteration under higher temperatures and salinity during burial (lower water/rock ratios).

The $\delta^{18}\text{O}_{\text{dolomite}}$ for the studied samples (range -1.90 to -10.31 ‰, PDB) reflects mostly different post depositional alteration histories. A mean $\delta^{18}\text{O}$ of -6.75‰ suggests that the Mistassini dolostones represent one of the least altered Aphebian sequences recorded. In contrast, the uniform $\delta^{13}\text{C}_{\text{dolomite}}$ dist-

tribution in the upper 4/5 of the Mistassini sequence gives way to second order oscillations toward the basin floor. The latter appear to reflect secular and facies controls, with only minimal overprint from alteration. A $\delta^{13}\text{C}_{\text{dolomite}}$ mean of +0.74‰ (range +4.70 to -6.08‰) is comparable to that of other Aphebian platform carbonates. Where sampled, limestones show a similar pattern, except for an offset to more ^{18}O and ^{13}C depleted values.

Syngenetic/early diagenetic, early to later diagenetic, late diagenetic and fault-related pyrites were analyzed for sulfur isotopes. An averaged scatter of -3 to +54 ‰ (mean $\approx$ 24 ‰ CDM) suggests that heavier seawater sulfate as well as sulfate reduction in a restricted basin may have been responsible for the isotopically heavy sulfides. Similarities in the ^{13}C and ^{34}S stratigraphic distributions are consistent with the existence of local, somewhat restricted basinal conditions.

A preliminary analysis of carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ indicates an increase in manganese and radiogenic strontium, toward the basin floor, with increasing degree of alteration. A preferred $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.706, a possible upper limit for isotopic composition for Mistassini seawater, is in agreement with reported values for other coeval carbonate sequences.

Résumé

Le Bassin de Mistassini (Aphébien) est composé d'une séquence (2.5 km) de carbonates peu métamorphisés et déformés. Celui-ci se situe à environ 80 kms au nord-est de Chibougamau, Québec.

Les dolomies de la Formation d'Albanel supérieure sont divisées en un membre stromatolitique supérieur et un membre de grès dolomitique inférieur. Par contre, les dolomies, calcaires et "shales" de la Formation d'Albanel inférieure sont caractérisés par des particules siliciclastiques détritiques à grains fins et angulaires et par des stratifications entrecroissées. L'environnement de déposition varie de péritidal à profond (marin) et anoxique. La salinité varie de normale à localement plus élevée.

La cimentation a été rapide et montre des évidences de diagénèse météorique dans les dolomies de la formation supérieure, tandis que des textures de diagénèse d'enfouissement sont présentes dans la formation inférieure. La pétrographie suggère que l'aragonite et la calcite magnésienne étaient présentes dans la formation supérieure, contrairement à la formation inférieure. L'épisode de dolomitisation est précoce quoiqu'un épisode plus tardive associée avec les failles est aussi présente.

Les dolomies de basses et hautes teneurs en strontium et les calcaires peuvent être identifiés isotopiquement et chimiquement. L'extrapolation a des valeurs moins altérées ce qui suggère la présence d'aragonite. Les dolomies de basse teneur en strontium, contrairement à la théorie, sont actuellement moins altérées selon les résultats des analyses isotopiques. Ce phénomène contradictoire peut s'expliquer en invoquant une minéralogie différente du carbonate précurseur. Les dolomies de basse teneur en strontium (stratigraphiquement supérieure) semblent avoir été affectées par une diagénèse caractérisée par des rapports élevés de eau/roche. Par contre, l'autre groupe de dolomies a été sujet à une altération post-dépositionnelle sous l'influence de température et salinité plus élevées (rapports eau/roche moins élevés).

La composition isotopique en oxygène des dolomies (-1.90 à -10.31% PDB) montre l'effet des différentes altérations post-dépositionnelles. Une moyenne en $\delta^{18}\text{O}$ de -6.75% indique que ces dolomies aphébiennes sont moins altérées. La distribution en $\delta^{13}\text{C}$ est uniforme dans les 4/5 de la section supérieure. Par contre, la partie inférieure montre des oscillations vers la base causées par des variations séculaires, des contrôles de facies et très peu d'altération. Une valeur en $\delta^{13}\text{C}$ moyenne de $+0.74\%$ ($+4.70$ à -6.08 PDB) est comparable à d'autres séquences aphébiennes. Lorsqu'échantillonnées, les calcaires montrent une distribution semblable sauf pour un déplacement en ^{18}O et ^{13}C ou les valeurs

sont plus basses.

Différentes générations de pyrite ont été analysées pour leurs isotopes de soufre. Une valeur moyenne de +24‰ (-3 à 54 CDM) suggère que la composition en sulfate du Bassin de Mistassini était plus élevée et que la réduction bactériologique des sulfates a eu lieu dans un bassin partiellement fermé. Une similarité avec les distributions en ^{13}C et ^{34}S supporte cette conclusion.

L'analyse en strontium isotopique des carbonates montre une augmentation en $^{87}\text{Sr}/^{86}\text{Sr}$ et en manganèse vers le fond du bassin, avec l'altération. Une valeur maximale préférée de 0.706 pour l'eau de mer aphébienne est en accord avec d'autres séquences du même âge.

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CHAPTER 1

GENERAL GEOLOGY OF THE MISTASSINI LAKE REGION1.0 OBJECTIVES OF THE STUDY

The primary objective of this research project was to study the trace element and isotopic stratigraphy of an Aphebian carbonate sequence, in order to determine whether second order secular variations are present and their origin. Such variations are known in Phanerozoic carbonates and appear to be related to tectonics. Additional objectives include information on the depositional environment and diagenetic history of the carbonates.

1.1 FIELD METHODS

Due to the nature of the investigation, a detailed sedimentological study was not attempted, nor were any sections measured. Only a limited area of the region was examined. Core samples from the lower portion of the Lower Albanel Formation were complemented with field samples collected from the remaining overlying portion of the latter and the Upper Albanel Formation. A sampled continuum of the carbonate sequence was desired for the study. Field sampling was hindered by the low regional dip of the rocks,

as well as the fact that much of the Upper Albanel Formation conforms to the boundary of Lake Albanel. Interpretations of the depositional environments are based upon this author's field and petrographic observations and complemented in whole or in part by those of previous authors.

1.2 Introduction: General Geology

The Mistassini Basin is located approximately 80 kilometers northeast of Chibougamau, Québec (Figure 1). It extends over 160 kilometers and has an approximate width of 50 kilometers. The basin occupies Albanel and Mistassini Lakes. The homocline dips gently to the southeast and reaches a thickness of about 2.5 kilometers. It overlies unconformably Archean metavolcanics and gneisses of the Superior Province. The strike of the shallow dipping sedimentary rocks of the Mistassini Basin swings eastwards (in the southern part of the basin) and the rocks are then truncated by the Mistassini Fault. This fault separates Aphebian sediments of the Superior Foreland from the Grenville Province.

1.3 Previous Work

The first report on the region was made by J. Richardson of the Geological Survey of Canada in 1872. McQuat (1872) first

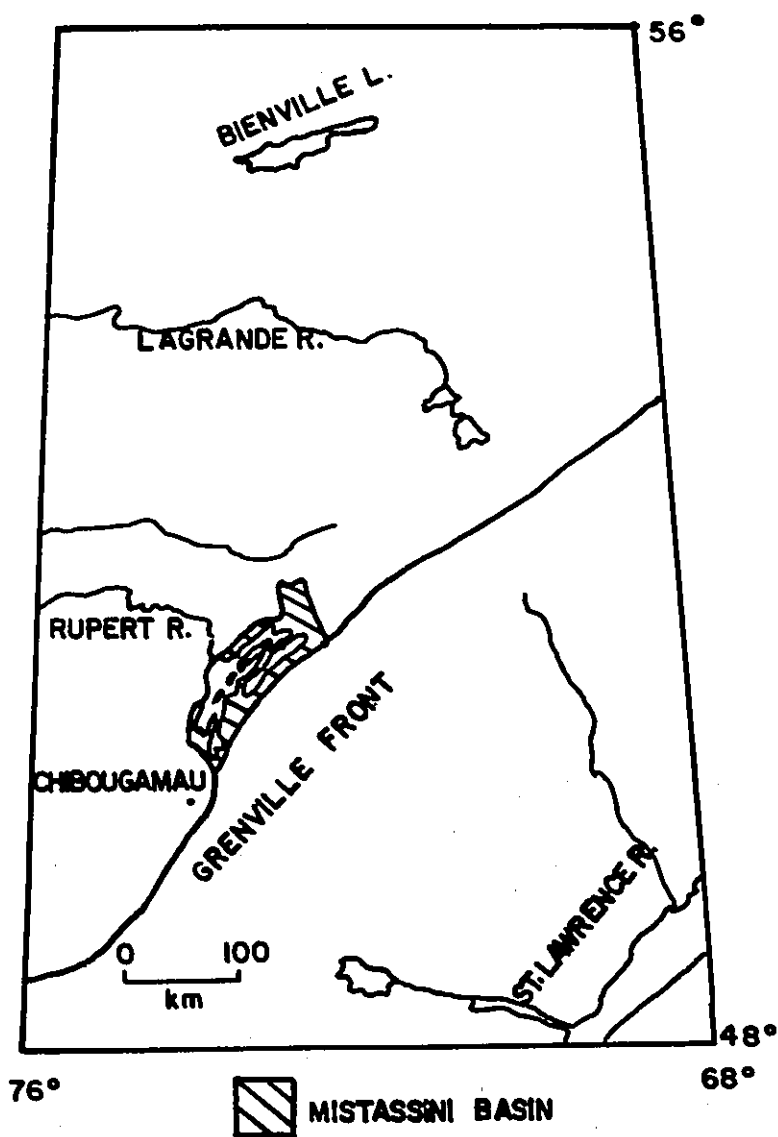


FIGURE 1: LOCATION MAP OF THE MISTASSINI BASIN, N. QUEBEC

described a contact between the carbonates and underlying basement. Low (1886, 1906) classified the carbonates as Cambrian, then as Upper Huronian. In 1910, Barlow et. al, assigned the rocks to the Ordovician. Norman (1940) recognized the Mistassini Fault, which thrust the Grenville rocks upon the carbonates. Neilson (1953, 1966) and Wahl (1953) of the Qu-bec Department of Mines made the first attempts to describe the stratigraphy of the basin. The discovery of mineralization in the late 1940's resulted in several research projects and publications. Quirke et al., (1960) and Quirke (1961) investigated the Temiscamie Iron Formation. In 1967, Deland and Sater made a detailed study of the southern extremity of the basin. Fryer (1972), on the basis of Rb-Sr age-dating, assigned an Aphebian age for the Temiscamie Formation. Discovery of the Icon Sullivan copper deposit resulted in Troop and Darcy's (1973) study of the ore body. Other reports on base metal occurrences include Kouassi's (1979) investigation on the geochemistry of shales. Caty and Chown (1973) established a stratigraphic correlation between the Mistassini and Otish Groups. Hofmann published two papers on stromatolite occurrences in 1978. Thorpe, et.al. (1981) and Roscoe (1984) investigated lead isotopes ages of sulfide occurrences in the Mistassini Basin (and local areas). A study of the Mistassini regolith was made by Caty and Chown (1983). Most recently, Chown (1984) reported on the controls of mineralization in the Chibougamau, Mistassini and Otish areas.

Although several publications on the economic and geological aspects are documented, a detailed geochemical, isotopic and diagenetic study of the carbonates has never been attempted. Furthermore, geologic mapping and interpretation of depositional environments are general and more specific information is desired.

1.4 Regional Geology

1.4.1 Archean Rocks

The east-west trending rocks of the Superior Province consist of migmatite, granitoid gneiss, metavolcanic and metasediment. The southern part of the basin is underlain by granitic gneiss, migmatite and granite (Deland and Sater, 1967). Along the western margin of the basin, migmatite, tonalite and quartz-feldspar gneisses are intruded by granodioritic plutons (Chown and Caty, 1983). The northern part of the basin is underlain by gneiss, amphibolite and metavolcanics of the Sam Gunner Group (Quirke, 1961). The latter is intruded by the Takwa Granitic Complex.

1.4.2 Aphebian Rocks

Felsite Porphyry Dikes: Felsite porphyry dikes, the oldest in the area, intrude late Archean granodiorites and are themselves cut by the Helikian Otish Dikes (Chown, 1984).

Mistassini Dike Swarm: These dikes consist of quartz tholeiite to peridotite compositions and extend northwest from (but do not intersect) Lake Mistassini to James Bay (Chown, 1984). Dates ranging from 1926 to 1960 million years were reported by Wanless (1972).

Mistassini Group: The Mistassini Group is divided into the Papasquasati, Cheno, Lower and Upper Albanel and Temiscamie Formations. The Cheno and Papasquasati Formations are believed to be time equivalent to the Lower Albanel Formation and outcrop only in the northeastern extremity of the basin (Caty and Chown, 1973). The relative stratigraphic positions are illustrated in Table 1. A short description of each unit will be made below:

a) Papasquasati Formation: It consist of a massive to cross-bedded quartzose to subarkosic sandstone and conglomerate. Chown and Caty (1973) interpreted the depositional environment as an alluvial fan-braided river system.

b) Cheno Formation: The dark colored sandstones and conglomerates of the Cheno Formation host dolomitic and stromatolitic dolostone interbeds. The formation is believed to represent a transitional facies between the continental Papasquasati and marine Lower Albanel Formations (Chown and Caty, 1973).

TABLE 1

STRATIGRAPHY OF THE MISTASSINI LAKE AREA

(MODIFIED FROM KOUASSI, 1979)

GROUP or COMPLEX	ROCK TYPE	AGE
	-ABITIBI DIABASE DIKE SWARM	1035 M.Y. *
GRENVILLE ROCKS	-GRANITIC INTRUSIONS	HELIKIAN
	-GABBRO + ANORTHOSITE	"
	-AMPHIBOLITE	"
	-QUARTZ-FELDSPAR GNEISS	"
	-OTISH DIKES	1465 M.Y. *
COOM LAKE INTRUSIVES	-MAFIC INTRUSIVES	?
MISTASSINI GROUP	-KALLIO FM.: SLATE + GREYWACKE	
	-TEMISCAMIE FM.: DOLOSTONE	1450 M.Y.**
	-U. ALBANEL FM.: DOLOSTONE	
	-L. ALBANEL FM.: CARBONATES + SHAL.	2100 M.Y.***
	-CHENO FM.: SANDSTONE + DOLOSTONE	
	-PAPASQUASATI FM.: SANDSTONE+CONGL.] 1	
	-MISTASSINI DIKE SWARM	1926-1960 M.Y.*
	-FELSITE PORPHYRY DIKES	?
TAKWA INTRUSIVE COMPLEX	-GRANITIC ROCKS	ARCHEAN
TICHEGAMI & SAM GUNNER GROUPS	-METAVOLCANICS & METASEDIMENTS	"
BASEMENT COMPLEX	- GNEISSES	"

1 = TIME EQUIVALENT

* = WANLESS, (1972)

** = FRYER, (1972)

*** = ROSCOE, (1985)

c) Lower Albanel Formation: Although it has been subdivided into different members by various authors, Lehmann's (1974) and Deland and Sater's (1967) subdivisions will be adopted. Table 2 illustrates a generalized stratigraphic section (based on drill data) representing most of the Lower Albanel Formation.

A basal stromatolitic dolostone and breccia unconformably overlies the Archean basement. This lithology is overlain by an interbedded shale-carbonate complex, which is defined by the presence of the lowermost and uppermost thick shale beds. This in turn is overlain by a thick banded (commonly cross-laminated) dolostone. A thinner interbedded shale and dolostone caps the banded dolostone (in drillhole LM-74-D2). The youngest unit represented by core (Lehmann, 1974) consists of an interbedded stromatolitic dolostone, breccia and dololomite. This unit however, is not represented in the sampled core and the presence of stromatolites was not recorded by previous authors. To simplify this situation, Deland and Sater's (1967) uppermost "Stratified Dolomite and Shale Unit" will be used. Stratigraphically, this member overlies and represents a vertical continuum with the eroded portion of the sampled drillhole LM-74-D2.

The contact between the Lower and Upper Albanel Formations is gradational (Wahl, 1953). It was originally distinguished by a change from greyish to more beige and pinkish colors and a more massive texture.

TABLE 2

GENERALIZED STRATIGRAPHY OF THE LOWER ALBANEL FORMATION

(Modified from Lehmann, 1974)

THICKNESS (METERS)	LITHOLOGY and STRUCTURES	DEPOSITIONAL ENVIRONMENT
<u>STRATIFIED DOLOMITE & SHALE UNIT</u>		
167.6-182.9	-Interbedded stromatolitic dolostone, algal dolostone breccia, grey dolomicrite & local shale beds -LLH stromatolites -flat pebble conglomerate -disrupted bedding -dessication features -quartz, carbonate & anthraxolite in vugs	supratidal to shallow subtidal marine
<u>UPPER BLACK SHALE COMPLEX</u>		
91.4 ?	-Interbedded graphitic (+pyrite) shale, argillaceous dolostone & grey dolostone. -planar lamination & bedding -algal laminations & clasts -dessication features -flat pebble conglomerate -cross-laminations -erosional features	Intertidal - subtidal zone (tidal flat)
<u>BANDED DOLOSTONE UNITS</u>		
>457.2	-Light & dark grey banded dolostone inter-bedded with argillaceous dolostone. Increasing % dolomitic limestone near base -parallel laminations & bedding -cross-laminations -cut & fill, convolute bedding	Shallow to deeper subtidal marine
<u>LOWER BLACK SHALE COMPLEX</u>		
45.7-147.8	-Black graphitic shale inter-bedded with argillaceous dolostone & dolomitic limestone to limestone. Local algal mats (?). - 2 to 5 shale beds -parallel bedding & laminations -local disrupted & brecciated bedding; crenulated laminations -pyrite lenses & disseminations	Deep subtidal marine (below wave base?)
<u>BASAL STROMATOLITIC DOLOSTONE</u>		
4.6-21.3	-Algal dolostone breccia inter-bedded with sandy dolostone. -lithoclasts & irregular laminations; mottled texture -quartz-carbonate & hydrocarbon vug fillings -erosional surfaces, slumping	Supratidal to shallow subtidal
0-27.7	-LLH & SH-V algal stromatolites -mottling & brecciation at base -quartz-carbonate vugs & veins	Unprotected intertidal zone
<u>REGOLITH</u>		
0-.6	-Regolith overlying basement intrusives, gneisses & meta-volcanics.	

REGRESSION

TRANSGRESSION

d) Upper Albanel Formation: Wahl (1953) assigned to this formation a lower, grey to pink cross-bedded sandy dolostone and an upper greyish laminated to banded stromatolitic dolostone member. The contact is somewhat arbitrary since lateral facies changes occur in the small (12 X 6 kilometer) area investigated by the present author. Although the contact between these two members is believed to be gradational, Wahl (1953) noted the presence of local scour channels and intraformational conglomerate at the contact.

The contact with the overlying Temiscamie Formation is very irregular and disconformable (Wahl, 1953).

e) Temiscamie Formation: Quirke (1961) subdivided the iron formation into six main members. The basal Boulder Bay Quartzite is overlain by the Lower Argillitic Member. The Lower Sideritic (chert and iron carbonate) Member contain minnesotaite. The economically interesting Magnetitic Chert Member is overlain by the (iron carbonate and stilpnomelane-rich) Upper Argillite Member. The latter contains lenses of magnetite-iron carbonate and silicate including stilpnomelane and minnesotaite. A second Sideritic Member lacking minnesotaite overlies the Upper Argillitic Member.

Although slate, argillite and greywacke were included in the Temiscamie Formation, Neilson (1966) indicated that they appear

to be disconformable to the Temiscamie Formation and may represent a younger, distinct unit (Kallio Formation).

Coom Lake Intrusive Complex: These igneous rocks intrude the Kallio Formation and consist of diorite, norite and aplite (Neilson, 1966). Their exact age is unknown.

1.4.3 Helikian Rocks

Otish Dikes: These north and northeast-trending olivine tholeiitic dikes intrude both the Mistassini and Otish Groups (Chown, 1984). The dikes were dated at 1465 million years by Wanless (1972).

Grenville Metamorphic Rocks: East of the Mistassini Basin, gneisses, amphibolites and granitic rocks of the Grenville Province are present. The Mistassini Fault separates the sedimentary rocks from the upthrusted Grenville metamorphic rocks. The fault is part of the Grenville Fault, which represents the western margin of the (10 to 50 kilometers wide) Grenville Front Tectonic Zone. The latter is characterized by zones of cataclasis and mylonitization. Kyanite, the dominant aluminosilicate, distinguishes this zone from the more common sillimanite-bearing rocks in other parts of the Grenville Province (Wynne-Edwards, 1972). The gneisses were commonly subjected to granulite facies metamorphism.

Abitibi Diabase Dike Swarm: These are the youngest dikes found in the Chibougamau area (Chown, 1984). Wanless (1972) reported a 1035 million year old date for diabase dikes.

1.5 Age of the Mistassini Basin

Fryer (1972) reported a Rb-Sr age of 1.749 - 0.054 Ga (recalculated using $^{87}\text{Rb} = 1.42 \times 10^{-11} / \text{y}$) for the Temiscamie Iron Formation. Galena occurrences from the Lower Alanel Formation were studied by Roscoe (1984). He concluded that if the lead source ages are assumed to be 2.71-2.63 Ga, then the age of mineralization is 2.07-2.13 Ga. Since a diagenetic origin was assumed for the mineralization, the age of the basin is anchored between 1.75 and (at least) 2.13 Ga.

An additional constraint on the age of the basin is suggested by the apparent cross-cutting nature of the Mistassini Dike Swarm (Figure 2), dated at 1926 to 1960 million years (Wanless, 1972). However, Chown (1984) specified that the dikes did not reach the basin and no contacts have been reported. Hence their exact chronological relationship to the basin is unknown.

This author collected a few shale samples from the Lower Black Shale Complex near the base of the Lower Alanel Formation. Although a preliminary 3-point errochron resulted in a 1.3 Ga

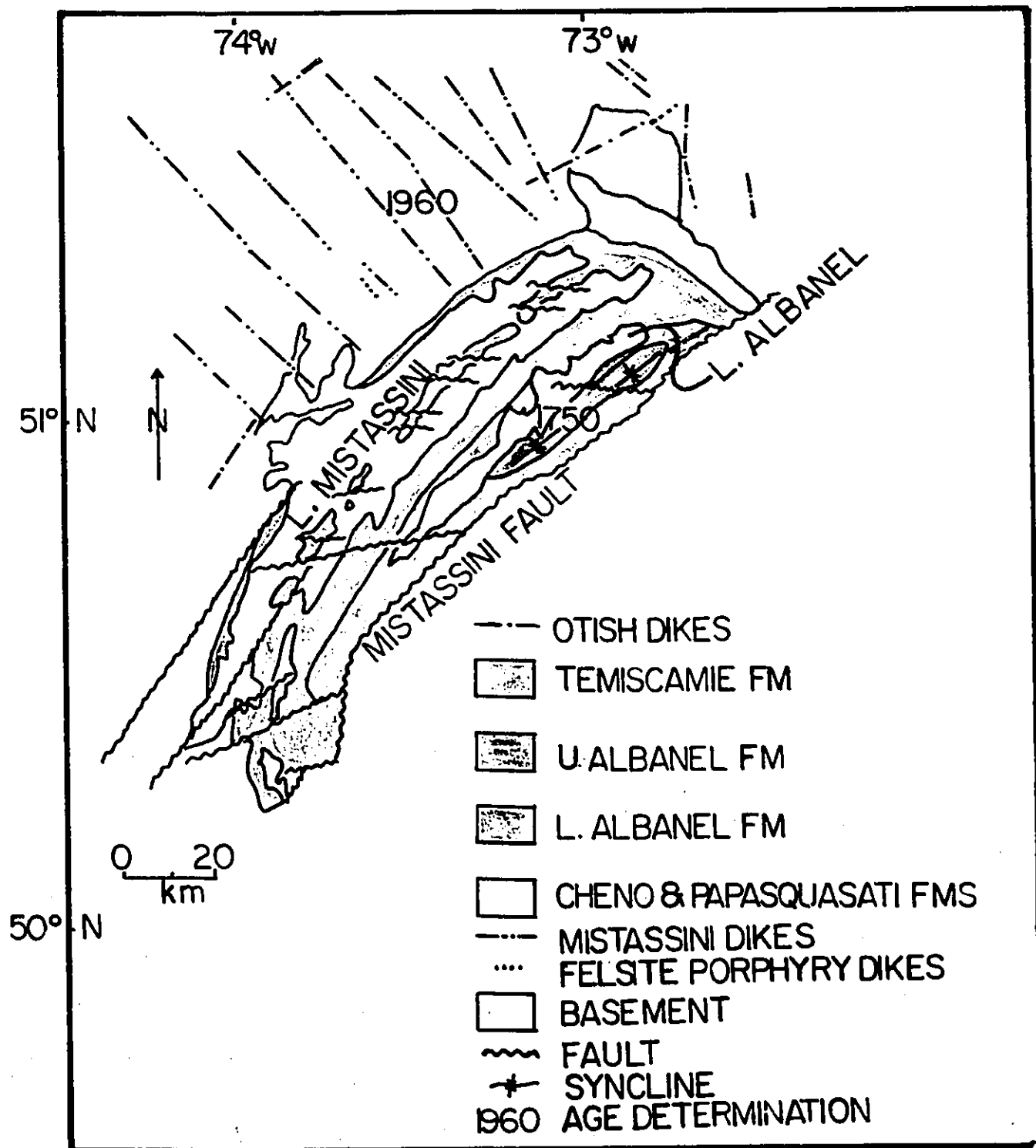


FIGURE 2: STRUCTURAL GEOLOGY OF THE MISTASSINI BASIN (MODIFIED FROM CHOWN, 1984)

age, a 2-point line gave a maximum age of approximately 1.9 Ga. However, more points are necessary to establish a meaning of these scatterchrons.

1.6 Metamorphism of the Mistassini Basin

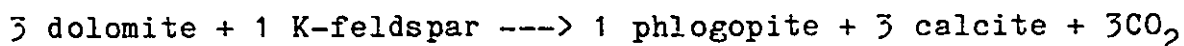
Rocks of the Mistassini Group suffer little from regional metamorphic effects. The following lines of evidence support this statement:

a) Stilpnomelane and minnesotaite occur in the iron formation and form in the subgreenschist facies. The absence of grunerite in parts of the Sokoman Iron Formation suggests that conditions associated with the biotite isograd of the greenschist facies (in pelitic rocks) were never attained (Dimroth and Dressler, 1978).

b) The stable coexistence of dolomite and quartz was noted in both the Lower and Upper Albanel Formations. The metamorphism of siliceous carbonates results in the formation of metamorphic minerals such as talc, tremolite, diopside and forsterite. The excellent textural preservation and the absence of metamorphic minerals points to subgreenschist metamorphic conditions.

However, a single occurrence of a micaceous mineral qualitatively

ively identified by microprobe as phlogopite, suggests higher local metamorphic conditions. The fine (<80 micrometers), euhedral crystals are often oblique to bedding. A detrital source is unlikely. Experimental work by Puhon and Johannes (1974) for the reaction:



suggests temperatures of 400 - 500° C. At higher H₂O-mole fractions, temperatures possibly less than 400° C are required. Fairchild (1979) came to a similar conclusion in reporting the presence of sporadic phlogopite in Precambrian dolostones of the Scottish Dalradian Bonahaven Formation. Thus the evidence suggests that metamorphic conditions up to the subgreenschist-greenschist boundary were attained in the Albanel carbonates.

c) The progressive metamorphism of pelitic rocks results in the sequential appearance of chlorite --> biotite --> garnet --> staurolite --> kyanite --> sillimanite. Kouassi (1979) indicated that shales of the Lower Albanel Formation contained quartz and illite. Minor chlorite was identified in some argillaceous dolostones. This phase originated from diagenetic transformation of aluminosilicates to chlorite and/or is of detrital or very low grade metamorphic origin. The presence of illite and the absence biotite in the shales suggests subgreenschist conditions.

1.7 Structural Geology of the Mistassini Basin

Faulting: Figure 2 illustrates the major structural features of the basin according to Chown (1984). The major northeast-trending faults are complemented by shorter, east-trending faults located in the central island chain of Lake Mistassini. The latter are often mineralized. This author noted the presence of discordant fault breccias in the Upper Albanel Formation and slickensides in the Lower Albanel Formation. Occasional minor flexures in the carbonates, noted by Norman (1940), may be related to local faults.

Minor strain-related structures are present in the Lower Albanel Formation. En-échelon calcite (and rarely pyrite) filled extensional fractures and fractured, early diagenetic pyrite nodules are occasionally present in the shales. These structures are formed by the initial loss of cohesion associated with faulting. In addition, pressure shadows of quartz, carbonate and chlorite commonly surround pyrite lenses. Burger et. al (1970) found that the quartz pressure shadows around authigenic pyrite were related to shear and extensional fractures.

Evidence of minor stress in the Upper Albanel Formation is indicated by the local presence of stylolites oblique to bedding and deformed chert beds.

Folding: The Temiscamie Iron Formation is folded into a large scale syncline. This is the only major fold in the basin; small local folds are common east of Lake Albanel. Norman (1940) found that the intensity of deformation increased towards the Mistassini Fault. West of a 1.5-6.5 kilometer zone, gentle flexures are locally present and may be related to faults. He also found a positive correlation between intensity of folding and thickness of sediments. This implies that thinner sequences are less susceptible to deformation, due to the more rigid nature of the basement rocks. Such is the case along the southern margin of the basin.

CHAPTER 2

Geology of the Upper and Lower Albanel Formations2.0 Introduction

The following descriptions of the Lower Albanel Formation are mostly based upon data collected by this author from drill-hole LM-74-D2 and complemented by a small number of field data (Appendix 2). Table 2 gives a general description of this formation based on numerous drill data (Lehmann, 1974). Descriptions of the Upper Albanel Formation consist of field data collected almost entirely from a small (12 by 6 kilometer) area in the central part of Lake Albanel (Appendix 1). The descriptions will proceed from the base of the Lower Albanel Formation and progress towards the summit of the Upper Albanel Formation. A generalized stratigraphic section is illustrated in Figure 3. Table 3 summarizes the general lithofacies, depositional environments and distribution in the Upper and Lower Albanel Formations.

2.1 Lower Albanel Formation

The Lower Albanel Formation is comprised of six units, five of which (excluding the basal stromatolite) were examined in some detail. Five general lithofacies were distinguished and a brief-

GENERAL STRATIGRAPHY OF THE UPPER & LOWER ALBANEL FORMATIONS

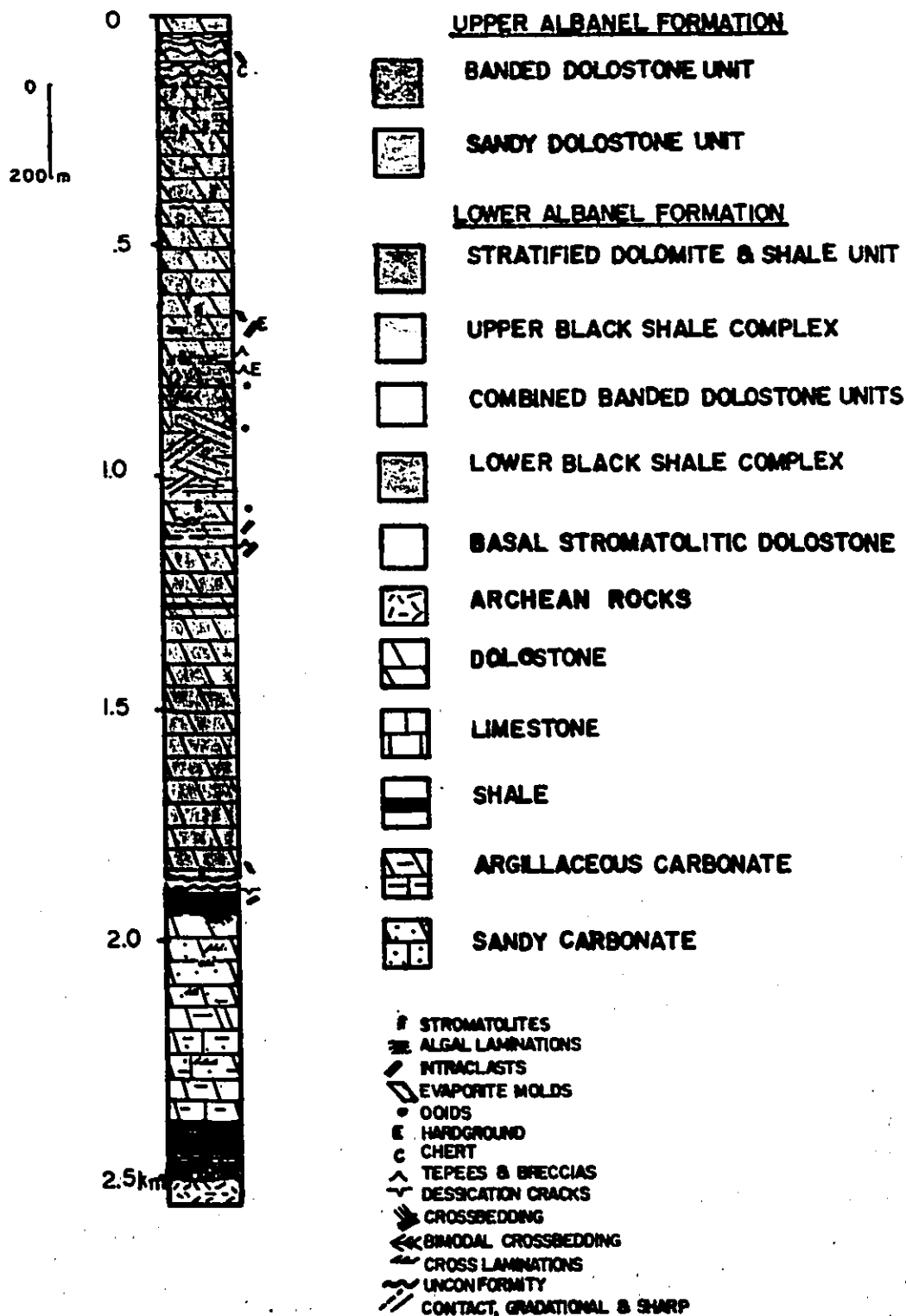


FIGURE 3: GENERAL STRATIGRAPHY OF THE UPPER AND LOWER ALBANEL FORMATIONS. Data for the Upper Albanel Formation and the Stratified Dolomite & Shale Unit is based on field observations. Data for the remaining underlying units of the Lower Albanel Formation was obtained from drill core (LM-74-D2).

introduction, in decreasing order of importance, will be presented. A more detailed description of the lithofacies as a function of their occurrence in each unit, will be presented in the following section:

(1) Dolomudstone - locally impure with minor silty-sandy clastics: grey to black, finely to more coarsely crystalline dolomite; impurities and minor silt to fine sand; laminated to massive; local algal structures; shallow water to peritidal deposition; mostly in the upper two units and base of section.

(2) Silty-sandy dolomudstone to dolomitic siltstone and arenite: laminated, cross-laminated and bedded; varying proportion of silty to very fine-grained immature siliciclastics; rare coarser-grained quartz arenites included; characteristic of the combined Banded Dolostone Units.

(3) Shale and related argillaceous varieties: pyritiferous and organic-rich; both shallow (abundant sedimentary structures) and deep water (few structures) shales included.

(4) Limestone: light to dark grey, laminated to cross-laminated and occurs as silty-sandy, argillaceous and mudstone varieties as described above; forms interlaminations and interbeds with dolostone and shale; more common in deeper water lithologies.

(5) Stromatolitic dolostone: grey laterally linked hemispherical (LLH) and stacked hemispherical (SH) stromatolites and may be associated with algal laminations, breccia and fenestrae in fine-grained dolomite.

TABLE 3
LITHOPACIES DESCRIPTION OF THE UPPER & LOWER ALBANEL FORMATIONS

LITHOPACIES	DESCRIPTION	DEPOSITIONAL ENVIRONMENT	DISTRIBUTION							
			1	2	3	4	5	6	7	8
SANDY DOLOGRAINSTONE TO DOLOPACKSTONE	Cross-bedded, coarse-grained rounded quartz & dolomite	Shallow subtidal, high energy shoal(?)	P	-	-	-	-	-	-	-
			-	-	-	-	-	-	-	-
DOLOMUDSTONE TO DOLOPACKSTONE	Grey to beige & pink, interlam- inated & bedded; fenestrae, flame structures, tepees, breccia, dis- rupted laminae & stromatolites	Low to moderate energy subtidal to peritidal	-	-	-	-	-	-	C	-
			-	-	-	-	-	-	-	-
DOLOMUDSTONE TO DOLOWACKSTONE	Grey, beige & pink, interbedded; fenestrae, tepees, breccias, dis- rupted laminae, shallowing cycles	Low energy subtidal (lagoon?) to peritidal	-	-	-	-	-	-	-	A
			-	-	-	-	-	-	-	-
MASSIVE TO FINEST- RAL DOLOMUDSTONE	Grey, beige & pink, laminated to bedded; fenestral & cryptalgal laminations, breccia	Protected shallow sub- tidal to peritidal	-	-	-	-	-	-	P	-
			-	-	-	-	-	-	-	-
CRYPTALGALAMINAT- ED DOLOMUDSTONE	Laminoid, crenulated & algal dis- torted fenestral laminae, tepees, early cements, erosional surfaces, water-escape structures, shallow- ing upward stromatolitic cycles	Intertidal to supra- tidal	-	-	-	-	-	-	-	C
			-	-	-	-	-	-	-	-
OOLITIC DOLOGRAINSTONE	Bedded to herring bone cross- bedded; grey to beige, grades into cross-bedded sandy dolopackstone	Tidal channels or bars	-	-	-	-	-	-	P	-
			-	-	-	-	-	-	-	-
STROMATOLITIC DOLOSTONE	Grey digitate, LM & SH varieties usually in fine-grained dolomite, forming shallowing upward cycles	Protected shallow sub- tidal to intertidal; one rare deep water example	A	-	-	-	-	C	P	C
			-	-	-	-	-	-	-	-
ONCOLITIC DOLOSTONE	Grey to beige & black (cherty), rounded to irregularly; many to few laminations; +/- sediment binding, grain to mud matrix	High to low energy shal- low subtidal & inter- tidal	-	-	-	-	-	-	P	P
			-	-	-	-	-	-	-	-
DOLOMUDSTONE	Grey, pure to impure, minor silty to sandy immature siliciclastics bedded, laminated to massive; local peritidal structures	Low energy, shallow subtidal lagoon & tidal flat	C	P	-	-	C	A	-	-
			-	-	-	-	-	-	-	-
SILTY-SANDY DOLOMUDSTONE TO SILTSTONE-ARENITE	Laminated to cross-laminated, immature, siliciclastic-rich; rare quartz arenite included	Deeper subtidal of mod- erate to low energy; coastal shelf	-	P	C	A	-	-	-	-
			-	-	-	-	-	-	-	-
SHALE & RELATED ARGILLACEOUS TYPES	Organic & pyrite-rich; bedded & laminated; calcite fractures; distinguish shales with few structures (1) and abundant (2) peritidal sedimentary structures	1-Deep stratified basin; 2-Tidal flat & shallow lagoon	-	A1	P	-	A2	-	-	-
			-	-	-	-	-	-	-	-
LIMESTONE	Grey beds & laminations; in shales, mudstones & siliciclastic rocks	Occurs in deeper sub- tidal environments	-	C	P	P	-	-	-	-
			-	-	-	-	-	-	-	-

A = Abundant (dominant); C = Common but not dominant; P = Present locally; - = Absent (or not applicable)
(units 1 to 8 in ascending order)

2.1.1 Basal Stromatolitic Dolostone Unit:

This basal unit was reported to lie upon either regolith or directly on unaltered basement (Caty and Chown, 1983). The thickness varies between 1.5 and 14 meters; a thickness of 9 meters is represented in hole LM-74-D2. It is characterized by stacked-hemispherical (SH) and laterally-linked-hemispherical (LLH) stromatolites (Lehmann, 1974). The small columns are interbedded with massive dolomitic to sandy dolomitic beds. The stromatolitic horizon becomes disrupted above and below to form a breccia. The upper breccia grades into an alternating massive to sandy dolostone.

Kouassi (1979) noted the presence of bedding, laminations, erosional channels, slumping and minor cross-laminations associated with this horizon.

Although present in the corelog, no samples were available to the author. Consequently, a few samples from drillhole LM-77-D12 (located approximately 6.5 kilometers west of borehole LM-74-D2) were collected to represent the characteristics of this stromatolitic unit. An example consists of a SH stromatolite surrounded by stromatolitic and grey dolomudstone fragments within a dolomudstone matrix. Light colored, coarser laminae alternate with darker, finer crystalline dolomite and light brown dolomitic crystals oriented perpendicular to the laminae. Unlike the common presence of alternating stromatolitic calcite and

dolomite laminations (Glebelein and Hoffman, 1973) only minor chert laminae are present in these dolomitic columns.

The stromatolitic unit is believed to have formed in a shallow subtidal to intertidal environment associated with a transgressive event (Hofmann, 1978). Lehmann (1974) invoked a supratidal environment for the breccia.

2.1.2 Lower Black Shale Complex:

This complex consists of up to five graphitic shale beds alternating with argillaceous carbonates and occasional dolomudstones and limemudstones. The complex extends vertically for 104 meters in the borehole and is defined by the lowermost and uppermost thick shale beds. These two beds are present throughout the basin (Kouassi, 1979); hence their stratigraphic marker potential.

The thinly to thickly-bedded graphitic shales and siltshales are interbedded with dark grey, argillaceous to light grey silty dolostone and limestone. The proportion of shale appears to be inferior to that of the carbonates. This unit hosts the largest proportion of limestone in the Lower Albanel Formation. Dolomudstones and limemudstones, with less siliciclastic content, are more common near the base of the unit. Contacts between limestone and dolostone may be sharp or gradational and incomplete dolomitization is common. Sedimentary structures observed in both shales

and carbonates are limited to laminations and bedding, although Kouassi (1979) recorded the presence of crenulations, slumping and occasional cross-laminations in other localities. Secondary structures such as calcite-filled "tension gashes", veins and slickensides occur occasionally. Diagenetic pyrite is ubiquitous in both shales and carbonates and occurs as nodules, laminations and disseminations. The nodules commonly exhibit pre-compaction features characteristic of early diagenetic origin. Such early diagenetic pyrite nodules form in euxinic environments where sulfate reduction is possible.

Kouassi (1979) indicated that the alternating nature of the shale and carbonates may be due to variations in eustatic sea level. Shales would be deposited during periods of maximum transgression, whereas carbonates would form during regressive periods. Such a mechanism would manifest itself throughout the whole basin. This is consistent with the widespread presence of the lower and uppermost thick shale beds. However, the local presence of up to three more shale beds between the marker shales suggests another mechanism (tectonic subsidence?; sedimentation rate?). Local topographic depressions where shale would form, was envisaged by Kouassi (1979); he showed that some of the local shale beds were indeed concentrated in circular troughs.

Based on the presence of thick organic-rich, pyritiferous black shales, fine-grained siliciclastics and a lack of sediment-

ary structures indicative of shallow water, a low energy, anoxic, deep (below wavebase?) subtidal depositional environment is inferred. This is consistent with Hofmann's (1978) conclusion that a stromatolitic occurrence from the Icon Sullivan Mine formed below wavebase in deep water. In contrast, Lehmann (1974) interpreted the complex as a shallow water(?) lagoon.

2.1.3 Banded Dolostone Units:

A sharp contact separates this unit from the underlying shale complex. The combined banded dolostone units attain a maximum thickness of 462 meters. The banded dolostone units can be subdivided into a lower more argillaceous carbonate and an upper silty to sandy dolostone.

The Lower Banded Dolostone Unit is characterized by more thinly interbedded, light to darker grey, argillaceous to (locally cross-laminated) silty dolostone and limestone. The carbonates become darker and more argillaceous toward the underlying formation contact. Although limestone is present, its proportion is inferior to that in the Lower Black Shale Complex. The siliciclastic content in the carbonates varies from high to low. Thin sandy dolostone beds occur rarely. Common sedimentary structures include cross-laminations, stylonodular and laminar fabrics, as well as ubiquitous bedding and laminations. Approaching and extending into the overlying unit, stylo-nodular and wispy to streaky laminations become more abundant. Pyrite occurs

as disseminations, laminae and lenses, although much less abundant.

The Upper Banded Dolostone Unit consists of light to dark grey, impure dolomudstones in the upper portion, with an increasing proportion of silty and sandy siliciclastics with depth. Impure limestone beds and thin beds of coarser, dolomitic quartz arenite occur only rarely. Bedding, laminations, cross-laminations and wispy to streaky laminations are common sedimentary structures. Less frequently, convolutions and erosional surfaces occur, as well as lenses, large cubes and disseminations of pyrite.

Based on the presence of ubiquitous fine-grained, immature siliciclastic grains, the Upper Banded Dolostone Unit is interpreted to have been deposited in shallow, more turbulent waters of a coastal shelf environment. The Lower Banded Dolostone Unit probably formed at somewhat greater depth, as suggested by the higher argillaceous content. The immature nature of the silicate detritus suggests a local source area with some topographic relief.

2.1.4 Upper Black Shale Complex:

The previous units grade upward into a finely to medium interbedded graphitic shale, argillaceous dolostone, grey dolomudstone with minor silty to sandy impurities and is devoid of

limestone. Only the lower 137 meters are represented in the sampled core. The interval exhibits distinctive sedimentary structures. Cut and fill structures, intraformational conglomerate, algal mats and crenulated layers, organic-rich limestone algal clasts (Plate 1), "wispy" laminations, cross-laminations and bedding are present. Occasionally, convolutions, spar-filled cavities (fenestrae or evaporite molds?), streaky laminations, as well as secondary calcite veins and "en-échelon" tension gashes are visible. Pyrite is also common and occurs as disseminations, replacement of algal mats and, in one case, as a disseminated mass preserving a cross-laminated texture.

On the basis of the above lithology and suite of sedimentary structures observed, a supratidal to low energy, shallow subtidal depositional environment is inferred. This is consistent with Lehmann's (1974) interpretation of this unit as a tidal flat and lagoon. He envisaged the migration and accumulation of subaqueous sand bars, resulting in restricted basin conditions.

2.1.5 Stratified Dolomite and Shale Unit:

Although Lehmann's (1974) stromatolitic dolostone member correlates with the lower portion of the Stratified Dolomite and Shale Unit, it is not represented in the drill core and its vertical extent is not known. Hence Deland and Sater's (1967) term was adopted since it directly overlies drillhole LM-74-D2

and thus forms a stratigraphic continuum for sampling¹ purposes.

This stratigraphic member of Deland and Sater (1967) is approximately 800 meters thick and consists of a grey, fine to coarsely bedded dolomudstone with minor dolomitic shale laminations. The bedded dolomudstone appears homogenous and is characterized by a general lack of detrital silicates. A cross-bedded arenaceous quartz dolostone (with frosted quartz grains) was reported near the base of this member (Deland and Sater, 1967). The bedded dolostones occasionally exhibit shallow undulating bedding and slumping, the former may be due to weak deformation. Dessication polygons, chert nodules and breccias were also noted by these authors. Kouassi (1979) noted the presence of concordant breccias and discordant solution collapse breccias. Near the summit, a tepee-like structure was observed, although the presence of nearby slickensides and associated vertical fractures in the tepee suggests some structural control.

Approaching the summit of the Lower Albanel Formation, a gradational change from grey to beige and pinkish colors and a more massive dolostone marks the contact with the Upper Albanel Formation.

Based on the presence of LLH stromatolitic dolomudstone,

¹Only a small number of samples were collected from this unit due to a lack of outcrop.

breccia and possible bird's-eye structures, Lehmann (1974) invoked deposition in an alternating supratidal-intertidal environment. However, this interpretation corresponds to the lower portion of the unit. The presence of cross-bedding and bedded massive dolomudstone implies deposition in shallow water higher and lower energy environments, respectively. The reported presence of dessication polygons and breccias, coupled with the observation of a tepee structure in dolomudstone, implies some subaerial exposure. Thus carbonates of the Stratified Dolomite and Shale Unit were deposited in environments ranging from supratidal-intertidal to shallow subtidal.

2.2 Upper Albanel Formation

The formation is approximately 1100 meters thick in the central part of Lake Albanel. Wahl (1953) subdivided it into a lower predominantly sandy and an upper banded (stromatolitic) dolostone unit (Figure 3).

The Upper Albanel Formation possesses general lithofacies that are in part common to both units. The general features will be briefly outlined below. A more detailed examination of the lithological characteristics of each unit will be presented in the following section:

- (1) Sandy dolopackstone to dolograinstone: Cross-bedded with

mature quartz and dolomite grains.

(2) Massive to fenestral dolomudstone: grey to pink, massive to fenestral dolostone.

(3) Oolitic dolograinstone: thickly bedded and locally bimodally-cross-bedded with recrystallized ooids; associated with cross-bedded sandy dolograinstone.

(4) Cryptalgalaminated dolomudstone: grey, well laminated and part of shallowing upward stromatolitic cycles; commonly cherty.

(5) Interbedded dolomudstone to dolopackstone: interbedded, grey to beige dolostone; various features indicative of shallow water to peritidal conditions.

(6) Interbedded dolomudstone to dolowackestone: similar to (5) but characterized by greyish colors and a lack of coarser fabrics.

(7) Stromatolitic dolostone: Includes small digitate, LLH and large SH stromatolites; in subtidal to intertidal and protected to higher energy environments.

(8) Oncolitic dolostone: includes beige to pink, well-rounded with numerous concentric laminations and evidence of coarser bedded clastics; also as grey irregularly laminated, organic and cherty varieties in a finer dolomite matrix.

2.2.1 Sandy Dolostone Unit:

The northeast to southwest-trending unit is distinguished by the presence of cross-bedded quartz dolopackstone to dolograinstone. However, lateral facies changes were observed and these

will be described below:

Sandy dolopackstone to dolograinstone: The northeastern margin of this area is dominated by this cross-bedded to bedded facies. Outcrops weather dirty grey to black ; fresh surfaces are lighter grey. Rounded quartz grains (<1 mm), rounded to ellipsoidal ooids (<4 mm) and subrounded intraclastic dolomudstone (<2 mm) occur in varying proportions. The particles are embedded in a fine grained dolomitic matrix. These rocks locally grade into dolomitic-quartz arenites and oolitic grainstones. To the southwest and west, the cross-bedded dolostone appears to thin out and is replaced by finer-grained and interbedded varieties, although cross-bedded dolostones were occasionally observed.

The rounded quartz grains are the sole dominant detrital silicates in the dolostones. This suggests that the craton has been eroded into a low relief topography, producing little if any detrital material. The textural maturity of the quartz grains may suggest several episodes of recycling. An offshore, shallow water, high energy environment (shoal ?) is inferred.

Massive to fenestral dolomudstone: This facies was observed in proximity of the Lower-Upper Albanell Formations contact. The pinkish to grey fenestral dolomudstone is laminated to bedded and is locally associated with oolitic beds. The fenestrae contain crystalline quartz (Plate 2), which accentuates the weathered surface. Occasionally, black, organic-rich laminations are

associated with the fenestrae and the former may represent algal mat remnants. One of the processes postulated for fenestrae formation involves the cavities left after decay of organic mats (Shinn, 1968). Near the Mistassini Post area, an intraformational breccia possessing fenestrae was found.

A protected intertidal to supratidal depositional environment is inferred, based on the presence of fenestrae, intraformational breccia, associated stromatolites, and cryptalgal laminations. Dolomudstones lacking these features may represent shallow subtidal sediments.

Oolitic dolograinstone: This lithology was observed near the northeast margin, where the thickness of the cross-bedded facies appears to thin out. Thicker beds appear to be bimodally cross-bedded (Plate 3). Outcrops weather dirty grey; fresh surfaces range from grey to oxidized beige and red. Rounded to ellipsoidal ooids and pisoids (<5 mm) protrude on the weathered surfaces; silicified varieties are especially discernable due to their large (<7 mm) size. Hand specimens rarely show more than a few concentric laminations and may be easily distinguished by changes in color, such as the presence of oxidized (organic iron-bearing coatings?) red cortices. Partially preserved to completely recrystallized textures were observed; diagenetic recrystallization is the probable cause of textural obliteration. Ooid nuclei range from quartz grains to a variety of dolomitic particles.

Thinner oolitic beds, laminations and (silicified) lenses were found to be locally associated with cryptalgalaminates, stromatolites, dolomudstones and an oncolitic dolostone. Many of these occurrences represent textural inversions. ie: higher energy ooids associated with lower energy dolostones. The ooids were probably deposited landward by storms. However, due to the low profile and poor exposure of certain outcrops, an autochthonous origin may be possible for some of the oolitic occurrences. If the ooids are indigenous, then a shoaling upward sequence may be colonized by algal structures if the substrate was previously stabilized.

A shallow, agitated and warm marine environment appears to be the optimum setting for the production of oolitic grainstones. This would correspond to Wilson's (1975) "winnowed platform edge sands" facies zone. Bimodally cross-bedded dolograins may represent tidal channels or bars.

The occurrence of associated cryptalgalaminates, ooid layers, (silicified) lenses in shallow depressions and small channels cutting into the laminates suggests intertidal (tidal flat?) to shallow subtidal depositional conditions.

Interbedded dolomudstone to dolopackstone: This facies is more common towards the southwestern portion of the area, where the

cross-bedded dolostone is less abundant. Quartz-bearing dolowackestone to dolopackstone (occasionally oolitic) are interlaminated and interbedded with dolomitic mudstone. Convolutions due to loading may occur in thinly bedded sediments; in thickly bedded varieties, flame structures result. Locally, overlying quartz-intraclastic dolopackstones are underlain by dolomudstone which often possesses "chaotic" laminations.

Cryptalgalaminates (locally brecciated) and stromatolites are occasionally present. One example of an algal laminated dolomudstone exhibits what may be a tepee structure. The brecciated fragments are surrounded by crystalline quartz and dolomite.

Deposition in subtidal to peritidal conditions is suggested. Local peritidal depositional conditions are inferred based upon the presence of stromatolites, fenestral fabrics, brecciated algal laminations and associated tepee structures. The latter would indicate deposition in a supratidal environment.

Stromatolitic dolostone: Only a few examples were found in the Sandy Dolostone Unit and may be due to the local inhospitable conditions and/or lack of outcrop exposure. The first example (A-13a-84) consists of alternating darker, quartz-rich dolowackestone and grey dolomudstone. Fresh surfaces range from beige and pink to grey colors. The quartz-rich dolomite layers tend to be pink and more fenestral. A peritidal environment is suggested,

based upon the association between stromatolites, fenestrae, intraformational breccia and possible cryptalgalaminates.

A second example involves a probable shallowing-upward sequence (one of several observed in the Upper Albanel Formation). Dolomudstone layers are displaced upward by oolitic beds, "stabilized" interlaminated oolitic and stromatolitic laminae and lenses. Frequently, tiny stromatolitic growths upon individual ooids are visible. The oolitic dolostone grades up into SH stromatolitic (<30 cm high) dolostone. Intercolumn space is occupied by dolomudstone, stromatolitic fragments, and dolospar and quartz-filled fenestrae and shelter porosity (Plate 4).

The sequence represents a shallow subtidal to intertidal environment. A nearby offshore ooid shoal supplied the ooids, which were trapped and cemented. Storms damaged the stromatolitic layers and broke-up the cemented oolitic layers into intraclasts (Plate 31).

Oncolitic Dolostone: Only one example of this facies was noted. The beige to pink oncolitic dolostone is interlayered with algal laminations. The well laminated, irregular to rounded oncolites reach diameters of 2 cm and are supported by a dolograinstone to dolopackstone matrix. The matrix is composed of smaller oncolites, intraclasts and minor ooids. Dolospar and quartz cemented shelter porosity and fenestrae are present (Plate 5).

Based on the presence of algal laminations and fenestrae, an intertidal to shallow subtidal depositional environment is inferred. Moderate energy conditions were intermittent, allowing the reestablishment of algal laminations.

2.2.2 Banded Dolostone Unit:

This unit occurs in the central island chain and extends to the southern shore of Lake Albanel (Appendix 1). Although the dolostones of the central island chain and south shore of Lake Albanel share certain attributes, significant differences do exist. The central island chain is dominated by buff to grey-colored, locally stromatolitic, laminated and interbedded dolomudstones, dolowackestones and rare dolopackstones. South of the lake, grey laminated to bedded stromatolitic dolomudstone is common; chert beds are also characteristic. Dolowackestones are less common and packstones seldom occur. The lithologies will be described in more detail below:

Stromatolitic dolostone: Stromatolites tend to be more common in the southwestern portion of the central island chain and very common along the southern shore of Lake Albanel. Stromatolites include SH (stacked-hemispherical with constant or variable radii) and LLH (laterally-linked-hemispherical) columns. Stromatolites tend to be circular in plan view; elongated stromatolites were not observed. Heights and diameters of columnar and LLH

varieties may reach tens of centimeters. One SH stromatolite however, possessing a Conophyton-like form, measured at least one meter in height (Plate 6) and is composed of alternating darker and lighter grey (organic-rich and poor) dolomite (Plate 7). Tiny digitate-like columns (a few centimeters high) also occur occasionally. Stratigraphically, a few meters may separate digitate (Plate 21) and larger columns. Laminae composing the columns consist of alternating dolomudstone and laminoid fenestrae composed of coarsely crystalline quartz and dolomite. These more resistant fenestrae enhance the stromatolitic laminations. Where observed, intercolumn fill usually consists of fine-grained dolomite, although rare coarser-grained fabrics may be present.

One such example consists of a quartz dolopackstone interbedded with dolomudstones, near the contact with the Sandy Dolostone Unit. Tiny columns (a few centimeters) and laminations are overlain by coarser subrounded feldspar, quartz and dolomitic grains, which are also lodged interstitially between the columns. Although the contact appears stylolitic, evidence of an erosional boundary is unequivocal. An attempt by the organisms to re-establish themselves was unsuccessful; the organisms were overwhelmed by the unstable, shifting clastics. A renewal of higher energy conditions is indicated here.

The ubiquitous presence of dolomudstone, stromatolites, laminoid fenestrae and frequent association with algal laminated

dolostone, all suggest a protected, shallow subtidal to intertidal depositional environment. Stromatolites overlain by cryptalgalaminated dolostone (Plate 8) and associated with tepee structures (Plate 9) represent shallowing upward stromatolitic cycles. Thus evidence for deposition in a supratidal zone is also present. The local presence of tiny, delicate digitate-like columns may represent deposition in quiet-water tidal ponds.

Some evidence suggests that the SH (Conophyton-like morphology) and LLH stromatolites appear to have formed in very different depositional environments. The typical fenestral fabrics and other evidence of peritidal deposition are lacking. Hofmann (1978) invoked a below-wave base depositional environment for a stromatolitic occurrence in the vicinity of that illustrated in Plates 6 and 7. Thus a quiet, deeper water environment is also suggested for this stromatolite.

Cryptalgalaminated dolomudstone: Aitken (1967) defined cryptalgalaminates as more or less planar laminations due to the sediment binding activity of blue-green algae. Numerous occurrences of cryptalgalaminates were noted in the island chain and south of the lake. The grey to beige and pink laminations are smooth or crenulated (Plate 9) and consist of alternating dolomudstone and quartz and dolomite-filled laminoid fenestrae. These algal laminations are usually associated with dolomudstones, although coarser fabrics were also found in the northeastern portion of

the island chain. Plate 10 illustrates a coarser-grained bed overlying a dark grey fenestral dolostone and separated by a sharp erosional surface. Erosion of early cements and straight vertical boundaries indicate early lithification. Examples of cryptalgalaminates associated with dolomudstones are numerous. Plate 11 illustrates a pink cryptalgal and fenestral dolomudstone, possessing an "undulating" fabric and is overlain by an intraformational breccia. This fabric may be similar to Keran's (1982) "curly bedding".

In the northeastern and southwestern regions of the island chain, certain finely laminated, light colored dolostones possess distinctive distorted textures. These deformed dolomudstones consist of finely laminated cryptalgal layers and may owe their origin to the loading of water saturated muds. Where fenestrae are present within the deformed laminae, they may enhance these chaotic textures. Plate 12 shows a distorted dolomudstone with preserved fenestrae. The preservation of the latter is the result of early precipitation within the cavities. Disrupted laminations were also noted to trend perpendicular to the bedding, suggestive of water-escape structures. In other cases, the fabrics appear more rigid and contrast readily with the more fluid matrix, as evident in Plate 13. This sample is also associated with a tepee breccia. These examples imply that sedimentary deformation occurred just after deposition but prior to complete lithification.

Cryptalgalaminated dolostones are also well developed south of Lake Albanel, where they form the chertified upper portions of shallowing upward stromatolitic cycles (Plate 8). Further inland and toward the Temiscamie Formation contact, interlaminated laminoid fenestral algal dolomudstones were found to vary from crenulated and tufted varieties to blister-like fabrics (Plate 14).

Algal laminated sediments are presently found in the intertidal to supratidal zone. Their upper and lower extent is presently controlled by dessication and grazing organisms, respectively. Since the latter was not a factor in the Precambrian, algal laminations would have extended down to the base of the intertidal zone (James, 1977), or beyond. Logan (1974) indicated that different algal mat fabrics occupy different locations in the peritidal zone at Shark Bay, Australia. For example, tufted and blister mats occur in the middle-upper intertidal and upper intertidal-supratidal zones respectively.

The cryptalgalaminated dolomudstones were shown to be associated with shallowing upward stromatolitic cycles (Plates 8 and 9), erosional surfaces (Plate 10), fenestrae, breccias (Plate 11), early lithification and tepee structures (Plate 9). The association of tepee structures with the other structures strongly supports a supratidal origin (Kendall and Warren, 1987).

The evidence suggests that the cryptalgalaminates were deposited in an intertidal to supratidal depositional environment.

Oncolitic dolostone: Only two examples were seen in the island chain and only in the southwestern region. In one case, well-laminated oncolites (less than 1 cm in diameter) occur with interbeds of tiny stromatolites (<1 cm), algal laminations and dolomudstone. The other consists of a beige to pink oncolitic-intraclastic dolostone of rudite size, interbedded with dolowackestone and algal dolomudstone. The oncolites and intraclasts may reach diameters and lengths of up to 10 and 20 millimeters, respectively. The underlying algal laminations are broken up into long, slender and imbricated fragments. Shelter porosity associated with the latter is obstructed by crystalline quartz and dolomite. Most of the matrix consists of rounded quartz and dolomite grains (<1 mm) and dolomitic intraclasts. Oncolitic cores are composed of locally derived dolowackestone and dolomudstone. Oncolitic laminations may contain quartz grains, implying sediment binding. These rounded and well laminated oncolites would correspond to Logan's et al. (1964) "type c" variety.

The presence of algal laminations and fine-grained dolostone implies quiet shallow subtidal to intertidal conditions. The oncolites and slender fragments of the first occurrence may have been disrupted by periodic higher energy conditions (ie: storms) and deposited in their present location. An allochthonous origin

is suggested since their almost spherical form suggests frequent agitation. This would be inconsistent with the enclosing sediment.

In contrast, several occurrences were found in outcrops along the south shore of Lake Albanel. Significantly they all differ from previous occurrences. The oncolites are distinguished from those in the underlying lithologies by the following traits:

- a) These dark grey oncolites are usually associated with finer-grained matrix.
- b) The irregular, less numerous organic-rich(?) and cherty laminations contrast with the fine, well laminated and numerous, organic-poor texture.
- c) The absence of evident sediment binding and possible evidence of precipitation within the algal sheaths.
- d) Grey and black (reduced) colors contrast with the beige (oxidized) oncolites of the island chain.

The oncolites may reach diameters of 1-2 centimeters. Alternating light and dark grey to black concentric laminations are composed of (organic-rich?) dolomite and chert. The matrix usually consists of dolomudstone and local dolowackestone. The relatively less defined, thicker and irregular laminations combined with an apparent lack of banded particles, may suggest possible precipitation of carbonates in mucilaginous sheaths.

A few unusual fabrics were observed, such as an oncolitic dolostone with little dolomudstone matrix and supported by interparticle dolospar and later crystalline quartz. The lack of fine-grained matrix implies winnowing by higher energy conditions. Petrographically, no evidence of algal binding was observed (in fact acicular crystals were seen in one structure). This would suggest that the oncolites formed locally in a tranquil environment and were then deposited (by storms?) in their present location. Remobilization and deposition occurred without major transport.

In another case, tapered, upward radiating crystal fans were found to project from a poorly defined circular (oncolitic?) structure.

Most of these specimens are inferred to have formed in a quiet, shallow subtidal (lagoonal?) depositional environment. However, the local occurrence with an overlying (≈ 50 cm) grey fenestral dolostone, possessing organic-rich(?) laminae, suggests shallowing upward peritidal cycles. In another example, the association of oncolites (Plate 23) with an apparently overlying fenestral dolostone possessing characteristics resembling caliche pisolites (Plate 24), is consistent with such an interpretation.

Interbedded dolomudstone to dolowackestone: The majority of the island chain is composed of grey, beige and pink dolomudstone and

dolowackestone. The proportion of dolopackstone is largely inferior to that of the dominating lithologies and tends to be more common in proximity to the underlying Sandy Dolostone Unit. Cross-bedding was occasionally observed. Where packstones tend to form thicker beds, contacts are occasionally erosional and sharp. Locally, sandy dolostones and underlying dolomudstones (with tepee-like structures) are separated by an erosional boundary. Various proportions (and sizes) of detrital quartz and dolomite constitute the bulk of the detrital material. Ooids may also occur locally.

Stromatolitic and cryptalgal dolostones are often associated. Tepee structures and intraclastic breccias (occasionally associated with the former) are locally present. Plate 15 illustrates a tepee which caps a shallowing upward stromatolitic cycle. Tepees were only observed in the southwestern part of the island chain (and adjacent mainland) investigated. Chaotic, fenestral dolomudstone (Plate 13) may also occur in proximity to the tepee breccias.

The south shore of Lake Albanel is also represented by these grey to tan-colored lithologies. Dolowackestone however, is less abundant and dolopackstones as well as coarser-grained dolostones seldom occur, compared to the island chain. Detrital grains include dolomitic particles, occasional quartz and rare chert grains. The unique occurrence of chert beds also serves to

differentiate this area from the underlying lithologies. Where exposed, these beds extend laterally for appreciable distances.

Although the dolostones are finely crystalline, a few samples such as that in Plate 16 are exceptions. The highly fractured dolostone is exceptionally coarsely crystalline; the latter imparts a pale color with the impression of translucency. The largest crystals (approaching one centimeter in length) are unique in that they occur as a long, slender and somewhat divergent mass, resembling a fan. The intense recrystallization and fracturing may be the result of local faulting. Evidence of faulting (narrow discordant breccias) south of the lake was observed by the present author and previously reported by others as well.

Sedimentary structures show little diversity. Laminated to bedded dolostones are commonly defined by a change in mineralogy and color (ie: dolomite vs chert). Apart from these and various algal (stromatolites, cryptalgalaminations and oncolites) structures, only local fenestrae, disrupted laminations and an intraclastic lens were found. The imbricated fragments of the latter, probably formed by disruption and transportation of lithified crusts, possibly during storms.

Deposition of dolomudstone and dolowackestone in both regions of the unit occurred in a low energy, subtidal (lagoona-

1?) to peritidal depositional environment characterized by numerous shallowing upward stromatolitic cycles. Local subaerial exposure is supported by the presence of the peritidal tepees previously described. The minor dolopackstones of the central island chain, occurring near the contact with the underlying Sandy Dolostone Unit were deposited in shallow, less protected and more turbulent waters. Erosional contacts between underlying peritidal dolostones (ie: fenestral dolostone and tepee structures) and overlying dolopackstones suggest reestablishment of subtidal conditions. A return to more turbulent water conditions however, is indicated by the presence of oolitic to granule-textured rocks of the overlying Temiscamie Iron Formation.

Note: To the southeast, the Upper Albanel Formation gives way to the Temiscamie Formation. Between the eastern margin of the Temiscamie Formation and the Mistassini Fault, a roadside exposure is characterized by alternating grey dolomite, dolomitic breccia and shale. These rocks may represent a turbidite deposit (Richard Bell, personal communication) beyond a platform margin, suggesting a return to deeper water depositional conditions.

2.3 Chapter Summary

The six units of the Lower Albanel Formation are generally composed of five major lithofacies. The depositional environments

and distribution of these lithofacies, in decreasing order of importance, is summarized as follows:

(1) Dolomudstone: Deposition in a low energy shallow subtidal lagoon and tidal flat; concentrated in the Stratified Dolomite and Shale, Upper Black Shale and Basal Stromatolitic Dolostone Units.

(2) Silty-sandy dolomudstone to siltstone-arenite: Deposition in a deeper subtidal, low to moderate energy coastal shelf environment; concentrated in the Upper and Lower Banded Dolostone Units and present in the Lower Black Shale Unit.

(3) Shale and related argillaceous types: Both deep restricted basin (Lower Black Shale Complex) and tidal flat-lagoon (Upper Black Shale Complex) depositional environments are included.

(4) Limestone: Observed in deeper subtidal depositional environments; major occurrence in the Lower Black Shale Unit and decreasing in importance in the Lower and Upper Banded Dolostone Units.

(5) Stromatolitic dolostone: Protected shallow subtidal to intertidal depositional environment; characteristic of the Basal Stromatolitic Unit and of the lower portion of the Stratified Dolomite and Shale Unit.

The Upper Albanel Formation can be generally described by eight lithofacies. Their depositional environments and distribution, in decreasing order of importance is described as follows:

(1) Sandy dolograinstone to dolopackstone: Deposited in a shallow

subtidal, high energy (shoal?) offshore environment; characteristic of the Sandy Dolostone Unit. Southwest extension of this lithofacies thins out and is replaced by the next lithofacies.

(2) Dolomudstone to dolopackstone: Deposition in a low to moderate energy shallow subtidal to peritidal zone; replaces lithofacies (1) in the Sandy Dolostone Unit.

(3) Dolomudstone to dolowackestone: Deposition in a low energy shallow subtidal lagoon(?) to peritidal zone; characteristic of the Banded Dolostone Unit.

(4) Massive to fenestral dolomudstone: Deposited in a shallow subtidal to peritidal depositional environment; occurs in the Sandy Dolostone Unit.

(5) Cryptalgalaminated dolomudstone: Deposited as shallowing upward stromatolitic cycles in the intertidal and supratidal zones; characteristic of the Banded Dolostone Unit.

(6) Oolitic dolograinstone: Deposition in tidal channels or bars; occurs in the Sandy Dolostone Unit.

(7) Stromatolitic dolostone: Most occurrences were deposited in a protected, shallow subtidal and intertidal depositional environment and represent the lower portions of shallowing upward stromatolitic cycles; more abundant in the Banded Dolostone Unit than in the Sandy Dolostone Unit.

(8) Oncolitic dolostone: Occurs in higher to lower energy, shallow subtidal to intertidal depositional environments; more common in the Banded Dolostone Unit than the underlying unit.

Rocks of the Lower and Upper Albanel Formations record a first order transgression and regression. The initial transgression over the Archean basement by the Basal Stromatolitic Dolostone Unit was followed by a maximum advance of the sea, reflected by the anoxic, deep water Lower Black Shale Complex. Additional fluctuations in depth and/or depositional conditions are suggested by the alternating nature of the shales and carbonates in this complex. Regression continued as evidenced by the deposition of the more argillaceous Lower Banded Dolostone and more silty to sandy Upper Banded Dolostone Units. Various low to high energy, shallow water to peritidal depositional conditions and local erosional surfaces in the overlying units suggest second order sealevel fluctuations.

CHAPTER 3

PETROGRAPHY3.1 Lower Albanel Formation

This chapter will present the petrography of the Upper and Lower Albanel Formation units, excluding the Basal Stromatolite Unit and regolith. The lithofacies will be described as a function of their dolomite, calcite and siliciclastic content in each unit of the Lower Albanel Formation.

3.1.1 Lower Black Shale Complex:

Graphitic shales: The high organic content and fine grain size hinders thin section examination. A few samples analyzed by X-ray powder diffraction denoted variable proportions of quartz, K-feldspar, plagioclase and phyllosilicates (chlorite and illite?). Interbedded carbonates are locally important. Kouassi (1979) reported a quartz-illite composition for the shales and an average of approximately 8 % organic matter.

Carbonates: The complex hosts a major portion of the (pure to impure) limestone. The limestones (and dolostones) are rather pure when compared to those of the overlying units. Calcite occurs as bedded hypidiotopic to xenotopic crystals (80 micrometers maximum) and in veins. Where porphyrotopic textures are

present, xenomorphic patches of up to 500 micrometers can be found (Plate 17). These patches commonly exhibit unit extinction, suggesting single crystal entities. Quartz, plagioclase, micas and dolomite are enclosed by the patches. These crystalline structures are believed to be of secondary origin. Porphyrotopic calcite may also occur as hypidiotopic crystals (<400 micrometers) along limestone-dolostone boundaries (Plate 18). Unlike the previous case, these lack inclusions, except for dolomitic rhombs. The layers probably represent incomplete dolomitized margins grading into limestone.

Impure dolostones grading into argillaceous varieties, are composed of idiotopic to hypidiotopic crystals, commonly less than 50 micrometers (up to 150-200). Dolomitization of limestone is ubiquitous; euhedral rhombs contrast readily against the less defined calcite crystals. Dolomite tends to be finer than the calcite. Microscopic gradations from limestone to dolostone are revealed by an intermediate porphyrotopic calcite zone and by the replacement of the latter by euhedral dolomite.

Siliciclastics: The proportion of silicates such as quartz, plagioclase, K-feldspar and micas increases in argillaceous to silty varieties. Quartz, the dominant silicate, is subangular and has a maximum dimension of 100 micrometers. The less abundant plagioclase and feldspar are similar in size and shape to quartz. The former is characterized by albite twinning, whereas the

latter possesses cross-hatch twinning.

A detrital origin for the plagioclase is indicated by the uniform small size, absence of inclusions, angularity and common polysynthetic twinning. Kastner (1971) found that cross-hatch twinning in authigenic microcline and polysynthetic twinning (ie: > 3 individuals) in authigenic albite does not occur. X-ray powder diffraction suggests a sodic-rich plagioclase.

Erosion of greenschist facies metamorphic rocks and albite granites represent the sole possible sources of detrital sodic plagioclase (Blatt et al., 1980). Just north of the Papasquasati Basin, greenstone rocks are present. Subsequent erosion, deposition in the clastic basin and redistribution into parts of the Lower Albanel Formation is the scenario envisaged. Note that Choquette and James (1987) indicated that albitization of calcium plagioclase can occur during burial.

Authigenic minerals: Pyrite is by far the most abundant, visible authigenic mineral. It forms nodules, laminations, disseminations, cubes of various sizes and rare tension gashes in shales as well as in carbonates. Several generations may be distinguished. Early diagenetic types displace the surrounding sediment and represent a pre-compaction stage. Later varieties cross-cut sedimentary structures, are usually poikilotopic and occur as lensoid masses and cubes. The latest pyrite forms anhedral masses

lining fractures, veins, tension-gashes and are associated with faulting. Note that pressure shadows of carbonate, quartz and chlorite surround several of the different generations of pyrite. This suggests that the early and some of later varieties are pre-deformational sulfides.

Quartz is the most common authigenic silicate, although it represents a minor portion of authigenic minerals noted. It occurs as large (< 1 mm) euhedral-subhedral, poikilotopic and often twinned crystals interrupting laminations. On occasion (Plate 17) it occurs as pseudomorphic rectangular crystals. Detrital and authigenic quartz are easily distinguished. Rare authigenic feldspar is present. Minor chlorite is present probably as detrital and authigenic components and as rare pressure shadows.

Textures: Ubiquitous bedding and laminations are enhanced by compositional and size variations. Shales, impure to purer carbonates, including organic and pyritiferous components constitute the compositional differences. Size variation is most evident in carbonates where coarser and finer bands appear lighter and darker respectively. The presence of siliciclastic lenses and laminations also contributes to the sedimentary structures in the carbonates.

Commonly, discontinuous filaments of brownish to black

argillaceous and opaque matter are present in carbonates. These filaments are usually low amplitude stylolites, which may impart a stylolaminated fabric. Wanless (1979) indicated that microstylolites ("wispy laminations") form in carbonates containing a significant proportion of fine insoluble platy particles.

3.1.2 Banded Dolostone Units:

The combined lower and upper segments are also dolomitic, but the proportion of limestone is reduced. The lower more argillaceous to silty portion hosts the bulk of the limestone; dolomite is the dominant carbonate. Rarely, the impure carbonates grade, or are in sharp contact with occasional coarse-grained, texturally mature and immature arenites, within the upper and lower portions respectively.

Carbonates: Dolomite, the most abundant mineral, occurs in the laminated, bedded and cross-laminated rocks. It forms idioblastic to hypidioblastic crystals usually less than 50 micrometers, but may reach 150 micrometers in length. The crystal size tends to increase with carbonate purity, as the summit of the unit is approached. Partial dolomitization of limestone is common. Dolomite also occurs as detrital sandy particles and as fine crystalline matrix. The sandy particles were deposited along with quartz and limestone.

The laminated, bedded and cross-laminated limestones consist

of hypidiotopic to xenotopic crystals (< 250 micrometers). Coarser (< 1 mm), rounded limestone grains are present in the arenitic beds. The co-occurrence of rounded detrital quartz and calcite is incompatible and implies a local carbonate source and a rapid removal from the active sedimentary environment. Other than a detrital origin, crystalline calcite is also present in veins. Porphyrotopic textures are absent. However, rare lenses containing a few calcite crystals (< 500 micrometers) are often bounded by stylolites. These secondary calcite lenses are associated with the latter and may have also been modified by pressure solution.

Siliciclastics: Quartz is by far the dominant silicate, although plagioclase, feldspar and micas are locally important. Feldspar appears to be subordinate to plagioclase. Higher concentrations of plagioclase were observed in thin section (and confirmed by XRF) in a limestone-rich and dolomitic interval, in the upper to middle portion of the Lower Banded Dolostone Unit. Clastics are subangular to subrounded and fine grained (< 100 micrometers) except in arenitic beds, where they are more rounded and coarser (< 250 micrometers).

Platy minerals include muscovite, chlorite and rare biotite. They are ubiquitous in the lower and common in the upper portions of the unit. The micas form subhedral to euhedral slender laths, a few hundred micrometers in length. The parallel alignment to

bedding and frequent bending due to compaction confirms a detrital origin. However, some of the chlorite is of diagenetic and metamorphic origin. The crystals tend to be shorter and appear more euhedral than the detrital micas. Metamorphic chlorite is found as local pressure shadows.

Authigenic minerals: Pyrite is the most conspicuous authigenic mineral and occurs as cubes, lenses and minor disseminations. The common bands and nodules commonly associated with argillaceous and/or organic matter, were not observed here. In addition, the sulfide is far less abundant than in the underlying shale unit and is often characterized by a poikilotopic texture. Paragenetically, many examples observed represent post-compaction features; however one example of a pre-compaction pyrite sphere clearly displaces the sediment around it. One unusual occurrence consists of small (< 250 micrometers) radiating clusters surrounded by calcite. The absence of a poikilotopic texture suggests early formation. An early diagenetic origin or possibly replacement of an early diagenetic precursor (or evaporites?) may be possible. Further discussion of this subject will be presented in Chapter 6.

Authigenic quartz is uncommon and was only noted in the lower portion of the combined units. The euhedral to subhedral (< 1 mm) poikilotopic crystals are frequently twinned. Where the crystals are elongated, they are aligned parallel or perpendicu-

lar to the bedding.

Textures: Bedding and laminations are similarly defined by changes in lithology and grainsize as previously noted. Contacts are commonly sharp and straight. The combined units are distinguished by the common presence of cross-laminations. "Wispy" laminations are frequent and consist of low amplitude micritic-litic fabric.

3.1.3 Upper Black Shale Complex:

Graphitic shale: Although the mineralogy is probably similar to that of the underlying shales, certain characteristics are different. A plethora of structures contrasts with a dearth in the underlying shales. The nodular pyrite occurrences characteristic of the latter were not observed in this unit. And finally, the abundant limestone in the Lower Black Shale Complex, contrasts with its absence here. However, calcite is present especially as conspicuous white fracture fillings related to faulting.

Carbonates: Dolomite takes the form of idioblastic-hypidioblastic crystals of decimicrometer (10-100) size, being mostly less than 50 micrometers. A rare presence of loaf-shaped dolomite crystals (< 200 micrometers) enhanced by interstitial opaque matter was noted, and resembles a limestone with a pseudospar fabric (formerly a micritic limestone) described by Folk (1965). Dolomitization (and previous diagenetic stabilization) may

obscure microscopic evidence of a detrital nature. Local cross-bedded dolostones are composed of interlocking, hypidiotopic crystals (< 75 micrometers) which no longer exhibit (microscopic) clastic traits.

Although limestone does not occur, minor calcite is present and occurs as fracture and cavity filling, along stylolites, and as occasional grains and xenotopic crystals (< 100 micrometers). Movement along fractures is indicated by the presence of strained crystals. Calcite in cavities usually occurs toward the center, with increasing size and surrounded by crystalline dolomite, quartz and opaques. The large (< 1 mm) cavities appear subangular to subrounded and may represent fenestrae or evaporite molds. Calcite also occurs as rare algal(?) clasts (Plate 1). The calcitic composition of the algal clasts contrasts sharply with its dearth in the surrounding dolomitic matrix.

Siliciclastics: The omnipresence of siliciclastics in the carbonates of the underlying units contrasts with their paucity in this unit. Generally, few silicates are visible in the thin sections examined; quartz being the dominant contributor. One specimen (D2-1-74) however, was observed to possess a high proportion of micas. Small (< 100 micrometers) euhedral laths appear randomly oriented in a dolomudstone. Qualitative microprobe examination revealed a Mg-K aluminosilicate believed to be phlogopite. Unlike other micas, the mineralogy, texture, size and

orientation suggests a metamorphic origin.

Authigenic minerals: Of those previously encountered, only minor pyrite was found. It usually forms disseminations. Noteworthy occurrences include a pyritized algal mat and cross-bedded dolostone. The former is comprised of fine subhedral crystals coalescing together by growth. Denser accumulations are found along algal laminae; inclusions are absent, although coalescing growth traps matrix between the crystals. The lenses and disseminations may be early diagenetic in origin.

Another unique pyrite specimen is characterized by a pyritized mass that transects the sedimentary structure, yet preserves the cross-bedding. Microscopically, hypidiotopic interlocking dolomite crystals (< 100 micrometers) and minor siliciclastics and non-metallic opaques contrast with the pyrite. The latter consists of subrounded (250 micrometers) to delicate coalesced grains extending over several hundred micrometers. The delicate nature of the interconnecting pyrite suggests precipitation in interstitial pores between carbonate grains. Subsequent growth and merging resulted in the present network of pyrite. The interstitial texture and preservation of cross-bedding suggests sulfide movement through porous clastics and precipitation along a reduction-oxidation front. Additional information will be presented in a later chapter.

Textures: The Upper Black Shale Complex distinguishes itself from underlying units by the presence of a spectrum of sedimentary (and other) structures. Cross-bedding, convolutions, intraformational breccia, cut and fill, erosional surfaces, algal(?) clasts, algal and deformed mats as well as bedding and laminations are present. Most of the particles range from silty to fine sandy (crystalline) dolomite; opaques and black particles (graphitic shale?) are also present. The structures are also defined by lithological and grain size variations. Discontinuous low amplitude stylolites, concentrating opaque matter along the length, are also visible locally. Strained carbonate crystals are frequent in fractures.

3.1.4 Stratified Dolomite and Shale Unit:

Carbonates: Dolomite is the sole carbonate present. Minor quartz grains and black organic streaks containing micas occur sporadically within the dolostone. Thin section study reveals a generally massive rock, devoid of any structures except for inconspicuous laminations and bedding. Dolostone specimens are composed of finer (< 50 micrometers) hypidiotopic to idiotopic crystals and coarser (< 250 micrometers) xenotopic to hypidiotopic crystals. Dolospar crystals in proximity to faults may reach 1 mm in length, appear strained and are oriented perpendicular to the cavity walls. The crystal cleavages (slightly curved) alter to a brownish color. The host dolostone also shows this cleavage alteration. These probably represent iron oxide concentrations

and/or substituted iron in dolomite.

Authigenic Minerals: No authigenic minerals were observed.

Textures: Other than bedding, laminations, rare cavity-filling dolomite and quartz, and evidence of faulting, the dolostones appear featureless. Laminations are defined by lighter (coarser-grained) and darker (finer-grained) dolomite crystals. Previous authors noted the presence of various breccias, nodules and rare dessication polygons. Lehmann (1974) petrographically observed small cavities with rectangular re-entrants, which he interpreted as evaporite molds. This author noted the presence of broken-up slabs of rippled dolostone along the lake edge and a possible tepee near the summit.

3.2 Upper Albanel Formation:

The distinctive nature of this formation is based upon numerous features. Lithology, depositional environment, textural maturity and color are all characteristic. The following descriptions will detail the inherent microscopic features of the various lithologies.

3.2.1 Sandy Dolostone Unit:

Sandy dolopackstone to dolograinstone: The cross-bedded dolostone

contains a variable proportion of dolomitic and quartzose clastics. Quartz, the unique siliciclastic, occurs as subrounded to rounded grains (up to 1 mm in diameter), although rare pristine feldspar and polycrystalline quartz grains were also identified. Quartz also occurs as ooid cores, as a detrital component in dolomitic intraclasts and as crystals within cavities.

Dolomite, the main clastic contributor, occurs as peloids (< 200 micrometers), various intraclastic particles and ooids. Dolomicritic peloids consist of dark, hypidiotopic crystals (< 25 micrometers). The subrounded and elongate intraclasts represent the largest particles and attain a few millimeters in length. Oolitic particles tend to be superficial-like (ie: possess few laminae). Recrystallized cores contrast readily with the commonly darker, less altered cortices.

Equigranular interparticle blocky dolospar appears to be the dominant matrix, although rare hypidiotopic, bladed crystals (< 600 micrometers) were observed to radiate from the clastics.

Textures: On account of the coarse nature, thin sections appear homogenous. Stylolites present are of the sutured (high amplitude) variety, unlike those of the Lower Albanel Formation.

Massive to fenestral dolomudstone: The dolomudstone is generally composed of finely crystalline (< 50-100 micrometers), hypidio-

topic dolomite. Isolated crystalline quartz and dolomite (< 3 mm) increase in size toward the center of cavities. Euhedral to subhedral dolomite line the cavities; coarse, anhedral quartz and dolomite may occupy the center. The dolomite bordering the cavity may be zoned, with darker, opaque cores. A few samples examined by cathodoluminescence, indicate two or three generations of dolospar. The darker (more opaque) zones are most luminescent with respect to the lighter zones.

Textures: Alternating coarser and finer laminations as well as cryptalgal evidence (fenestrae) are the sole structures observed.

Oolitic dolograinstone: Dolomitic ooids and quartz grains are the main clastics. A maximum diameter of 4 mm was noted for the former (termed pisoids). The spherical to elliptical particles are usually superficial-like (possessing few laminae). The coated grains are supported by a blocky dolospar matrix, up to several hundred micrometers in diameter. Concentric laminations consist of alternating coarser and finer dolospar, which may be modified by replacive and precipitative quartz. Coarser dolomite crystals are usually found in the more poorly preserved ooids, consistent with the degree of recrystallization. Dark cortices are common; these dolomicritic envelopes may represent the sole distinguishable evidence of ooids, especially if diagenetic alteration is extreme. Reddish-colored cortices may be due to interparticle precipitation of oxides (Plate 40) and within cortices.

Oolitic nuclei range from quartz grains to various dolomitic particles, including dolomicritic and dolospar allochems. Some ooids seem to lack nuclei.

Thin oolitic and intraclastic beds and laminations may be interlayered with lower energy (peritidal) dolostones. The numerous ooid varieties (Plate 19) and textures of these muddy dolostones contrasts with the recrystallized ooids of the cross-bedded facies. Normal, micritic, superficial, compound and dissolved varieties are commonly found together (with other detritus). The micritic types include both normal and superficial. The normal micritic variety exhibit fine and numerous (up to ten in one case) concentric laminations. The compound varieties also occur in these fine sediments and consist of several dolomicritic envelopes surrounding multiple oolitic nuclei (Plate 19). The resulting particle clusters are often asymmetrical in shape. Other particles, such as the dissolved ooids, are abundant here and are not found in the dolograinsstones. Dark dolomicritic envelopes surrounding dolospar-filled roofs and sediment-filled bases is characteristic (Plate 33). Occasionally the dolomicritic cortices of these grains are cracked due to compaction and/or to veins (Plate 34). The various particles may be modified partially or completely by numerous diagenetic processes (ie: diagenetic stabilization, dolomitization and silicification). The implications of diagenesis will be discussed in a later segment.

Textures: The oolitic grainstones exhibit no obvious structures in thin sections on account of their coarse granularity. However, ooids associated with dolomudstones are laminated, bedded and have sutured stylolites. A rare example of imbricated, oolitic intraclasts was found associated with algal laminations and columnar stromatolites. This outcrop also hosts rare "T"-shaped fenestrae-like cavities, several ooid varieties and a unique euhedral mold of a crystal cluster (Plate 19). The crystal cavity may have been occupied by an evaporitic mineral. However, qualitative microprobe analysis indicates remnants of a chlorite-like mineral, believed to be of a secondary (unknown) origin.

Interbedded dolomudstone to dolopackstone: Various proportions of quartz, dolomitic intraclasts, peloids and ooids, make up the main detrital elements of these rocks. Except for the ooids and intraclasts, diameters are usually less than 1 mm. Quartz occurs as (+ strained) single and polycrystalline crystals, some of which possess sutured boundaries. All these particles usually occur together in the limited dolopackstone occurrences and are supported by (50-250 micrometers) hypidiotopic dolospar.

Certain dolomudstone layers and intraclasts appear extremely fine-grained (dolomicritic). The hypidiotopic crystals are less than 25 micrometers in size. Dissolved, superficial and micritic (normal) ooids are common.

Minor particles observed include feldspar, chert and radial fibrous grains. Of these, the radial fibrous allochems are the more abundant and distinctive particles. They are characterized by brownish, irregular to smooth laminations, within which fibrous-like dolomite is oriented perpendicular to the latter. Based on several clastic (and "in situ") occurrences, the fabric forms by early precipitation in cavities or on surfaces. The entrapment of quartz grains supports this interpretation.

Textures: Excluding the ubiquitous laminations and bedding, distorted and disrupted laminations are present and are believed to have originated by compaction of water-saturated mud. The disrupted fabric is typified by irregular curly laminations that often separate and are filled by quartz. A dessication-dehydration mechanism may be involved.

Imbricated oolitic intraclasts were noted in thin interbeds of oolitic dolopackstone-grainstone (Plate 31). Bedding, laminations and high amplitude stylolites are present in most lithologies. Rare microstructures, characterized by several thin dolocrystalline laminae are visible in thin section. These laminations appear to contour over an irregular clastic surface and the dolomitic allochems in contact do not show any dissolution effects. The structure appears to be a precipitated surface, possibly of algal origin.

Oncolitic dolostone: The oncolitic dolostone appears to be grain-supported (Plate 20) and is also interlaminated and bedded with cryptalgal laminations (and locally in stylolitic contact with dolomudstone). Numerous concentric to irregular laminations are composed of fine dolomitic crystals (< 75 micrometers). Occasional imbedded quartz grains indicate algal binding. Smaller oncolites act as nuclei for growth. The matrix consists of intraclasts and smaller oncolites. Coarse dolospar and crystalline quartz occupy the numerous cavities.

The finely crystalline (< 25 micrometers) algal laminations form discrete bands and commonly grow over and conform to the stabilized oncolites.

Textures: Excluding algal laminations and stylolites, fenestral cavities and shelter porosity constitute the most obvious structures. Shelter porosity forms when clastics of various diameters are imperfectly stacked (Plate 20). It was previously believed that the presence of fenestrae in grainstones was indicative of subaerial exposure. However, Shinn (1985) found that such fabrics may form in subtidal environments as well.

3.2.2 Banded Dolostone Unit:

Stromatolitic dolostone: Both larger and smaller columns were observed along the island chain. The latter appear to be textura-

lly unlike the larger types and shall be examined below.

Small stromatolites are associated with both coarse and fine sediment. An example of the former consists of tiny columns and laminations overlain by a quartz dolopackstone layer. Alternating coarser (< 70 micrometers) and finer (< 25 micrometers) crystalline dolomite define the laminations. Fine (<100 micrometers) quartz grains are intermittently imbedded in the structures, implying algal binding.

In rare instances, digitate stromatolites are associated with larger fenestral domes and cryptalgalaminates, representing an upward shallowing stromatolitic cycle. The tiny columns are imbedded in laminated light to dark grey (organic-rich?) dolomudstone. The delicate columns (a few centimeters high) are composed of alternating coarser and finer dolospar. However, the laminations are distinguished by a faint, elongate fabric perpendicular to the latter (Plate 24). The slender structures (a few hundred micrometers) are enhanced by dark micrite, outlining the margins. The interior is presently composed of a crystalline mosaic of dolomite. Intercolumn fill consists of precipitative dolospar and/or dark, decimicrometer-sized dolomite sediment. Where both occur together, the dolospar occupies the upper and the dark sediment fills the lower portion of the cavities respectively.

Although peritidal stromatolites are common south of Lake

Albanel, one example of a possibly deeper water occurrence was already presented. The alternating black and grey dolomitic layers of the deeper water forms are surrounded by finely crystalline (< 40 micrometers) dolospar; fenestrae are absent. The hypidiotopic crystals are homogeneous, except for faint coarser bands which seem to grade imperceptibly into the fine dolospar.

The stromatolitic upward cycles are characterized by laterally linked hemispherical columns overlain by partially chertified cryptalgalaminates, showing extensive laminoid fenestrae alternating with dolomudstone. The encasing dolostone is composed of hypidiotopic (50-100 micrometers) crystals. Infrequent coarser and finer grained patches are present within the otherwise homogenous dolomite. Rare detrital (< 50 micrometers) quartz is dispersed throughout.

Small (< 10 cms) digitate columns were observed at another locality. The dark stromatolitic dolomudstone is surrounded by grey dolomitic crystals (< 100 micrometers) that appear featureless, except for ubiquitous sutured stylolites. The notable feature of this occurrence is that the stromatolites appear to have colonized a low energy trough-shaped depression (tidal pool?).

Textures: Laminated and bedded sedimentary structures are

ubiquitous. Additional structures include eroded stromatolites, high amplitude stylolites, cemented domal fenestrae, intercolumn sediment and dolospar-fillings and an acicular to bladed fabric.

Cryptalgalaminated dolostone: Although most were found in the southwest extremity, cryptalgalaminates are also present on the northeastern islands of the map area. These rocks are characterized by both distorted and planar fabrics. Plate 8 illustrates a dark, fenestral cryptalgalaminate overlain by dolowackestone and dolopackstone. Dolomite-filled fenestrae are truncated by an erosional surface. A closer inspection discloses the presence of local radial fibrous dolospar crystals (< 100 micrometers) forming irregular laminae (Plate 22). The significant feature is that this fabric is not entirely found within the fenestrae, but is also found in the surrounding dolomite. The fabric is not extensive and is most evident just below the erosional contact. The fibrous crystals formed in syn-depositional cavities or as crusts, probably related to the presence of algal mats. Fragments of a similar fabric were noted in the overlying clastics, confirming a syn-sedimentary origin. This fabric is not unlike the Aphebian cryptalgal tufas found by Grotzinger and Reed (1983). Eriksson (1977) described fibrous blades oriented perpendicular to algal laminae in the Aphebian Malmani dolomite, and interpreted as algal moulds. A direct or indirect algal role may be involved here.

The straight, erosional contact also hosts microrelief. Microscopically, the sharp vertical walls of the microcavities, filled with fine detritus, imply erosion of a lithified surface.

As previously noted, stromatolites along the south shore of Lake Albanel grade upward into smooth, scalloped and blister-like cryptalgalaminates. Microscopically, the lithology consists of finely crystalline dolostone devoid of detrital quartz. Certain laminae consist of alternating finer (< 25 micrometers) and coarser (< 75 micrometers) crystalline dolomite forming a continuous to discontinuous fabric. Irregular blotches and streaks of brownish micritic dolomite are commonly interlaminated with coarsely crystalline dolomite and quartz fenestrae. Bands of brownish micritic dolomite, apparently unrelated to the mats, occasionally host cubic to rectangular, poikilotopic quartz pseudomorphs (< 75 micrometers) possibly after evaporites.

Limited amounts of oval-shaped peloids (< 1 mm) formed by the erosion of porphyrotopic dolomicrite (hosting poikilotopic quartz crystals), is found in some of the dolomudstones. Fabrics resembling a clotted texture consist of isolated patches of fine dolospar surrounded by coarser dolomitic spar. An algal fragment (< 1 cm long) with a faint linear fabric perpendicular to the laminations, resembling the radial fibrous laminae commonly observed in oncolites and stromatolites, was also noted.

Textures: Distorted to planar laminae, fenestrae, erosional surfaces and radial fibrous fabrics complement the usual sedimentary structures.

Oncolitic dolostone: Only a few examples were noted in the central island chain. Rudite-sized oncolites associated with an intraclastic layer possess numerous concentric laminations, which smoothly surround the rounded to rod-shaped nuclei. The laminae are composed of alternating finer and coarser decimicrometer-sized dolomite crystals. The shape of the core dictates the morphology of the oncolite. Quartz grains, dolomitic intraclasts, slender algal "rods" and radial fibrous clasts compose the matrix. The improper packing of these particles results in abundant cemented shelter porosity. According to Logan et al. (1964), the oncolites would correspond to type "c" structures, which form in shallow waters of frequent turbulence.

Concordant cavities unrelated to sediment packing are also present. Both types of cavities are lined by several generations of dolospar; quartz and iron oxides concentrate toward the center. The presence of radial bundles of acicular (Fe-oxide enhanced) crystals projecting downward into the cavity (Plate 35) was also observed. Such gravity-controlled pendant cements would be expected to form in the marine vadose zone.

More tranquil conditions characterize the second occurrence.

The specimen consists of alternating bands of algal laminations and tiny laterally-linked stromatolites interlayered with dolowackestone and dolopackstone. The latter contains peloids, algal fragments and dolospar surrounded by micritic cortices. The finer grained, darker matrix hosts traces of replacive quartz. Algal laminations commonly overly and contour the stationary oncolites. The latter (< 1 cm) are composed of alternating fine and coarser, decimicrometer-sized dolomite crystals. Evidence suggests that the laminae were partially rigid (ie: brittle), yet other portions were sufficiently flexible to enable folding upon itself due to turbulence. Oncolites are irregular in morphology; nuclei are composed of smaller, truncated oncoids. The sequence: growth ---> inversion ---> erosion ---> re-established growth on the inverted surface, represents the sequence of events typical of type "I" oncolites (Logan et al., 1964).

All but one of the oncolites found along the south shore of the lake consist of quiet water varieties. The oncolites (< 2 cm) are generally composed of alternating, irregularly interlaminated coarser and finer dolospar, and chert. Chert appears fabric selective, often forming concentric zones within the interior. Several oncolites possess truncated internal structures, suggesting growth, inversion, erosion and/or dissolution and periodic agitation resulting in subsequent growth in new orientations.

A rare rudite-sized oncolitic dolostone appears to be

grain-supported and is associated with peloids and various micritic intraclasts, set in a dolospar and quartz matrix. Plate 23 also illustrates a radial, bladed to acicular fabric (enhanced by micrite) commonly seen in various algal structures. In the cavities, mega-quartz usually obstructs the center, whereas dolomite lines the openings. The fabric selective chert is paragenetically earlier than the mega-quartz.

A few questionable oncolitic occurrences were also noted. One consists of a brownish micritic dolostone with abundant coated grains and spar-filled cavities. The largest measured was 10 mm in diameter; however most are less than 2 mm. The coated particles consist of few, poorly defined concentric laminae. Coarser dolospar, chert and micrite make up the latter. Detrital porphyrotopic dolomicrite, peloids and rare dissolved ooids occasionally form the nuclei. An in situ formation of the coated grains is suggested (Plate 24) on the basis of similarity between the particle fabric and that of the matrix. Fenestrae, brecciation and non-tectonic fractures are locally visible. The exterior concentric lamina is often spar-filled and suggestive of circumgranular cracking. Similar traits and related spar-filled cavities characterize caliche pisoids (Esteban, 1976). Although the irregularly laminated and brecciated nature is consistent with such an interpretation, a more detailed investigation of this occurrence may be required to ascertain its exact origin.

Another dubious example is represented by a poorly concentric fabric illustrated in Plate 25. A concentric shape is suggested by the fabric-selective chert laminae and remnant dolospar arcs. This unique specimen is distinguished by divergent tapering rays (< 3 mm in length) of acicular habit, now replaced by polycrystalline (< 75 micrometers) dolospar. The rays are best developed in the upper portion and diminish in extent and preservation laterally due to more intense chertification, stylolitization and/or inhibition of lateral growth. Lateral obstruction resulted as several fans diverged by growth. The rays are enhanced by dark dolomicrite, believed to be of detrital origin, based on the presence of silt-sized quartz grains interstitial to the rays and in the overlying dolomicrite matrix. The crystals may have grown unhindered into the overlying water; settling and infiltration of dolomicrite was synformational with growth. Alternatively, the rays may also have grown within the sediment, pushing it aside as growth proceeded. In any case the rays were at least 3 mm high before an intraclastic layer was deposited, with little apparent damage.

Assereto and Folk (1980) described unusual diagenetic carbonate fabrics occurring within tepee cavities. These include paleo-aragonitic flowstones, giant (raggioni) and microscopic paleo-aragonitic crust and hemispheres. However, many of the radial-fibrous occurrences described in the present author's investigation are related to algal structures and a cavity and

vadose origin for the paleo-aragonitic structures described by these authors is not entirely applicable here. The presence, however, of gravity cements in cavities (Plate 35) is consistent with a marine vadose origin.

Textures: The most distinctive structures include the alternating algal structures and clastic layers, the oncolitic symmetry versus asymmetry and radial fibrous cement fabrics. Bedding, laminations and stylolites are ubiquitous.

Interbedded dolomudstone to dolowackestone: The central island chain and south shore of the lake are dominated by these lithologies, although minor dolopackstone and intraclastic layers occur sporadically in the former area. The sole conspicuous detrital component (if present) in the dolomudstones is quartz. Dolomudstones consist of finely crystalline, hypidiotopic dolomite, which may reach micritic dimensions. Under the microscope, these layers appear dark brown and not uncommonly show evidence of replacement. Rectangular to ellipsoidal cavities (centimicrometer-sized) are filled with polycrystalline dolomite or poikilotopic mosaic quartz. Inclusions in the latter consist of unreplaced dolomite. Based on their rectangular to cubic form, occurrence in micritic dolostone and locally associated with intraformational breccias and cryptalgalaminations, evaporites are inferred. These finely crystalline dolostones also occasionally host sporadic centimicrometer-sized micaceous patches of unknown origin.

Clastics in the dolostones include subrounded to subangular quartz (minor chert) as well as dolomitic peloids, intraclasts and rare ooids. Less commonly, dolomitic micrite and pseudospar surrounded by micritic envelopes are present. Although not abundant, a few grains of brownish radial fibrous spar are usually present in the coarser-grained samples. The largest fragment observed (<3 mm) consists of several thin laminae of perpendicular acicular to bladed dolomite crystals. Where laminae are straight, extinction is complete; if curved, a sweeping (undulose) extinction is characteristic. The crystals are a few tens to hundreds of micrometers long and formed as crusts or along cavity walls. One example of a brownish (finely bladed) lamina was observed at the base of a clast, suggesting a pendant cement. A syndepositional origin for some of these fabrics at or near the surface (marine vadose zone?) would be consistent with their common detrital occurrence.

Spar-filled cavities are ubiquitous and take the form of laminar to discontinuous pods and fenestrae. Numerous generations of dolomite line the openings; quartz and iron oxides usually occur toward the center. The red and yellowish oxides probably represent hematite and goethite respectively, although Fischer (1963) indicated that goethite is rare in ancient sedimentary rocks since it ages to hematite. A unique example of a black

mineral suspected to be magnetite was noted in the center of a cavity. A decrease in Eh towards the center of cavities, during progressive cementation is a common diagenetic phenomenon. Chevé et. al. (1985) reported a similar decrease within birdseyes of Aphebian dolostones, aided by cathodoluminescence, microprobe, as well as observing the presence of sulfides. Evidence indicates that much of the dolospar precipitated early (near surface) and during later burial; a detailed distinction was not attempted. However, the more coarse dolomite (and quartz) in the center of cavities, as well as tectonic-related dolomite are unequivocal examples of late cements.

The southern shore is underlain by similar lithologies. Most of the dolostones studied consist of hypidiotopic (< 25-50 micrometers) crystals. Peloids and intraclasts represent the coarsest dolomititic allochems; the latter may attain a maximum of a few centimeters. Quartz grains (< 1 mm) never reach more than a few volume percent. Several examples of (inferred) evaporite molds and pseudomorphs of various crystal habits are commonly found in darker micritic and cryptalgal dolomudstones (Plates 26 and 27), suggesting more arid conditions.

Although fine crystalline size is the norm, coarsely crystalline dolomite fabrics occur locally. A thin section of the severely recrystallized dolostone (Plate 16) presented in the previous chapter, reveals an inhomogenous distribution of size

and shape of the dolomitic crystals. The somewhat radiating fabric is characterized not by a fine mosaic, but by slender bladed crystals (< 1 cm) with serrated boundaries (Plate 28). The presence of abundant fractures and associated fragments, occasional strained precipitative megaquartz, as well as the severe recrystallization, suggest a tectonic influence. The radiating fabric may represent a vestige (aragonitic?) cement fan after fault-induced recrystallization.

The area is distinguished by the unique presence of chert beds, laminae and nodules. The laterally extensive layers are composed of a fine (< 25 micrometers) quartz mosaic replacing and isolating dolomitic patches and crystals. Chertification appears to be post-dolomitization, although early. A late silica precipitate consists of coarsely crystalline megaquartz occluding the central portions of cavities.

East of the zone bordering the southern shore of Lake Albanel, the dolomudstones to dolowackestones are stratigraphically overlain by higher energy sediments of the Temiscamie Formation. More agitated conditions are represented by outcrops of oolitic iron formation. The latter is characterized by magnetite granules set in a cherty matrix (Plate 41).

Textures: Ubiquitous bedding, laminations and stylotites are complemented by various algal structures, evaporites, distorted

laminations and cement fabrics. Contacts between finer and coarser lithologies may be straight or irregular and commonly sharp. Where sharp contrast in lithology is evident, stylolites are usually responsible for the juxtaposition.

3.3 Precursor Mineralogy of the Mistassini Carbonates

Petrographic and field evidence suggests that the carbonates were deposited in generally warm, shallow marine water of normal to elevated salinities. Today the most common carbonate minerals in such environments are high magnesium calcite and aragonite. Based on textural evidence, it is suggested that both HMC (LMC ?) and aragonite were initially present. A case shall be developed for each in the following section.

3.3.1 Evidence for Aragonite:

The presence of radial acicular (long fiber) and tapered fabrics (growing downward from cavities, Plate 35; upward from sediment, Plate 25; and as slender crystalline pointed to square-tipped forms in algal structures, Plates 21, 23 and 37), dissolved ooids (indicative of oomoldic porosity, Plate 33), recrystallized oolitic dolograins (Plate 40) and the rare presence of (dissolved?) intraclasts now occupied by coarse precipitative spar (Plate 31), all suggest an aragonitic precursor in the Upper Albabel dolostones. The inferred warm, semi-arid depositional

environment, including local above normal salinity, would certainly be conducive to aragonite precipitation. The presence of precursor aragonite in other Aphebian dolostone sequences has already been demonstrated by Grotzinger and Read (1983).

The absence of internal fabric preservation is consistent with the accepted notion that the inversion of aragonite to low magnesium calcite results in the obliteration of textural integrity (Given et al., 1985). Zenger (1982) noted that early dolomitization (especially of HMC) resulted in good textural preservation, unlike aragonite. For example, Loucks and Folk (1976) described dolomitized aragonitic cements, which were characterized by preservation of the exterior morphology only. Furthermore the simultaneous occurrence of different ooid textures suggests different metastable mineralogies, although different crystal size (hence solubility) could also be involved.

In contrast, the Lower Albanel Formation carbonates show no petrographic evidence of a former aragonitic precursor. The absence of textural evidence for aragonite may be due to the different depositional setting (ie: deeper water), where a significant portion of finer-grained carbonates may have been of detrital origin or to lower sample resolution due to the nature of the core sampled. Alternatively, these sediments could have had a calcitic precursor.

3.3.2 Evidence for (High Magnesium) Calcite:

The occurrence of acicular, short fiber cements (Plate 22), radial acicular to bladed dolospar (Plate 36), rare isolated ooids with preserved concentric fabrics (compared to the obliterated aragonitic fabrics), as well as the simultaneous occurrence of different ooid textures, suggest an original magnesium calcite mineralogy in the Upper Albanel Formation. Tucker (1982) reasoned that good fabric preservation in Precambrian ooids probably indicated a HMC mineralogy, whereas fabric obliteration suggested dolomitization of stabilized aragonite. The vast majority of ooid fabrics are textually altered, but rare cases of isolated dolomicritic ooids are an exception. Observed locally in dolopackstones, certain dolomicritic ooids were seen to possess numerous concentric laminations. The preservation may be a function of lower permeability and initial HMC mineralogy.

The Lower Albanel Formation is devoid of any petrographic evidence for original magnesium calcite. Chemical and isotopic data, however, suggest the existence of both precursor aragonite and magnesium calcite, and will be presented in the appropriate chapters.

3.4 Chapter Summary

The lower units of the Lower Albanel Formation contain a variable proportion of finely crystalline dolomite, coarser primary and secondary calcite and argillaceous to immature silty and sandy siliciclastics. Authigenic minerals include coarsely crystalline quartz as well as early to later diagenetic pyrite. Dolostones in the Stratified Dolomite and Shale Unit and overlying Upper Albanel Formation consist of finely to very coarsely crystalline dolomite. The immature siliciclastics of the Lower Albanel Formation are replaced by mature coarse-grained quartz and various dolomitic allochems in the Upper Albanel Formation. The latter formation also hosts numerous dolomitic cement and ooid fabrics suggesting the existence of both aragonite and HMC precursors.

CHAPTER 4

DIAGENESIS4.0 Introduction

Samples of the Upper and Lower Albanel Formations have been subjected to diagenetic processes and evidence for the latter will be presented in this chapter. A general summary of the diagenetic processes and inferred paragenetic sequence is illustrated in Figure 4.

4.1 Upper Albanel Formation

4.1.1 Silica Diagenesis:

The portion of the Upper Albanel Formation investigated is characterized by the presence of replacive chert, minor replacive and abundant precipitative crystalline quartz.

The majority of the chert observed is found south of Lake Albanel, occurring as beds, laminations and nodules. The chert appears fabric selective (Plate 8), as it is frequently associated with algal structures. The remainder of the underlying formation is dominated by late precipitative crystalline quartz (of various sizes) and only minor replacive chert. Chert occurs

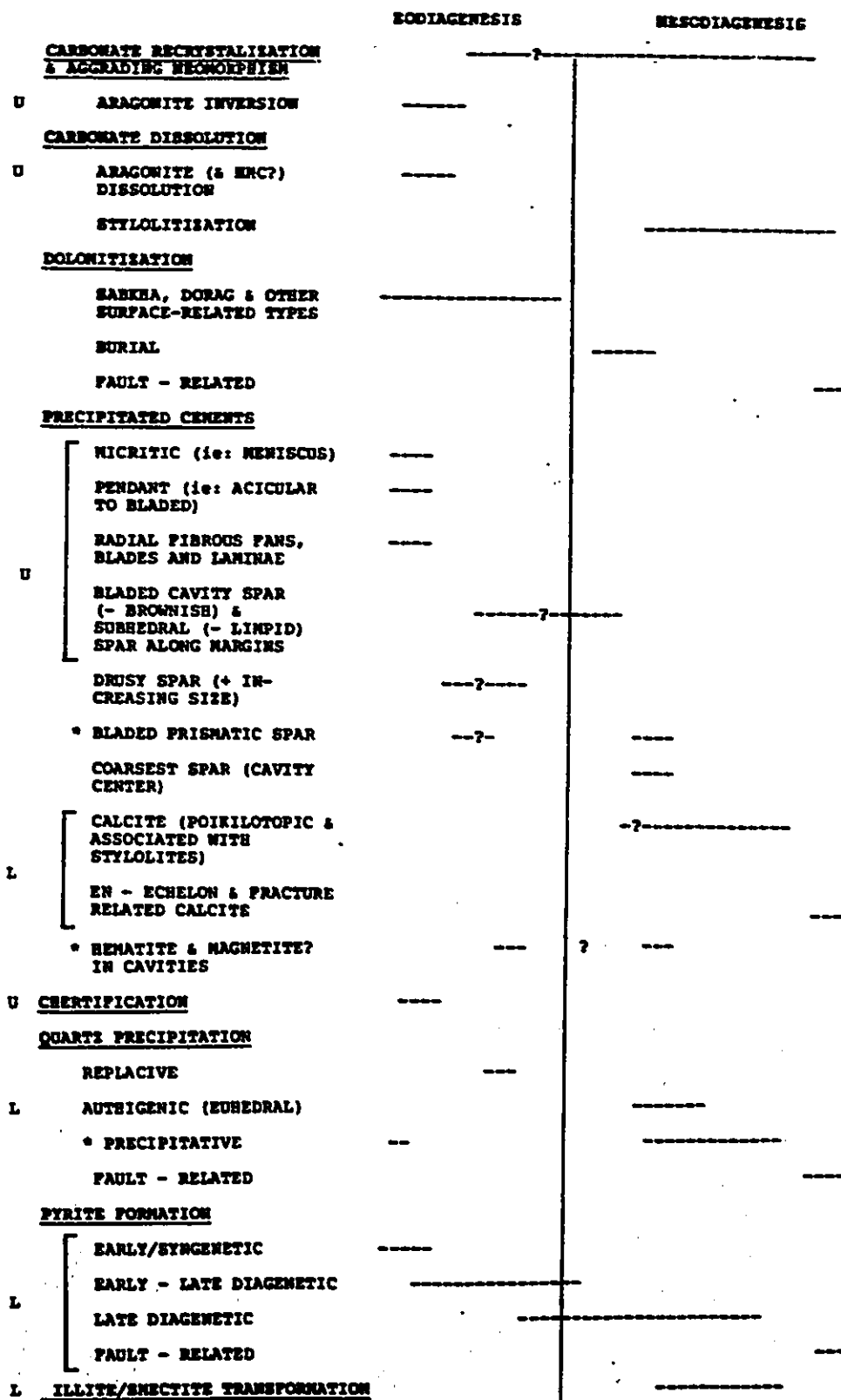


FIGURE 4: GENERAL SUMMARY OF DIAGENETIC PROCESSES AND INFERRED PARAGENETIC SEQUENCE FOR SAMPLES OF THE UPPER & LOWER ALBANEL FORMATIONS. Horizontal lines represent inferred relative sequence of events. The relative sequence between certain diagenetic processes can only be approximated. Early cements include micritic, pendant and various radial fibrous fans, blades and laminae. Later cements include bladed, drusy, subhedral-euhedral, prismatic and very coarse spar. Due to lack of resolution, certain cements are grouped together or denoted by "?". All cements are dolomite, unless otherwise indicated. An "*" denotes both apparently early and late cements. Occurrence in the Upper (U), Lower (L), or combined formations (unmarked) is indicated as shown.

as rare nodules in dolomudstone, as detrital grains, ooid nuclei in the coarser grained facies, as chertified ooids and as a rare cavity precipitate.

Excluding the dominant quartz fabrics, minor replacive quartz and chert are also present in the Sandy Dolostone Unit. Chert grains, ooid nuclei, and chertified oolitic dolostones were observed. The chertification may locally exhibit a sharp boundary within a single thin section. Plate 29 represents the lower portion of a thin section of an oolitic dolograinstone. The chertified portion is sharply separated from the overlying dolomitic-cemented dolograinstone (showing little evidence of chertification).

In the Banded Dolostone Unit, quartz also occurs as either individual crystals or crystal mosaics in the finest, dark brown (micritic) dolostone components. Occasionally they occur in cryptalgalaminates. The quartz can take the form of poikilotopic, anhedral crystals or pseudomorphic replacements with rectangular edges, possibly after evaporites.

The timing of chertification appears to be early although post (early) dolomitization. The fabric selectivity of chert, the presence of detrital chert grains as well as occurrence in oolitic dolostones suggests an early process. Chertification of oolitic layers suggests that porosity must have been still

available (hence an early process for the silica solutions to migrate). The contrasting nature between chertified and pristine oolitic dolograins segments, as observed in thin section (Plate 29) suggests that the latter upper portion probably owes its survival to an anterior cementation by precipitation of carbonate into the pores. The lower cherty part was probably more permeable and porous; waters of the proper chemistry were permitted to migrate and react. Silicification appears to affect either the core, cortex or the whole ooid. Although dolomitization is usually earlier, the euhedral dolomite crystals forming the cortices or within the ooids compared to the subhedral recrystallized cores, suggests that the former are post chertification (Plate 38).

Paragenetically, precipitation of the majority of the coarsely crystalline quartz occurred last, during and after burial. The coarse, increasing crystal size and its central position in cavities supports this. However, some evidence of earlier crystallization was found in certain algal structures. The preservation of algal (fenestral) cavities in stromatolitic domes by precipitating quartz (and in part by carbonate cementation of the column), prevented subsequent compaction. A striking example of early precipitation is shown by a distorted cryptalgal dolostone (Plate 12). The distorted nature indicates plasticity of the initial mud; yet such deformation should have obliterated the fenestrae. Hence early precipitation would have prevented the

obliteration of the cavities as deformation ensued.

Examples of early chertification and silicification imply less alkaline pore water conditions. A unique example of the effect of higher alkalinity on quartz was observed in thin section. Plate 30 is a photomicrograph of a dolomitized, intensely recrystallized (< 500 micrometers) oolitic pseudospar. The oolitic fabric is barely discernible. The quartz layer is composed of serrated detrital quartz. Significantly, this is the only specimen showing both intense recrystallization and dissolution of detrital quartz. This may suggest that the higher pH may have affected both quartz dissolution and dolomite recrystallization.

The source of silica for chert appears to be the contemporary seawater. Due to the probable higher concentration of dissolved silica combined with the absence of silica-secreting organisms in the Precambrian, Holland (1984) suggested that mildly evaporative environments would be favorable to chert precipitation, consistent with the described depositional setting. The commonly observed association of chert and stromatolites appears to be the result of a decrease in pH due to the decomposition of organic matter (Veizer, 1978b).

The major source of late silica is the dissolution of silica phases during diagenesis. Kerans (1982) suggested that the

dissolution of detrital quartz may be a source of silica for overlying strata.

4.1.2 Carbonate Diagenesis:

1) Early Cementation: Although later cavity-filling is commonplace, numerous examples of early cementation were observed especially in the Upper Albanel Formation. This may be due to the availability of core instead of field evidence, or simply to the preponderance of submerged conditions in the Lower Albanel Formation. Evidence of early cementation appears more varied in peritidal to shallow water depositional conditions, where the diagenetic potential is enhanced. Such appears to be the case for the Upper Albanel Formation.

Examples of syndepositional cementation were observed both in the field and in thin sections. The presence of intraformational breccias (Plate 11), broken and plastic fragments, straight erosional surfaces (Plate 10), tepee structures (Plates 9 and 15), as well as preservation of fenestrae (Plate 2), are some field examples. Lithified surfaces (subaerially exposed) are occasionally visible (Plate 10). Other evidence involves stromatolites, which are an adaptation to colonizing rigid surfaces. The occurrence of tiny algal columns upon distorted (previously fluid) dolomudstone suggests colonization of a rigid surface, after distortion and cementation. In another instance, small columns (< 10 cm high) appear to occupy a partially filled

depression (channel or pond?), whose surface must have been cemented.

Abundant petrographic evidence is reflected by the presence of various syn-sedimentary precipitates. For example, truncated cement fabrics (Plate 10) are also accompanied by sharp micro-relief along erosional surfaces and can only be explained if the latter was a cemented surface. Further evidence is found in the formation of compound ooids (Plate 19). Compound ooids form in less frequently agitated environments (Flügel, 1982) where precipitation during (by algal CO₂ intake?) periods of "rest" would permit cementation. But unlike grapestones, these would be later agitated and transported elsewhere. The resulting allochem would host not one, but several (oolitic or other) nuclei. A different example involving ooids is illustrated in Plate 31. Here, an oolitic layer was sufficiently undisturbed to be cemented, but not to withstand periodic high energy conditions (storms ?), resulting in break-up and imbrication.

The precipitation within cavities was found to be both early and late (burial stage). The source of precipitated early spar is due to early diagenetic processes at or near the surface. The common presence of concordant and discordant spar-filled cavities such as sheet cracks, probably occurred early. The precipitation of diverse fibrous to bladed fabrics (some presumably aragonitic and others possibly of algal origin) occur as laminae, fans and

ray-bundles. Such fabrics probably formed on and within (peritidal) algal framework (or cavities) and subsequent erosion resulted in their deposition in the overlying sediments (Plate 10). Most of these allochems were found on islands located at the southwestern margin of the island chain (Appendix 1), within coarser-grained interbedded dolostones.

Another example of early precipitation consists of detrital allochems with quartz grains imbedded within (Plate 32). The incorporation of detrital quartz along laminae, followed by additional growth and subsequent erosion and deposition, is quite evident.

The early precipitation of carbonate in cavities was often forceful. The expansive nature (known as the "force of crystallization") is well illustrated in peritidal tepee structures (Plate 15). Assereto and Kendall (1977) initially indicated that in subarid conditions, sufficient force could be exerted by carbonates to deform beds, providing that supersaturation in cavities prevailed. They indicated that supersaturation could be more easily maintained in more arid environments, where little dilution, frequent changes in temperature as well as maintaining an ion supply by waves, dessication and seaspray, would be likely.

2) Diagenetic Stabilization - Evidence of vadose and phreatic

diagenesis: A shallow water to peritidal depositional environment represents an active diagenetic environment conducive to the stabilization of metastable phases. Diagenetic stabilization of metastable phases occurs in the vadose and phreatic zones, under the influence of meteoric water. Field evidence (already presented) as well as additional petrographic evidence shall be offered below.

a) Dissolved Ooids: These occur as interlamination and beds within dolomudstone. The fabrics are characterized by micritic envelopes and by the conspicuous presence of dolospar roofs and basal internal sediment (Plate 33). Thus dissolution (ooidic porosity), deposition of sediments and subsequent precipitation of spar (now dolomitized) is envisaged. Dissolution in the meteoric vadose or phreatic zones is indicated; where a meniscus-like fabric is also present (Plate 33), the former environment was likely.

The micritic envelopes which contrast readily with the recrystallized interior could have been indirectly algally generated. Organic substrates are known to enhance nucleation of carbonates as well as inhibit dissolution (Carlson, 1983). The latter combined with the algal content of ooids, suggests that organic matter may form lower-energy surfaces with carbonates. Plate 34 illustrates rupturing of the micritic cortex indicating that the mold was unable to withstand the compressive growth of

coarse crystals nearby or the loading. The following sequence of events is suggested: dissolution--> deposition--> cortex rupture--> and either precipitation of spar and dolomitization, or early dolomitization followed by precipitation of spar and later dolomitization. Further evidence of early dissolution is indicated by the rare presence of detrital, thin concave fragments interpreted as micritic envelopes of ooids. If this interpretation is correct, then the oomolds were exposed to erosion and hence not buried.

The stylolitization of dissolved oolitic allochems indicates a pre-stylolite origin, consistent with an early dissolution event.

b) Recrystallized Ooids: The presence of coarsely crystalline oolitic dolograins (Plates 29 and 40) is consistent with the diagenetic stabilization of an aragonitic precursor in a meteoric phreatic environment. This is supported by the isotopic composition of the oolitic dolograins, which will be presented in chapter 6.

c) Meniscus Cements: Rare meniscus-like dolomicritic cements (Plates 31 and 33) were found in an imbricated oolitic dolostone and in an interlaminated oolitic dolomudstone, respectively. If these indeed were meniscus cements, then a vadose zone is indicated. Such fabrics form where capillary water adheres to the

grains and precipitation is favored there.

d) Pendant Cements: Plate 35 illustrates several generations of dolospar. One of the earliest is a gravity controlled cement underlying an algal allochem. The acicular to bladed crystals are enhanced by iron oxides and appear to form tapered, radiating fans interpreted as aragonite. Such fabrics are expected to form in a marine vadose zone. The presence of a brownish (<50-100 micrometers), bladed cement underlying clasts in a dolopackstone, has already been presented.

e) Caliche-like Fabric: An example of a caliche-like (?) fabric is shown in Plate 24. The underlying oncolitic and cherty beds appear to be overlain by a fractured, fenestral dolomicrite with a pisolitic fabric. Although a detrital origin is suggested, a closer examination discloses interesting characteristics. The textural similarity between allochems and matrix as well as the prominent spar-filled cortices (circum granular cracking?), suggest a caliche origin (Harrison and Steinen, 1978). If correct, these fabrics and associated clotted and fenestral textures indicate subaerial (vadose) diagenesis. Nearby radial fibrous to bladed bundles growing downward from cavities, imply the influence of nearby seawater.

f) Various Radial Fibrous-Bladed Occurrences: The various cement fabrics may be the result of both inorganic and possibly (indire-

ctly or direct) algal-mediated carbonate precipitation. Examples of the former include pendant, upward radiating, irregular crusts(?) with detrital quartz grains and certain cavity cements. The fibrous to bladed fans growing downward into a cavity (Plate 36) are composed of elongate crystals and not mosaics. This specimen underlies the caliche-like(?) fabric just described and is consistent with a vadose depositional environment. The habit of these crystals suggests the occasional influence of seawater. The crystalline fans host fine, concordant cherty laminae consistent with an early origin.

A unique upward-radiating fan, possessing a tapered fabric is composed of a fine crystalline dolomitic mosaic (Plate 25). This structure may represent a marine acicular aragonitic cement. The unique growth orientation, coupled with fine detrital sediment interstitial to and overlying the acicular fabric, suggests growth in shallow tranquil seawater or within the sediment.

Mazzullo (1980) described botryoidal and fan-shaped acicular marine cements that formed in cavities or precipitated on the seafloor. Superficially, the set of divergent fans (Plate 25) resembles that described by this author. Grotzinger and Reed (1983) noted the presence of upward growing cement fans in Aphebian dolostones of the Rocknest Formation (N.W.T.). They concluded that these aragonitic fans formed subtidally in a

shallow marine shelf environment. The occurrence in peritidal dolostones indicates shallow water conditions.

One unusual specimen is fractured and intensely recrystallized, as indicated by the coarse crystal size and serrated crystal borders (Plate 28). Its coarse texture suggests that it may represent a vestige of an aragonitic ray-bundle after fault-related recrystallization. XRF analysis of the bulk rock as well as microprobe examination revealed no indication of an aragonitic precursor.

The reported occurrence of radial-fibrous laminated fabrics in stromatolites is common. Hofmann (1978) noted the presence of "radiofibrate" microstructures in certain Belcher Island stromatolites. Hofmann and Grotzinger (1985) suggested that the precursor of the radial-fibrous microstructure in Frutexitites was probably aragonitic. Hofmann and Jackson (1987) suggested that a chemical or biologic origin may be distinguished by examining the cross-section of the fabric.

Many of the biogenic structures observed are characterized by fibrous to bladed dolomite (centimicrometer) crystals, aligned perpendicular to the laminations. The resultant structures (now comprised of polycrystalline dolomite) often resemble "crowns". They occur in stromatolites, oncolites and cryptalaminates, as well as detrital particles. The algal association (Plates

21,22,23 and 37) is well founded and may suggest some sort of algal influence (Hofmann and Jackson, 1987). The concomitant lack of evident binding textures, as observed in other samples, is consistent with a precipitative hypothesis.

3) Burial Cementation : Although no detailed attempt was made to distinguish between burial and near surface cements, the following observations suggest the existence of burial cements:

- a) coarse xenotopic dolomite and quartz occupying cavity centers.
- b) fault associated coarse dolomitic and calcitic spar.
- c) occasional presence of elongate prismatic crystals. (Choquette and James, 1987) in the cavity center (Plate 35). (Note that certain bladed ($\pm$ prismatic) cements may probably be early, near surface precipitates, as suggested by the truncation of cements by erosion (Plate 22).)

The source of such late cements are the abundant zones of dissolution, indicated by ubiquitous high amplitude stylolites.

4) Dolomitization : The frequent excellent preservation of microtextures, common finely crystalline dimensions, lack of post-stylolite dolomite fabrics as well as the associated shallow water to peritidal depositional environments all suggest that most of the dolomitization episode was penecontemporaneous to early diagenetic. Since primary dolomitization cannot be unequiv-

ocally ascertained, the dolomitization process is assumed secondary (ie: replacive) as evidenced by the presence of various fibrous fabrics. Due to severe kinetic obstacles, primary dolomite in such crystal habits is not to be expected (Ricketts, 1983). Dolomitization of samples exhibiting sharp textural contrasts (ie: Plate 33), and features such as the preservation of dolomicritic ooids with numerous concentric laminae, all attest that early dolomitization was required to conserve the delicate textural integrity. This suggests that textural destruction may commonly be due to pre-dolomitization diagenetic processes (ie: dissolution-precipitation, inversion, aggrading neomorphism, etc.). Thus subsequent dolomitization inherits the anterior fabric whether primary or altered. Coarser fabric-destructive dolopseudospar probably resulted from more intense diagenesis (Plate 40), later burial dolomitization, recrystallization¹ and possibly from local tectonically-related recrystallization.

Evidence of later dolomitization is suggested by the presence of euhedral rhombs in chertified ooids, large euhedral zoned crystals and by coarse, xenotopic crystals. Plate 38 illustrates the contrast between euhedral rhombs in cherty ooid cortices and apparently earlier subhedral crystals in the core. Such a fabric implies post-chertification dolomitization (Swett,

¹recrystallization includes the transformation of strained--> unstrained crystals and unstrained ----> finer or coarser unstrained crystals up to and including metamorphism (Folk, 1965).

1965).

Later dolomitization also preserves anterior chemical signals and records the changing chemical conditions in the precipitating solutions. Plate 39 denotes several generations of dolospar including coarsely crystalline zoned dolomite. The zoning and relation to the cavity indicates that the dolomitization was subject to fluctuating fluid conditions but before final blocking of the cavity (hence surface related). Dull cathodoluminescence in dolomite indicates low (or inhibited) manganese concentrations.

The latest dolomite occurs as coarsely crystalline and xenotopic, fabric-destructive textures (Plate 30) and as fault dolomite. However, the difficulty in distinguishing specific dolomitization paragenesis is more pronounced in wholly dolomitized sections (as noted by Zenger, 1972).

Dolomitization Mechanisms: A penecontemporaneous to early dolomitization event has been advanced for much of the formation sampled. Early dolomitization includes such processes as reflux, Dorag, and "organic" dolomitization as used by Mattes and Mountjoy (their table 1, 1980). The relative timing of such processes would correspond to Choquette and Pray's (1970) "eogenic" stage, whereas later processes such as burial dolomitization falls into the "mesogenic" stage. These terms refer to

time intervals during which diagenetic processes are dependent upon, and independent of, surface processes, respectively. Based on the available evidence, two dominant eogenic dolomitization mechanisms are feasible. The sabkha and mixing models will be discussed below:

(1) Sabkha Model: Several lines of evidence are favorable to this mode of dolomitization. The Upper Albanel Formation reflects shallow subtidal to peritidal conditions. The carbonates were deposited in warm seawater, based on the presence of oolites and inferred aragonite mineralogy. Local elevated salinity due to higher evaporation is suggested by occasional scattered evaporites and chert beds. These molds and pseudomorphs after evaporites are commonly concentrated in (the darkest) micritic dolostone, the latter associated with stromatolites, cryptalgal structures, fenestrae, local intraformational breccias and tepee structures. Although Kendall and Warren (1987) showed that tepees can form in different environments, the association of tepee structures with shallowing upward stromatolitic cycles in the Upper Albanel Formation confirms a peritidal origin. These authors suggested that peritidal tepees form in areas of climatic extremes (semiarid climate?).

Such conditions would be expected to be highly conducive to early dolomitization by a sabkha-like mechanism, although the lack of more abundant evaporites is troubling.

Evidence of semiarid conditions by no means prevents the existence of seasonally more humid conditions. A prime example is the Precambrian Yalco Formation of the MacArthur Group, Australia (Muir et al, 1980). The Yalco Formation is an Australian Proterozoic equivalent of the Coorong model. The evaporation of alkaline ephemeral lakes results in a reflux plume responsible for dolomitization and silicification in the Yalco carbonates. Unfortunately, these authors made no attempt to study trace elements and isotopes; thus a comparison is not possible. These authors showed that seasonal humid and arid conditions existed. During dry seasons, structures typical of an arid climate (dessication, tepees, chert, evaporites) were formed, whereas during humid seasons evaporites dissolved.

(2) Mixing Model: Petrographic (and partial chemical and isotopic) data favor a model which requires the participation of meteoric water. Unquestionable petrographic evidence of meteoric water is found in the dissolution and recrystallization of oolitic samples (and probably accounts for the dissolution of evaporites). Since meteoric fluids were present during stabilization, their participation in dolomitization is feasible.

Dunham and Olson (1980) have invoked dolomitization of certain Paleozoic carbonates by mixing of fluids, whereas others such as Taylor and Sibley (1986) called upon shallow burial at

higher temperatures. Based on textural grounds, deep burial dolomitization is not believed to have been of major importance in the Upper Albanel dolostones investigated. Gregg and Sibley (1984) concluded that coarsely crystalline, fabric-destructive, xenotopic dolomite does not form at temperatures below 50° C, which is the critical roughening temperature for dolomite. Below this temperature, fine-grained idiomorphic crystals are energetically favored and consistent with the petrographic evidence.

4.1.3 Diagenesis of the Iron Formation:

A sample collected adjacent to the Upper Albanel Formation contact consists of an oolitic iron-rich specimen composed of magnetite and hematite and set in a quartz matrix (Plate 41). The ooids (up to granule size) are poorly preserved: at best only a few concentric quartz laminae can be distinguished. Unlike previous examples of ooids, these are commonly flattened, reflecting the effects of compaction while still unhardened. Carbonate appears translucent (hematitic) to opaque (magnetitic), indicating unequivocal evidence of replacement by iron oxides.

4.2 Lower Albanel Formation

Many examples of early diagenetic processes characteristic of the Upper Albanel Formation are entirely lacking in the Lower Albanel Formation. Probable reasons for this difference include

deeper and/or continuous subtidal conditions as well as the fact that the vast majority are core samples.

4.2.1 Silica Diagenesis:

Although the presence of chert in this formation was noted by several authors, it was not observed in the borehole investigated. Caty and Chown (1983) reported on the early chertification of the basal stromatolites. The fabric-selectivity (algal structures) of chert has already been discussed.

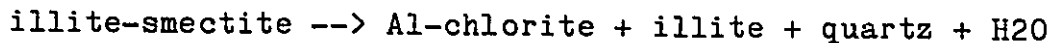
Excluding the dominant detrital origin, most silica takes the form of late cavity and fracture fillings, as well as in the form of authigenic and replacive quartz. The common euhedral form, large size ($< 1-2\text{mm}$), frequent twinned nature, and crosscutting fabrics (elongated either parallel or perpendicular to laminae) all indicate an authigenic origin. However, some are replacive in origin. Such is the case in Plate 17, which consists of a ($< 1\text{mm}$) quartz crystal with rectangular corners. Rarely it occurs with pyrite.

Authigenic crystals occur in the lower portions of the formation, and may be related to the diagenetic transformation of clays or greater organic content found there. Since silica precipitation is favored by a decrease in pH, such fluids (decomposition of organics?) would be expected to precipitate silica within or above the Black Shale Unit due to compaction.

An abundant detrital source and subsequent dissolution by stylolitization would result in an ample supply of secondary silica.

4.2.2 Clay Diagenesis:

The reported presence of illite in rocks of argillaceous composition in the Mistassini Basin, is compatible with a burial diagenetic origin. Frey (1970) proposed the following reaction to explain the disappearance of illite-smectite mixed layers in the anchizone (200-300°C):



The presence of chlorite and authigenic quartz in these rocks can also be explained as a by-product of this reaction.

4.2.3 Carbonate Diagenesis:

1) Early Cementation: Evidence for early cement is far less evident compared to the overlying strata. Most of the evidence is found in the upper portion of the formation, especially in the Upper Black Shale Unit, which is interpreted as a tidal flat and lagoon. This unit hosts intraformational breccias, preserved vugs, deformed and broken algal mats, as well as erosional structures. Such examples of early lithification are anticipated in a tidal flat environment.

Even fewer examples were observed in the underlying units. One example consists of rare quartz arenite beds with detrital calcite and dolomite. In another case, the bending of mica laths around detrital carbonate (and quartz) grains was also observed. These examples indicate an early lithification, erosion and deposition of the carbonates.

The reported presence of algal breccias near the base of the formation (Kouassi, 1979) is also indicative of early lithification in a peritidal depositional environment.

2) Burial Cementation: Evidence of late precipitation of carbonates is suggested by the following²:

- a) fault related white calcite, occurring as en-échelon veins, strained crystals in veins and fault dolomite
- b) coarse xenotopic calcite along stylolites and as poikilotopic crystals
- c) the ferroan and 180-depleted nature of certain carbonates (to be presented later)
- d) compaction of unlithified (deeper water) sediments, as suggested by bent micas in contact with silicates and draping of laminae around early/syngenetic pyrite (Plate 43) imply later cementation.

Dissolution along low amplitude stylolites are the source of such

²Some of these and other criteria were listed by Choquette and James (1987) as evidence of burial cementation.

cements.

3) Dolomitization: Much of the Lower Albanel dolostones samples mostly consist of deci-micrometer-sized idiotopic to hypidiotopic crystals (often < 50 micrometers). Macrofabrics appear well preserved (ie: cross-laminae), but detrital nature is obscured by idiotopic to hypidiotopic dolomite. Evidence of early as well as later dolomitization shall be presented below.

Any models applied to account for dolomitization of the Lower Albanel Formation will be constrained by (a) abundance of limestone associated with shale, (b) variable depositional environments, and (c) evidence of early dolomitization. In addition, the later discussed broad isotopic variation must also be accounted for. Again, establishing the exact mechanism may be difficult where dolomitization is complete.

(a) Shale-Limestone Correlation: Most of the limestones occur within, or in proximity to, the Lower Black Shale Complex, although beds, grains and secondary patches (ie: along stylolites) are found locally also in some overlying units. Rare limestone algal(?) clasts were observed in the Upper Black Shale Complex (Plate 1). Various degrees of dolomitization were observed. Contacts between limestone and dolostone can be sharp, but microscopically a "patchy" transition zone is apparent (Plate 18). The distribution of dolomitization appears to be controlled

by sedimentological boundaries, suggesting that dolomitizing fluids migrated through permeable pathways.

The preservation of limestone may be a function of water depth and/or distance from shore (or of inhibiting effects of organic matter?). This implies that the majority of dolomitization in samples of the Lower Albanel Formation is surface-related (ie: eogenic) and hence must be an early diagenetic process. The shale-limestone association also suggests that dolomitization by compaction flow has not been an effective dolomitization process (see also Ricketts, 1983 and Dunham and Olson, 1980).

(b) Depositional Environments: Field relations and petrographic evidence have already been shown to indicate the presence of several depositional environments. Local peritidal, and extensive shallow and deeper subtidal environments were present. Thus the likelihood of different mechanisms by which dolomitization may have proceeded, is augmented.

(c) Early Dolomitization: Several lines of evidence have been advanced to suggest an early episode of dolomitization:

a) The fine crystallinity and preservation of both macro and microtextures (< 1 mm) imply an early process. Most evident in fine carbonates, only the detrital character of the allochems is overprinted by the hypidiotopic-idiotopic dolomite crystals.

- b) Confinement of dolomitization to stratigraphic boundaries (hence permeable pathways such as laminae and beds) indicates that pore occlusion was not yet attained, implying shallow depth to surface conditions. The concordant limestone-dolomite contacts and common fine crystal size would be inconsistent with a major, late burial dolomitization event.
- c) The absence of post-stylolite dolomitization (see Mattes and Mountjoy, 1980) is consistent with an early event.
- d) The occurrence of both polycrystalline limestone and dolostone grains in a quartz arenite bed implies early dolomitization. Further evidence was noted in a rare mature quartz arenite bed. Both quartz and limestone grains are cemented by dolomite. This implies an early process, unlike later discordant dolomitization.

The case for early dolomitization appears firmly established. However, some late dolomitization is expected in any thick ancient sequence, as is well exemplified by local coarsely crystalline, massive beds and fracture-related, white vein dolomite (Plate 49). Fault dolomite can also be characterized by very coarse, strained and iron rich (brownish) crystals and/or opaque material. Hence several episodes of dolomitization appear to have been operative.

Dolomitization Mechanisms: Although several processes are possible, the sabkha, Dorag and a few other models will be

presented here. In general, parts of the trace element and isotopic data, can be reconciled which will be dealt with in a subsequent section.

(1)- Sabkha Model: Portions of the Upper Black Shale Complex and Stratified Dolomite Unit were interpreted to have formed under peritidal conditions. Sedimentary structures, early cementation, fine crystallinity as well as evidence of subaerial exposure characterize the former. The algal portion of the overlying Stratified Dolostone Unit was interpreted by Lehmann (1974) as an intertidal-supratidal deposit. Reported (Lehmann, 1974) and petrographically observed evidence suggestive of evaporites suggest above normal salinities, which are compatible with the above interpretation. Note that a sabkha depositional environment has been proposed by Caty and Chown (1983) for the basal stromatolite and for the regolith (not represented in the core investigated). These authors also reported evidence of high salinities and the presence of anhydrite in fluid inclusions found within carbonate veins hosted by the regolith.

The remaining, underlying units represent shallow to deeper water deposits; no evidence of emergence was observed. The common (fine-grained) immature silicilastic content of the carbonates suggests the contribution from a distal fluvial source. Fluvial and transitional deposits are present to the northeast (Papasquasati Basin) and were interpreted as syn-depositional with the lower part of the formation (Chown and Caty, 1973). Its clastic

character would imply porous and permeable conditions and a mixing zone dolomitization model may be feasible. Furthermore, the lack of subaerial exposure, greater water depth, favorable hydrologic conditions and evidence of meteoric fluids, do not contradict such a model. Ricketts (1983) indicated that continentally derived meteoric waters can extend for considerable distances under modern continental platforms.

The foregoing discussion does not preclude the existence of other dolomitization mechanisms. Burial and fault-related dolomitization has already been mentioned. Another possibility includes Lippman's (1973) "organic" dolomites, related to sulfate reduction. Baker and Kastner (1981) found that sulfate inhibits dolomitization; hence sulfate reduction generates conditions (including an increase in alkalinity) that favors its formation. The presence of early diagenetic pyrite, frequently associated with deeper water organic-rich deposits, favors local dolomitization by such a process.

Machel and Mountjoy's (1986) comprehensive review of dolomitization revealed several other dolomitization possibilities. They believed that subtidal and subsurface dolomitization account for the majority of ancient dolomites observed. The shallow subtidal model Sass and Katz, (1982) is attractive, but difficult to prove for ancient carbonates. The subsurface dolomitization alternative involves magnesium supply by compacti-

on flow, hydrothermal flow or topography-driven flow. Compaction flow is an unlikely dolomitizing agent due to its impoverishment in magnesium (Land, 1985). Hydrothermal flow is an unlikely alternative as no evidence of magmatism has been observed. Topography-driven flow is possible, since the presence of immature clastics implies a hinterland with some relief. However, the latter model is based on a laterally extensive Cambrian dolostone bed, averaging only 6 meters in thickness (Gregg, 1985). Dolomitization of several hundred meters is required for much of the Lower Albanel Formation. Petrographically, the coarse crystallinity and abundant xenotopic texture is generally lacking in the Lower Albanel carbonates, except a few samples from the upper unit. In addition, topography flow can occur long after compaction flow has ceased. This suggests that much of the permeability may no longer be present, especially in rapidly-cemented carbonates. This, as well as evidence of early dolomitization requires rejection of most such models.

Dolomite Inhibitor: Factors that encourage and inhibit dolomitization are both numerous and poorly understood. Machel and Mountjoy (1986) indicated that several factors interact (often with opposite consequences) in enhancing or reducing kinetic barriers. This aspect is illustrated by Plate 1, which show finely crystalline, organic-rich (limestone) algal clasts set in a dolomitic matrix. The presence of certain organic compounds was found to inhibit dolomitization (cf. Machel and Mountjoy, 1986).

It is believed that the latter and possibly lower permeability(?) may have been responsible for preserving the calcite.

Geochemistry5.0 Introduction:

This chapter deals with the geochemical results of the Mistassini carbonates, which were obtained by XRF, AAS (Appendix 3) and electron microprobe analyses (Appendix 4).

5.1 Factor Analysis of XRF Data

A total of 162 carbonate samples from the Upper and Lower Albanel Formations were pulverized in a tungsten carbide ring mill and analyzed as whole rocks on a Philips 1410 automated XRF at the University of Ottawa. The determinations were made on fused $\text{Li}_2\text{B}_4\text{O}_7$ and Li_2CO_3 discs. The accuracies, based on comparison of average concentrations from ten discs of SY-2 syenite standard, and precisions are listed in Veizer et al., (1983).

The chemical data, which is lognormally distributed, was subjected to log transformation prior to statistical analysis; this tends to clarify the chemical trends. For data reduction and compilation, the SPSS package, version 6 (Nie et al., 1975) was employed. Factor analysis was carried out by the Pal procedure

with Varimax rotation, using an IBM 360 computer at the University of Ottawa. The results of the whole rock factor analysis are illustrated in Table 4.

Factor 1 represents potassium-rich aluminosilicate phases (ie: illite and K-feldspar). Veizer and Garrett (1978), in their study of carbonates, found these phases to be the dominant potassium sources. Most of the trace elements (Rb, Ba and Sr) substitute for potassium whereas Ti^{+3} (and iron) replace Al^{+3} . An example of the stratigraphic distribution of Al^{+3} is illustrated in Figure 5. As expected, elevated values are encountered in the argillaceous lithologies (ie: shale complexes) as well as in those with abundant detrital aluminosilicates (ie: Banded Dolostone Units) of the Lower Albanel Formation.

Factor 2 likely signifies the presence of quartz and Na-rich aluminosilicates (ie: plagioclase) versus dolomitic limestone. Although quartz is by far the dominant silicate, Na-plagioclase is locally important. For example, the distribution of Na_2O (Figure 6) indicates a peak concentration within the Lower Banded Dolostone Unit, corroborating the petrographic observations. Additional evidence is derived from a $Na_2O-Al_2O_3$ plot showing the compositional ranges of the most likely mineral contributors. Figure 7 confirms that most of the first order sodium content is controlled by the proportion of plagioclase and K-feldspar. Most samples that cluster in the upper right corner are from the

TABLE 4

FACTOR ANALYSIS OF ALL XRF SAMPLES

N = 162

	FACTOR 1	FACTOR 2	FACTOR 3	COMMUNALITY
LSiO ₂	.443	.652	.278	.699
LaI ₂ O ₃	.696	.580	.352	.945
LFe ₂ O ₃	.551	.454	.593	.862
LMgO	-.563	-.521	-.024	.590
LCaO	-.097	-.858	.029	.746
LNa ₂ O	.414	.642	.119	.598
LK ₂ O	.713	.443	.367	.840
LTiO ₂	.666	.536	.431	.917
LMnO	.185	-.009	.896	.838
LS	.762	.114	-.138	.613
LBa	.612	.521	.347	.768
LCr	.379	.589	-.011	.491
LZr	.657	.535	.319	.822
LSr	.759	.324	.314	.781
LRb	.618	.637	.335	.901
LY	.811	.073	.297	.752
LNb	.043	.558	.521	.585
LZn	.087	.476	.291	.320

FACTOR	% VARIATION	INTERPRETATION
1	60.4	ALUMINOSILICATE PHASES (PREDOMINANTLY ILLITE AND K-FELDSPAR) VS. DOLOMITE
2	7.1	Na-PLAGIOCLASE AND QUARTZ VS. DOLOMITIC LIMESTONE
3	6.1	IRON AND MANGANESE OXIDE COATINGS

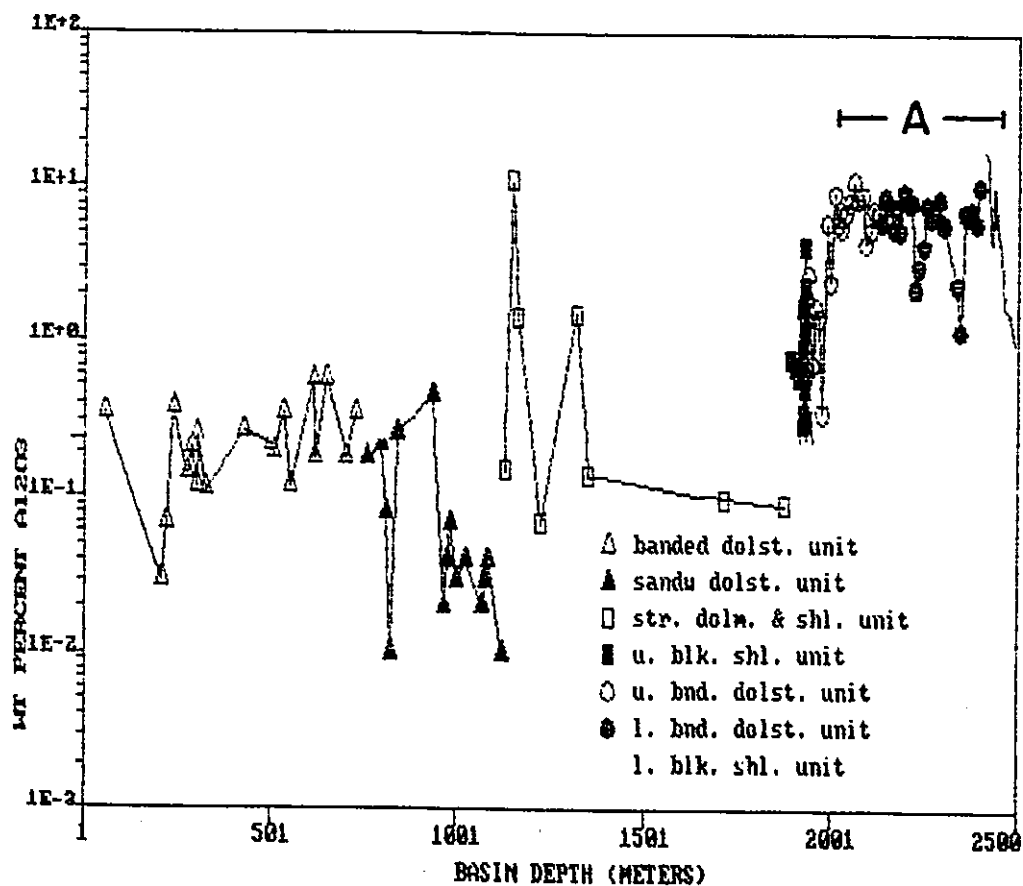


FIGURE 5: DISTRIBUTION OF LOG AL₂O₃ VERSUS SAMPLE DEPTH. XRF analyses of Mistassini carbonates are divided according to relative stratigraphic unit position. High - Sr dolostone interval indicated by "A"; all other dolostone samples belong to the Low - Sr Dolostone Group.

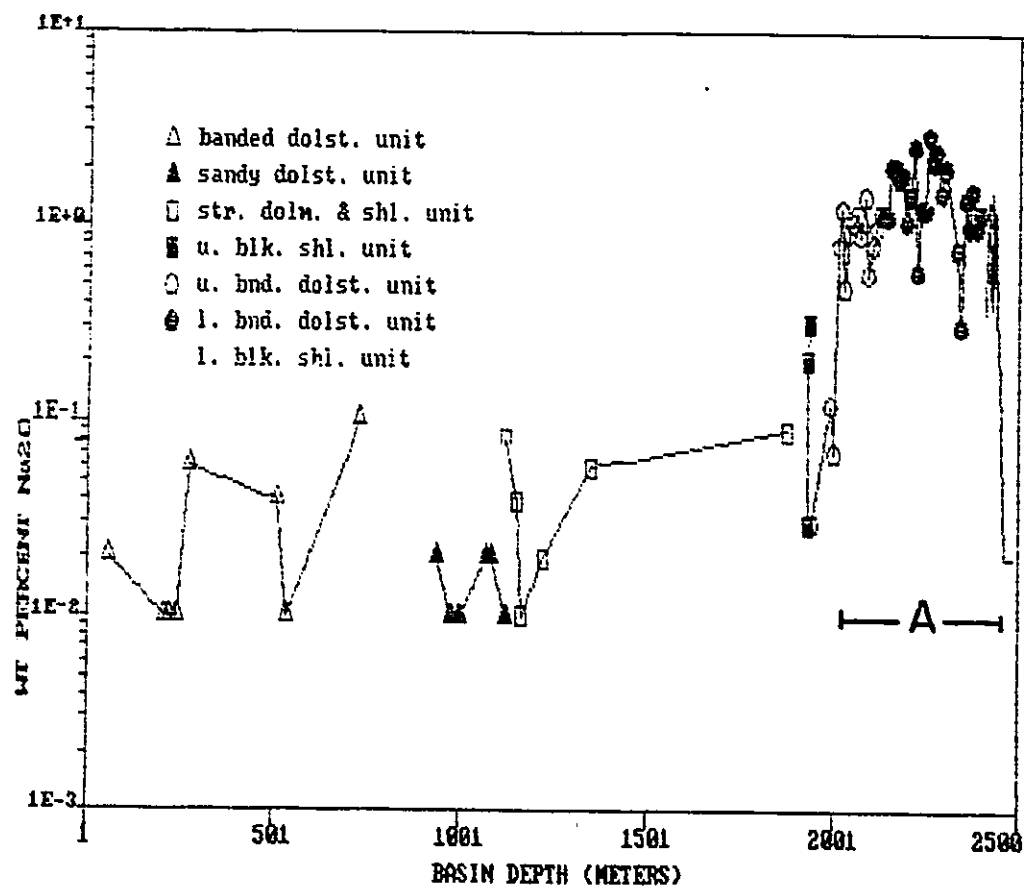


FIGURE 6: DISTRIBUTION OF LOG Na₂O VERSUS SAMPLE DEPTH. XRF analyses of Mistassini carbonates are divided according to relative stratigraphic unit position. High - Sr dolostone interval indicated by "A". Lack of apparent data points in the upper - 1.5 km. of section corresponds to XRF concentrations below the detection limit.

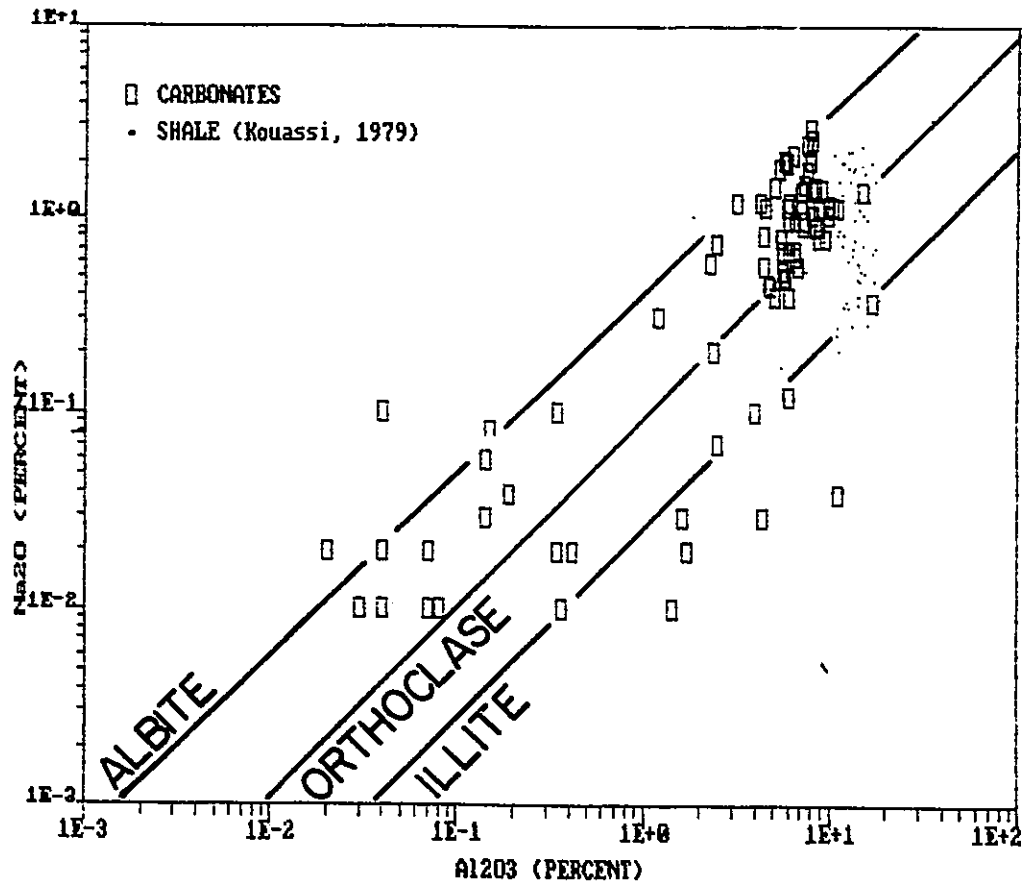


FIGURE 7: MINERALOGICAL CONTROLS ON Na_2O AND Al_2O_3 . XRF analyses of Mistassini carbonates and shales are plotted relative to the illite, orthoclase and albite compositional lines. [Compositional lines reproduced from Veizer (1977)].

plagioclase-rich horizons described in the petrography (Chapter 3). A plot of Kouassi's (1979) shale data (Figure 7) indicates a dual illite and feldspar control.

Factor 3 assigns positive, but different loadings to manganese and iron, suggesting somewhat different controls. For the latter, a plot of total iron versus alumina (Figure 8) indicates that most of the carbonate samples plot above the illite domain and on either side of the chlorite line. Since these phyllosilicates are minor constituents, other carrier phases are required. Veizer (1978) concluded that iron oxide coatings exerted a primary control, whereas substitution into carbonates (similarly for manganese) represented a secondary control. A similar conclusion is favored for the Mistassini samples based on the wide scatter present. The local presence of pyrite may represent an additional contributor. As for the shale, the points fall close to the illite compositional line, suggesting an important control by clays.

An attempt to establish whether additional factors exerted some subsidiary control was tested by repeating the statistical analysis on samples with more and less than 1% Al_2O_3 . (Alumina was preferred over silica since the latter occurs mostly as detrital quartz throughout much of the basin). The Al-poor group revealed little new information. Consequently only the samples with > 1% Al_2O_3 shall be discussed in detail (Table 5). This

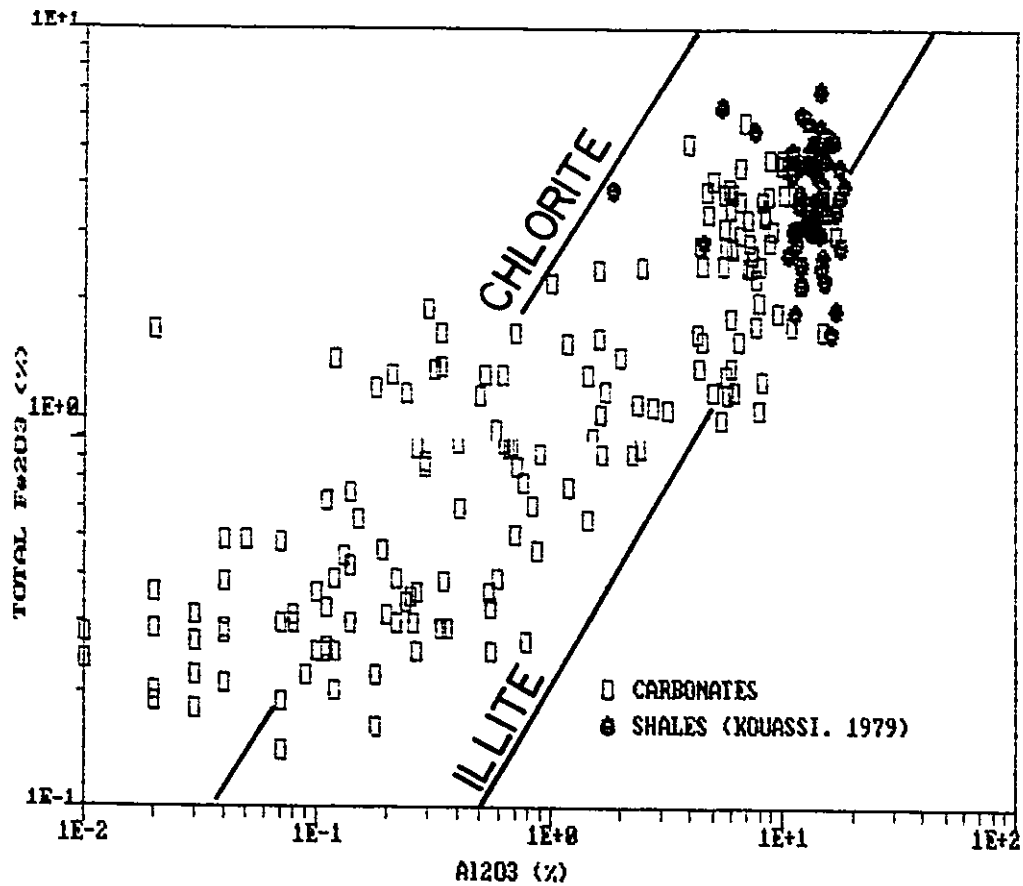


FIGURE 8: MINERALOGICAL CONTROLS ON TOTAL Fe_2O_3 AND Al_2O_3 . XRF analyses of Mistassini carbonates and shales are plotted relative to the illite and chlorite compositional lines. [Compositional lines reproduced from Veizer (1978b)].

effectively exempts the entire Upper Albanel and parts of the Lower Albanel samples.

Factor analysis reveals the existence of four factors. Factor 1 is interpreted as an aluminosilicate (ie: plagioclase, feldspar and illite) versus a limestone control. The observed occurrence of limestone and plagioclase in the lower portion of the stratigraphy confirms this result.

Factor 2 is characterized by loadings of zinc, barium and magnesium and probably represents dolomite (or chlorite?). Due to the low average concentration of zinc in this group (average = 16 ppm) its significance can be discounted. The magnesium-barium correlation is not due to substitution, (due to ionic radii incompatibility). Thus the correlation is probably fortuitous.

The comparable loadings for strontium and calcium indicate calcite as the controlling mineralogy in factor 3. The expected substitution of Sr^{+2} for calcium as well as its presence (as limestone) in the Lower Albanel Formation are consistent with this interpretation.

Factor 4, has positive loadings for iron, manganese and niobium, and a negative one for sulfur. Niobium may be discounted due to its low average concentration of 1 ppm. The oxide coatings control for iron and manganese has already been advocated.

TABLE 5

FACTOR ANALYSIS OF XRF SAMPLES WITH AL₂O₃ >1%

N = 75

	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4	COMMUNALITY
LSiO ₂	<u>.908</u>	.212	-.115	-.037	.885
La ₂ O ₃	<u>.975</u>	.003	-.087	.087	.965
LFe ₂ O ₃	<u>.580</u>	.351	.156	<u>.519</u>	.755
LMgO	-.219	<u>.851</u>	.058	<u>.151</u>	.799
LCaO	-. <u>.632</u>	-. <u>.151</u>	<u>.653</u>	.106	.860
LNa ₂ O	<u>.803</u>	-.380	.290	.012	.874
LK ₂ O	<u>.712</u>	.423	-.413	.200	.898
LTiO ₂	<u>.817</u>	.194	-.110	.451	.922
LMnO	-.057	.118	.311	<u>.825</u>	.796
LS	.046	.274	.048	-. <u>.585</u>	.423
LBa	.216	<u>.716</u>	-.363	-.071	.697
LCr	.495	-.094	.090	-.260	.330
LZr	<u>.839</u>	-.126	.001	.072	.726
LSr	<u>.283</u>	-.436	<u>.775</u>	-.099	.883
LRb	<u>.804</u>	.360	-. <u>.253</u>	.229	.893
LY	-.112	.134	<u>.811</u>	.107	.700
LNb	.424	.171	-. <u>.217</u>	<u>.585</u>	.599
LZn	.459	<u>.555</u>	.066	-.066	.552

FACTOR	% VARIATION	INTERPRETATION
1	42.0	ALUMINOSILICATES VS. LIMESTONE
2	15.4	DOLOMITE (?) OR CHLORITE (?)
3	11.6	CALCITE (LIMESTONE)
4	7.1	OXIDE COATINGS VS. SO ₄ - REDUCTION

However, the antithetic sulfur loading suggests that sulfate reduction may also have played a role. This is supported by early diagenetic nodules and abundant pyrite in the organic-rich (deeper water) shales. Wedepohl (1978) indicated that the reduction and mobilization of manganese in shales could be identified if a negative correlation between C_{org} and manganese were present. Such a plot (Figure 9) does indeed show a negative correlation, although just barely statistically significant at the 95% confidence level. Furthermore, the high manganese concentrations in the associated carbonates support the existence of such a process.

Further examination of second order controls of chemistry, due to carbonate-bound cations, shall be dealt with in the next section. However, because of the chemical evolution of carbonate chemistry during their diagenetic history, an insight into the theory of carbonate diagenesis must first be presented.

5.2 Trace Elements in Carbonates

5.2.1 Partition Theory of Trace Elements:

Trace elements enter the carbonate structure by substitution for Mg and Ca, by occupation of vacant sites, along crystallographic planes, and by surface adsorption. At the moment, most is known about the first mechanism. Substitution is described by the

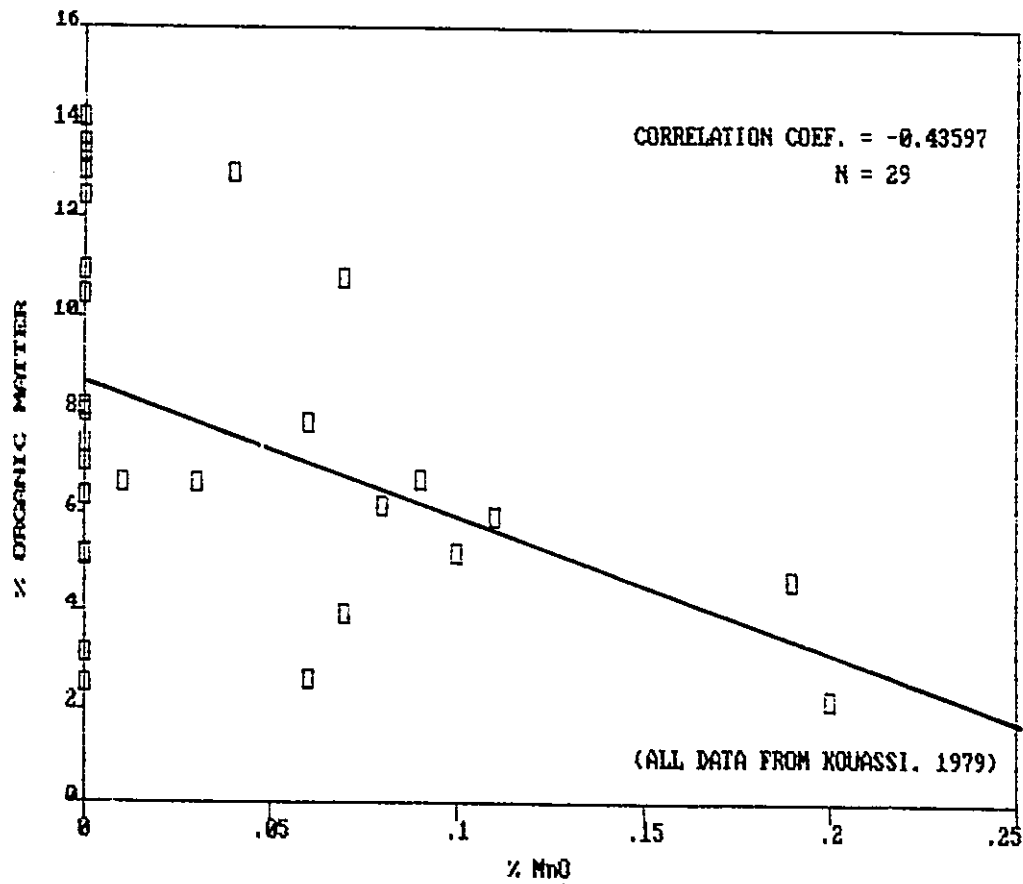


FIGURE 9: CORRELATION DIAGRAM BETWEEN % C_{ORG} AND % MnO . The regression line based on XRF analyses of Mistassini shales results in a negative correlation, consistent with SO_4 - reduction. Regression line is statistically significant at the 95 % confidence level.

distribution coefficient "D", given by:

$$D(M_{Me}/M_{Ma})_l = (M_{Me}/M_{Ma})_s$$

where Me = molar concentration of trace element

Ma = " " " major " (Ca and Mg)

and l = liquid, s = solid phase.

This is valid when the system is at equilibrium at constant T and p and corresponds to a case where the liquid dominates the amount of solid. Where the opposite is true, the system is governed by the heterogeneous distribution law (in Veizer, 1983):

$$\log (m_{eo} / m_{ef}) = D * \log (m_{Cao} / m_{Caf})$$

where D = distribution coefficient, and "o" and "f" represent the initial and final concentrations.

Consequently, any value > 1 for the distribution coefficient (D) signifies an enrichment in the trace element concentration within the precipitating carbonate (D < 1 represent depletions). The distribution coefficient varies for each element and carbonate mineral. It is controlled by numerous factors such as crystal structure, ionic radius, T, p, precipitation rate, cation abundance (a function of complexing) and more. In most cases "D" represents approximate values or ranges; much data is still

lacking, especially for dolomite.

Marine carbonates are primarily composed of aragonite and high magnesium calcite (HMC) which are stable in seawater (Allan and Mathews, 1977). Although calcite is thermodynamically favored, magnesium in seawater exerts a kinetic barrier (Lippman, 1973), thus permitting the precipitation of aragonite and HMC in chemical equilibrium with ambient seawater. In the presence of meteoric water, these phases are no longer stable and dissolve with a concomitant precipitation of diagenetic low magnesium calcite (dLMC).

During diagenetic stabilization, a repartitioning of the constituents (ie: cations and isotopes) takes place. The final composition of the diagenetic phase (whether LMC or dolomite) will depend upon the extent of the repartitioning, which is a function of several factors:

- 1- The direction and the amount of deviation from unity for each distribution coefficient.
- 2- The original mineralogy, which exerts control on the composition of the ambient diagenetic waters.
- 3- The amplitude of the chemical (and isotopic) difference between the initial marine and later diagenetic fluids. For example, marine waters are enriched in Na, Mg, Sr, Ba and U but depleted in Mn, Fe, Co, Cu and Zn, (Veizer, 1983).

4- The water/rock ratio involved in the diagenetic stabilization. This ratio expresses the relative contribution of an element from the diagenetic fluids versus that from the dissolving carbonate. This is controlled by hydrologic parameters, such as porosity and permeability.

5- Other complicating factors include the disequilibrium (cation and isotopic) precipitation of carbonates due to biological fractionation (Veizer, 1983).

With respect to water/rock ratios, high values characterize open systems (ie: precipitation of cements) whereas low ratios indicate closed systems. Note that each of these extremes may exert a dominant control over certain constituents. For example, calcium, magnesium and carbon originating from the solid phase would exert a dominating influence over the fluid. The final concentration of the trace elements would thus depend on the above factors. An example of fluid phase control, even in a partially closed system is illustrated by oxygen isotopes (unless the precipitation of the diagenetic phase is rapid, as indicated by Veizer, 1983). In this case, the isotopic composition of the resulting phase would reflect the isotopic composition and the temperature of the fluid. A diagenetic system may be therefore open for some constituents, but closed for others (Veizer, 1983).

A high water/rock ratio characterizes a diagenetic mechanism where the dissolving phase is in equilibrium with the bulk

aquifer fluid. However, such a model would require a ludicrous number of recrystallizations, in order to explain cation depletions observed in carbonates (Morrow and Mayers, 1978). Veizer, (1983) indicated that diagenetic transformation of most carbonates occurs in low to intermediate water/rock ratios, which is in accord with the frequent preservation of textural integrity and chemical inhomogeneity. He proposed the "bulk solution disequilibrium" model, whereby a dissolving phase is separated from the bulk solution by a liquid film which is in kinetic equilibrium with the former but in disequilibrium with the liquid. Thus the necessary trace element depletions as well as the fabric preservation can be obtained with a minimal number of recrystallization episodes.

5.2.2 General Characteristics of Trace Elements:

This section will cover the pertinent characteristics of some trace elements incorporated into carbonates.

Sodium: The ionic radius of Na^+ ($0.97\text{\AA}$) corresponds closely to that of Ca^{+2} ($0.99\text{\AA}$) and substitution is expected. The difference in charge may be compensated by hydrogen ion (Land and Hoops, 1973), by anion vacancies and/or interstitial cation substitution (White, 1977). In addition, Billings and Ragland (1968) proposed a coupled substitution of Na^+ and a trivalent cation. Sodium may also occur as fluid and solid inclusions (Speer, 1983), as well as a constituent in aluminosilicates.

Based on crystallo-chemical considerations, calcite should contain more Na^+ than dolomite, but less than aragonite. However, White (1977) found that Na^+ co-precipitation in carbonates is independent of Mg concentration, and Speer (1983) noted that Na^+ is not preferentially incorporated in either calcite or aragonite. The latter even suggested that Na^+ (and Mg^{+2}) in aragonite should be treated as an adsorbed cation or as inclusions. Indeed, Amiel et al., (1973) discovered that portions of Na^+ and Mg^{+2} in aragonitic corals are associated with organics and as adsorbed ions. Land and Hoops (1973) reported that dolostones with < 1000 ppm Na^+ either lost Na^+ during recrystallization, or that the dolostones formed in hyposaline waters.

Various authors have reported on the use of Na^+ as a paleosalinity indicator. This is reflected by the high and low sodium values reported in hypersaline and late hyposaline diagenetic dolostones (Veizer et al., 1977). These authors assigned a boundary between hypersaline and normal marine Lower Paleozoic Arctic carbonates at ≈ 230 ppm.

Iron: The ionic radius of Fe^{+2} ($0.76 \text{ \AA}$) compares favorably with that of the Mg^{+2} ion ($0.65 \text{ \AA}$). As a result, it is expected to be more abundant in dolomite. However a troublesome source of Fe^{+2} in carbonates is the associated insoluble residue. In a study of secular variations, Veizer (1978) found it as an oxide coating on

clays and as a constituent in clays and chlorite.

Friedman (1969) discovered that the higher concentrations of Fe^{+2} (and Mn^{+2}) associated with freshwater could be used to distinguish brackish lagoonal from marine carbonates. The generally weakly acidic freshwaters contain more Fe^{+2} . Thus discharge and mixing of such waters with seawater results in the precipitation of Fe (and Mn) colloids.

Iron (and Mn^{+2}) enrichments, due to leaching of supratidal carbonates was observed by Fruth and Scherricks (1975). They found that Fe^{+2} (as well as Mn^{+2} , Zn^{+2} and I.R.) was more abundant in the supratidal-intertidal than the intertidal-subtidal zones.

Other authors (ie: Eriksson, et al., 1975) reported high Fe^{+2} (and Mn^{+2}) concentrations in Precambrian carbonates of the Transvaal Supergroup. The high concentrations in the carbonates are related to their proximity to iron formations, and ultimately reflect the higher soluble Fe^{+2} (and Mn^{+2}) in the waters at that time. Veizer (1978) established that Fe^{+2} and Mn^{+2} content in carbonates increases into the Proterozoic and Archean eons. The less oxidizing (lower P_{O_2}) atmosphere-hydrosphere that prevailed then is the accepted cause of iron-manganese enrichments in carbonates (and other sediments). Holland (1984), however, argued that the higher concentrations may be attributed to a greater

abundance of colloidal Mn-Fe oxides and/or hydroxides. He indicated that incorporation of these tracers into carbonates during diagenesis would therefore not reflect the oxidation state of the oceanic surface waters.

Manganese: Although a few authors still dispute whether Mn^{+2} is carbonate or silicate-bound (ie: Flugel, 1982), most accept the former view. The Mn^{+2} ion (0.80 Å) substitutes for both Mg^{+2} (0.65 Å) and Ca^{+2} (0.99 Å). Wildeman (1969) reported on the distribution of Mn^{+2} in carbonates, aided by electron paramagnetic resonance. He discovered that manganese was more populated in the distorted Mg-sites in dolomite. In co-precipitated carbonates, dolomite was found to contain 20 times more Mn^{+2} than calcite (Atwood and Fry, 1967). On account of its smaller size, it will preferentially enter rhombohedral carbonates over aragonite. Bencici and Turi (1974) found that dolomitization results in little change in manganese concentration, unlike strontium.

The manganese content of ancient carbonates may indicate paleodepositional environments. The elevated concentration in fresh versus marine waters is reflected in the higher manganese content in brackish versus marine carbonates (Friedman, 1969). According to Flugel (1982), the predominance of Mg-calcite in lagoons results in an elevated manganese signature relative to aragonitic sediments. In a study of Mesozoic carbonates, Bencici and Turi (1974) observed low values in shallow water (aragonitic)

and enriched concentrations in deeper water (calcitic) carbonates. They cited several possible reasons for the increased manganese: intense continental weathering, submarine volcanism and submarine anaerobic conditions.

The leaching of detrital material constitutes the source of manganese in normal continental shelves (Presely, et al., 1967). They noted that where volcanism was active, leaching of volcanic products and injection of juvenile metal-rich fluids were additional contributors of manganese. Another means of concentrating manganese offshore lies in biological fixation by organisms in zones of high organic productivity. Reduced (deep sea) clay sedimentation and dissolution and concentration in subaerially exposed carbonates (Flügel, 1982) represent additional processes.

Since manganese is easily oxidized, it can only enter the carbonate structure under reducing conditions, such as produced during sulfate reduction. This process should reflect an inverse relationship between manganese and organic carbon in shales (Wedepohl, 1978). The existence of this inverse relationship was cited by Wedepohl (1978) as proof for the mobilization of manganese in areas of high organic productivity. Bivalent manganese may subsequently be incorporated in carbonates or diffuse upwards until re-oxidation results in precipitation. (Iron is not as mobile in such environments, since reaction with hydrogen sulfide results in precipitation of pyrite.)

Strontium: The ionic radius of Sr^{+2} (1.13 Å) lies between that of Ca^{+2} (0.99 Å) and K^{+} (1.33 Å). Strontium preferentially enters 8-fold coordination. Its substitution for calcium (6 and 8-fold coordination) and potassium (up to 12-fold coordination) in minerals renders the prediction of substitution more difficult.

Although it occurs in the lattice of carbonates and aluminosilicates, there is disagreement on whether it is absorbed on clays. Flugel (1982) cites references that report increases in strontium in limestones with clay content. Possible mechanisms include diagenetic release of strontium and subsequent adsorption on clays and the impeding effects of clays on coalescent neomorphism.

Excluding strontium minerals, the feldspar group represents the dominant Sr-bearing silicates. Others, such as pyroxenes and amphiboles, contain much lower concentrations of strontium (Wedepohl, 1978). Micas, which are rich in potassium, actually harbor little strontium. This is due to the 12-fold coordination of K^{+} , which results in an excessively large site for strontium to occupy.

In carbonates, the larger aragonitic cell can accommodate more strontium than calcite or dolomite. In terms of decreasing abundance, the sequence: aragonite > calcite > dolomite, records

the progressive decrease in the distribution coefficients. Since strontium occupies calcium sites, dolomite should have about half the strontium content of calcite (Jacobson and Usdowski, 1976).

Variety sedimentary rocks (ie: sandstones, shales, etc...) contain up to a few hundred ppm strontium (Veizer, 1978a). The concentration will, in general, depend on the mineralogy (feldspar, plagioclase, carbonates) as well as the relative abundance of the latter. Recent (aragonitic) carbonates can accommodate up to approximately 8,000 - 10,000 ppm strontium. Ancient limestones usually have concentrations of several hundred ppm, whereas dolostones rarely exceed a few hundred ppm strontium. The low values are due to numerous factors, but in general, the initial precipitation and subsequent diagenetic stabilization via low distribution coefficients appear to be the primary cause of depletions (Veizer, 1983). In addition, Veizer (1978b) uncovered a secular variation which asserts itself as a strontium decrease in Precambrian dolostones with age. The cause lies in the augmented substitution of manganese and iron in older dolostones. Thus the strontium dependence upon numerous factors will dictate its final concentration in the carbonate.

The value of strontium (in conjunction with other trace elements) as a tool in the study of facies has proved its usefulness. Due to its greater abundance in aragonite, the initial facies distribution would be reflected in the strontium

values (after diagenetic stabilization is accounted for). For example, Veizer and Demovic (1974) reported higher strontium values in hypersaline and deep sea carbonates relative to shallow water organodetrital varieties. These authors also indicated that the mineralogy of the dolomitized carbonate may be implied from the strontium content of the dolostone.

Strontium (low D) can be used in conjunction with manganese (high D) as a sensitive indicator of intensity of diagenetic alteration. Brand and Veizer (1980) were able to trace a diagenetic alteration trend of the fossils and matrix, as well as infer the precursor mineralogy using such a technique.

5.3 Analysis of Carbonate Bound Cations

5.3.1 Analytical Procedures:

Atomic Absorption Spectrophotometry: A total of 142 samples were selected for analysis. Samples were powdered to <200 mesh, dried at 110°C for 1 hour and approximately 1 gram weighed out. Digestion in 20 mls 8% v/v HCl proceeded on a shaker table for 4 hours. Samples were then filtered (Watman filter 43) into 25 ml volumetric flasks. Solutions were brought to the mark with deionized water. The gravimetric determination for the insoluble residues have been listed in Brand and Veizer, (1980). All results were recalculated on insoluble residue-free basis.

Aluminium, calcium, iron, magnesium, manganese, strontium and sodium were determined on a Varian-Techtron 6R Atomic Absorption Spectrophotometer at the University of Ottawa. Strontium and aluminium were analyzed in an acetylene-nitrous oxide flame; the remaining elements were analyzed in an acetylene-air flame. Additions of 2000 ppm CsCl were made to all samples and 5000 ppm $\text{Sr}(\text{NO}_3)_2$ was added to all calcium samples.

The average accuracies, as compared with the recommended values for the Z.G.I.-KH and TB (Flanagan, 1973) and NBS-88A (Church, 1981) standards, and precisions are as follows: Al (3.8%, 7.8%), Fe (4.6%, 3.2%), Mg (2.5%, 6.8%), Ca (7.1%, 6.9%), Na (13.8%, 10.3%), Sr (6.4%, 12.9%) and Mn (6.3%, 6.0%). Accuracy is expressed as the relative accuracy, which is defined as (editors of Analytical Chemistry, 1972):

$$\text{relative accuracy} = ((X_m - X_{\text{rec}}) / X_{\text{rec}}) * 100\%$$

where X_m = mean of the results

X_{rec} = recommended value

Precision is expressed as the relative standard deviation, defined by the following (editors of Analytical Chemistry, 1972):

$$\text{relative standard deviation} = (S / X_m) * 100\%$$

where S = standard deviation of the results

X_m = mean of the results

The statistical treatment of the data is similar to that described in the previous section.

5.3.2 Trace Element Geochemistry of the Mistassini Carbonates:

The stratigraphic distributions of the carbonate-bound cations (and insoluble residue) are illustrated in Figures 10 through 14. (Calculated population means correspond to arithmetic means). Overall, the concentrations usually increase with unit depth.

5.3.2.1 General Trends - Upper and Lower Albanel Formations:

1- Insoluble Residue (IR): The higher IR content in the Sandy Dolostone Unit (B) of the Upper Albanel Formation (Figure 10) is due the presence of mature detrital quartz and pore- filling silica. The increase in the IR with depth (Figure 10) for both dolomite and calcite, in the Lower Albanel Formation, is due at first to an increase in coarser (immature) siliclastics and below the banded dolostones (E, F) to a finer (argillaceous) component in the basal shale complex (G).

2- Strontium: The strontium distribution (Figure 11) for both, limestones and dolostones increases with depth to a peak in the Lower Banded Dolostone Unit, which hosts most of the sampled limestone. As expected, limestones contain more strontium than dolostones. The wide scatter in the strontium distributions observed suggests the presence of at least 2 strontium populatio-

DISTRIBUTION OF INSOLUBLE RESIDUE IN THE MISTASSINI CARBONATES

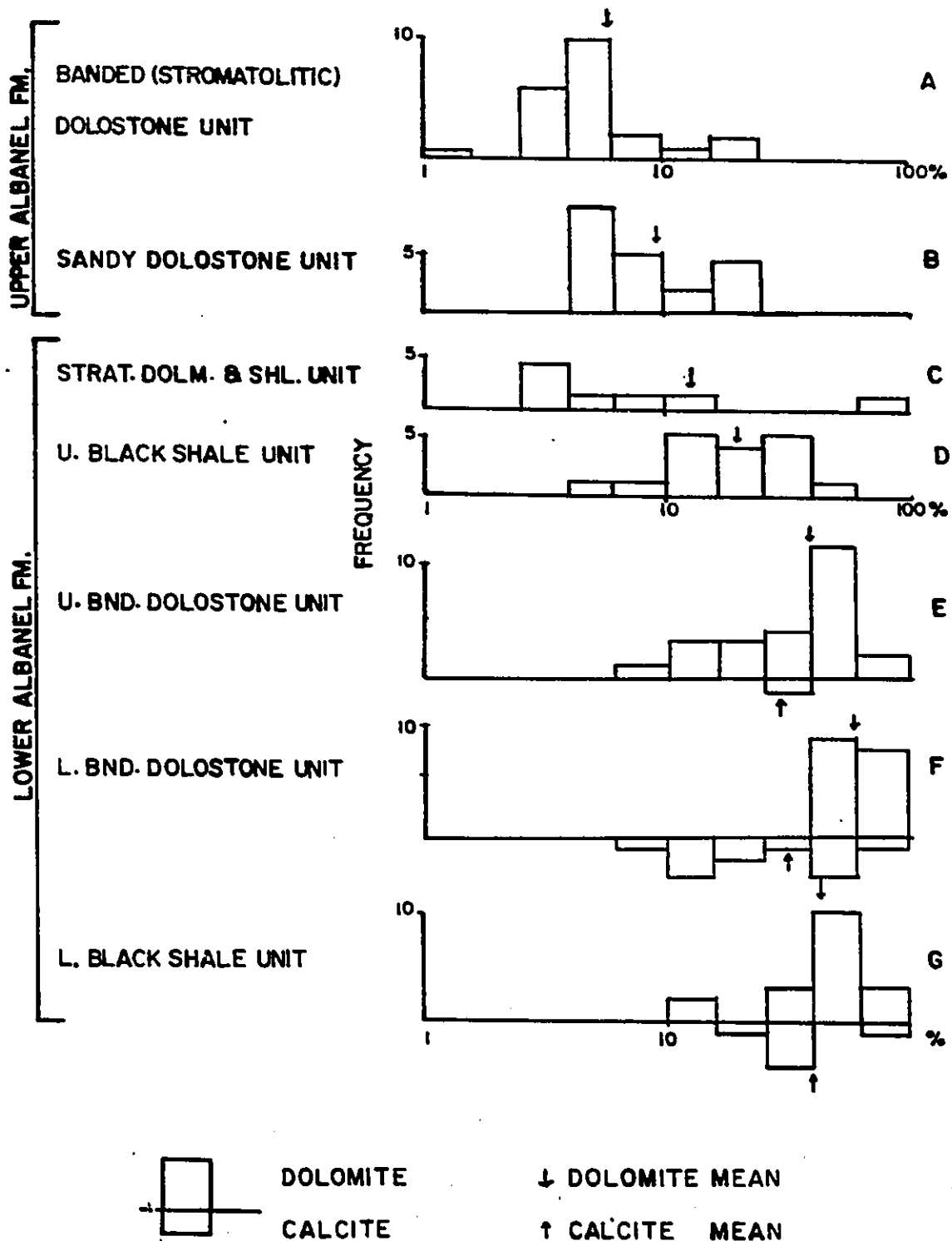


FIGURE 10: DISTRIBUTION OF INSOLUBLE RESIDUE IN THE MISTASSINI CARBONATES. Sample insoluble residues are plotted relative to the stratigraphic unit positions. Histograms for each unit are divided into limestones (bottom) and dolostones (top); sample means are also included.

DISTRIBUTION OF STRONTIUM IN THE MISTASSINI CARBONATES

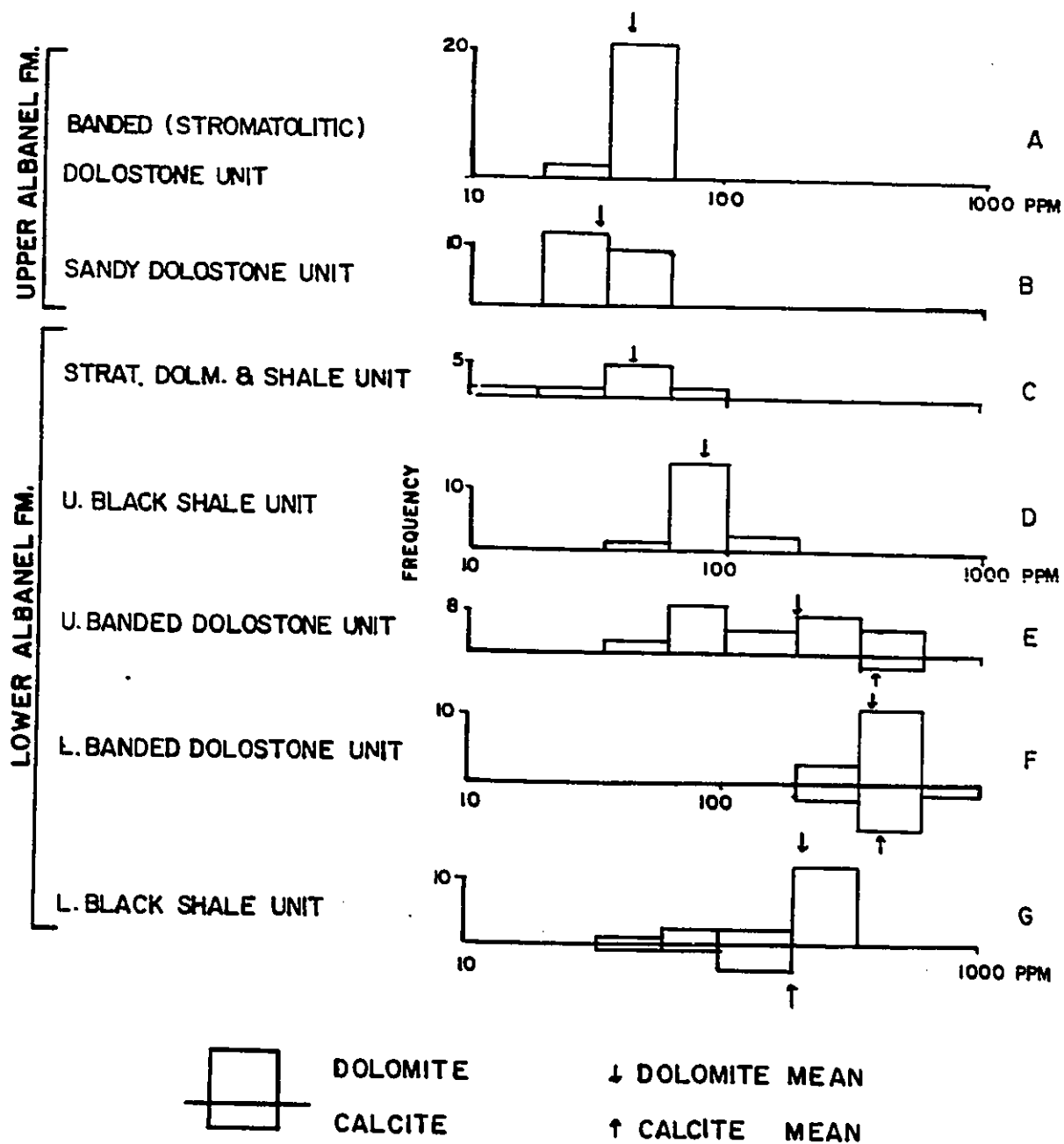


FIGURE 11: DISTRIBUTION OF STRONTIUM IN THE MISTASSINI CARBONATES. AAS analyses of strontium in carbonates were recalculated on a 100 % IR - free basis and plotted relative to the stratigraphic unit positions. Histograms for each unit are divided into limestones (bottom) and dolostones (top); sample means are also included.

DISTRIBUTION OF SODIUM IN THE MISTASSINI CARBONATES

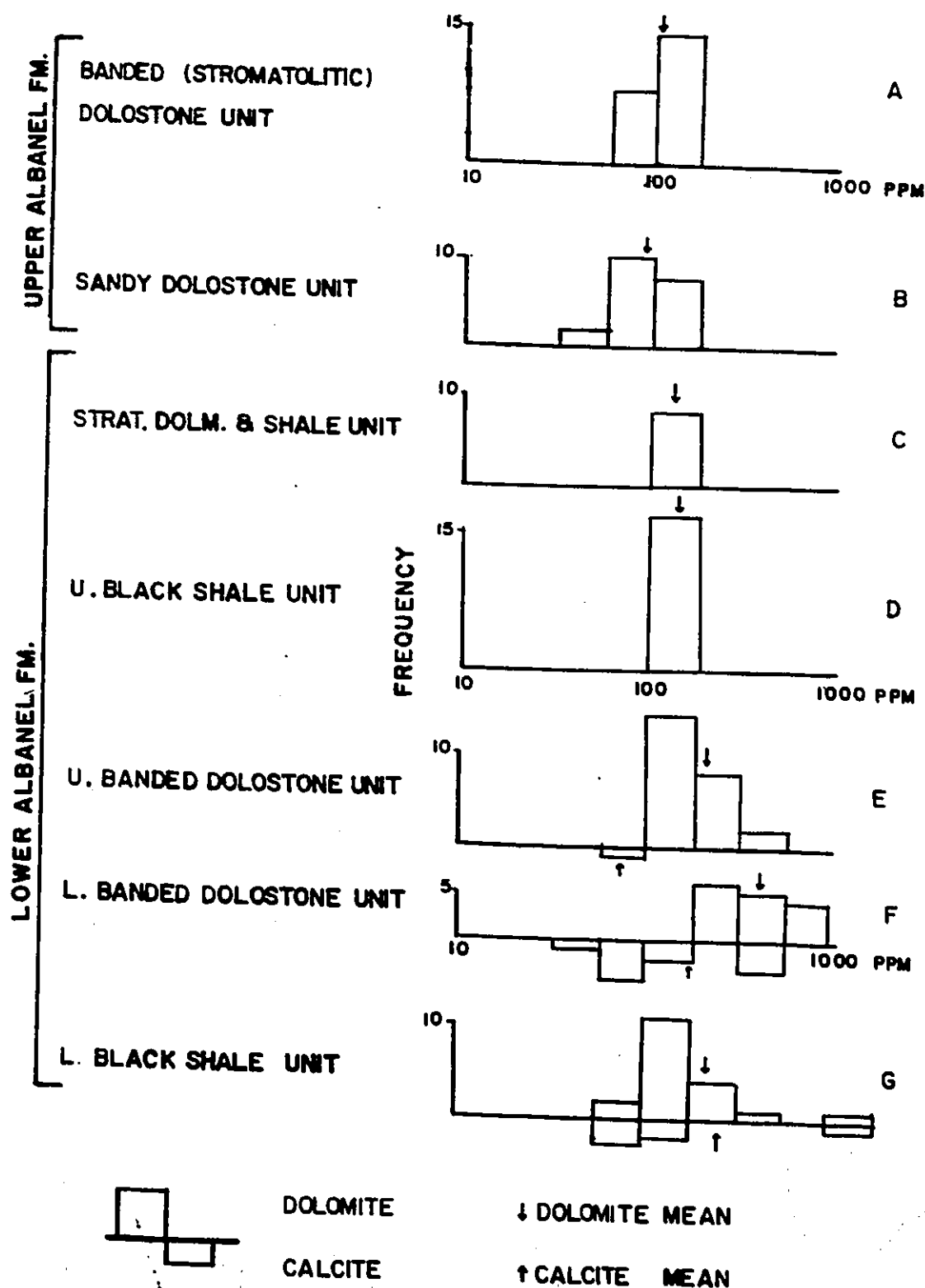


FIGURE 12: DISTRIBUTION OF SODIUM IN THE MISTASSINI CARBONATES. AAS analyses of sodium in carbonates were recalculated on a 100 % IR - free basis and plotted relative to the stratigraphic unit positions. Histograms for each unit are divided into limestones (bottom) and dolostones (top); sample means are also included.

DISTRIBUTION OF IRON IN THE MISTASSINI CARBONATES

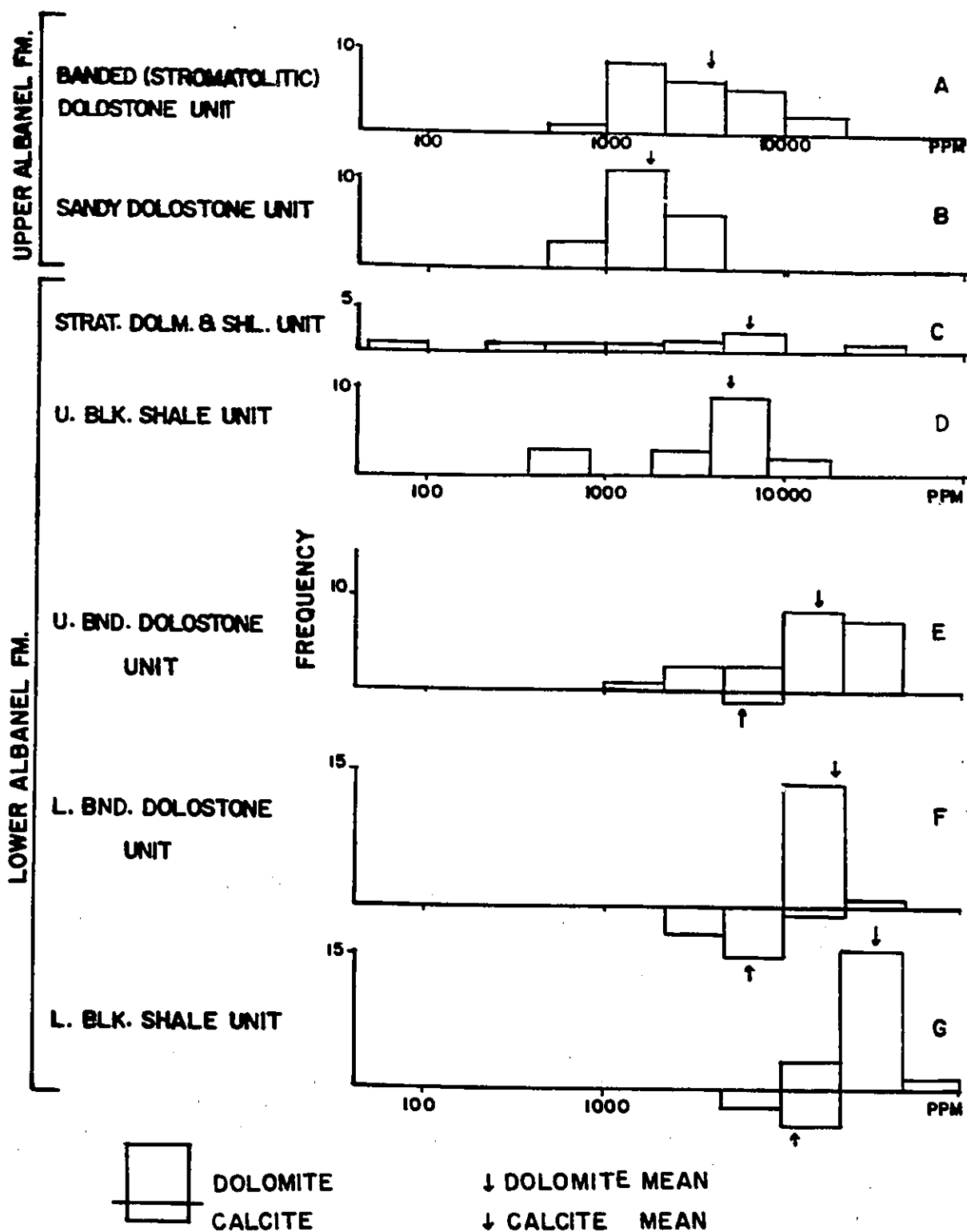


FIGURE 13: DISTRIBUTION OF IRON IN THE MISTASSINI CARBONATES. AAS analyses of iron in carbonates were recalculated on a 100 % IR - free basis and plotted relative to the stratigraphic unit positions. Histograms for each unit are divided into limestones (bottom) and dolostones (top); sample means are also included.

DISTRIBUTION OF MANGANESE IN THE MISTASSINI CARBONATES

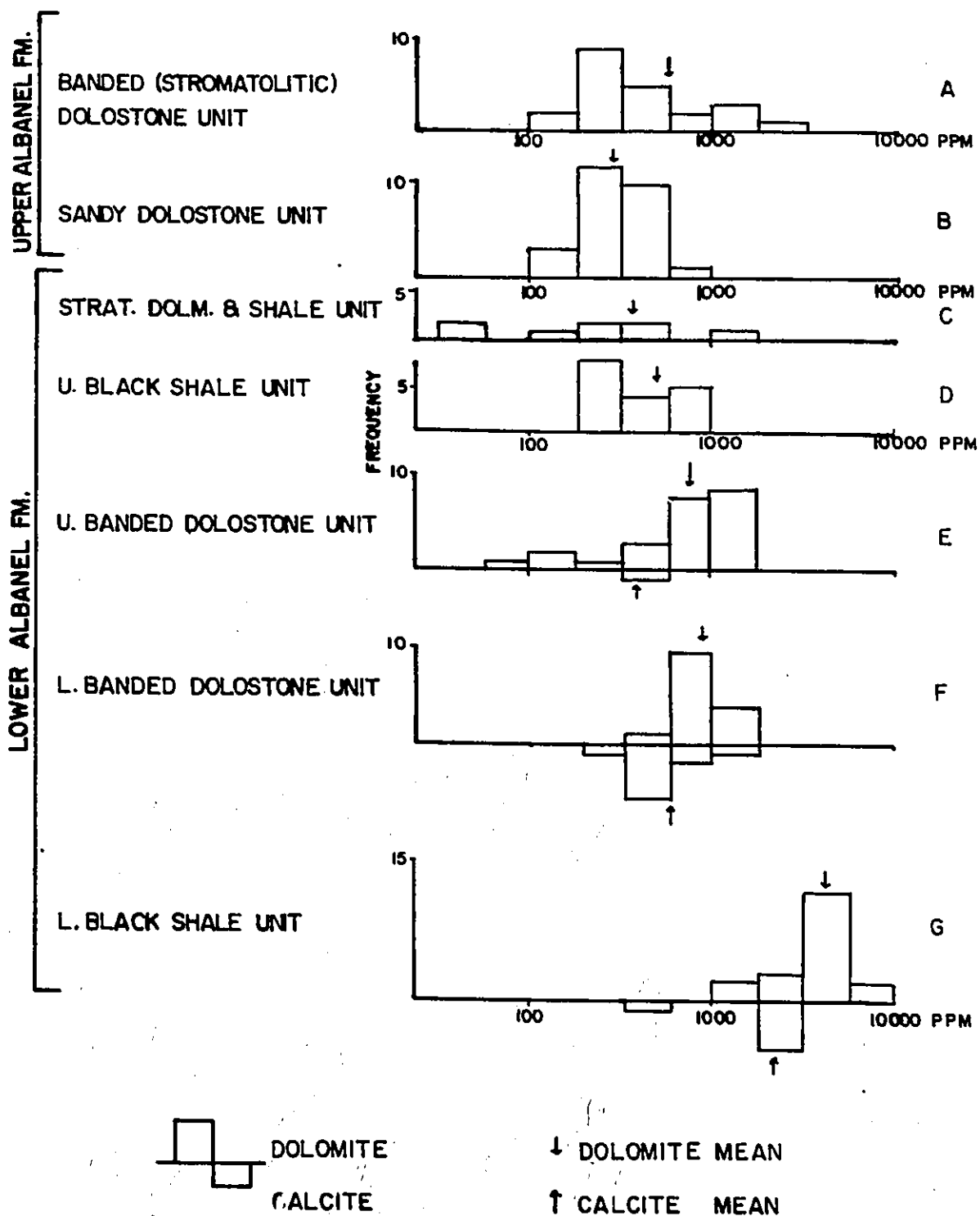


FIGURE 1.: DISTRIBUTION OF MANGANESE IN THE MISTASSINI CARBONATES. AAS analyses of manganese in carbonates were recalculated on a 100% IR-free basis and plotted relative to the stratigraphic unit positions. Histograms for each unit are divided into limestones (bottom) and dolostones (top); sample means are also included.

ns; the Upper Albanel dolostones exhibit generally uniform, depleted concentrations.

3- Sodium: This cation displays a similar trend to that of strontium. The upper portion of the sequence has a narrow distribution (Figure 12), suggesting control by comparable processes. The scatter increases toward the base, reflecting additional sodium controls. For example, the divergence of the sodium means in the Lower Banded Dolostone Unit may be due partially to its IR content, since limestones have greater purity than dolostones (Figure 10).

4- Iron: In the Upper Albanel Formation, iron concentrations are higher in the finer grained Banded Dolostone Unit, compared to the coarser grained underlying Sandy Dolostone Unit (Figure 13). The generally greater permeability of the latter unit should render it more susceptible to alteration. The Fe^{+2} (and Mn^{+2}) are not in accord with this postulate, since they should increase with alteration. This implies that the higher average iron values reported for the Banded Dolostone Unit (A) may be controlled by additional variables such as facies (ie: the proximity to the overlying iron formation, or local deeper and/or less oxygenated waters), concentration of these cations by dissolution in the supratidal zone, or possibly by concentration in organics (Kouassi, 1979) related to the abundant stromatolites.

The increasing concentrations with depth, in the Lower Albanel Formation, culminate with a maximum within the basal Black Shale Unit (G). This is consistent with the fine grain size of particles associated with deeper water milieus and suggests a partial IR control of iron concentrations. The large dispersion of data in the Stratified Dolomite and Shale Unit, as well as local low values, further suggest the complexity of iron controls.

5- Manganese: This element shows a pattern somewhat similar to that of iron, suggesting similar controls. The general increase in manganese with depth (Figure 14) also suggests partial IR control of its distribution. As expected, dolostones contain more manganese than limestones. The distinguishing features of the manganese distribution are the significantly elevated values in the basal shale complex, despite its lower percentage of IR (Figure 10) relative to the overlying unit. This suggests that much of the cation could be carbonate bound. Indeed, Kouassi (1979) found an excellent positive correlation between MgO and MnO , attributed to carbonates in the shales and dispelling any silicate contribution. In contrast, his shales have low MnO concentrations (0.06 %), which preclude their role as a source of Mn^{+2} . Since manganese is easily oxidized, its reduction to a soluble form is favored in anaerobic environments where sulfate reduction is possible. Thus the elevated values could have resulted by such a process.

Note that similar elevated manganese concentrations are common in ancient carbonates. For example, the Permian Kupferschiefer carbonates range from 2000 to 6000 ppm Mn (Wedepohl, 1978) and the Paleozoic Michigan Basin carbonates possess several thousand ppm manganese (Taylor and Sibley, 1986).

In conclusion, a general increase in trace elements with depth is apparent and it reflects the interplay between facies, diagenetic reactions, initial mineralogy and possibly secular variations. Unequivocal confirmation of the controlling factors will require factor analysis of the carbonate-bound cations, the subject of the next section.

5.4 Factor Analysis of the Carbonate-Bound Cations

5.4.1 Limestones:

Factor analysis of 17 limestone samples from the Lower Albanel Formation (Table 6) reveals 3 controlling factors. Factor 1, with positive loadings of Na^+ , Al^{+3} and IR and negative ones for Ca^{+2} and $\delta^{13}\text{C}$, represents an antithetic relationship between limestone purity and their aluminosilicate content. The covariance between $\delta^{12}\text{C}$ and the aluminosilicate fraction probably reflects diagenetic generation of CO_2 from C_{org} in more argillaceous samples. Factor 2, may represent a combination of diagenetic

TABLE 6

FACTOR ANALYSIS OF AAS DATA - LIMESTONES

N = 17

	FACTOR 1	FACTOR 2	FACTOR 3	COMMUNALITY
LSr	-.235	-.032	.865	.804
LNa	.940	.018	.080	.891
LA1	.872	.195	-.264	.869
LMn	-.114	.912	-.150	.867
LCa	-.792	.082	.553	.942
LMg	.130	.938	.028	.899
LFe	.345	.899	-.119	.943
LIR	.893	.373	.117	.950
O13 CAL	-.056	.531	-.656	.716
C13 CAL	-.840	.057	.291	.795

FACTOR	% VARIATION EXPLAINED	INTERPRETATION
1	47.3	LIMESTONE VS. ALUMINOSILICATES (AND ^{12}C GENERATED FROM C_{ORG})
2	26.2	DOLOMITIZATION & DIAGENETIC ALTERATION
3	13.2	DIAGENETIC ALTERATION

(Note: If the analysis is repeated with the exclusion of two anomalous IR & organic-rich samples (D2-93-74 and D2-95-74), the following results are found:

factor 1: Na, Al, Mg, Fe, IR versus Ca - limestone versus aluminosilicates.

factor 2: Mn, Mg, Fe, ^{18}O versus Sr & Ca - diagenetic alteration - dolomitization.

factor 3: ^{13}C - secular variation ?

Thus two samples appear to influence the contribution of organically-derived ^{12}C , as well as of $^{18}\text{O}/^{16}\text{O}$.)

alteration (Mn^{+2} and Fe^{+2}) and degree of dolomitization. The ^{18}O loading on this factor is consistent with the fact that dolomite should be $\approx 3\%$ heavier than calcite (Land, 1980). The third factor, with positive loadings of Sr^{+2} , Ca^{+2} and ^{16}O , may reflect a combination of preferential substitution of Sr^{+2} for Ca^{+2} and diagenetic loss of heavy ^{18}O . The similar Sr^{+2} and ^{16}O loadings are puzzling and may be due to insufficient sample size or inclusion of anomalous samples. Additional factor analysis (cf. Table 6) suggests that the latter proposition may be involved.

The antithetic strontium and manganese relationship in the limestones suggests an alteration trend (Figure 15). However, the limestone populations are too small for further statistical treatment.

5.4.2 Dolostones:

Factor analysis of 125 dolostone samples yielded three factors (Table 7). Factor 1 has positive loadings of Sr^{+2} , Na^{+2} , Al^{+3} , Mn^{+2} , Fe^{+2} and IR, and negative loadings of Mg^{+2} and ^{18}O . Factors 2 and 3 have unique loadings of Ca^{+2} and ^{13}C , respectively. The first factor represents an IR control for all cations versus dolomite content (Mg^{+2} loading), the latter associated with heavy ^{18}O . Factors 2 and 3 represent the calcite admixture and a possible secular control for carbon, respectively.

The dolostones must be subdivided into representative

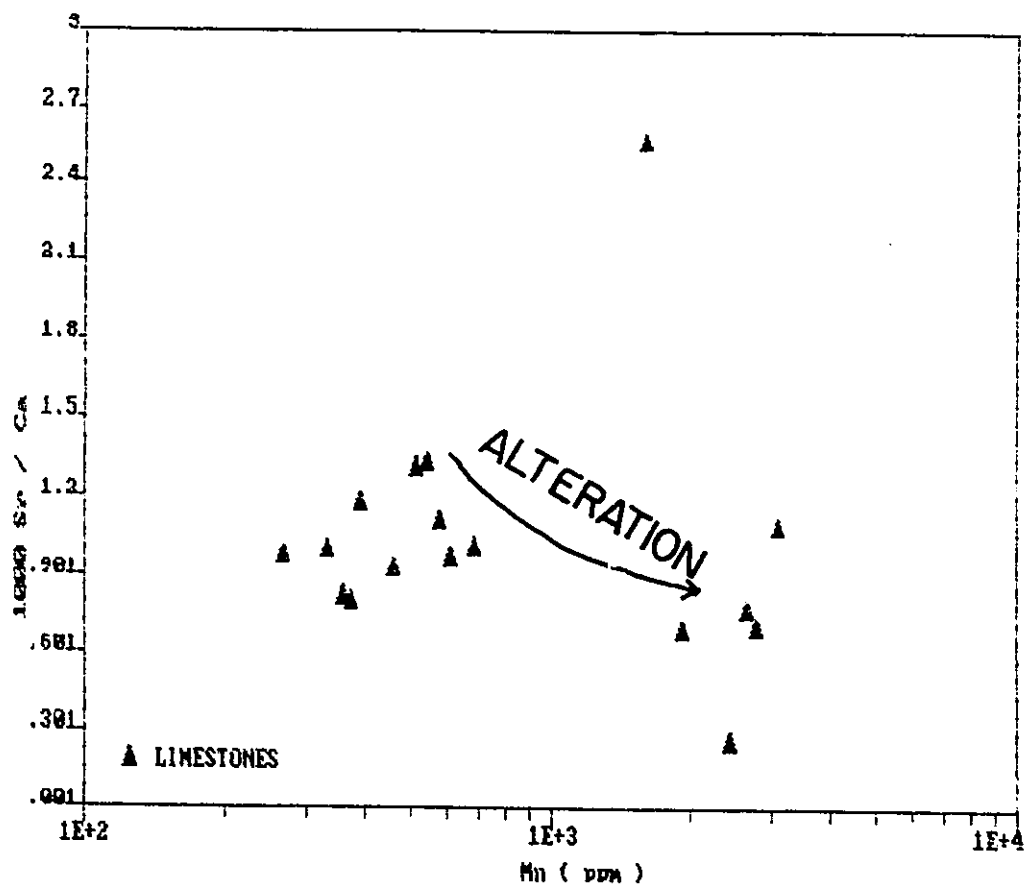


FIGURE 15 : LIMESTONE ALTERATION TREND- SCATTER DIAGRAM OF 10^3 Sr / Ca VS. Mn. AAS analyses of limestones were recalculated on a 100 % IR - free basis. Limestone samples are from the Banded Dolostone and Lower Black Shale Units of the Lower Albanel Formation. Arrow represents alteration trend.

TABLE 7

FACTOR ANALYSIS OF AAS DATA - ALL DOLOSTONES

N = 125

	FACTOR 1	FACTOR 2	FACTOR 3	COMMUNALITY
LSr	<u>.927</u>	.063	-.008	.864
LNa	<u>.796</u>	-.408	.095	.809
LA1	<u>.892</u>	.132	-.030	.815
LMn	<u>.728</u>	.258	-.367	.732
LCa	.150	<u>.919</u>	.004	.867
LMg	-.805	-.073	.120	.668
LFe	<u>.878</u>	.168	-.082	.806
LIR	<u>.884</u>	-.015	-.042	.784
O18 DOL	-.745	-.179	-.047	.590
C13 DOL	-.031	.010	<u>.972</u>	.946

FACTOR	% VARIATION EXPLAINED	INTERPRETATION
1	57.0	ALUMINOSILICATES VS. DOLOMITE AND 18O IN DOLOMITE
2	11.8	LIMESTONE CONTENT
3	10.0	SECULAR VARIATION ?

segments for identification of secondary factors. The presence of at least two dolostone populations, with high and low trace element concentrations, was suggested in histograms of carbonate-bound elements (Figure 11). Ideally strontium and manganese are employed as discriminating variables of carbonate diagenesis (Veizer, 1983).

All measured samples were plotted in terms of their $1000 \text{ Sr}^{+2}/\text{Ca}^{+2}$ against Mn^{+2} concentrations (Figure 16). This plot divides dolostones into two populations. For this reason, the dolostones shall be divided in further discussion into low ($1000 \text{ Sr/Ca} \leq \approx 0.65$; Group 1) and high ($1000 \text{ Sr/Ca} \geq \approx 0.65$; Group 2) strontium groups. Stratigraphically, the high-Sr group represents the lower, and the low-Sr group the upper, portion of the Mistassini sequence, the transition confined to the Upper Banded Dolostone Unit (Figure 11).

5.4.3 Factor Analysis of Dolostone Groups:

High Sr Dolostones

Table 8 indicates three dominant factors. The high and opposite loadings of the Mn^{+2} - Fe^{+2} versus Sr^{+2} - ^{13}C pairs on factor 1 are consistent with alteration trends predicted by theory. Factor 2 allots opposite Al^{+3} , Na^{+} and IR versus Ca^{+2} loadings. This represents leaching of insoluble residue, as well as the presence of a limestone component in the IR - poor samples. The positive Mg^{+2} and barely significant (.49) ^{18}O

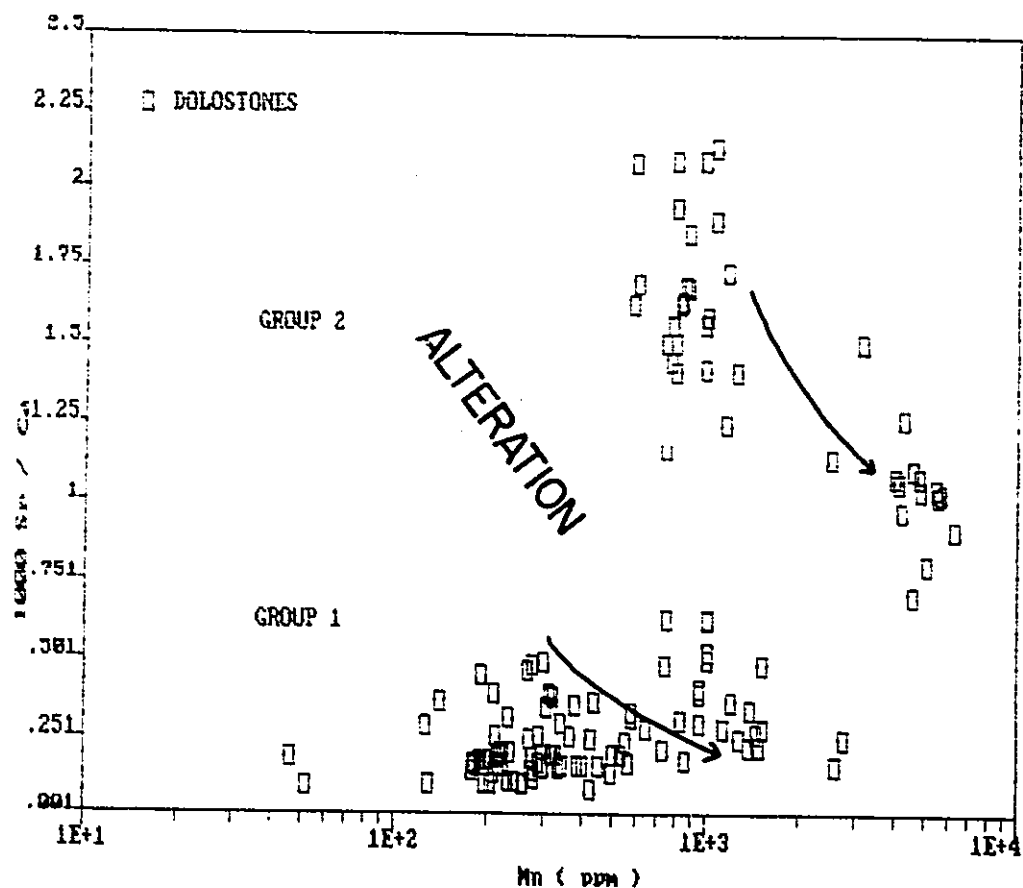


FIGURE 16: DOLOSTONE ALTERATION TREND- SCATTER DIAGRAM OF $10^3 \cdot \text{Sr/Ca}$ VS. Mn. AAS analyses of dolostones were recalculated on a 100 % IR - free basis. Dolostone samples are from both the Upper and Lower Albanel Formations. Arrows represent alteration trend.

loadings of factor 3, are tentatively interpreted to represent the fractionation of the heavier isotope into dolomite (and/or less susceptibility to subsequent alteration).

Low Sr Dolostones

Two factors control the variation of chemical and isotopic components (Table 9). Factor 1 assigns positive loadings to Sr^{+2} , Al^{+3} , Mn^{+2} , Fe^{+2} and IR and a weak negative loading to Mg^{+2} . This factor represents some leaching from the insoluble residue during acid digestion, versus dolomite content. Factor 2, characterized by positive Sr^{+2} , Na^{+} , IR, ^{18}O but negative ^{12}C loadings, is difficult to interpret. It may reflect a facies signature (ie: salinity) or lower degree of alteration, all characterized by elevated Sr^{+2} , Na^{+2} and ^{18}O concentrations. The low IR loading probably reflects the presence of detrital or pore-filling quartz. The salinity interpretation is certainly consistent with the field and petrographic evidence for local elevated salinity (sections 2.1.4 and 2.1.5). The sign of the ^{13}C loading is contrary to that expected from theory if salinity or the decrease in alteration were the controlling factors. This suggests that CO_2 generation from decomposition of C_{org} may have been involved. Discussion of this problem shall be delayed until a later section.

5.5 Primary Versus Secondary Chemical Trends

TABLE 8

FACTOR ANALYSIS OF AAS DATA - HIGH SE DOLOSTONES

N = 41

	FACTOR 1	FACTOR 2	FACTOR 3	COMMUNALITY
LSr	.919	-.073	-.190	.887
LNa	.474	.798	-.144	.884
La1	-.404	.649	.014	.585
LMn	-.935	-.116	-.306	.982
LCa	.177	-.774	-.266	.702
LMg	-.108	-.166	.908	.864
LFe	-.904	.000	.020	.817
LIR	.456	.780	-.053	.820
O18 DOL	.204	.239	.491	.340
C13 DOL	.673	.167	.428	.664

FACTOR	% VARIATION EXPLAINED	INTERPRETATION
1	39.1	POST-DEPOSITIONAL STABILIZATION
2	22.0	ALUMINOSILICATES VS. LIMESTONE COMPONENT
3	14.4	DOLOMITE COMPONENT

TABLE 9

FACTOR ANALYSIS OF AAS DATA - LOW SR DOLOSTONES

N = 84

	FACTOR 1	FACTOR 2	COMMUNALITY
LSr	.525	.728	.807
LNa	.164	.765	.613
LAl	.650	.446	.622
LMn	.832	-.028	.693
LCa	.346	-.038	.121
LMg	-.512	-.007	.262
LFe	.890	.090	.800
LIR	.528	.544	.575
O18 DOL	-.593	.732	.690
C13 DOL	.396	-.537	.445

FACTOR	% VARIATION EXPLAINED	INTERPRETATION
1	35.5	ALUMINOSILICATES (LEACHING) VERSUS DOLOMITE CONTENT AND MN AND FE IN THE DOLOMITE LATTICE
2	20.0	PREFERENTIAL PRESERVATION OF ARGILL- ACEOUS FACIES (- SALINITY) AND ¹² C CONTRIBUTION FROM THERMAL DECOMPOSIT- ION OF ORGANIC CARBON

TABLE 10

SUMMARY OF (AAS) CHEMICAL COMPOSITION OF CARBONATE GROUPS

	N = 125	N = 41	N = 84	N = 17
	ALL DOLOSTONES	HIGH SR DOLOSTONES	LOW SR DOLOSTONES	LIMESTONES
Sr (ppm)	89	304	49	286
Na "	156	275	118	131
Al "	317	3101	104	1010
Mn "	627	1646	392	804
Ca (%)	21.60	22.18	21.32	30.72
Mg "	11.69	9.29	13.09	2.28
Fe "	0.65	2.61	0.33	0.77
IR "	17.17	54.28	9.79	28.90
6O18 (‰ PDB)	-6.75	-9.09	-5.64	-11.85
6C13 "	0.74	0.37	0.91	-0.58

The presentation in Figure 16 indicates a bimodal distribution of chemical attributes for dolostones, with $1000 \text{ Sr/Ca} \leq 0.70$ being the discriminant. This represents ≈ 130 ppm strontium in pure dolomite. The factor analysis for the high-Sr dolostone group (Table 8), yields results compatible with the theory of diagenetic alteration. The opposite loadings of Sr^{+2} , ^{13}C , Fe^{+2} and Mn^{+2} (factor 1) suggest that diagenetic alteration has been the controlling parameter of their chemistry. The Lower Black Shale carbonates appear consistently more altered (having higher manganese; Figure 14) relative to the overlying Lower and Upper Banded Dolostone carbonates.

The projection of Sr^{+2} - Mn^{+2} trend for the high-Sr group to the "least altered" values yields Sr^{+2} concentrations of $\approx 400 \pm 80$ ppm ($1000 * \text{Sr/Ca} \approx 2 \pm 0.4$). Such high strontium concentrations in dolostones usually require the presence of a high Sr phase such as aragonite, during the process of penecontemporaneous-early diagenetic dolomitization (Veizer et al., 1977). The summarized petrographic observations neither refute nor support this assertion.

In contrast, the low-Sr group of dolostones appears to be, in terms of Sr^{+2} content, at the end of the alteration trend with the loss of Sr^{+2} to levels expected for open meteoric systems. Yet, as a group, these dolostones contain petrographic evidence

(section 3.3; page 80) for at least local presence of aragonite and HMC precursors. What could have been their original relative abundance is impossible to estimate. These dolostones are usually fine grained, interpreted as having formed in locally hypersaline environments and, as will be discussed later, have heavier ($\approx 4\%$) $\delta^{18}\text{O}$ than the high-Sr group. All these features suggest, if anything, less alteration for the low-Sr group. If so, the difference in Sr^{+2} content between these two groups of dolostones must be due to factors other than just a difference in the degree of post depositional alteration. The difference in original Sr^{+2} content, hence mineralogy of the precursors, the nature and temperature of dolomitizing fluids and other factors could be involved.

A microprobe (Appendix 4) examination of certain (aragonitic?) cement fabrics, as well as ion probe analysis of ooids (Veizer et al., 1987) indicated Sr^{+2} levels below 200 ppm. If these ooids were originally aragonite, the conclusion of large scale post-depositional alteration for the low-Sr dolostone group would be difficult to refute. However, Mg-calcite ooids have been reported in the literature (Flügel, 1982), supporting the possibility of different metastable precursors. In their investigation of Aphebian dolostones, Grotzinger et al., (1983), concluded that aragonite cements were initially present, based mostly on petrographic grounds as the majority of their microprobe results were under 200 ppm strontium. Similarly, an aragonite

mineralogy is inferred for certain cement fabrics of the Upper Albanel Formation, despite their low strontium concentrations. Thus the equivocal chemical (and microprobe) evidence may underestimate the qualitative proportion of aragonite.

In conclusion, based on separate petrographic and chemical evidence amassed so far, the existence of both aragonite and HMC is suggested.

ISOTOPE GEOCHEMISTRY6.1 Carbon and Oxygen Isotopes in Carbonates

6.1.1 Analytical Procedure:

Approximately 10 milligrams of carbonate was placed in a reaction vessel and evacuated for 1 hour. Samples were equilibrated for half an hour in their respective water baths, then reacted. Calcite samples were reacted for 4 hours in a 25°C water bath, whereas dolomite for 22 hours in a 50°C bath. An attempt was made to extract calcite and dolomite fractions where possible. After extraction of calcite carbon dioxide, the reaction vessel was placed in the dolomite bath. Extracted CO₂ gas was transferred into breakseals and analyzed on a SIRA mass spectrometer at the University of Ottawa. The precision for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are 0.24 and 0.35‰ PDB respectively. The precision was calculated from twenty one duplicate samples, using the following mathematical expression (Youden, 1951):

$$\text{standard deviation} = (\sum d^2 / 2n)^{1/2}$$

where d = the difference between values in each duplicate.

n = number of duplicate samples.

The notation for expressing isotopic composition is:

$$\delta(x) = (R_x - R_{std} / R_{std}) * 1000$$

where R_x = heavy/light isotope of sample

R_{std} = heavy/light isotope for standard,
in this case Pee Dee Belemnite (PDB).

6.1.2 Distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the Mistassini Carbonates:
Dolomite: Figure 17 illustrates the stratigraphic distribution of $\delta^{18}\text{O}$ in the Mistassini samples. The $\delta^{18}\text{O}$ at first increases with depth, reaching a unit average maximum in the Stratified Dolomite & Shale (arithmetic mean = -4.46‰) and Upper Black Shale (-4.04‰) Units. Subsequently, a rapid decrease results in a minimum mean of -9.35‰ in the Lower Black Shale Complex.

The $\delta^{13}\text{C}$ histogram (Figure 18) shows much smaller variations, with scatter increasing in the inferior four units. The heaviest average $\delta^{13}\text{C}$ of 2.54‰ has been observed in the Upper Banded Dolostone Unit, whereas the lightest mean values of -1.64 and -1.47‰ have been established in the Upper and Lower Black Shale Complexes, respectively.

Calcite: These analyses include limestones as well as calcite extracted from dolostones, all from the Lower Albanel Formation.

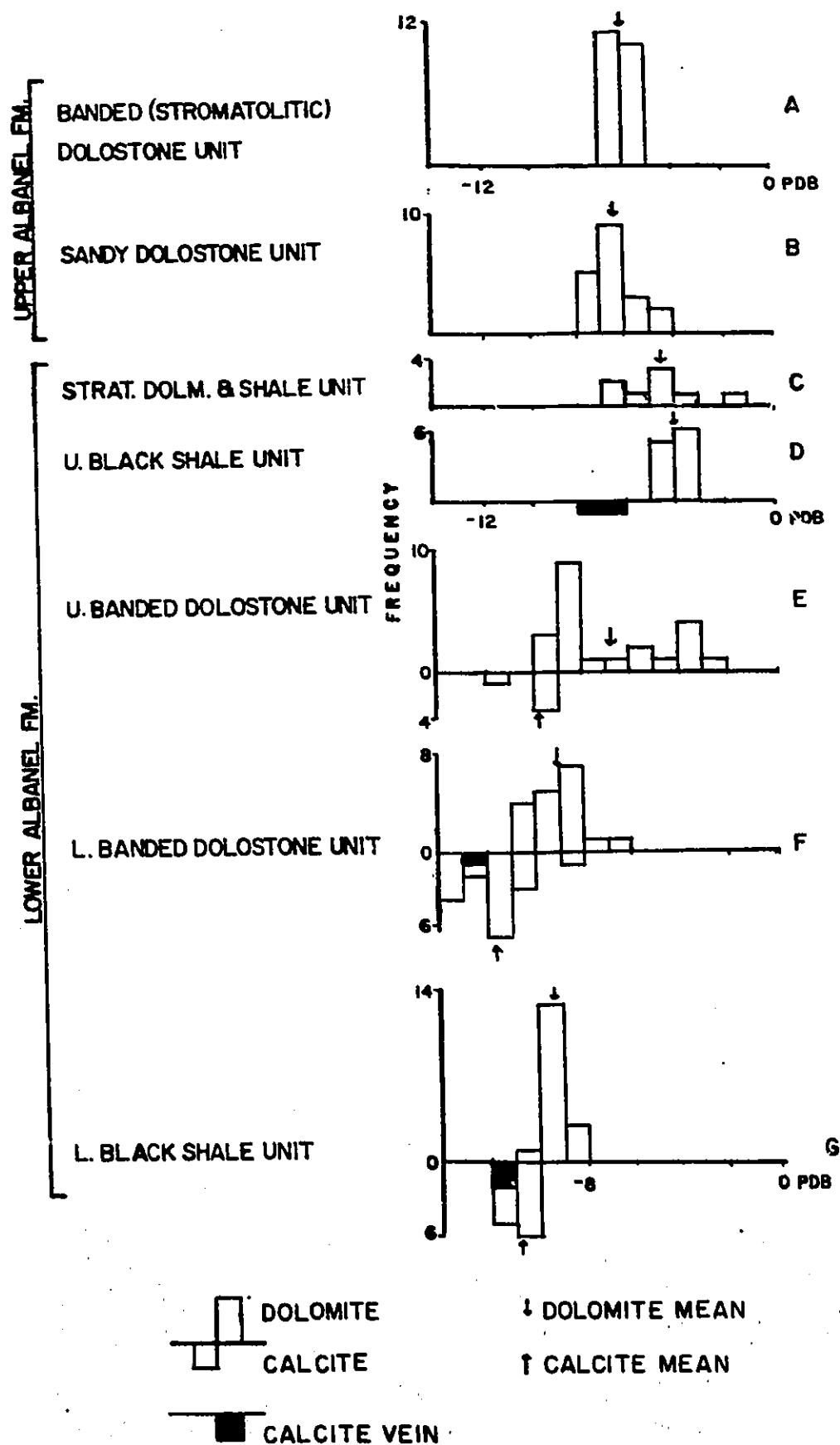
DISTRIBUTION OF $\delta^{18}\text{O}$ IN THE MISTASSINI CARBONATES

FIGURE 17: DISTRIBUTION OF $\delta^{18}\text{O}$ IN THE MISTASSINI CARBONATES. Dolostones, limestones and calcite veins were selected for isotopic analysis. Where possible both calcite and dolomite fractions were extracted and analyzed. Isotopic results are plotted relative to unit stratigraphic position. Population means are shown in the figure.

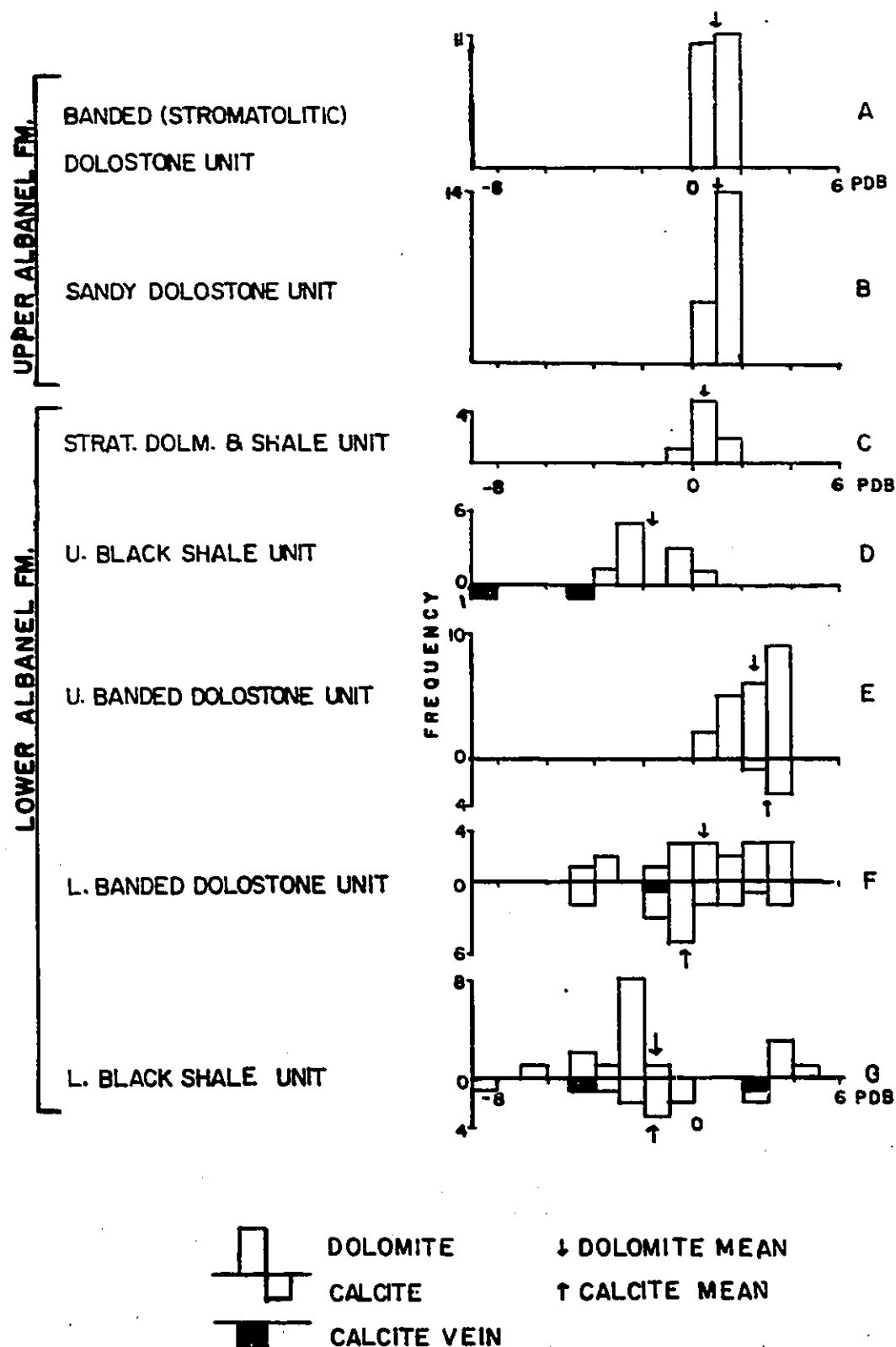
DISTRIBUTION OF $\delta^{13}\text{C}$ IN THE MISTASSINI CARBONATES

FIGURE 18: DISTRIBUTION OF $\delta^{13}\text{C}$ IN THE MISTASSINI CARBONATES. Dolostones, limestones and calcite veins were selected for isotopic analysis. Where possible both calcite and dolomite fractions were extracted and analyzed. Isotopic results are plotted relative to unit stratigraphic position. Population means are shown in the figure.

The lightest average $\delta^{18}\text{O}$ of calcite measured (-11.68‰) was found in the Lower Banded Dolostone Unit (Figure 17), which also contains the most $\delta^{18}\text{O}$ -depleted ($\approx -13\%$) samples. Relative to dolomite, calcite is also consistently depleted in ^{18}O .

The stratigraphic distribution of carbon isotopes (Figure 18) in calcite is similar to that of dolomite. Where co-existing calcite and dolomite could be separated, the difference in isotopic composition was found to be almost always small, with dolomite usually heavier than calcite.

Calcite Veins: Four en- $\acute{e}$ chelon veins and one cavity filling, associated with an early diagenetic (?) pyrite nodule (Plate 42), have been measured. Figures 17 and 18 show that the en- $\acute{e}$ chelon veins are usually more depleted than other calcites in ^{13}C as well as ^{18}O . The single calcite sample associated with pyrite (D2-153-74) has a distinctly different $\delta^{13}\text{C}$ value (2.02‰), unlike the surrounding carbonates and en- $\acute{e}$ chelon veins. This implies (along with the textural difference) a different mode for its origin.

6.1.3 Theory of Incorporation of Stable Isotopes in Carbonates:

The incorporation of oxygen and carbon isotopes into carbonate minerals is defined by a fractionation factor, which is analogous to the distribution coefficient for trace elements.

This fractionation factor " " is defined as: $\alpha = R_{x_a} / R_{x_b}$

Where Rx_a = ratio of heavy/light isotope in a, and

Ry_b = ratio of heavy/light isotope in b

Since $1000 \ln (1.00x)$ is approximated by x , the fractionation factor can be defined in terms of the difference in isotopic composition between the two substances:

$$\Delta_{a-b} = \delta a - \delta b = 1000 \ln \alpha_{a-b} \quad (\text{O'Neil, 1977})$$

The fractionation factor is temperature dependent and decreases with increasing temperature.

Fractionation mechanisms involve equilibrium and kinetic processes. The slightly different atomic masses, resulting in different chemical reactivity, are responsible for kinetic processes. Equilibrium fractionation involves a thermodynamic redistribution of isotopes such as to attain a minimum free energy at a particular temperature (in systems where no chemical transfer, except isotopic, occurs).

6.1.3.1 Factors Controlling Stable Isotopes in Carbonates:

The following factors influence the isotopic composition of carbonates (Brand and Veizer, 1981):

- a) Mineralogy exerts a control on the isotopic composition. Unlike calcite, fractionation factors for dolomite-water systems are less unequivocal since they are based

upon extrapolations from high temperature, and are thus uncertain. Land's (1980) literature review suggests that $\alpha^{18}\text{O}_{\text{dol-cal}}$ is +1 to +7‰. The $\alpha^{13}\text{C}_{\text{dol-cal}}$ is < 2 -3‰ (Anderson and Arthur, 1983).

- b) Fluid temperatures, because fractionation factor (α) is inversely proportional to the square of temperature and thus appreciable at near surface conditions.
- c) Fluid $\delta^{18}\text{O}$, which depends on a number of factors, such as salinity, because of kinetic fractionation associated with the evaporation of seawater. Fresh water, as a result of Rayleigh distillation, is depleted in ^{18}O . This depletion increases with latitude and altitude. The $\delta^{13}\text{C}$ of seawater depends on the interplay of the composition of upwelling cold water, organic productivity, temperature, age of water and the rate of CO_2 infusion and escape. Several of these factors are related to depth (Anderson and Arthur, 1983). Also, hypersaline or stagnant depositional environments appear to exhibit heavier $\delta^{13}\text{C}$ values compared to their less restricted, normal marine counterparts.

The unresolved question is the $\delta^{18}\text{O}$ of past sea water. The available data indicate a lighter isotopic composition for ancient, particularly Precambrian, sea water

(cf. Veizer, 1983). Nevertheless, the issue is still hotly debated. In contrast, the $\delta^{13}\text{C}$ does not show any unidirectional secular trend (Schidlowski et al., 1975), but second order secular variations have been clearly established (Veizer, et al., 1980).

- d) Certain organisms secrete their carbonate shells in apparent isotopic equilibrium, but others - such as corals and echinoderms - exhibit a "biological" fractionation effect (Anderson and Arthur, 1983). In the latter, the incorporation of metabolic "light" CO_2 results in isotopic disequilibrium with the surrounding fluids.

6.1.3.2. Factors Controlling Stable Isotopes in Diagenetic

Carbonates:

Much of the diagenetic stabilization of platform carbonates occurs in the meteoric vadose and phreatic zones. Allan and Mathews (1977) found depletions in ^{18}O and ^{13}C in altered carbonates, due to the involvement of "light" metabolic CO_2 from the soil. However, Land (1986) indicated that ^{13}C -depleted carbonates would not be expected in arid areas (ie: little vegetation; also applicable to pre-Silurian carbonates) or where a large reservoir of "heavy" carbonate could buffer the system.

Brand and Veizer (1980, 1981) showed that during the wet

chemical stabilization of carbonates, the increase in Fe^{+2} , Mn^{+2} is complemented by a decrease in Sr^{+2} , Na^{+} , ^{18}O and $\pm \delta^{13}\text{C}$. The precipitation of late diagenetic phases only exaggerates the enrichments and depletions. The extent of this alteration was found to be a function of the stability of the precursor, water/rock ratio, differences in fluid composition (marine versus meteoric), as well as the magnitude and sign of the distribution coefficient and fractionation factors. As sediments, particularly organic-rich ones, pass through different burial zones, characterized by different diagenetic processes, carbonate precipitation is dominated sequentially by bacterial oxidation, sulfate reduction, fermentation and decarboxylation. The expected ^{13}C would be of -25, -25, +15 and -20 (?) ‰, respectively (Curtis, 1978). Furthermore, the isotopic composition of carbonates can be altered by exchange reactions at depth. O'Neil (1977) stated that massive ^{18}O exchange was possible at high grade diagenetic (200-300°C) to low grade metamorphic temperatures. The rate of exchange is a function of temperature, mineralogy and structure (Longstaffe, 1986). Carbonates (especially calcite) undergo isotopic exchange (recrystallization) at lower temperatures than do silicates. Degens and Epstein (1964) found that dolomite is much more resistant to recrystallization than calcite. However, Land (1980) believes that ancient, depleted dolostones could have resulted from recrystallization at basinal temperatures exceeding 100°C. The structural and textural inhomogeneity of dolomite, as illustrated by SEM studies (Wenk et

al, 1983), suggests that perhaps dolomite goes through stabilization reactions resulting in a more "ideal" dolomite composition (Land, 1986).

In the extreme case, the metamorphism of carbonates results in decarbonation reactions. The liberated CO_2 is enriched in the heavy isotope, especially for oxygen (Sheppard and Schwarz, 1970), resulting in a depleted residual carbonate. Such reactions are expected in siliceous carbonates. However, intense metamorphism of pure carbonates can still result in an unaltered initial carbon isotopic composition (Sheppard and Schwarz, 1970).

6.1.4 Diagenetic Imprint and Stable Isotopic Composition of the Mistassini Carbonates:

The oxygen-carbon isotopic composition of studied samples is summarized in Figure 19. This summary shows that the three groups of carbonates defined on the basis of chemical data have distinctive isotopic compositions. The low Sr dolostones of the upper part (top of the Upper Banded Dolostone Unit and above) of the sequence have the heaviest ^{18}O and the least variable ^{13}C . The Sr-rich dolostones and limestones of the bottom part of the sequence are depleted in ^{18}O and contain some strongly ^{13}C depleted samples. On average, limestones are about 3‰ lighter in ^{18}O than are the stratigraphically equivalent dolostones. Finally, calcites (and 1 dolomite) from veins within the Lower Albanel Formation are usually depleted in ^{13}C and ^{18}O if compared

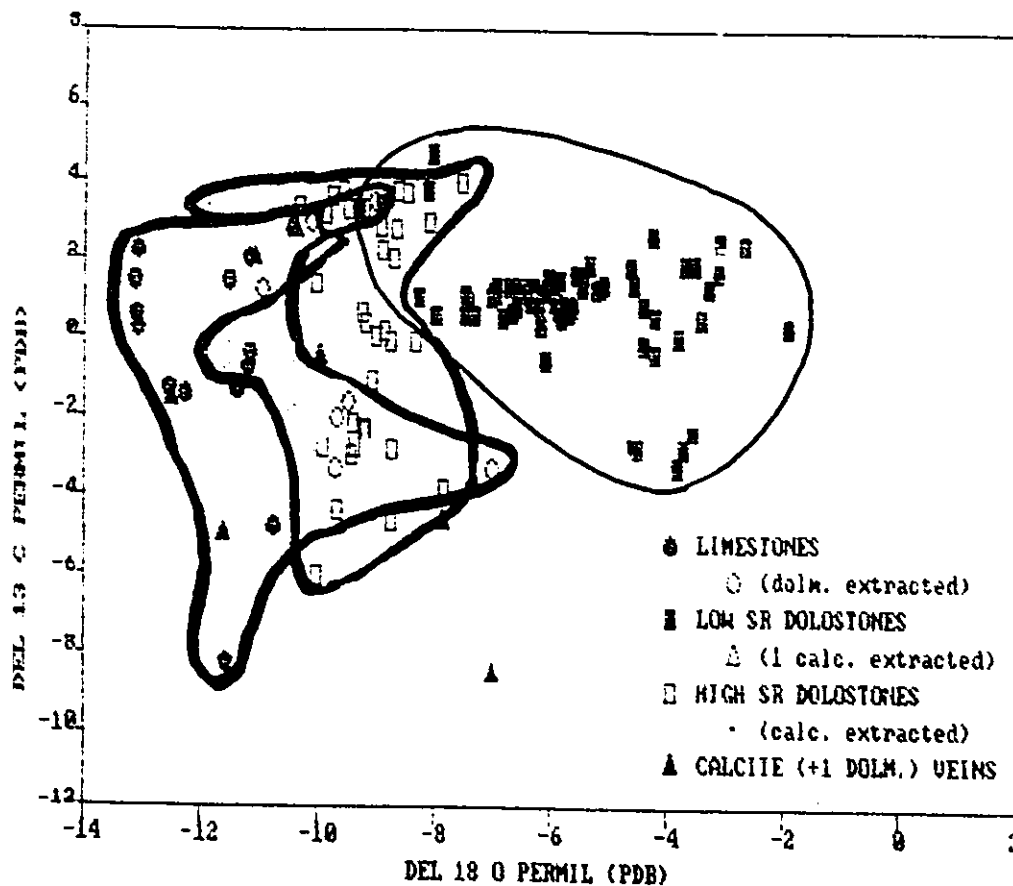


FIGURE 19: SCATTER DIAGRAM OF $\delta^{13}\text{C}$ VS. $\delta^{18}\text{O}$ OF THE MISTASSINI CARBONATE GROUPS. The Limestone group includes the calcite fraction, as well as extracted dolomite (○). The Low Sr Dolostone Group includes the dolomite portion and one extracted calcite fraction (△). The High Sr Dolostone Group is represented by both dolomitic and extracted calcitic (●) fractions. Major fields are encircled, except for the 5 calcite (of which 4 are of the en - echelon type) and one dolomite vein samples.

to their enclosing rocks, suggesting an autochthonous carbonate source. The ^{18}O of the calcite reflects that of the surrounding carbonates, modified by the temperature and salinity of the fluids.

Low-Sr Dolostones

Statistical evaluation of trace element and isotope data (Table 9) shows that both, oxygen and carbon isotopes load - albeit antithetically - on the same factor 2. This has been interpreted as post-depositional alternation (or degree of preservation), but probably incorporates several processes. Firstly, it likely represents increasing recrystallization at elevated temperatures and/or in progressively more open systems in the presence of meteoric waters. This results in generally low Sr and Na contents as well as their continuous depletions (Figures 20 and 21) with increasing alteration. The degree of alteration increases from the bottom to the top of the sequence and therefore correlates with texture. The Upper Albanel is commonly coarser and its oolitic grainstones possess the most negative $\delta^{18}\text{O}$ values. This strongly suggests that it was not the increase in temperature, but the permeability and thus the high water/rock ratios which controlled the ^{18}O shift of $\approx 8\%$ for the low Sr dolostones. The projection to "least altered" values (Figures 20 and 21) yields dolostones with ^{18}O of $\approx -2.5 \pm 1\%$, $\text{Sr}^{+2} \approx 90 \pm 50$ ppm and $\text{Na}^{+} \approx 150 \pm 50$ ppm.

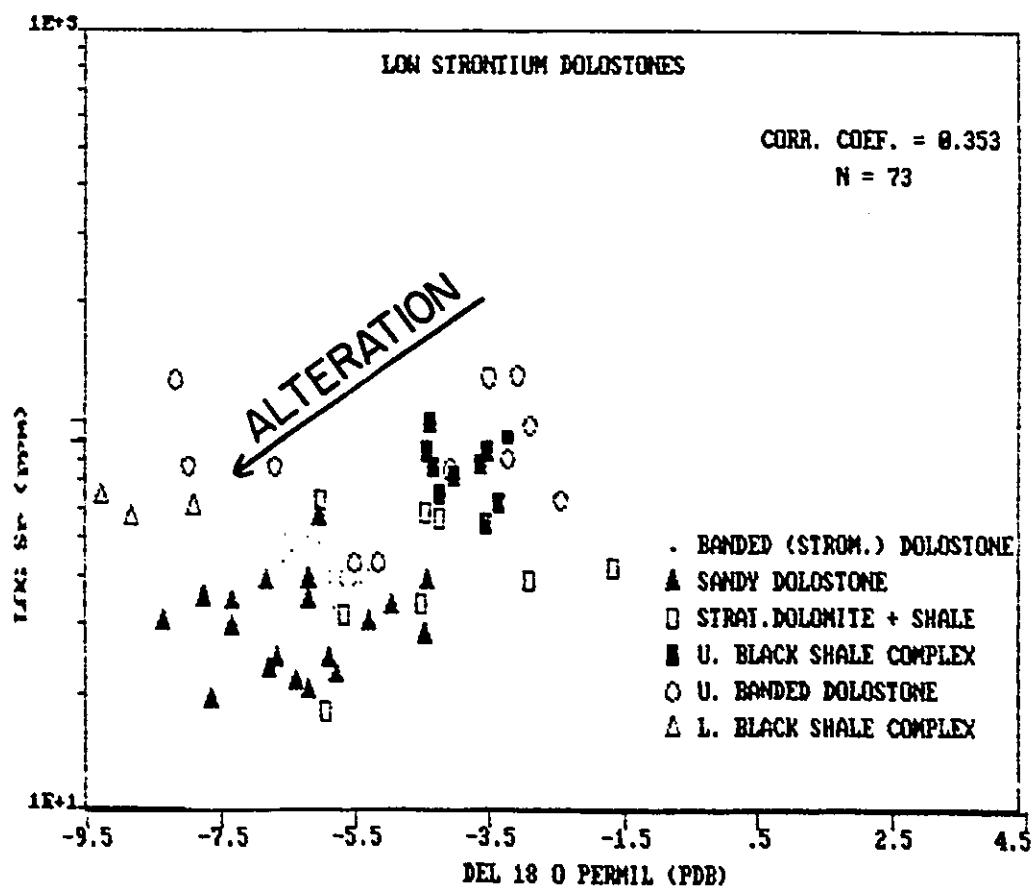


FIGURE 20: CORRELATION DIAGRAM BETWEEN LOG Sr AND $\delta^{18}\text{O}$ FOR THE LOW Sr DOLOSTONE GROUP. The symbols correspond to samples from the different units. The positive correlation obtained is consistent with that expected for diagenetic alteration (arrow), and is statistically significant at the 99 % confidence level.

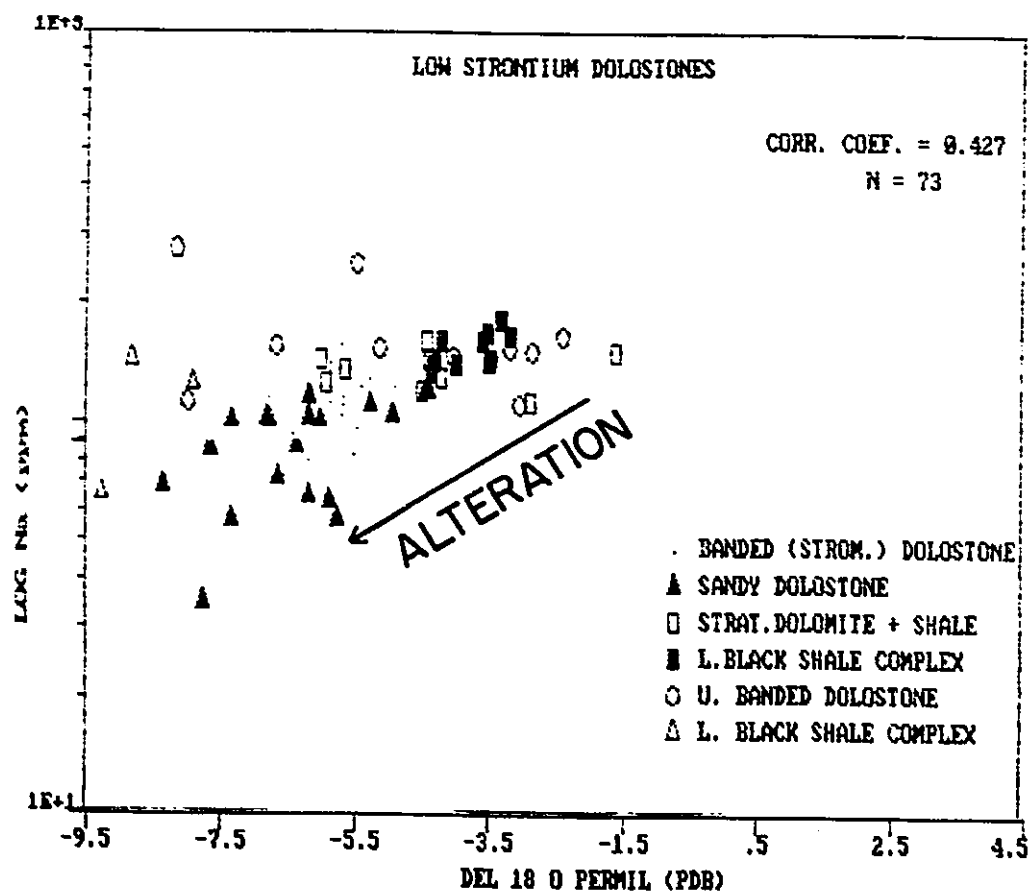


FIGURE 21: CORRELATION DIAGRAM BETWEEN LOG Na AND $\delta^{18}\text{O}$ FOR THE LOW Sr DOLOSTONE GROUP. The symbols correspond to samples from the different units. The positive correlation obtained is consistent with that expected for diagenetic alteration (arrow), and is statistically significant at the 99.9 % confidence level.

The ^{13}C during recrystallization has been buffered by the large reservoir of carbon in the carbonates and therefore reflects the original values of $\approx 2 \pm 2\%$. (Figures 19 and 22). The only exception are the samples from the Upper Black Shale Unit, with $\delta^{13}\text{C}$ of about -3% . Because of the association of these dolostones with the organic rich sequence, it is reasonable to assume that they incorporated some CO_2 derived from oxidation of organic matter.

High-Sr dolostones

Statistical evaluation of trace element and isotope data (Table 8) suggests that ^{13}C in this population is controlled by the degree of post depositional alteration (factor 1). For oxygen the ^{18}O enrichment appears to correlate somewhat with the Mg content of the rocks (factor 3). The shift towards ^{12}C enrichment clearly relates to recrystallization accompanied by a loss of Sr^{+2} and gain of Mn^{+2} . The latter is particularly pronounced in the shaly unit with high C_{org} content (Figure 23) and may suggest the superposition of an additional facies factor (ie: sulfate reduction effects) to account for the distinct Mn and ^{13}C change defined by the lithological boundary. As in the previous example, the existence of ^{13}C depleted values can reasonably be attributed to incorporation of $< 1/3$ of "organic" CO_2 into such dolostones. The projection to the 'least altered' values for this population of dolostones yields ^{13}C values of perhaps $+2 \pm 2\%$, Sr^{+2} content of $\approx 375 \pm 75$ ppm, (Figure 22) and Mn^{+2} values of $\approx 1000 \pm$

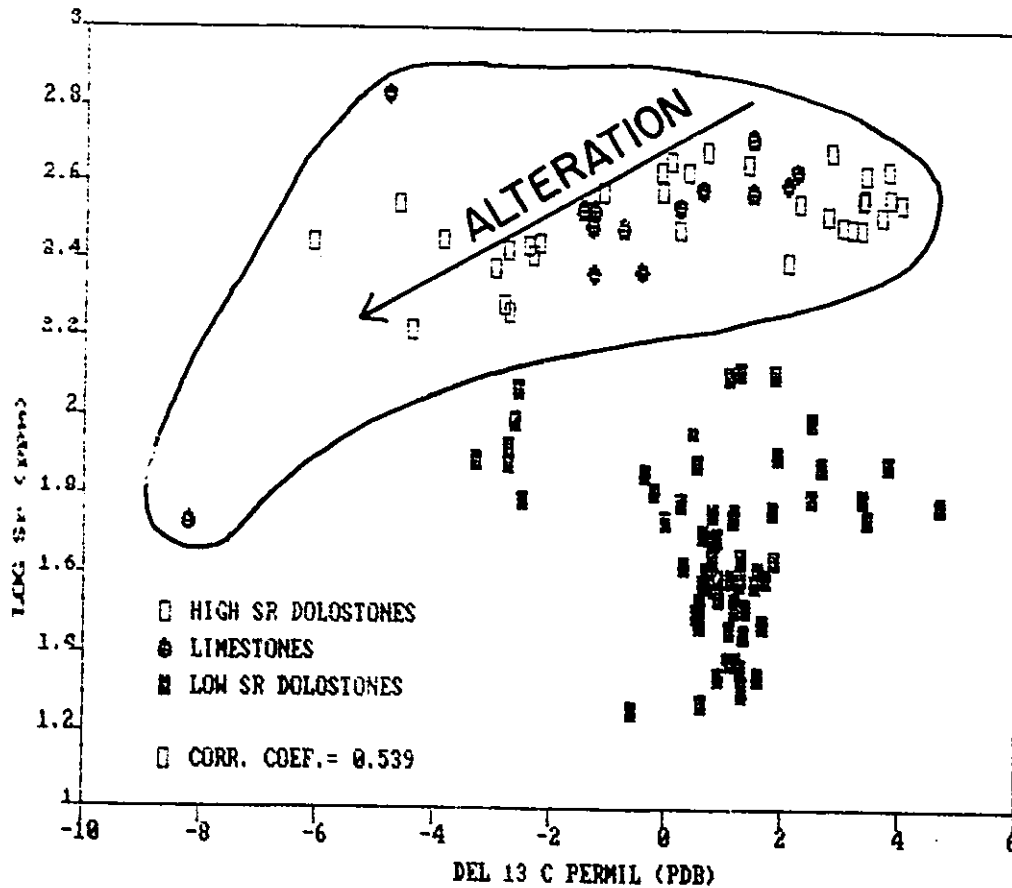


FIGURE 22: SCATTER DIAGRAM OF LOG Sr VERSUS $\delta^{13}\text{C}$ FOR THE MIST-ASSINI CARBONATE GROUPS. High and Low Sr Dolostone, as well as Limestone Groups, are illustrated. Diagenetic alteration is indicated by arrow. The positive correlation obtained for the High Sr Dolostones is consistent with alteration and is statistically significant at the 95 % confidence level.

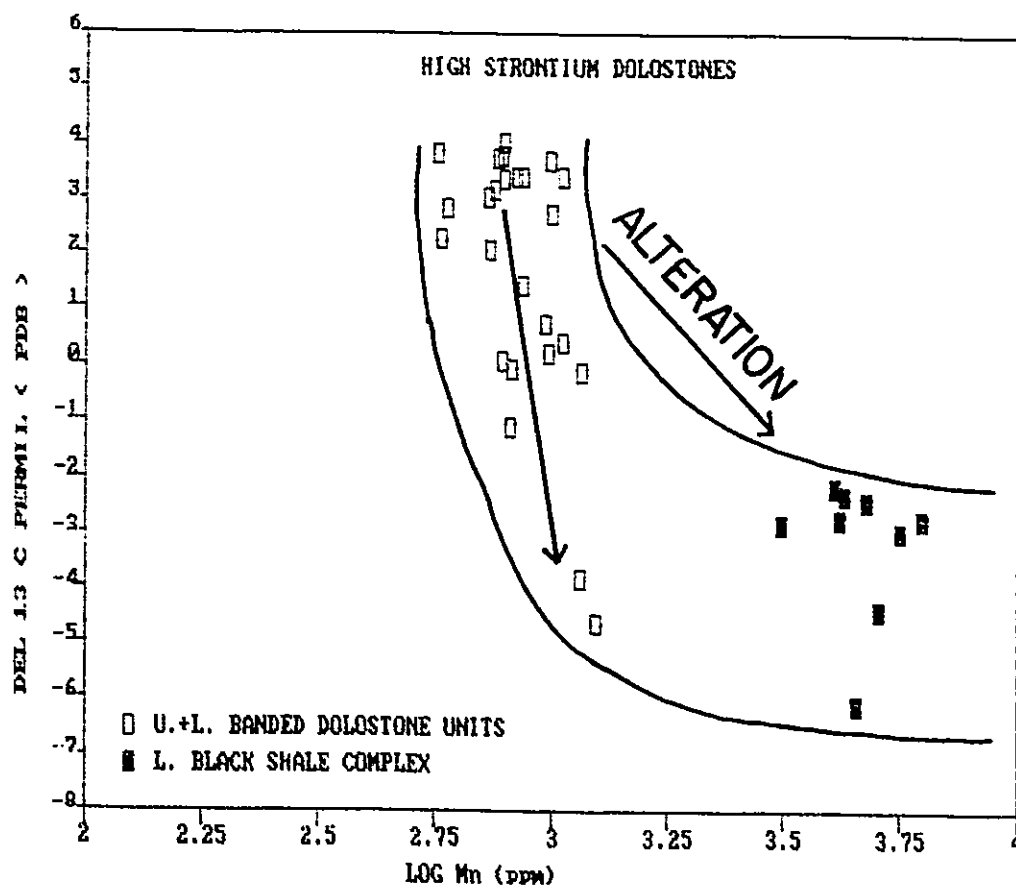


FIGURE 23: SCATTER DIAGRAM OF LOG Mn VS. $\delta^{13}\text{C}$ FOR THE HIGH Sr DOLOSTONE GROUP. Direction of diagenetic alteration indicated by arrows. The marked increase in manganese levels coinciding with change in lithology implies an additional (facies) control.

400 ppm (Figure 23). The $\delta^{18}\text{O}$ of $\approx -9 \pm 2\%$ is distinctly lighter than that of the stratigraphically higher low Sr dolostones (Figure 19). In contrast to the latter group, the depletion in ^{18}O appears to be correlated with depth (cf. Figure 17). Since, it is the less permeable Lower Black Shale Unit that has more ^{18}O depleted values, it appears that temperature and not water/rock ratio may have been the major reason for the observed oxygen isotopic shift. Other things being equal, the temperature difference between the Upper Banded Dolostone and the Lower Shale Units could have been 18°C ($\approx 4\%$), consistent with ≈ 500 meters deeper burial depth for the latter (cf. Figure 3).

Limestones

In many respects, the limestone isotope pattern (Figure 19) resembles that of the co-stratigraphic high Sr dolostones, but with approximately -3% $\delta^{18}\text{O}$ offset. Again, introduction of ^{13}C depleted signal is associated with shaly sequences rich in organic matter (Table 6, factor 1 & Figure 18), pointing to thermal cracking and decarboxylation of organic matter during burial as its cause. The projection to 'least-altered' values (Figure 22) suggests, similar to the high Sr dolostones, the $\delta^{13}\text{C}$ of $\approx 2\%$ and a Sr^{+2} content of $\approx 450 \pm 75$ ppm. The dispersion of $\approx 3\%$ in $\delta^{18}\text{O}$ is related to recrystallization (Table 6, factor 3). However, the loss of Sr^{+2} accompanied by an ^{18}O enrichment, is difficult to interpret. Although the sample population is small, exclusion of two "anomalous" samples results in a clarification

of interpretation. The latter assigns the ^{18}O -control to dolomite.

Interim summary

The previous discussion indicated $+2 \pm 2\%$ as possible primary values for $\delta^{13}\text{C}$ of all populations. The perusal of ^{18}O data suggests that the stratigraphically higher low-Sr dolostones varied this parameter from $\approx -2.5 \pm 1$ to -8% with increasingly open system alteration. The subjacent high-Sr dolostones range from ≈ -7 to -11% and the co-stratigraphic limestones from ≈ -10 to -13% . This may suggest an increasing degree of alteration in this order, with the shift caused by recrystallization at higher temperatures and/or in more open systems. Yet, as a group, the dolostones and limestones in the lower portion of the sequence show petrographic (fine grained textures) and chemical (higher Sr^{+2}) characteristics, which are difficult to reconcile with a more open diagenetic system, if compared to that of the upper part of the section. It would appear that these two intervals of the Mistassini sequence had separate post-depositional histories. Starting from the top of the Upper Banded Dolostone unit and upwards, the alteration trends are related to relatively open system near-surficial circulation cells. These led to dolomitization and leaching of trace elements (e.g. Sr^{+2}) at near-surface temperatures. In contrast, the subjacent interval may have been subjected to alteration by fluids at lower water/rock ratio (and thus more concentrated solutions) and at elevated

temperatures. This could explain the higher trace element (e.g. Sr^{+2}) content and the depleted ^{18}O signal of both limestones and dolostones. If so, the difference in temperature between the two systems would have to be a minimum 25°C ($\approx 6\%$), and likely more because the more saline deeper fluids were probably enriched in ^{18}O , if compared to those in the shallower circulation cell.

It is possible that the deeper (high Sr^{+2}) dolostones and limestones both equilibrated with these fluids and the observed $\Delta^{18}\text{O}$ dolomite-calcite of $\approx 3\%$ (Figure 19) is a near-equilibrium fractionation (cf. also Milliken et al., 1981). If the calcite and dolomite extracts from the same sample are considered (Figure 24), the overall $\Delta^{18}\text{O}$ appears to be $\approx 2\%$, but decreases to $\approx 0.5\%$ for pure dolomitic samples. I do not have a satisfactory explanation for this relationship, except perhaps to suggest that the extraction of 'calcite' in progressively more dolomitic samples may have incorporated some dolomitic CO_2 .

6.1.5 Implications of ^{18}O and ^{13}C on Dolomitization:

Although Figure 19 defines five dolostone sub-populations, these represent different diagenetic histories, differential alteration, facies and secular controls rather than distinct dolomitization mechanisms. However, some isotopic evidence is consistent with certain dolomitization mechanisms.

Sabkha Model:

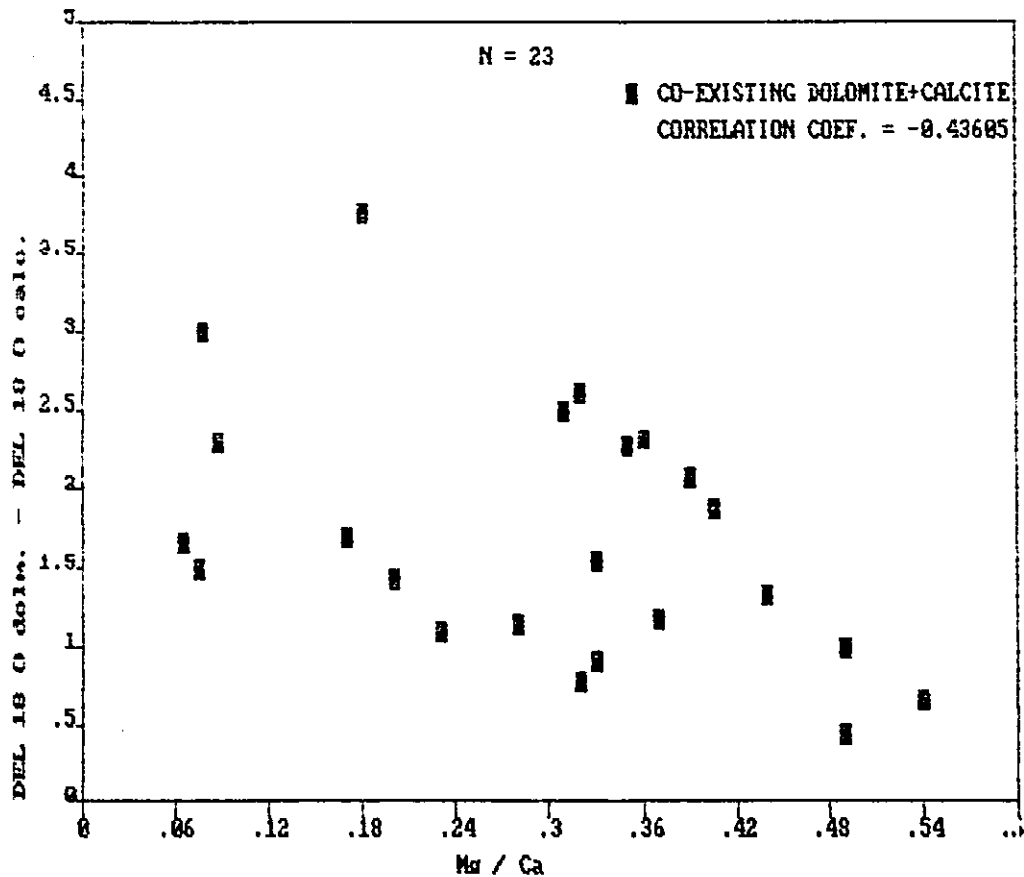


FIGURE 24: CORRELATION DIAGRAM BETWEEN $\Delta_{\text{DOL-CAL}}$ AND Mg/Ca. Co-occurring calcite and dolomite were extracted and analyzed. The negative correlation (statistically significant at the 95 % confidence level) suggests that more dolomitic samples may have suffered some premature dissolution during the phosphoric acid attack of calcite. Mg/Ca values correspond to weight ratios.

- 1) The ^{18}O -enriched stratigraphic interval (Figure 27) also exhibits evidence of peritidal depositional conditions (sections 2.1.4 and 2.1.5).
- 2) The increasingly heavy ^{13}C trend near the base (Figure 26) is consistent with the inferred peritidal depositional conditions (Hofmann, 1978; Lehmann, 1974) for the Basal Stromatolite Dolostone. A sabkha model was previously suggested by Chown and Caty (1983), with supporting evidence of fluid inclusion anhydrite.

Dorag Model:

The presence of local meteoric diagenesis (coarsely crystalline fabrics, ^{18}O depleted signatures and stabilization of metastable phases, suggest that dolomitization by such a model is feasible.

Organic Dolostones:

A portion of the ^{13}C -depleted dolostones in the Lower Black Shale Unit could conceivably have been formed as a result of increased alkalinity related to SO_4 -reduction (Lippman, 1973).

Burial and Fault Dolomitization:

Local coarsely crystalline fabrics and ^{18}O -depleted values suggest a burial dolomitization episode. The latest episode of dolomitization is indicated by coarse, white fault dolomite (Plate 49).

6.1.6 Evidence for a Primary Carbon Isotopic Signal:

Figure 25 illustrates the variation in $\delta^{13}\text{C}$ with basin depth. The upper 4/5 is relatively uniform, followed by large oscillations in the remaining 1/5 of the section. A stable $\delta^{13}\text{C}$ implies a generally stable marine depositional setting whereas a fluctuating signal reflects the changing nature of the depositional environment, secular changes and/or differential alteration. Recent marine carbonates display the $0 \pm 4\%$ range (Hudson, 1977), whereas ancient carbonates oscillate about $0 \pm 3-5\%$ (Veizer et al., 1980). Thus the vast majority of the Mistassini carbonates analyzed represent about normal marine conditions.

Post-depositional alteration was found to account for the negative (less than 0) $\delta^{13}\text{C}$ values in the organic-bearing shale complexes. Veizer et al., (1980) indicated that carbonates usually faithfully record the initial composition within -1% PDB. Thus the remaining variations, except for those in the Upper and Lower Shale Complexes, may represent a primary signature, reflecting facies or a secular trend.

The following observations favor the existence of a primary carbon isotopic signature:

1. Elevated $\delta^{13}\text{C}$ values are almost always sequential (forming a smooth trend) and partially correlated with facies and/or depositional unit.

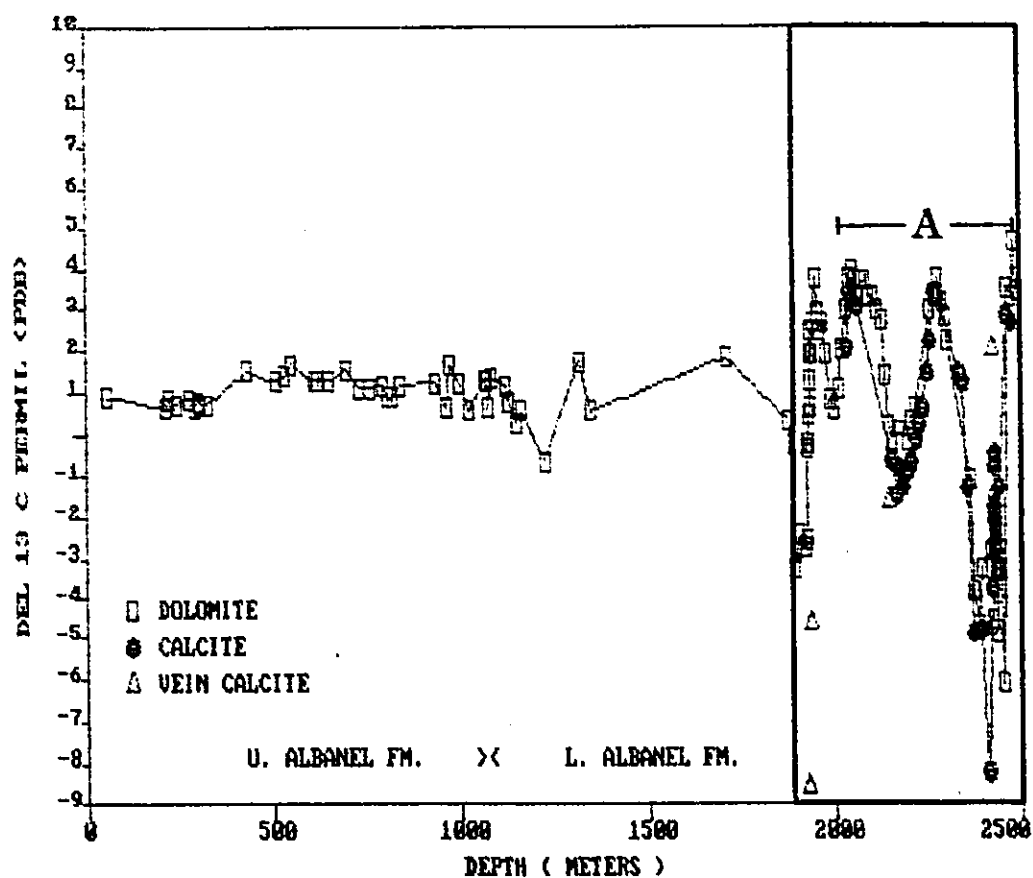


FIGURE 25: $\delta^{13}\text{C}$ STRATIGRAPHY OF THE MISTASSINI CARBONATES. Calcite, dolomite and vein calcite were analyzed. The high Sr interval is indicated by "A". Highlighted rectangle represents portion of sequence where greater resolution is desired (next figure).

2. Co-existing dolomite and calcite are characterized by a parallel $\delta^{13}\text{C}$ trend, calcite being always lighter, and by "smooth" transitions in the $\delta^{13}\text{C}$ pattern with depth (Figure 26).

Whether the primary signature represents a secular or facies control is more difficult to decide. This would require analysis of different boreholes throughout the basin and from other carbonates of similar age (any secular variations would have to be global). The following discussion will investigate the role of facies, with any residual fluctuations assigned to secular changes.

Figure 26 illustrates the $\delta^{13}\text{C}$ trend with greater resolution. Four peaks are evident; the younger two appear to form two cycles. Although the two older peaks are separated by depleted values (diagenetic reactions involving ^{12}C), the downward trend may still be real. Three peaks are located in the combined Banded Dolostone Units; the fourth is represented by the lowermost four samples (dolomite and calcite) extending over ≈ 30 meters. This last peak is corroborated by a published analysis of the basal stromatolitic unit, unavailable to this author. Schidlowski et al. (1983) reported a $\delta^{13}\text{C}$ of +6.36‰, for a stromatolitic dolostone interpreted as peritidal (Lehmann, 1974), and with fluid inclusion evidence supporting local elevated salinities (Caty and Chown, 1983). Thus the suite of heavier $\delta^{13}\text{C}$ values may be

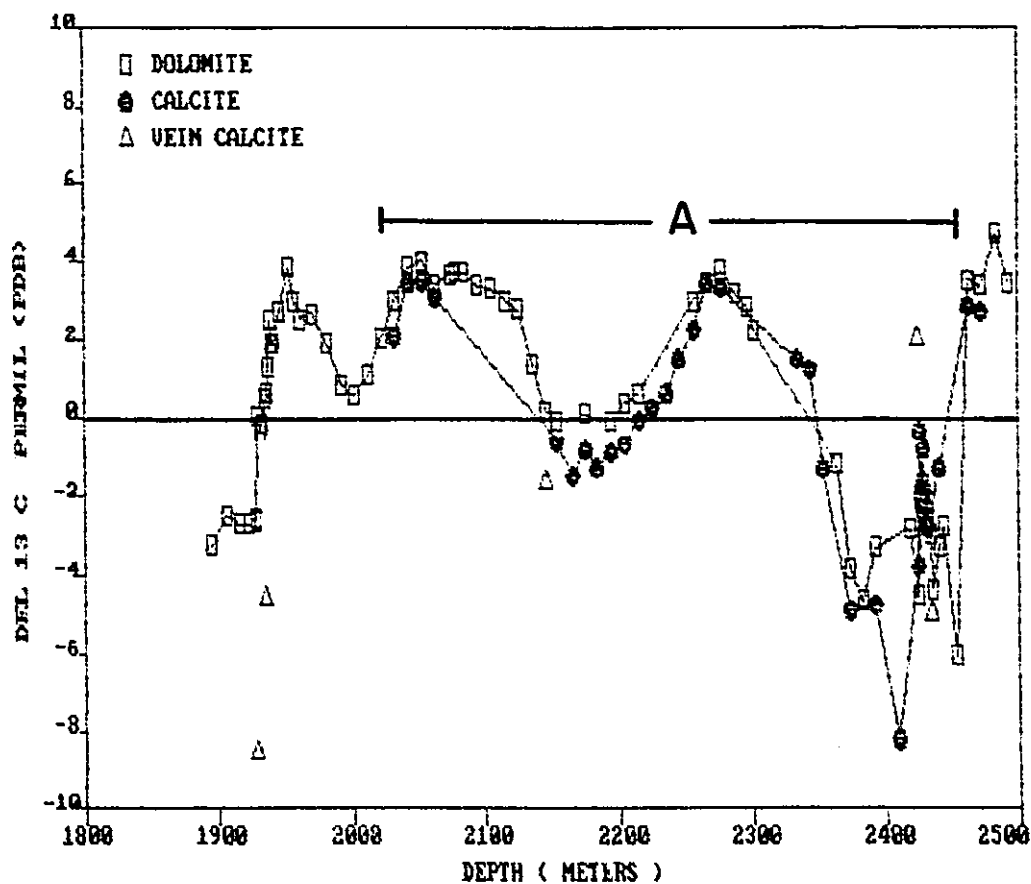


FIGURE 26: HIGH RESOLUTION $\delta^{13}\text{C}$ STRATIGRAPHY OF THE LOWER ALBANELL CARBONATES. The Stratified Dolomite and Shale Unit was omitted. Calcite, dolomite and vein calcite were analyzed. The high Sr interval is indicated by "A". Horizontal line defines boundary below which samples are more altered.

associated with a restricted (?), more saline environment indicating a facies control.

The causes of the remaining three oscillations in the overlying carbonates are less obvious. The Banded Dolostone section has coarser clastics (insoluble residue) in the upper and more argillaceous contribution in the lower unit. Similarly the trace element and isotopic composition evolves across this interval (low versus high Sr groups), yet this does not appear to influence the carbon isotope signal. The apparent lack of evident facies control suggests a possible secular control. The above variations may represent basinal or global fluctuations; the confirmation of the latter requiring additional measurements in coeval basins. For example, similar variations have been demonstrated for the (restricted) Lomagundi Dolostones (Schidlowski et al., 1975), where the heavy $\delta^{13}\text{C}$ has been ascribed to the sequestering of ^{12}C into organics.

In summary, a combination of secular controls with some facies influence are believed to have been responsible for the observed fluctuations in $\delta^{13}\text{C}$.

6.1.7 Stratigraphic Signal for Oxygen Isotopes:

The vast majority of $\delta^{18}\text{O}$ values represent different degrees of alteration (a function of diagenetic susceptibility) and reflect the composition of the fluid. It is apparent that the

$\delta^{18}\text{O}$ variation with depth (Figures 27 and 28) is not simply a function of fluid temperature, as a continuous ^{18}O depletion with burial depth would be expected. As discussed previously, the two-fold $\delta^{18}\text{O}$ pattern may perhaps reflect two diagenetic systems, a relatively open near surficial one and another more restricted, deeper and with higher salinity and temperature.

6.1.8 Comparison of Isotopic Signatures with other Sequences:

Figures 29 and 30 show the mean $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for several Proterozoic platform dolostone sequences (Veizer, unpublished). All dolostones were considered in the Mistassini study. Exclusion of "altered" samples with negative $\delta^{13}\text{C}$ values would result in a somewhat higher $\delta^{13}\text{C}$ than that presented here. The Mistassini mean $\delta^{13}\text{C}$ (0.74‰ PDB) is consistent with other sequences of Aphebian age (Duck Creek and Coronation dolostones) and may represent an increasing burial flux of $\text{C}_{\text{organic}}$, resulting in a heavier $\delta^{13}\text{C}$ of oceanic TDC, relative to the younger, McArthur dolostones.

For oxygen isotopes, the Mistassini dolostone average represents the heaviest Proterozoic sequence (-6.75‰ PDB), with the Malmani dolostones a close second. This is true even if the Mistassini dolostones are compared with a larger set of published values listed in Schidlowski et al. (1975). No overall secular trend is evident from this compilation, except that all early Proterozoic dolostones are relatively light, with average $\delta^{18}\text{O} <$

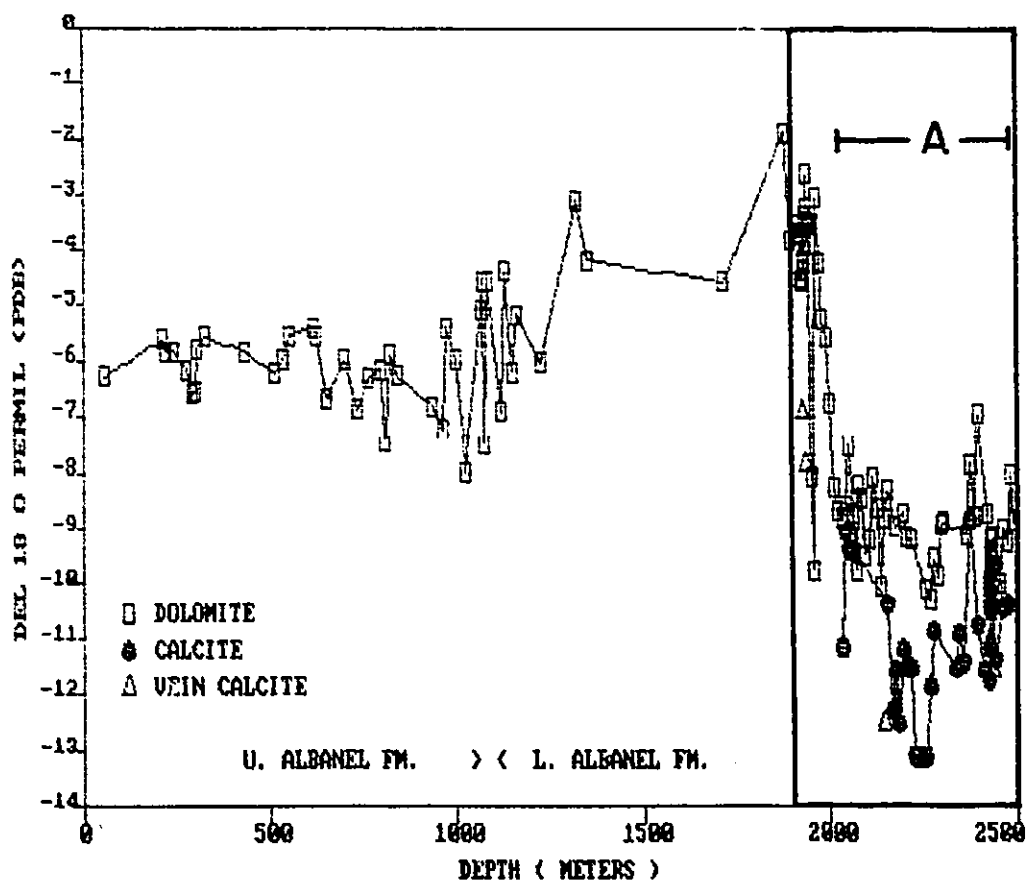


FIGURE 27: $\delta^{18}\text{O}$ STRATIGRAPHY OF THE MISTASSINI CARBONATES. Calcite, dolomite and vein calcite were analyzed. The high Sr interval is indicated by "A". Highlighted rectangle represents portion of sequence where greater resolution is desired (next figure).

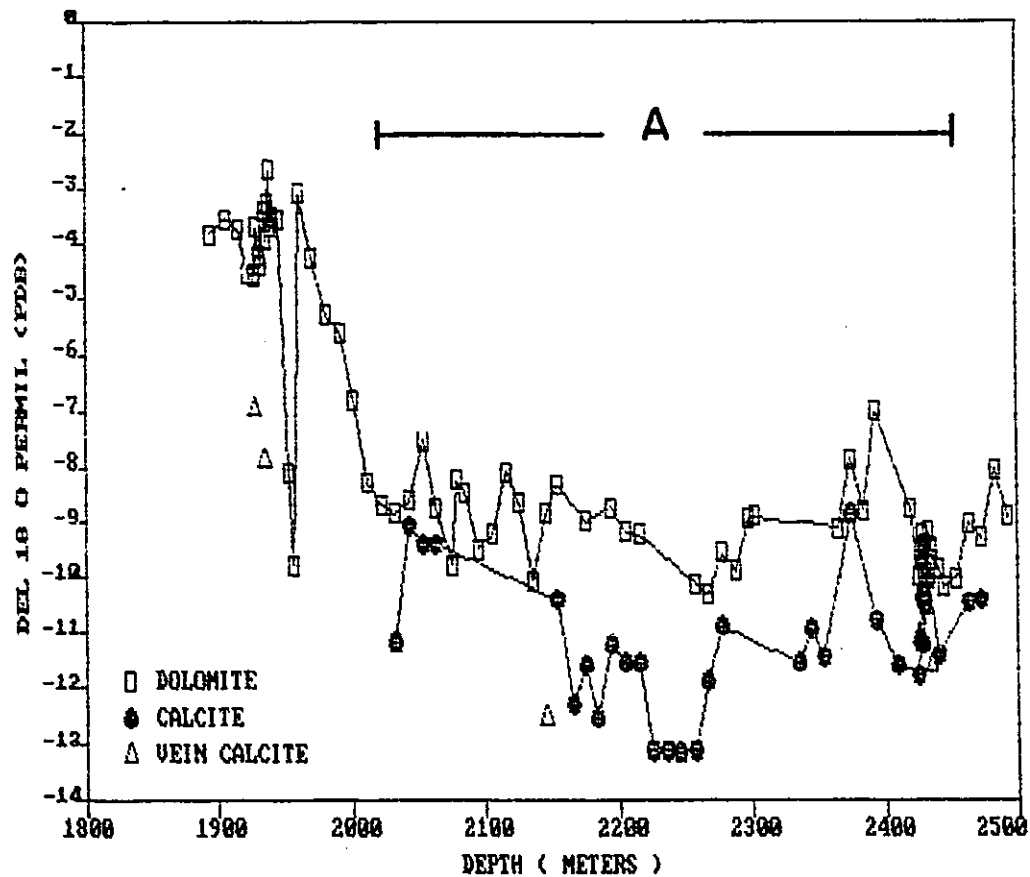


FIGURE 28: HIGH RESOLUTION $\delta^{18}\text{O}$ STRATIGRAPHY OF THE LOWER ALBANIEL CARBONATES. The Stratified Dolomite and Shale Unit was omitted. Calcite, dolomite and vein calcite were analyzed. The high Sr interval is indicated by "A".

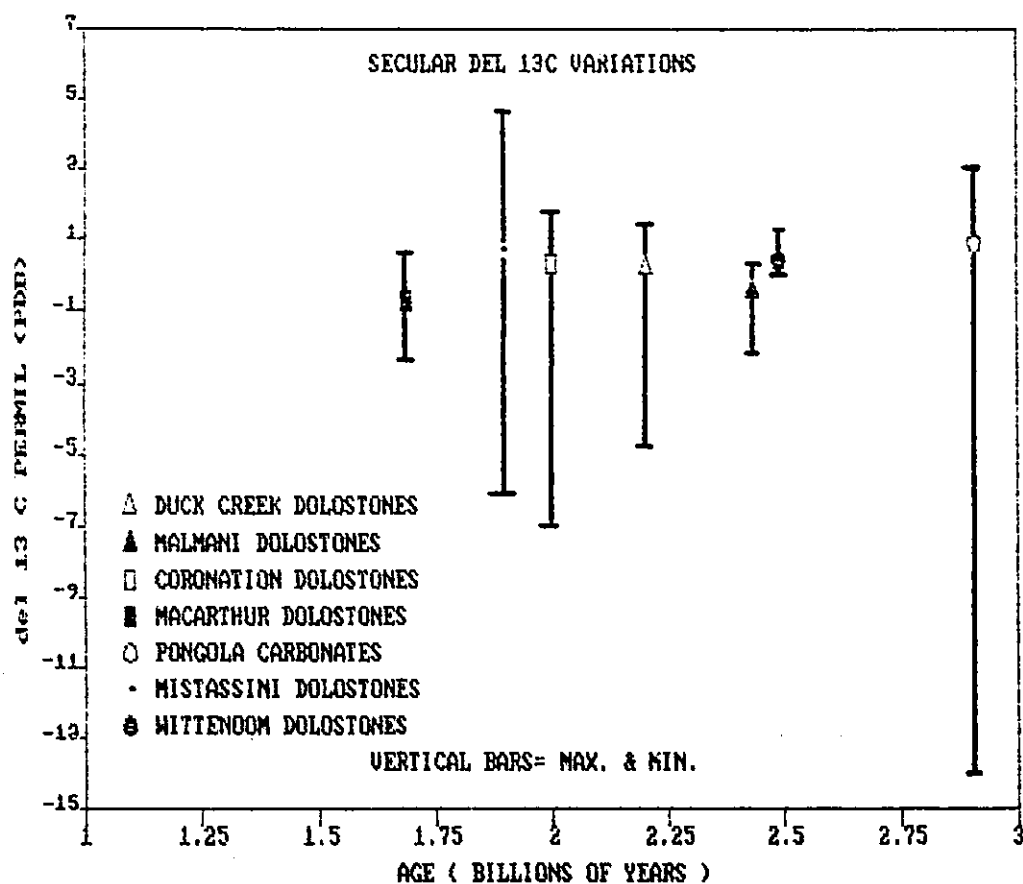


FIGURE 29: COMPARISON OF $\delta^{13}\text{C}$ TO OTHER PRECAMBRIAN PLATFORM SEQUENCES. $\delta^{13}\text{C}$ means and ranges of the different sequences are plotted in order of increasing age. A Mistassini mean of +0.74 ‰ (N=125) represents a minimum value, due to inclusion of $\delta^{13}\text{C}$ -depleted dolostones. Unpublished data from Veizer (1988).

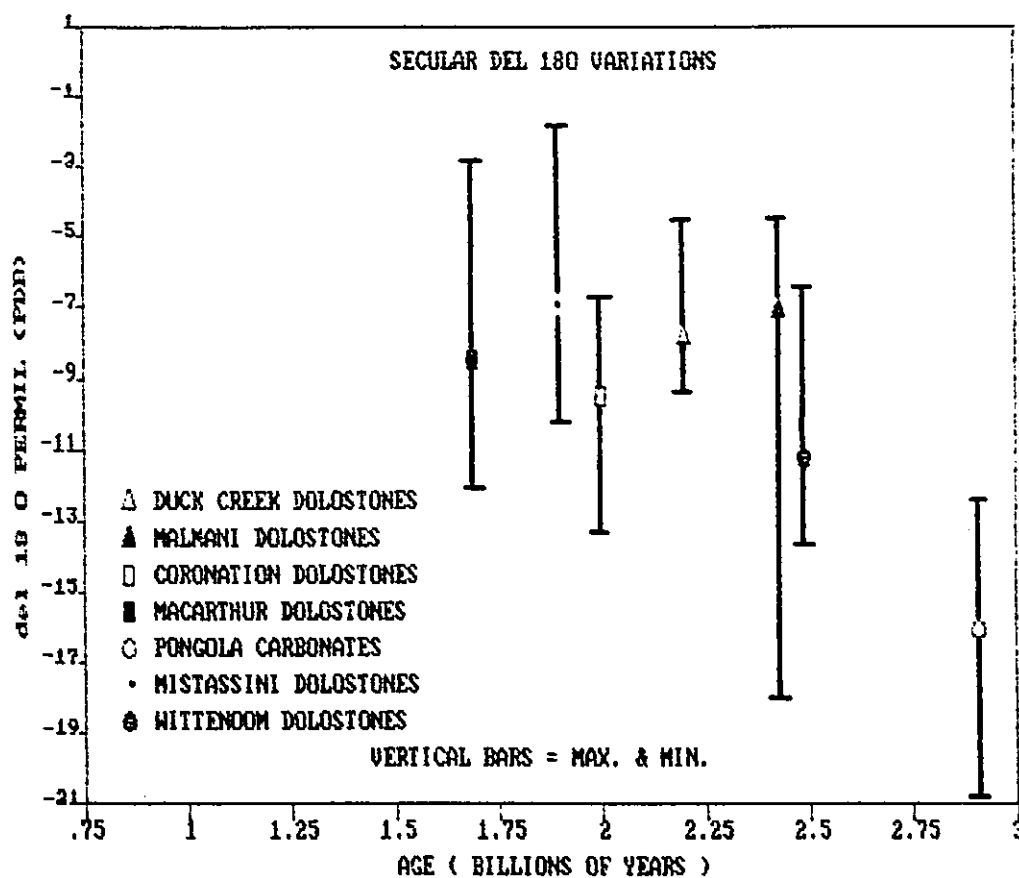


FIGURE 30: COMPARISON OF $\delta^{18}O$ TO OTHER PRECAMBRIAN PLATFORM SEQUENCES. $\delta^{18}O$ means and ranges of the different sequences are plotted in order of increasing age. A Mistassini mean of -6.75 ‰ (N=125) indicates that the latter is less altered than the other sequences. Unpublished data from Veizer (1988).

-6 ‰ PDB.

6.2 Sulfur Isotopes

6.2.1 Analytical Procedures:

Accessible pyrite samples were cut, crushed and mixed until homogenized with Cu_2O . The mixture was burned for 15 minutes at 1000°C . The evolved SO_2 was isolated from other gases using a dry ice - liquid nitrogen slurry. The final SO_2 product was transferred into breakseals and analyzed on a 602E mass spectrometer at the University of Ottawa. The sample precision, based on twelve duplicate samples (Youden, 1951), was found to be 0.51‰CDM.

A few samples where disseminated pyrite was observed, but too fine to remove, were extracted chemically. The Kiba method (Sakia et al., 1979) employs Tin (II) - strong phosphoric acid to extract sulfur as H_2S .

6.2.2 Theory of Sulfur Isotopes:

Primordial sulfur has a $\delta^{34}\text{S}$ near 0 ‰ CDM. This source is partitioned into two dominant reservoirs: sulfate and sulfide. The former consists of seawater sulfate and evaporites; the latter is dominated by pyrite. Sulfates are ^{34}S - enriched ($\delta^{34}\text{S} \approx 20\%$) whereas sulfides are depleted, with an average ^{34}S of $\approx -15\%$ (Kaplan, 1983). Thus primordial sulfur is partitioned into

a heavy and light isotopic reservoir. Such a large fractionation is explained by dissimilatory sulfate reduction by bacteria at low temperature (Trudinger et al., 1985).

During sulfate reduction, the incorporation of SO_4^{-2} necessitates several chemical reactions, which result in different fractionations (Kaplan, 1983). The extent of fractionation will be determined by the environmental conditions to which the bacteria are exposed. The former will be a function of several parameters:

- (a) metabolic rate (depending on temperature, nutrients)
- (b) the composition and availability of sulfate.

The sulfur isotopic composition of sulfate has varied through time and reflects the oscillating fluxes of the sulfate and sulfide reservoirs. The availability of sulfate reflects either the sedimentation rate or the extent of contact with the oceanic reservoir (Maynard, 1980). High rates of sedimentation result in decreased diffusion of overlying seawater sulfate; subsequently, the rate of sulfate reduction increases, with a corresponding decrease in fractionation. Such a mechanism is characterized by low total sulfur ($< 0.3\%$) in the sediments (Maynard, 1980). In the second case, progressive sulfate reduction in a basin isolated from its sulfate source results in a culminating $\delta^{34}\text{S}$ pyrite composition similar to that of the original sulfate. In both cases, such "closed systems" result in an

increase in the $\delta^{34}\text{S}$ of the residual sulfate and consequently lead to the formation of heavier pyrite, which can be defined by a Rayleigh distillation process.

Therefore a changing $\delta^{34}\text{S}$ of pyrite may give an insight as to the evolution of the basin, that is record the extent of contact of sediments with the overlying water and of isolation of a basin from open seawater sulfate.

Where evidence indicates higher temperature ($> 100^\circ \text{C}$) of sulfide formation, biological sulfate reduction must be excluded. Ohmoto (1972) showed that sulfur species in ore solutions will exchange isotopes and attain an equilibrium fractionation. The final isotopic composition will be a function of P_{O_2} , pH and T. Thus a reconstruction of the initial $\delta^{34}\text{S}$ source will depend on the amount and type of sulfur species as well as on chemical parameters of the fluid.

Inorganic sulfur reduction by ferrous ion or organic matter is definitely known to occur at temperatures above 250°C (Trudinger et al., 1985). Examples of Archean sulfides known to deviate from $\approx 0\%$ (Thode and Goodwin, 1983) can be explained by the incorporation of some seawater sulfate during circulation of seawater through hot basalts. These authors indicated that the resulting sulfides cannot have a $\delta^{34}\text{S}$ greater than that of the seawater sulfate source.

6.2.3 Pyrite Occurrences in the Mistassini Basin:

Several varieties of pyrite were observed and these will be organized in a generalized and overlapping paragenetic sequence.

(a) Syngenetic/early diagenetic pyrite - This type occurs as lenses, nodules or spherical masses that show sediment displacement indicative of pre-compaction growth. The pyrites are agglomerations composed of coalescing crystals of various sizes. Individual crystals host no inclusions. Incomplete coalescing may preserve the matrix and/or a mosaic of quartz-carbonate. Larger examples may possess fractures healed by calcite. Associated organic rich sediments are common. Examples are illustrated in Plates 42 to 44.

(b) Early (?) to later diagenetic pyrite - Some examples are difficult to classify as unequivocal pre-compaction pyrite. These occur as fine disseminations or masses, are frequently associated with organic matter ($\pm$ algal mats), and may adopt discontinuous to laminar fabrics. These characteristics suggest (but do not prove) an early origin; hence they are included in this group (Plates 45 and 46).

A unique example is a pyritized cross-bedded dolostone (Plate 47), perfectly preserving the sedimentary

structure. The time of formation is constrained by the presence of interparticle porosity. The preservation can be explained by intergranular precipitation related to a migrating redox front after consolidation but before extensive cementation.

In another case, unique radiating clusters are surrounded by calcite (evidence of sulfate reduction ?; initially evaporites ?; Plate 46).

- (c) Late diagenetic pyrite - This type is commonly distinguished by coarser size (≤ 6 mm), is frequently euhedral and distinctly poikilotopic, cross-cuts fabric and is often observed to be associated with sedimentary boundaries. The latter feature suggests a post-consolidation origin (Plate 48), yet before complete occlusion of permeable pathways.
- (d) Fault-related pyrite - This is the latest in the paragenetic sequence of pyrite formation. Examples consist of discordant bands, fracture-fillings and possibly cubes. An example of cubic pyrite occurs in a brecciated dolostone from the epigenetic Icon Sullivan copper deposit. Plate 49 illustrates a typical example of fault-related mineralization.

6.2.3.1 Origin of Pyrite in the Mistassini Basin (Lower Albanel Formation):

The existence of bacterial sulfate reduction appears to be supported by the following observations:

- (a) The major concentration of both finer and coarser grained pyrite is in shale complexes.
- (b) The pyrite is commonly of precompaction origin (replacement of sulfide precursor ?), and/or is locally associated with organic matter, and is always concordant to bedding.
- (c) High manganese (and Fe) concentrations in the Lower Black Shale carbonates are coupled with the inverse Mn^{+2} - $\delta^{13}C$ correlation (see page 172 and Wedepohl, 1978).
- (d) The disruption of the parallel $\delta^{13}C$ trend in the Lower Black Shale Unit (Figure 26; in the interval between $\approx$ 2426 and 2441 meters) could have also resulted from the incorporation of some (buffered) biogenic HCO_3^- during SO_4 reduction. This interval also hosts a wide range in $\delta^{34}S$, to be presented shortly (Appendix 5).
- (e) There is a lack of evidence for other mechanisms, such as hydrothermal activity. This does not preclude pyrite

formation in fault veins.

- (f) The S/C ratios in the shales of the Temiscamie and Albanel Formations (0.31 and 0.36, respectively) are consistent with dissimilatory sulfate reduction (Cameron and Garrels, 1979).

Bacterial reduction can proceed at temperatures less than 100° C (Trudinger et al., 1985). Nevertheless, other pyrite-forming processes must have also been active. For example, the fault-related pyrite occurs as the first precipitate, lining the cavity and surrounding the stromatolitic fragments (Plate 49). In this case, precipitation of sulfides has been likely controlled by changing fluid conditions and presumably occurred at higher temperatures. The ubiquitous association of sulfides with organic - bearing stromatolites could suggest the importance of organics (reductant, iron or sulfur source ?) for pyrite formation (Plates 45, 46 and 49). This does not exclude the possibility of local inorganic sulfate reduction (> 250° C).

The occasional presence of large (< 1 cm) euhedral cubes in coarser-grained, higher energy impure carbonates suggests an intermediate pyrite-forming episode relative to the two obvious extreme occurrences, early diagenetic and late fault-related pyrite.

6.2.4 Isotopic Composition of Pyrite

6.2.4.1 Geological Examples of Heavy $\delta^{34}\text{S}$ Pyrite:

The process by which increasingly heavy sulfides can form is highlighted by numerous ancient basins that possess such values. A notable example is illustrated by the early Paleozoic Selwyn Basin (Goodfellow and Jonasson, 1984). Pyrite $\delta^{34}\text{S}$ variations parallel those of sulfate, reflecting the changing isotopic composition of the overlying sulfate. Positive $\delta^{34}\text{S}_{\text{pyrite}}$ excursions up to $\approx 35\%$, corresponding to restricted conditions, were noted by these authors.

Proterozoic sulfides are distinguished by heavy $\delta^{34}\text{S}$ also attributed to restricted conditions. Lambert (1984) indicated that the propensity of heavy sulfides may represent a sampling bias, such that more restricted basins tend to be better preserved. Furthermore, heavy values must be balanced by lighter ones elsewhere, as required by the mass balance relationship.

Examples of heavy Proterozoic sulfides, including the Mistassini Basin, are many (Wedepohl, 1978) but a notable example is the Australian Paradise Valley Cu-deposit. Scott et al. (1985) reported a maximum $\delta^{34}\text{S}$ of 51‰ for a syngenetic pyrite and Lambert et al. (1984) reported values up to +45‰ for syngenetic / diagenetic sulfides for this late Proterozoic occurrence. These examples were introduced to show that syngenetic / diagenetic pyrites can be isotopically heavy. Examination of heavy Mistass-

ini pyrites shall be presented below.

6.2.4.2 $\delta^{34}\text{S}$ of Mistassini Pyrite:

Appendix 5 summarizes the pertinent information for the samples analysed. The subsequent discussion will entail characteristics of the entire sample groups, with a later focus on a few individual samples. Since only one pyrite sample was found in the Upper Albanel Formation, it will be disregarded in the discussions.

The distribution of $\delta^{34}\text{S}_{\text{pyrite}}$ for the different groups is shown in Figure 31. As a whole, these pyrites are enriched in ^{34}S , with a mean and standard deviation of 24.01‰ and 11.96‰, respectively. The range for samples with averaged values is $\sim -3\%$ to $\sim +54\%$ CDM, but if individual analyses of nodules are considered, the range increases from -7% to $+60\%$.

In general, the early diagenetic and early to later diagenetic pyrites exhibit the widest range of $\delta^{34}\text{S}$. Both the later diagenetic and fault-related pyrites have more restricted ranges; the former being heavier than the latter. The heaviest average $\delta^{34}\text{S}$ have been observed in the coarse grained pyrites of the Upper Banded Dolostone and in nodules of the Lower Black Shale Complex (Figure 32), reflecting the isotopic composition of the late and syngenetic /early diagenetic groups, respectively. In the Lower Black Shale nodules, both different and individual specimens

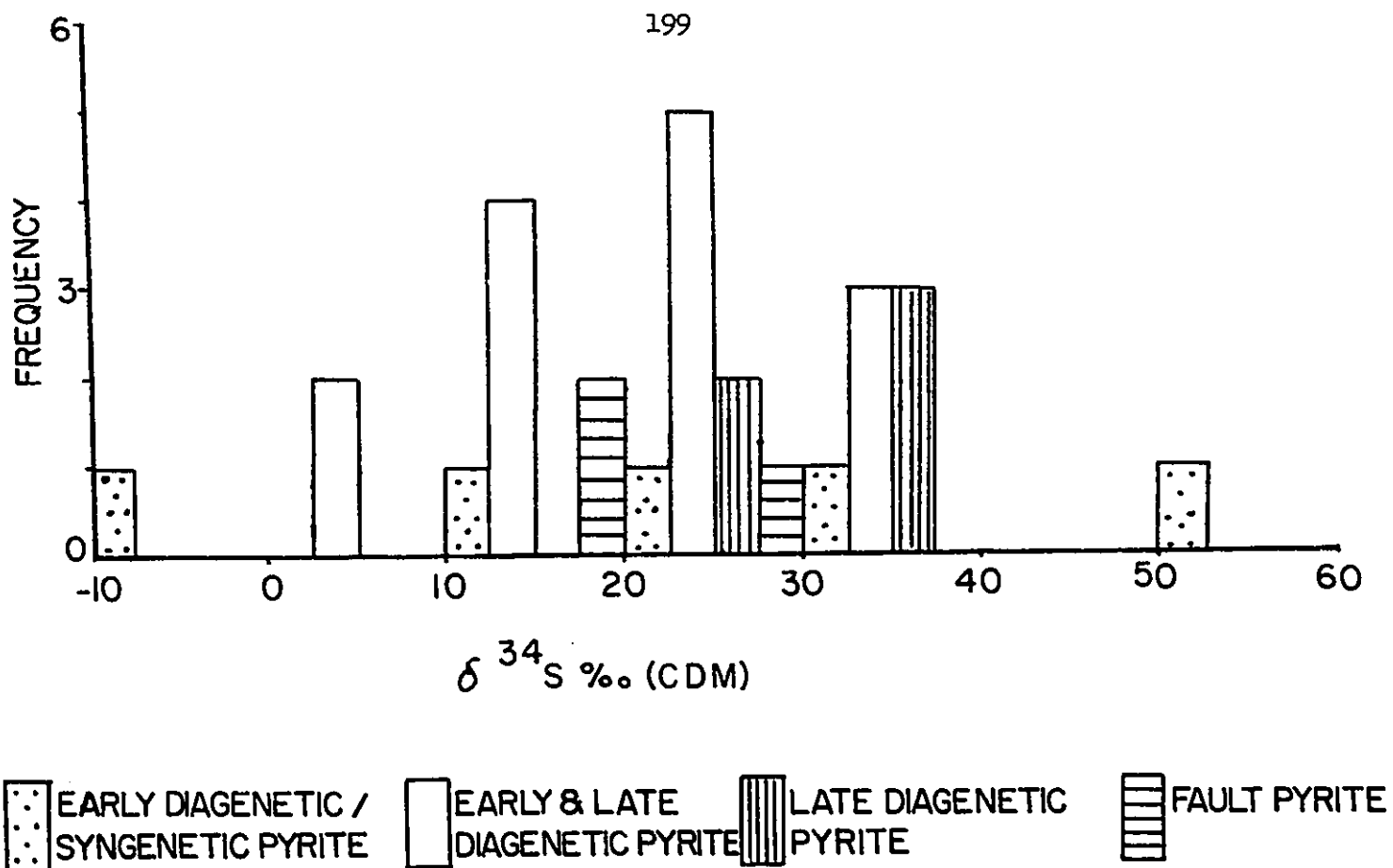


FIGURE 31: $\delta^{34}\text{S}$ DISTRIBUTION OF MISTASSINI PYRITE. The majority of pyrites analyzed are from the Lower Albanel Formation, except for one sample ($\delta^{34}\text{S} \approx 27\%$). Four pyrite groups are defined relative to their inferred paragenetic sequence. All multiple sample analyses were averaged.

exhibit a wide range in $\delta^{34}\text{S}$, observable over short distances (Figure 32). Hence pyrite formation in a system "closed" to sulfate appears to have been the norm, although fluctuations toward more "open" (lighter) $\delta^{34}\text{S}$ compositions are also suggested (Plate 44; $\approx -3\%$).

Whether these characteristics reflect the isotopic composition of the dissolved sulfate can be tested by comparison with other parameters. A plot of $\delta^{34}\text{S}$ versus depth (Figure 32) shows that despite low sample resolution, isotopic fluctuations are considerable. If the trend toward heavier values were to represent more restricted basin conditions, then the $\delta^{13}\text{C}$ should show a similar trend and correlate positively with $\delta^{34}\text{S}$. Superposition of these isotopes versus depth (Figure 33) suggests local coincident positions for certain maxima and minima. Furthermore, a positive correlation between these isotopes was indeed observed, although its statistical significance just barely failed to reach the 95 % confidence level.

Previously it has been suggested that both facies (restriction +/- evaporation) and secular changes may have controlled the $\delta^{13}\text{C}$ distribution. For S isotopes, the parallel trend between $\delta^{34}\text{S}$ of sulfate and sulfide, as observed by Goodfellow et al., (1984) in the Selwyn Basin, indicates the intimate association between the two phases via dissolved sulfate. Although no preserved

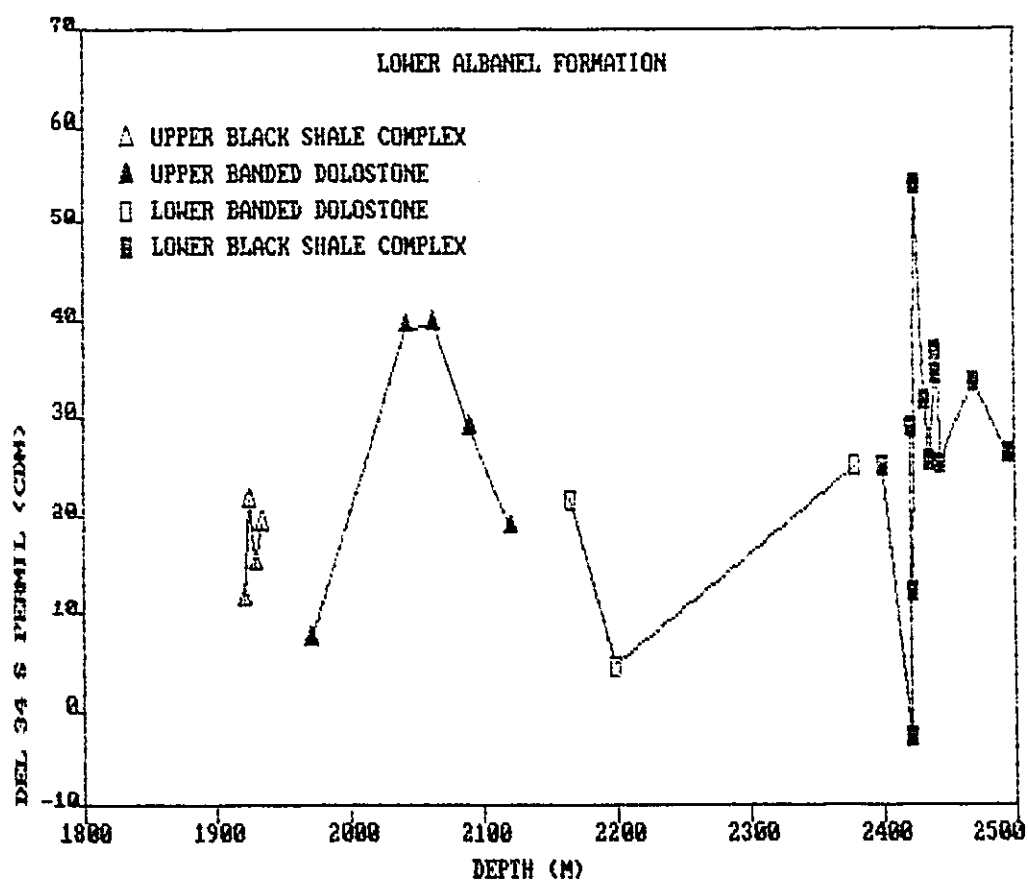


FIGURE 32: $\delta^{34}\text{S}$ STRATIGRAPHY OF MISTASSINI PYRITE. The $\delta^{34}\text{S}$ results of pyrite are plotted relative to stratigraphic unit position. All multiple sample analyses were averaged.

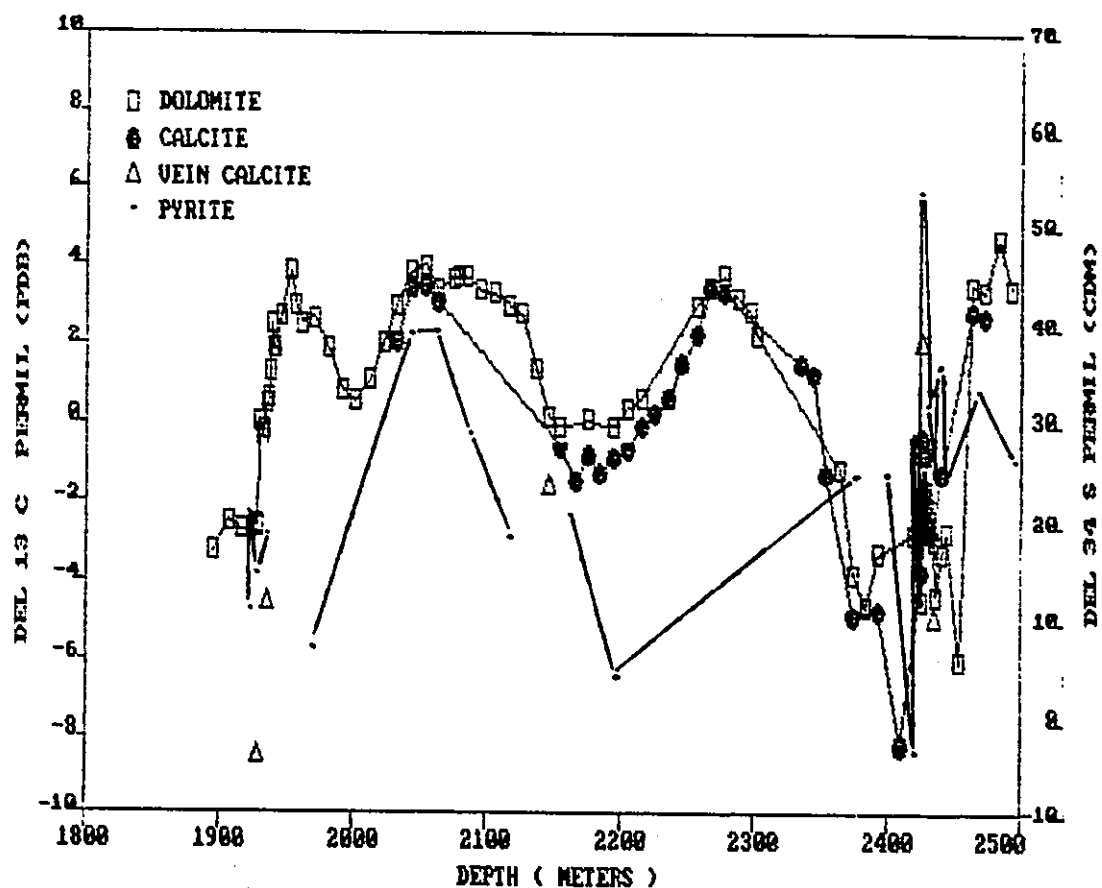


FIGURE 33: SUPERPOSITION OF $\delta^{13}\text{C}$ AND $\delta^{34}\text{S}$ STRATIGRAPHY IN THE LOWER ALBANELL FORMATION. The $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ isotopic scales are indicated along the left and right sides of the vertical axes, respectively. Additional information as indicated on previous diagrams.

sulfate¹ was observed in the Mistassini Basin, it is conceivable that a portion of the observed fluctuation could have been of a secular and/or facies nature and be reflected in the sulfide.

The sulfate composition of the Mistassini basin waters is difficult to establish since preserved sulfates are absent. It will depend on the range of the fractionation factor (0 to + 50‰; Kaplan, 1983) and degree of openness of the basin. The original sulfate values could have been quite variable. Nevertheless, with whatever assumptions, most of the sulfate values would have to be $\approx +20 \rightarrow >+50$ ‰ CDM. These are rather heavy values, but not totally unrealistic. For example, the Phanerozoic Selwyn Basin sulfates range from $\approx +20$ to $\approx +47$ ‰. A sulfate value of $\approx +35$ ‰ was reported for the latest Precambrian (in Anderson and Arthur, 1983), and Smith et al. (1978) reported values of 25 ± 5 ‰ for the mid Proterozoic of Australia. Probably the best evidence of heavy sulfate values for a coeval dolostone sequence is offered by Ueda (personal communication, 1987). Ueda extracted traces of sulfate from molds in the - 1.9 Ga Belcher Group, N.W.T. A $\delta^{34}\text{S}$ sulfate value of +27.8‰ supports the existence of (at least locally) heavy Aphebian seawater sulfate. Similarly, heavy values could have conceivably existed in the Mistassini Basin.

¹Examples of evaporite molds have traces or margins of chlorite, opaques and $\pm$ dolomite and evaporites.

$\delta^{34}\text{S}$ of Selected Samples

This section presents insights for unusual pyrite specimens.

(a) Early diagenetic pyrite displacing sediment (Plate 42).

This pre-compaction pyrite is characterized by an increasing $\delta^{34}\text{S}$ ($\approx +48$ to $\approx +60\%$) as the base of the pyrite mass is approached. This suggests that sulfate became increasingly enriched in $\delta^{34}\text{S}$ with progressing sulfate reduction. Calcite-healed fractures support Solomon's (1965) observation that pyrite, unlike other sulfides, can transmit stress.

Other examples of pyrite that displaces sediment either possess pronounced $\delta^{34}\text{S}$ variations or may be depleted in ^{34}S (Plate 44, with average $\delta^{34}\text{S}$ of $\approx -3\%$). An apparent (unexpected) increase in $\delta^{34}\text{S}$ towards the center (Plate 44) corresponds to an increasing crystal size and more extensive coalescence, compared to the margins. This suggests that growth originated along the margins (?) and terminated in the center, resulting in greater coalescence.

(b) Individual samples with distinct pyrite types or sizes are apparent (Plate 45 and sample D2-29-74) but may not show variable $\delta^{34}\text{S}$. Although coarser grained pyrite is expected to be isotopically heavier, Maynard (1980) also found that silt-sized pyrite had similar values to

nodular varieties. Hence the general observation that coarser pyrite necessarily forms later and has heavier $\delta^{34}\text{S}$ values is not without exception. (However, if all samples are considered, coarser (late diagenetic) varieties are usually heavier (Figure 31)).

- (c) Radiating pyrite clusters surrounded by calcite (Plate 46) may represent a by-product of sulfate reduction(?).
- (d) A large pyritized, cross-laminated dolostone (Plate 47) was sampled in three locations from edge to center along the core boundary. A range of 14.83 to 15.16‰ CDM lies within the uncertainty of analysis. Such homogeneity reflects that of the fluid and is compatible with a redox front-precipitation mechanism.
- (e) Pyrites associated with faulting (Samples D12-A-77 and D12-B-77, Plate 49) have lighter and more uniform $\delta^{34}\text{S}$ (Figure 31). Two samples from drillhole D12-77 have similar values, just under $\approx 20\text{‰ CDM}$. Since these $\delta^{34}\text{S}$ are similar to other pyrites, the samples may represent remobilization of early sulfides at somewhat elevated temperatures.

6.4 Strontium Isotopes

6.4.1 Analytical Procedures:

Approximately 1 gram of carbonate was digested in 8% v/v ultrapure HCl for one hour and subsequently filtered. A 1 milliliter (ml) aliquot of sample solution was placed upon resin (Biorad AG50W-X8) in an ion exchange column, previously equilibrated with 2.5 N ultra pure HCl. Once absorbed, two additional 1 ml and one 2 ml HCl washings were added. After absorption, 120 mls was added to the acid reservoir. An eluted 20 ml volume of acid containing the strontium was collected, evaporated to dryness and transferred to teflon sample holders. Each column was subsequently rinsed with 100 mls of 6N HCl and equilibrated with 2.5N HCl, respectively.

Isotope measurements were made on a Finnigan-MAT 261 multi-collector machine at Carleton University. Strontium was run as the phosphate using a single tantalum filament. Reproducibility, including chemical preparation, of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is considered to be 0.004% of the quoted value at the 2 sigma level. The NBS 987 standard gives a ratio of 0.71023 ± 0.00003 and the E. and A. standard a value of 0.70802 ± 0.00003 .

6.4.2 Strontium Isotopes in Carbonates:

Unlike carbon and oxygen, strontium isotope 87 forms by the radiogenic decay of rubidium via beta decay. Strontium enters the carbonate structure without undergoing isotopic fractionation

(Veizer, 1983). A precipitating carbonate should reflect the $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater, even in restricted basins, since the residence time for strontium is much greater than the rate of seawater mixing (Veizer, 1983).

That strontium isotopic composition of seawater has varied during the Precambrian is well documented (Veizer and Compston, 1976). Basalt-seawater exchange introduces less radiogenic strontium into the oceans, whereas river discharge from old continents (high in K^+ and Rb^+) results in a highly radiogenic strontium. River flux is buffered by carbonates with their high Sr^{+2} concentration at isotopic composition of ≈ 0.708 . This may be a dominating contributor to the river flux of strontium (Wadleigh et al., 1985).

A first order seawater $^{87}\text{Sr}/^{86}\text{Sr}$ trend is characterized by a general increase in this ratio to the present, with a sharp rise near the Archean-Proterozoic boundary (Veizer, 1983). This variation appears to reflect the different tectonic regimes that have characterized the Archean, Proterozoic and Phanerozoic eons. Superimposed on the latter are second and higher order fluctuations which are not only related to other parameters (ie: $\delta^{13}\text{C}$, $\delta^{34}\text{S}$ and sea level), but appear to be all controlled by tectonic processes (Veizer, 1983).

6.4.3 Preservation of $^{87}\text{Sr}/^{86}\text{Sr}$ Signal:

As previously discussed, metastable carbonates become stabilized with a concomitant decrease in strontium concentration, especially in the presence of meteoric fluids. Nevertheless, diagenetic stabilization in seawater causes no change in the strontium isotopic ratio. For meteoric waters, the extent of alteration would obviously depend on the diagenetic history of the carbonates, such as water/rock ratios, number of diagenetic transformations and isotopic composition of all the phases involved. Nevertheless, meteoric water has considerably lower Sr/Ca ratios than most of the carbonate minerals. Since D^{Sr} of calcite (dolomite) is < 1 , recrystallization results in strontium partitioning into the fluid. This strontium overwhelms the diagenetic environment and is subsequently sequestered into successor phases. Consequently the original isotopic signature can be preserved in carbonates.

A more serious problem is the diagenetic exchange of Sr between silicate and carbonate phases. Although the evidence is conflicting (Veizer and Compston, 1976), at least some exchange is feasible. Veizer and Compston (1976) found that exchange with K^+ (Rb^+)-bearing silicates and laboratory leaching both result in an increase in the $^{87}Sr/^{86}Sr$ of the carbonate. Thus samples with the lowest values are expected to be the least altered and hence reflect most the primary composition of the ambient water.

6.4.4 $^{87}Sr/^{86}Sr$ of the Mistassini Carbonates:

The positive correlation of $^{87}\text{Sr}/^{86}\text{Sr}$ with manganese (Figure 34) indicates that the addition of ^{87}Sr is due to post-depositional alteration, mostly to growth of late diagenetic ferroan (?) spar. Figure 34 shows that the lowest ratios occur in the low strontium dolostones, especially in the ^{18}O -enriched interval. Relative to depth, the $^{87}\text{Sr}/^{86}\text{Sr}$ records an increase to extreme values (≥ 0.725) near the base. This may be the result of increasing silicate-carbonate exchange with burial depth. The presence of ubiquitous low amplitude stylolites, diagenetic illite as well as ^{18}O -depleted carbonates suggests that carbonate and clay diagenesis continued during burial.

Employing Veizer et al. (1983) alteration criteria, the most likely strontium ratio representing the Mistassini seawater is ≈ 0.7060 (Appendix 6). Due to low sampling resolution and exchange with silicates, examination of basinal secular variations was not attempted. Some samples possessing similar manganese concentrations (alteration) have somewhat more radiogenic strontium ratios (Figure 34). Whether, this reflects a primary signature is not known and will tentatively remain unsolved. The observation that two samples with similar isotopic compositions (≈ 0.706) are separated by an estimated thickness of ≈ 800 meters may indicate some isotopic uniformity in the waters during this interval.

The Mistassini value of 0.706 is comparable to that of roughly coeval Proterozoic carbonates. For example, Veizer and

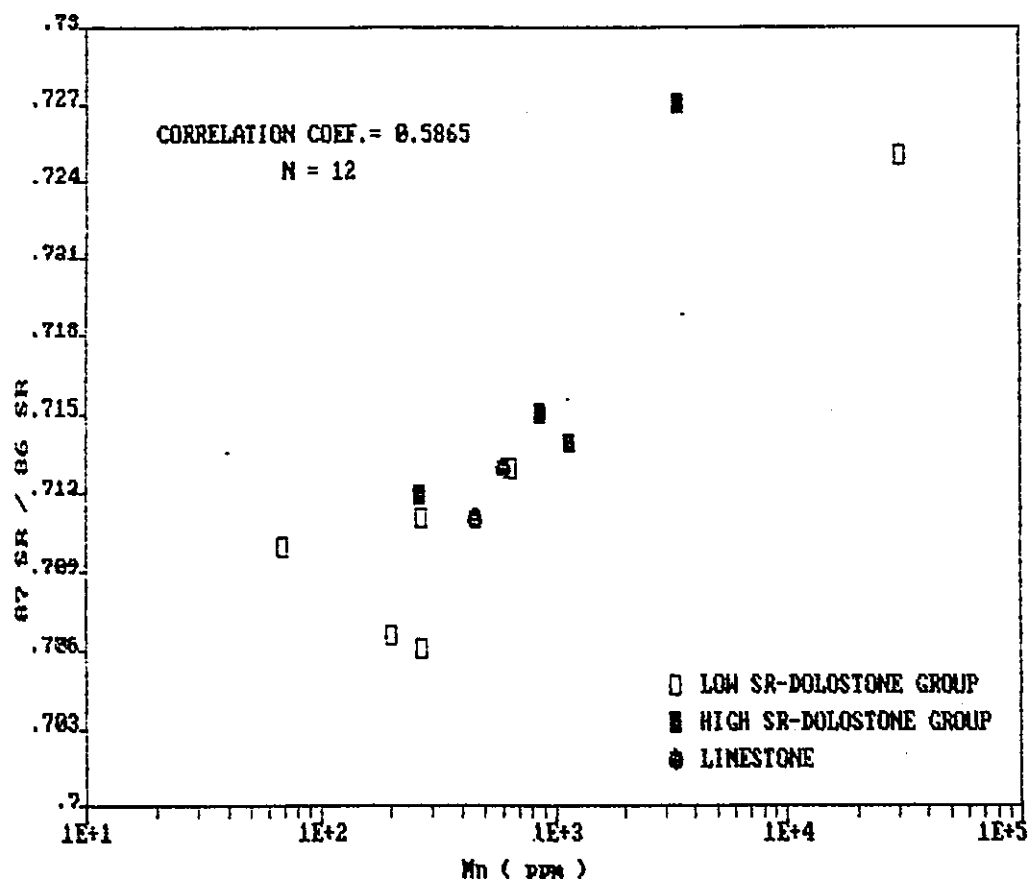


FIGURE 34: CORRELATION DIAGRAM BETWEEN $^{87}\text{Sr}/^{86}\text{Sr}$ AND Mn FOR THE MISTASSINI CARBONATES. Isotopic analyses of selected samples include dolomite from the Low and High Sr Dolostone Groups, as well as two limestones from the latter group. The positive correlation (statistically significant at the 95 % confidence level) is consistent with diagenetic alteration.

Compston (1976) reported $^{87}\text{Sr}/^{86}\text{Sr}$ values for the McArthur Group (≈ 1.5 billion years), Gunflint Formation (≈ 1.7 billion years) and Mt. Bruce Supergroup (≈ 2.0 billion years) of 0.7061, 0.7051 and 0.7050, respectively. Since the reported age range for the Mistassini Basin lies between ≈ 1.75 to 2.1 billion years, a value of 0.706 is appropriate, although a slightly lower value would ideally be expected.

SUMMARY AND CONCLUSIONS

The undeformed and unmetamorphosed Aphebian Mistassini carbonates are divided into a Lower and Upper Albanel Formation. The former and the latter formations can be described by five and eight lithofacies, respectively. The Basal Stromatolite Unit of the Lower Albanel Formation marks the initial transgression over the Archean basement. The Lower Black Shale Unit (shale, limestone and dolostone) represents the maximum transgression and reflects a deep, anoxic depositional environment. The Lower (silty to argillaceous carbonates) and Upper (silty to sandy cross-laminated dolostones) Banded Dolostone Units represent less deep and shallower water depositional conditions, respectively. The Upper Black Shale Unit (shale to dolomudstone) and the uppermost Stratified Dolomite and Shale Units (dolomudstones) were deposited in quiet, shallow water with local peritidal affinities. The Upper Albanel Formation is composed of two units; the lower Sandy Dolostone Unit (crossbedded sandy dolograinstones to dolomudstones) represents a shallow high and low energy (locally peritidal) depositional setting. The upper Banded Dolostone Unit (stromatolitic dolomudstone and dolowackestone) was deposited in a protected subtidal to peritidal environment and is characterized by shallowing upward stromatolitic cycles.

Finely to coarsely crystalline fabrics characterize the

Upper Albanel dolostones. Allochems include intraclasts, various ooid fabrics and eroded cements; mature detrital quartz implies erosion of a low relief topographic source. Peritidal tepees and evidence of evaporites and suggest a local semi-arid climate, whereas ooids suggest deposition in warm waters of normal to elevated salinity. Truncated tepees, cements and fenestral algal dolostones indicate local subaerial exposure. Fine to coarse crystalline dolomite as well as the lower proportion and scarce siliciclastics characterize the Upper Black Shale and Stratified Dolomite and Shale Units, respectively. The subjacent Upper and Lower Banded Dolostone Units contain immature silty-sandy (cross-laminated) and silty-argillaceous (locally cross-laminated) siliciclastics, respectively, suggesting erosion of a higher relief source and local deposition. The shaly and argillaceous-silty carbonates of the Lower Black Shale Unit become increasingly pure near the base.

Ubiquitous cavity-filling quartz and selective chertification of the Upper Albanel algal dolostones contrasts with the authigenic and fracture-filling silica observed in the Lower Albanel Formation. This distinction is a result of different diagenetic setting and timing. The Upper Albanel Formation exhibits abundant evidence of early cementation; meniscus and pendant fabrics imply vadose, whereas recrystallized and dissolved ooids suggest meteoric water diagenesis. Based upon ooid and cement fabrics, aragonite and high magnesium calcite precursors

are suggested. In contrast, scant evidence of early cements and no petrographic evidence of metastable phases was observed in the Lower Albanel Formation. The (permanently?) submerged Upper and Lower Banded Dolostone and Lower Black Shale Units show evidence of compaction, stylolite formation and precipitation of burial cements. On textural grounds, dolomitization in both formations is early and near surface, although later episodes are indicated. Possible (but not only) dolomitization mechanisms include sabkha, Dorag, sulfate-reduction, burial and fault-related.

Factor analysis of whole rock data indicates that illite, K-feldspar, albite, iron oxides, dolomite and quartz are the dominant mineralogical controls. Carbonate-bound trace elements, insoluble residue and Al^{+3} generally increase with unit depth, due to facies, mineralogy and diagenetic history. On the basis of Sr/Ca and Mn^{+2} concentrations, limestone and high and low Sr dolostone groups can be distinguished. Although only first order mineralogical controls are revealed for the limestones, factor analysis indicates post depositional alteration as the dominant factor for the high Sr dolostones. The highest Sr^{+2} concentrations require the existence of an aragonitic precursor, despite the absence of petrographic evidence. Factor analysis of the low Sr dolostones indicates a more pristine nature, contradicting the apparent extreme diagenetic loss of Sr^{+2} . The difference between the high and (a portion of the) low Sr dolostones may be due to different precursor mineralogy and/or alteration history and not

to the intensity of alteration.

The carbonate groups are also similarly defined on the basis of stable isotopes. Statistical analysis suggests that selective recrystallization of the low Sr dolostones is related to permeability and occurred in nearsurface higher meteoric water/rock circulation cells. Projection to "least altered" values suggest $\delta^{18}\text{O} \approx -2.5 \pm 2 \text{‰}$, $\text{Sr}^{+2} \approx 90 \pm 50 \text{ ppm}$ and $\text{Na}^{+} \approx 150 \pm 50 \text{ ppm}$. The uniform $\delta^{13}\text{C}$ values were buffered by the large carbonate reservoir, except for the organically derived ^{12}C in Upper Black Shale Unit. The elevated Sr^{+2} concentrations, despite post deposition alteration of the high Sr dolostones, can best be reconciled if recrystallization proceeded under higher temperatures and salinity (lower water/rock ratio). Extrapolation to "least altered" values suggests $\delta^{13}\text{C} +2 \pm 2 \text{‰}$, $\delta^{18}\text{O} \approx -9 \pm 2 \text{‰}$, $\text{Sr}^{+2} \approx 375 \pm 75 \text{ ppm}$ and $\text{Mn}^{+2} \approx 1000 \pm 400 \text{ ppm}$. Similarly $\delta^{13}\text{C} \approx +2 \text{‰}$ and $\text{Sr}^{+2} \approx 450 \pm 75 \text{ ppm}$ are suggested for the coeval limestones.

The $\delta^{18}\text{O}$ distribution of Mistassini dolostones increases to an average unit maximum in the Stratified Dolomite-Shale (-4.46‰) and Upper Black Shale (-4.04‰) Units, followed by a marked decrease to a minimum (-9.35‰) in the Lower Black Shale Unit. Calcite (range -8.08 to -13.10‰) exhibits a similar pattern, although offset to lighter values as a result of burial recrystallization. Differential diagenetic alteration in near surface, higher and subsurface lower water/rock ratios controls the $\delta^{18}\text{O}$

distribution. The $\delta^{18}\text{O}$ of calcite veins reflects that of the enclosing rocks, modified by fluid temperature and composition. A $\delta^{18}\text{O}$ mean of -6.75 (range -1.90 to -10.31 ‰) for the Mistassini dolostones suggests that these samples represent one of the least altered Aphebian sequences.

The uniform $\delta^{13}\text{C}$ distribution in the upper 4/5 of the section becomes increasingly oscillating toward the base. An average maximum (+2.54‰) in the Upper Banded Dolostone contrasts with average minima in the Upper (-1.64‰) and Lower (-1.47‰) Black Shale Units, due to incorporation of organic carbon. The parallel nature and consistent offset between dolomite and calcite curves suggests a primary signal, excluding locally altered ($\leq 0\%$) values. The $\delta^{13}\text{C}$ distribution reflects secular and facies controls; alteration is subordinate in importance. The ^{13}C depleted calcite veins appear to reflect the amount of available authochthonous C_{org} . A mean $\delta^{13}\text{C}_{\text{dolomite}}$ of +0.74‰ (range -6.08 to 4.70‰) is compatible with that of other Aphebian sequences.

Lower Albanel pyrite is divided into early/syngenetic, early to later diagenetic, late diagenetic and fault-related groups, with a mean $\delta^{34}\text{S}$ of $\approx +24\%$ (mean range -3 to +54‰). Such heavy values can be explained by sulfate reduction of initially heavier $\delta^{34}\text{S}_{\text{SO}_4}$ in a restricted basin characterized by a limited sulfate reservoir. The similar $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ distribution patterns

further suggests basin restriction.

The positive correlation obtained from a $^{87}\text{Sr}/^{86}\text{Sr}$ versus Mn plot of dolostones and limestones indicates increasing radiogenic strontium with alteration and basin depth. The lowest (least altered) $^{87}\text{Sr}/^{86}\text{Sr}$ values occur in the high $\delta^{18}\text{O}$ interval of the low Sr dolostone group, corroborating the existence of a more pristine nature. A preferred $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.706 for Mistassini seawater compares favorably with that of other coeval platform carbonates.

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APPENDIX 1

SAMPLE LOCATIONS FOR XRF, AAS, ISOTOPE AND MICROPROBE
ANALYSES AND ADDITIONAL PETROGRAPHY AND PHOTOGRAPHS

INDEX FOR LOCATION OF (FIELD) SAMPLES

(Photographs and AAS, XRF, Isotopic & Microprobe Analyses)

LOWER ALBANEL FORMATION IN THE MISTASSINI POST AREA

(Stratified Dolomite and Shale Unit)

1 M-7b-84	4 M-11-84	7 M-1-84	10 M-8a-84
2 M-6-84	5 M-3-84	8 M-2-84	11 M-9-84 *
3 M-5-84	6 M-12-84	9 M-4-84	12 M-10a-84 *

(* including two adjacent Upper Albanel samples)

UPPER ALBANEL FORMATION IN THE TEMISCAMIE RIVER AREA

1 A-1a-84	21 A-48b,g & h-85	40 A-8-85
2 A-31-84	22 A-36b-85	41 A-60-85
3 A-30mi-84	23 A-32b-85	42 A-74-85
A-30ma-84	24 A-12b-84	43 A-29-84
4 A-28a-84	25 A-13a1-84	44 A-23-84
5 A-27a-84	A-13a2-84	45 A-17b-85
6 A-24a-84	A-13a3-84	46 A-49b-85
7 A-72bg-85	A-13a4-84	47 A-38a-85
8 A-79b-85	A-13a5-84	48 A-58b-85
9 A-26a-84	26 A-30a-85	49 A-71c-85
10 A-2a-84	27 A-15a-84	50 A-82c-85
11 A-59a-85	28 A-43b-85	51 A-83-85
12 A-3a-85	29 A-44b-85	52 A-78b-85
13 A-4ami-84	30 A-20-84	53 A-5a-84
A-4ama-84	31 A-21-84	A-5b-84
14 A-52a-85	32 A-47b-85	54 A-6-84
15 A-54a-85	33 A-22-84	55 A-8-84
16 A-7bmi-84	34 A-25a-85	56 A-9a-84
A-7rmi-84	35 A-14d-85	57 A-14a-84
17 A-55a-85	36 A-35-85	58 A-16-84
18 A-56a-85	37 A-69-85	59 A-25a-84
19 A-10-84	38 A-5-85	60 A-17-84
20 A-62b-85	39 A-2-85	61 A-18-84
		62 A-19-84

[Where thinsections were available, petrographic descriptions are included in the sample description (Appendix 2) of those analyzed.
1

Additional Petrography

56 A-9-84	69 A-20-85	45 A-17b-85
63 A-40-85	70 A-6-85	48 A-58b-85
64 A-33B-85	39 A-2-85	47 A-38a-85
15 A-54d-85	71 A-13-85	58 A-16-85
65 A-52e-85	44 A-23-84	46 A-49b-85
40 A-8-84	49 A-71c-85	21 A-48b, h-85
66 A-65b-85	52 A-78b-85	23 A-32c-85
67 A-66b-85	50 A-82c-85	35 A-14d-85
68 A-11b-85	72 A-17h-85	36 A-35-85

(No AAS chemical analyses were made on the above samples.)

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NOTICE

AVIS

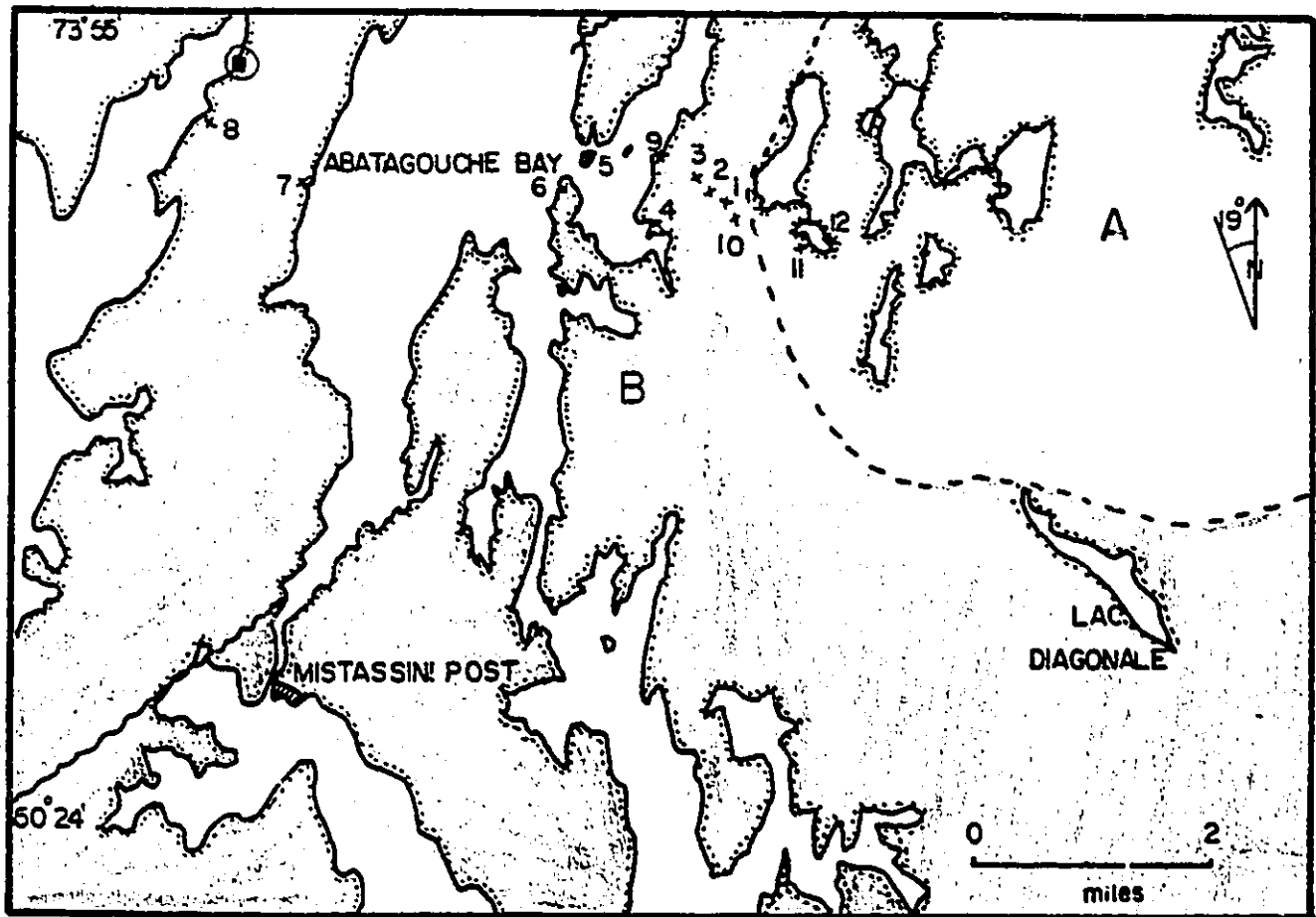
**THE QUALITY OF THIS MICROFICHE
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ILLUSTRATIONS EN COULEURS DE CETTE
THESE NE PEUVENT DONNER QUE DES
TEINTES DE GRIS.**

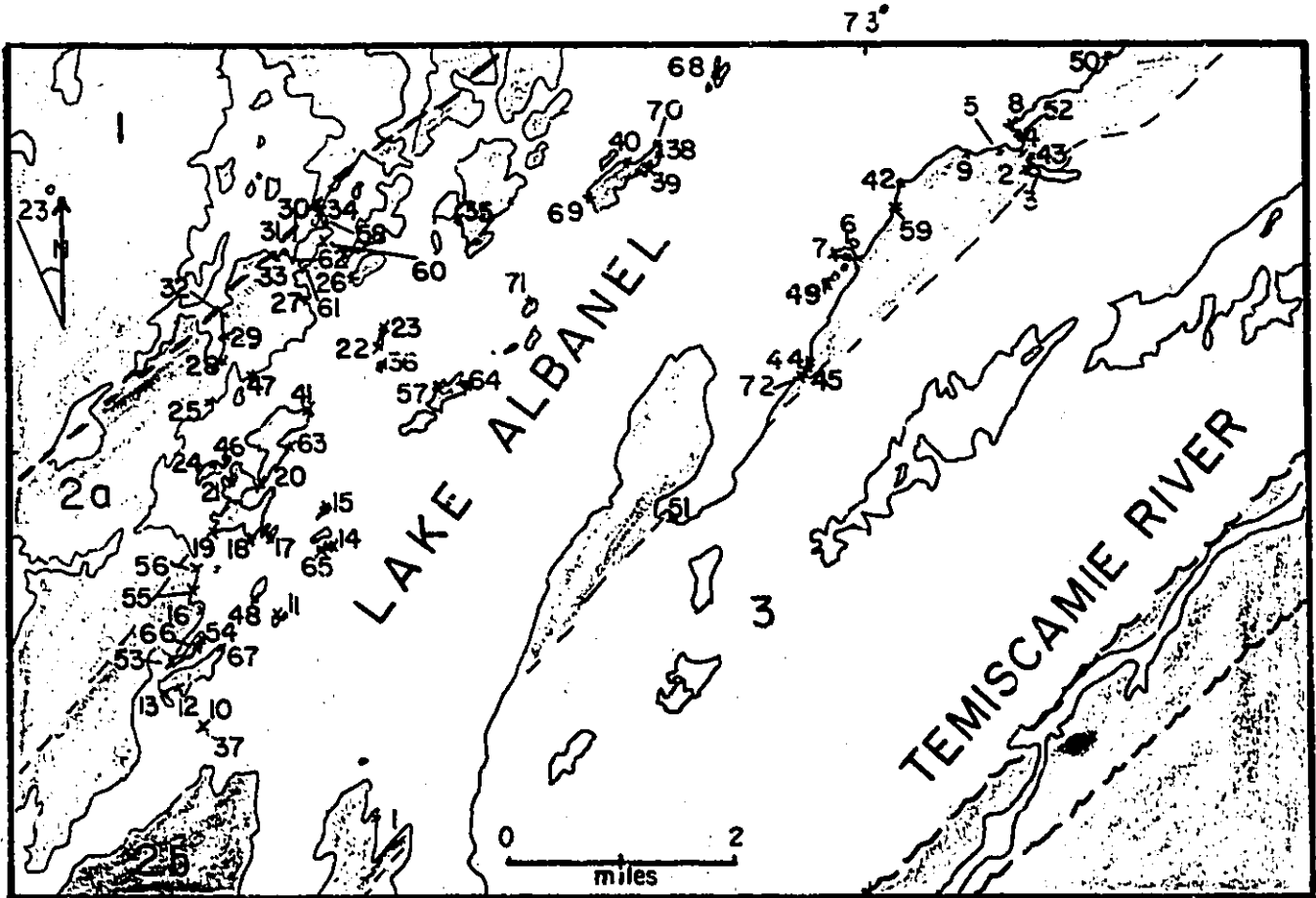
SAMPLE LOCATIONS IN THE MISTASSINI POST AREA



(MODIFIED FROM DELAND & SATER, 1967)

-  UPPER ALBANEL FORMATION
-  LOWER ALBANEL FORMATION
-  BOREHOLE LM-74-D2
-  SAMPLE LOCATION
-  GEOLOGICAL CONTACT
-  FAULT
-  SHORELINE

SAMPLE LOCATIONS IN THE LAKE ALBANEL AREA



(MODIFIED FROM WAHL, 1953)

- 3** TEMISCAMIE FORMATION
- U. ALBANEL FORMATION
- 2a** SANDY DOLOSTONE UNIT
- L.** ALBANEL FORMATION
- GEOLOGICAL CONTACT
- - - FAULT
- 3x SAMPLE LOCATION

APPENDIX 2

DESCRIPTION OF ANALYZED CARBONATE AND PYRITE
SAMPLES AND ADDITIONAL PETROGRAPHIC SAMPLES

DESCRIPTION OF ANALYZED MISTASSINI CARBONATE SAMPLES

UPPER ALBANEL FORMATIONBanded Dolostone Unit

- A-31-84 Cryptalgal laminated dolomudstone:
alternating l. & d. grey irregularly laminated
dolomudstone and dolomite - quartz fenestrae; alter-
nating hypidiotopic ($\leq 30 \mu$) & coarser ($\leq 200 \mu$) dolo-
mite (Plate 14).
- A-30ma-84 Dolomudstone:
medium grey mudstone (analyzed) with discontinuous
black (organic ?) laminations; hosting a lighter grey
mudstone layer; ($\leq 25\text{--}250 \mu$); evaporite molds? hosting
Fe-oxides (Plate 26).
- A-30mi-84 Dolomudstone:
light grey (1 cm) mudstone layer within darker dolo-
mudstone matrix (see above); hypidiotopic ($< 20 \mu$) $\approx$
massive dolomite.
- A-28-84 Laminated dolomudstone:
grey dolomite; alternating medium and dark laminae;
minor quartz and dolomite-filled vugs.
- A-27-84 Laminated dolomudstone:
grey dolomite alternating medium + dark + discontinu-
ous irregular laminae ($\leq 25 \mu$, hypidiotopic); abundant
quartz and dolomite fenestrae of centimicron-sized
crystals; quartz pseudomorphs after evaporites?
- A-1-84 Stromatolitic dolomudstone:
dark grey dolomite; weak alternating lighter ($\leq 50 \mu$)
& dark (10-20 μ) grey hypidio- idiotopic dolomite;
stylolite; micaceous mineral(?) (Plate 7).
- A-24-84 Laminated dolomudstone:
alternating light ($\leq 70 \mu$) and dark ($\leq 25 \mu$) grey
hypidio- idiotopic dolomite laminae; rare isolated
linear patches; stylolites present; evaporite molds?
(Plate 27).
- A-72bg-85 Interbedded dolomudstone:
light grey dolomudstone layer (analyzed) underlain by

'In the following descriptions, " μ " represents micrometers

an imbricated and thickly laminated light ($\leq 30 \mu$) and dark ($\leq 20 \mu$) grey laminated layer in a ($\leq 100 \mu$) hypidiotopic matrix; stylolites and hairline fractures present.

- A-79b-85 Dolomudstone:
irregularly laminated and discontinuous dolomudstone of light grey to beige color; minor black chert laminations and stylolites.
- A-26a-84 Dolomudstone:
medium grey dolomudstone with dark patches, wisps and a few peloids ($< 5-10\%$); hypidiotopic ($\leq 25 \mu$) dolomite; quartz pseudomorphs (after evaporites?); dolomite & quartz cavity filling with d. brown laminae showing a faint acicular (algal?) fabric.
- A-2a-84 Stromatolitic dolomudstone
alternating irregular laminated m. ($\leq 200 \mu$) and d. ($\leq 20 \mu$) grey dolomudstone; quartz and dolomitic laminations $\pm$ tiny algal bulbs (subsequently removed); stylolite & micaceous? mineral; underlying sample in Plate 9.
- A-59a-85 Laminated dolomudstone:
light and dark grey laminated to disrupted dolomudstone; rare quartz dolowackestone lenses.
- A-3a-84 Laminated dolomudstone:
disrupted & irregularly laminated m. and d. grey dolomudstone with quartz and dolomite interlaminations and vugs; hypidiotopic ($\leq 20 \mu$); evaporite? molds with traces of hematite within; cavities have ≥ 3 dolomite generations.
- A-52a-85 Laminated stromatolitic dolomudstone:
alternating light and dark grey (organic-rich? dolomudstone) laminated dolomudstone with occasional tiny stromatolitic bulbs (a few mm high).
- A-4ma-84 Sandy dolopackstone:
various dolomitic intraclasts (≤ 2 mm), peloids, quartz grains (≤ 1 mm) and rare ooids, chert and radial fibrous grains (≤ 3 mm $\pm$ silicified) set in a finer grained arenitic to muddy matrix; several generations dolospar; hosting & in stylolitic contact with brecciated dolomudstone.
- A-4mi-84 Laminated dolomudstone:
brecciated beds of laminated dolomudstone, bounded by stylolites and hosted by the dolopackstone (above); hypidiotopic, ($\leq 20 \mu$); several generations of fine to

coarse dolospar surrounding fragments suggesting early brecciation.

- A-54a-85 Dolomudstone:
poorly laminated light grey dolomudstone with ($\leq 10\%$) quartz grains; stylolites present; associated with sandy dolopackstone.
- A-7r-84 Red laminated dolomudstone:
red band of dolomudstone exhibiting both a "fluid" & "rigid" texture (Plate 13); $\leq 10\%$ peloids; tepee breccia is associated; hypidiotopic ($\leq 20\ \mu$) dolomite.
- A-7b-84 Fenestral dolomudstone:
beige, irregularly laminated to distorted fenestral (early quartz?) dolomudstone overlying red dolomudstone sample (A-7r-84); quartz and dolomite of filling fenestrae; hypidiotopic ($\leq 20\ \mu$) dolomite.
- A-55a-85 Laminated dolomudstone:
beige, light and dark grey irregularly laminated dolomudstone; minor stylolites and fenestrae.
- A-56a-85 Laminated dolomudstone:
alternating light grey and black (organic ?) fine laminations; stromatolites located nearby.
- A-10-84 Interbedded oolitic dolopackstone & dolomudstone :
white ooid-rich layers of normal, compound & micritic (>6 laminae) ooids, interlayered with dolopackstone and light grey dolomudstone and dolomite-quartz cavity filling brecciated fragments; minor detrital quartz; stylolites associated; hypidiotopic ($\leq 30\ \mu$) dolomite matrix.
- A-5a-84 Sandy dolopackstone-dolograinstone:
grey color; $\approx 35\%$ mature quartz in detrital dolomitic matrix; sample A5b84 represents the buff-colored, altered margin.
- A-6-84 Dolomudstone:
grey laminated dolomudstone; $\pm$ dolomite and quartz-filled vugs.
- A-8-84 Dolomudstone:
laminated l. & d. grey (algal?) dolomudstone; concordant dolomite & quartz cavities (fenestrae?); dolomite & quartz precipitate.
- A-9a-84 Sandy dolopackstone-dolograinstone:
grey color; $\approx 35\%$ mature quartz grains in a ($\pm$ oolitic) detrital dolomitic host; associated with tiny stromat-

olites (a few cms high).

- A-14a-84 Sandy dolowackestone:
l.-m. grey dolostone; $\pm$ laminated & stylolitic; $\approx 25\%$ mature quartz ($\leq .6$ mm); some sandy lenses; associated with imbricated sandy dolomite.
- A-25a-84 Dolomudstone:
m.-d. grey dolostone associated with small (≤ 10 cms) stromatolites occupying a shallow (cemented?) depression; $\approx < 100 \mu$ hypidiotopic massive dolomite; $\approx 10\%$ crystalline quartz along stylolites.

Sandy Dolostone Unit

- A-62b-85 Stromatolitic dolomudstone:
interlaminated light and dark grey dolomudstone and fenestral quartz-dolomite; local stromatolitic domes within laminated host.
- A-32b-85 Cryptalgal dolomudstone:
partially oxidized (orange) grey irregularly laminated dolomudstone. Light grey and black (organic-rich) continuous to discontinuous laminations and patches; minor fenestrae; associated with silicified ooid lenses+ sandy dolopackstone occupying shallow channels(?).
- A-48g-85 Stromatolitic dolomudstone:
grey algal laminated and stromatolitic dolomudstone with oolitic-rich lenses and laminae (only the dolomudstone was analyzed); underlying columnar stromatolites.
- A-36b-85 Oolitic dolograinstone:
grey dolomite; dolomitic ooids (60-70 %) < 2 mm in diameter; 10-15 % quartz (≤ 1 mm) grains; matrix (≤ 15 %); ($< 150 \mu$) hypidiotopic interparticle dolomite.
- A-12b-84 Cryptalgal dolomudstone:
alternating light and dark grey dolomudstone; irregularly laminated to brecciated ($\neq$ tepees) and overlain by sandy dolopackstone. (Minor peloids + stylolites); hypidiotopic-idiotopic ($\leq 30 \mu$) dolomite.
- A-30a-85 Oolitic dolograinstone:
partially silicified ooids (≤ 5 mm) ≈ 70 %; chert and xenotopic ($< 500 \mu$) interparticle dolospar constitute ≈ 30 %; stylolites; hypidiotopic-xenotopic dolomite ($< 600 \mu$) in cores contrast with the later idiotopic rhombs in the silicified cortices (Plate 29).

- A-13b-84 Sandy dolowackestone:
pink dolowackestone with distorted and quartz-rich laminae ($\approx 20\%$); fenestrae have oxidized margins, filled with dolomite & quartz.
- A-13c-84 Interbedded dolomudstone & algal intraclastic dolostone:
dark grey weakly laminated (to discontinuous patches) dolomudstone (analyzed) $\leq 20 \mu$ and interbedded with intraclastic band showing shelter porosity; frequent stylolitic contacts; a few feldspar & quartz grains $\pm$ chert with idiopathic, later dolomite.
- A-13a1-84 Stromatolitic dolomudstone & dolowackestone:
(top of slab) red, poorly laminated dolomudstone to quartz dolowackestone.
- A-13a2-84 Stromatolitic dolomudstone & dolowackestone:
beige poorly laminated mudstone and red quartz dolowackestone + minor quartz fenestrae.
- A-13a3-84 Stromatolitic dolomudstone:
beige, poorly laminated dolomudstone; little quartz present.
- A-13a4-84 Stromatolitic dolomudstone:
red to beige dolomudstone with local quartz fenestrae.
- A-13a5-84 Stromatolitic dolomudstone to dolowackestone:
alternating beige dolomudstone and red quartz dolowackestone; local quartz fenestrae; base of slab.
- A-15-84 Sandy dolopackstone-dolograinstone:
pink dolomite; intraclasts, peloids and ooids ($\approx 50-60\%$) ($\leq 3 \text{ mm}$) in a hypidiotopic dolomite ($\approx 20-600$) matrix; 15% mature quartz grains ($< 1 \text{ mm}$).
- A-43b-85 Dolomudstone and dolowackestone:
weakly laminated light grey dolomudstone and quartz ($\leq 1 \text{ mm}$) dolowackestone; $\approx 15\%$ quartz; local black streaks (organics?) in dolomudstone; associated with fenestral dolomudstone & nearby ooliticolograinstone.
- A-44b-85 Ooliticolograinstone:
80% dolomitic ooids ($\leq 2 \text{ mm}$); normal ooids with various nuclei; 15% hypidio-xenotopic dolospar ($\leq 200 \mu$) matrix; 5% quartz grains.
- A-20-84 Fenestral dolomudstone:
light grey dolomudstone with quartz - filled fenestrae; rare 1.5 cm chert nodule associated.

- A-21-84 Fenestral dolomudstone:
light grey dolomudstone with discontinuous black (organic?) streaks and quartz-filled fenestrae.
- A-47b-85 Quartz dolowackestone:
pink-orange dolowackestone with (15 %) mature quartz grains and ooids (1 cm); lenticular to oval quartz-filled fenestrae minor; associated with nearby fenestral dolomudstone.
- A-22-84 Bedded dolomudstone:
thinly bedded pink dolomudstone with numerous brownish-yellow Fe-oxide fractures and a minor quartz-filled cavity; vertical fractures and "v"-shaped opening $\approx$ dessication? feature. Interlocking hypidiotopic (30-50 μ) crystals up to a maximum of 250 μ .
- A-25a-85 Dolomudstone and dolowackestone:
white dolomudstone with fine fenestrae overlying dolowackestone with 10-15 % peloids.
- A-16-84 Dolomudstone & sandy dolowackestone:
grey; 15-30% allochems (ooids, intraclasts & peloids) and 15% mature quartz ($< .5$ mm); in stylolitic contact with an underlying laminated dolomudstone (≤ 30 μ) and coarser laminae.
- A-17-84 Sandy dolopackstone-dolograinstone:
grey; 20 % mature (≤ 1 mm) quartz & 40 % dolomite grains ($\approx \leq .5-1$ mm) in dolomitic matrix; local outcrop cross-bedding.
- A-18-84 Sandy dolopackstone-dolograinstone:
grey; $\approx 30\%$ mature quartz ($\approx .2$ mm), and dolomitic grains in dolomitic matrix; local outcrop cross-bedding.
- A-19-84 Brecciated dolomudstone:
buff colored, laminated (algal?) & brecciated (1-2 cms) dolomudstone (≤ 100 μ) with coarser sediment infilling interstices; (dessication?); local chertification.
- M-9-84 Dolomudstone:
grey $\approx$ massive dolomudstone; minor fracture dolomite.
- M-10a-84 Sandy dolopackstone-dolowackestone:
grey color; $\approx 35\%$ (≤ 1 mm) mature quartz (< 1 mm) & dolostone grains in a hypidiotopic (200 μ , max. ≈ 350 μ) dolomitic matrix; rare feldspar grains; associated with fenestral intraclastic ($\pm$ imbricated) dolostone.

LOWER ALBANEL FORMATIONStratified Dolomite & Shale Unit

- M-8a-84 Fractured dolomudstone:
grey $\approx$ massive dolomudstone; hypidiotopic dolomudstone ($\leq 100 \mu$) brownish (Fe-rich?) crystals; abundant dolomite- ($\pm$ Fe oxide) filled veins; associated with brecciated dolostone and slickensides; associated with teepee? structure.
- M-7b-84 Laminated dolomudstone:
grey, coarsely laminated mudstone with darker laminae (organic or argillaceous); on a larger scale the laminations form shallow domes and depressions; laminae displaced by thin fractures.
- M-7a-84 Dolomudstone:
1. grey to buff colored dolomudstone; abundant coarsely crystalline dolomite vugs with Fe-oxides toward center. Sample $\approx$ 1 meter above M7b84.
- M-6-84 Dolomitic siltshale:
weakly laminated light to dark grey and black; weathers a rusty brown; quartz, dolomite, illite and chlorite dominate; minor plagioclase?
- M-5-84 Laminated dolomudstone:
weakly laminated dolomudstone with light and dark grey colors.
- M-4-84 Dolomudstone:
grey dolostone with a few (1-3 mm) lighter grey, coarser crystalline laminae; $\leq 250 \mu$ and xenotopic to hypidiotopic; minor detrital quartz; stylolites.
- M-11-84 Medium crystalline dolomite:
medium grey, crystalline ($\leq 300 \mu$) hypidiotopic dolomite; massive; minor stylolites.
- M-3-84 Dolomudstone:
medium grey dolomudstone with minor black discontinuous streaks.
- M-12-84 Laminated dolomudstone:
weakly laminated medium grey dolomudstone; hypidiotopic dolomite ($\leq 40 \mu$; maximum of $\leq 100 \mu$); 10-15 % dark ($\leq 200 \mu$) patches; < 5 % detrital quartz and plagioclase.
- M-1-84 Dolomudstone:
medium grey dolomudstone; massive.

- M-2-84 Dolomudstone:
medium grey; massive; a few black (organic and/or argillaceous) streaks; hypidiotopic dolomite ($\leq 30 \mu$; maximum of 60μ); $< 5\%$ detrital quartz, feldspar and micas.

Upper Black Shale Complex

- D2-1-74 Impure dolomudstone:
poorly laminated to patchy black (organic) and medium grey dolomudstone ($\leq 25 \mu$); mostly hypidiotopic dolomite, lesser quartz and euhedral, randomly oriented phlogopite? ($\leq 120 \mu$) minor chlorite (?) & calcite; 3 mm oval cavity filled with dolomite, calcite & opaques.
- D2-3-74 Impure dolomudstone:
dark grey poorly laminated dolomudstone; minor quartz and feldspar; stylolites; dominant dolomite, lesser quartz and minor k-spar (?).
- D2-5-74 Impure dolomudstone:
patchy light and dark grey dolomudstone with minor calcite ($\leq 500 \mu$) along stylolites and organic-rich patches; idio-hypidiotopic dolomite ($\leq 50 \mu$, max 100) also showing unique "loafish" texture with segregation of organics interstitially; minor quartz and mica.
- D2-7-74 Silty and laminated dolomudstone:
light and dark grey dolomudstone; laminations partially developed and irregular; white calcite fractures; minor quartz and feldspar; abundant quartz and minor k-spar and chlorite.
- D2-113-74 Sandy dolograinstone:
fine grained, laminated to cross-laminated impure dolomite; local erosional surface; medium to dark grey with dolomite and quartz dominating and minor plagioclase, feldspar and mica (possibly chlorite ?).
- D2-114-74 Silty dolomudstone:
light and dark grey dolomite and shale laminae; erosional surface; minor mica, calcite and pyrite; abundant quartz.
- D2-115-74 Sandy dolomudstone:
light (fine sandy) and dark grey to black impure dolomite; laminations and stylonodular texture; dominant dolomite and abundant quartz, minor k-spar and mica ?; pyrite lenses.

- D2-116-74 Silty dolomudstone:
dark grey and black impure dolostone; stylonodular texture; more argillaceous toward base; dominant dolomite, abundant quartz, minor calcite, pyrite and possibly chlorite.
- D2-117-74 Impure dolomudstone:
laminated, darker argillaceous layer grades into lighter fine sandy(?) layer; calcite fractures; abundant quartz and dominant dolomite.
- D2-118-74 Pyritized cross-bedded arenaceous dolostone:
medium grey, pyritized fine grained arenaceous dolostone to dololomite ($\leq 50 \mu$); mostly hypidiotopic dolomite, abundant quartz and minor k-spar, chlorite and mica; 20-30 % pyrite ($\leq 250 \mu$) (Plate 47).
- D2-119-74 Silty dolomudstone:
layers of laminated dark argillaceous dolostone and lighter mottled impure dolostone; dominant dolomite, abundant quartz, minor k-spar pyrite and possibly micas (?).
- D2-120-74 Silty dolomudstone:
dark grey, mottled dolomudstone with minor pyrite and calcite along erosional surface; dominant dolomite, abundant quartz, minor k-spar and micas.
- D2-121-74 Arenaceous dolostone:
dark grey laminated to weakly cross-laminated, fine-grained; erosional surface present; abundant quartz, minor calcite, k-spar, pyrite and possibly micas, dominant dolomite.
- D2-122-74 Vuggy and organic-rich dolomudstone:
weakly laminated, dark grey to black organic streaks (1 mm) and 10 % vugs (evaporite molds?); ($\leq 100 \mu$, often $< 20 \mu$) hypidio-idiotopic dolomite ($\leq 15 \mu$) crystals; abundant quartz and minor ($\leq 200 \mu$) calcite along stylolites, k-spar and micas; calcite, dolomite, quartz and opaques fill the vugs.
- D2-123-73 Silty dolomudstone:
d. grey with stylonodular clastic lenses and thin fissile shale laminae; dominant dolomite, abundant quartz and minor calcite, k-spar, plagioclase and chlorite.
- D2-124-74 Silty dolomudstone:
medium to dark grey poorly bedded with fine argillaceous laminae, stylonodular lenses and erosional surface present; abundant quartz, dominant dolomite, minor k

-spar, plagioclase, calcite and possibly micas (?).

- D2-125-74 Impure dolomudstone:
light and medium grey, weakly laminated (white calcite fracture); dominant dolomite, abundant quartz, minor chlorite (?).

Upper Banded Dolostone Unit

- D2-127-74 Arenaceous dolostone:
light to medium grey, weakly laminated to cross-laminated; local darker argillaceous laminae; abundant quartz and minor k-spar and pyrite; dominant dolomite.
- D2-128-74 Silty dolomudstone:
light to medium grey massive dolostone with shale and stylonodular layers; dolomite and quartz are abundant; minor pyrite.
- D2-129-74 Silty dolomudstone:
light to medium grey banded, massive dolostone with darker stylolaminar zones and calcareous laminae; abundant quartz and possibly minor mica; dominant dolomite.
- D2-9-74 Silty dolomudstone:
medium and dark grey bands of massive to stylonodular dolostone; abundant quartz and minor pyrite; dominant dolomite.
- D2-130-74 Silty dolomudstone:
light to medium grey dolostone with weak bands of calcareous dolostone, stylonodular and laminated dolostone; abundant quartz and minor calcite and mica; dominant dolomite.
- D2-131-74 Silty dolomudstone:
light to medium grey weakly banded dolostone with stylonodular to stylolaminar and dark argillaceous zones; abundant quartz and minor calcite and k-spar (and chlorite ?); dominant dolomite.
- D2-132-74 Silty dolomudstone:
light to medium grey dolostone with gradational change from stylonodular to laminar fabric; local thin shaly laminae; abundant quartz and minor k-spar and chlorite; dominant dolomite.
- D2-11-74 Silty dolomudstone:
medium grey, weakly laminated dolostone; abundant quartz; dominant dolomite.

- D2-13-74 Silty dolomudstone:
medium grey weakly stylolaminar to crenulated; abundant quartz and minor k-spar; dominant dolomite.
- D2-15-74 Silty dolomudstone:
medium grey dolostone with stylolaminar to wispy texture; abundant quartz and minor k-spar and pyrite; dominant dolomite.
- D2-17-74 Impure dolomudstone:
medium to dark grey massive to weakly laminated dolostone; dominant dolomite, lesser quartz and minor plagioclase and k-spar.
- D2-19-74 Sandy dolomudstone
medium grey interlaminated dolomudstone and very fine grained arenite ($\leq 100 \mu$); stylolaminar to lenticular texture; abundant subangular quartz ($< 100 \mu$) and minor k-spar, calcite and plagioclase (and chlorite ?); mostly hypidic-idiotopic dolomite ($< 100 \mu$).
- D2-21-74 Banded dolomudstone & sandy dolostone:
medium to dark grey beds of cross-laminated and finely laminated to massive and stylolaminated dolostone; abundant quartz and minor k-spar, mica and plagioclase; dominant dolomite.
- D2-23-74 Dolomitic arenite:
medium to dark grey well laminated to weakly cross-laminated; very fine grained; dominant quartz, abundant dolomite and minor k-spar, plagioclase, chlorite and mica.
- D2-25-74 Dolomitic arenite:
medium to dark grey beds of massive and weakly cross-laminated (very fine grained) arenite; dominant dolomite and quartz and minor k-spar, plagioclase, mica, pyrite, calcite and chlorite.
- D2-27-74 Silty dolomitic limemudstone:
light grey bands of limestone ($\leq 50 \mu$, mudstone hypidic-xenotopic) and dolostone ($\leq 15 \mu$, idiotopic) with stylolaminar texture; hypidiotopic calcite ($\leq 50 \mu$) dominant with abundant subangular quartz ($\leq 50 \mu$) and lesser dolomite and minor plagioclase, chlorite ($< 25 \mu$), fracture calcite & (bent) micas.
- D2-29-74 Dolomudstone & silty to sandy dolomudstone:
medium to dark grey well laminated to cross-laminated (very fine grained); large pyrite cubes present; mostly hypidic-idiotopic dolomite ($< 50 \mu$), subrounded quartz

(< 100 μ) and minor hypidiotopic calcite, plagioclase, k-spar and micas; both detrital & pressure shadow chlorite (around pyrite cube) are present.

- D2-31-74 Dolomitic arenite & dolomudstone:
medium to dark grey bands of massive and light grey lenticular, very fine grained arenite (< 100 μ); quartz major & hypidiotopic dolomite (< 25 μ) important; minor calcite streaks, k-spar, micas and plagioclase; clastics ($\leq$ 100 μ) often concentrated in lenses; stylolaminar texture, calcite lenses (< 5 mm) bounded by stylolites.
- D2-33-74 Quartz arenite & dolomitic arenite:
bedded coarse grained quartz arenite ($\leq$ 1 mm) with dolomitic matrix ($\pm$ 500 μ calcite grains) and overlies a grey finely laminated, dark grey dolomitic arenite; quartz (50-80 μ) dominant, hypidiotopic dolomite (< 30 μ , $\pm$ 500 μ patches) important with lesser calcite, k-spar, plagioclase and micas; pyrite ($\leq$ 4 mm) cube; sharp contact.
- D2-35-74 Dolomitic arenite:
upper part is finely laminated, lower part is stylolaminar, very fine grained; dolomitic arenite; dominant quartz (< 100 μ), then hypidiotopic-idiotopic dolomite (< 50 μ) with less calcite, chlorite, k-spar, micas and plagioclase.
- D2-37-74 Dolomitic arenite:
bedded light grey stylolaminar, very fine grained arenite and dark grey impure massive dolostone; quartz dominant, important dolomite and minor calcite, plagioclase, micas and k-spar.
- D2-39-74 Silty to sandy dolomudstone:
bedded dark grey massive dolomite and laminated to stylolaminar; lensoidal lighter grey zones are coarser grained and calcite bearing; quartz dominant with dolomite next and minor calcite, k-spar, micas and plagioclase.
- D2-41-74 Dolomitic arenite:
medium grey, very fine grained arenite; stylolaminar texture; lighter grey lenses are calcitic; quartz and dolomite dominant, micas significant and minor plagioclase, k-spar and calcite.
- D2-43-74 Dolomitic arenite:
dark to medium grey bedded stylolaminar arenite and laminated to weakly cross-laminated, very fine sandy to silty; quartz and dolomite abundant; minor k-spar,

plagioclase and micas.

- D2-45-74 Dolomitic arenite:
medium to dark grey, very fine grained arenite with lighter grey band of impure dolostone with stylolaminar texture; quartz dominant, significant dolomite and minor plagioclase and k-spar (chlorite?).

Lower Banded Dolostone Unit

- D2-47-74 Calc-dolomitic siltstone:
dark grey, $\approx$ massive, very fine grained lime-dolomitic (arenite?); minor black (organic?) streaks; quartz is dominant with important dolomite and lesser calcite; minor k-spar, plagioclase and micas.
- D2-49-74 Dolomitic siltstone:
dark grey, $\approx$ massive, very fine grained (arenite?); white calcite fractures; dolomite and quartz dominant; minor plagioclase, micas and k-spar.
- D2-51-74 Calc-dolomitic siltstone:
dark grey, massive except for minor black streaks, very fine grained (arenite?); dolomite and quartz dominate, significant calcite and plagioclase and minor micas and k-spar.
- D2-53-74 Sandy dolomitic limewackestone:
bedded light grey with intraclastic wackestone (≤ 1 mm) and darker argillaceous dolomitic limestone with black streaks; dominant quartz and calcite and important dolomite with minor micas, k-spar, plagioclase and fine disseminated pyrite.
- D2-55-74 Calc-dolomitic siltstone:
dark grey, massive, very fine grained (arenite?); dominant quartz, important dolomite and calcite and minor plagioclase, k-spar, micas and pyrite.
- D2-57-74 Sandy dolomitic limewackestone:
medium to dark grey with carbonate intraclasts (≤ 1 mm); weakly laminated to massive; quartz (≤ 1 mm) and calcite dominant with lesser dolomite and minor k-spar, plagioclase and chlorite.
- D2-59-74 Calc-dolomitic siltstone:
light and dark grey, very fine grained (arenite?) with darker (organic and/or argillaceous) and lighter carbonate zones; ≤ 5 % pyrite in the former; quartz dominates with important dolomite and calcite and minor plagioclase, k-spar and micas.

- D2-61-74 Banded calc-dolomitic siltstone:
medium grey limy-dolomitic, very fine grained stylolam-
inar bands interlaminated with darker grey dolomitic
siltshale; quartz dominates with important dolomite,
plagioclase, calcite and minor k-spar and micas.
- D2-63-74 Calc-dolomitic arenite:
light to medium grey, fine grained cross-laminated
arenite; quartz and plagioclase dominant with important
dolomite, lesser calcite and minor micas and k-spar.
- D2-65-74 Banded silty limemudstone & dolomudstone:
medium to dark grey banded dolomitic ($< 30 \mu$, idio-
hypidiotopic) and limestone ($< 30 \mu$) rich laminae;
hypidiotopic calcite dominates with appreciable micas
and lesser dolomite, subangular ($< 50 \mu$) quartz and
feldspars; transition marked by scattered idiotopic
dolomite.
- D2-67-74 Silty limemudstone:
dark grey, finely but weakly laminated; calcite
dominates with lesser plagioclase and quartz and minor
dolomite, chlorite, plagioclase and k-spar.
- D2-69-74 Silty limemudstone:
medium grey, finely but weakly laminated; calcite
dominates, plagioclase and quartz important with lesser
dolomite, and minor k-spar chlorite and pyrite.
- D2-71-74 Banded calcareous & dolomitic arenite:
medium grey, finely laminated to weakly cross-laminated
very fine grained arenite; quartz ($< 80 \mu$) and calcite
($< 100 \mu$) dominate; significant mica ($< 200 \mu$, often
bent) and plagioclase, dolomite ($\leq 100 \mu$, idio -
hypidiotopic) and minor chlorite and k-spar; authigenic
quartz as subhedral, twinned ($< 1 \text{ mm}$) & poikilotopic
crystals parallel or perpendicular to bedding.
- D2-73-74 Calc-dolomitic arenite:
medium grey, very fine grained, massive arenite;
dominant quartz and dolomite, significant calcite,
plagioclase and minor chlorite, mica and k-spar.
- D2-75-74 Dolomitic arenite:
medium grey, finely laminated, very fine arenite;
quartz ($\leq 20 \mu$) and $\approx$ idiotopic dolomite ($\leq 40 \mu$)
dominant, significant plagioclase and minor hypidioto-
pic ($< 100 \mu$) calcite, k-spar, chlorite and bent mica
($< 150 \mu$); subangular clastics ($\leq 60 \mu$).
- D2-77-74 Dolomitic siltstone to arenite:

dark grey, very fine grained, $\approx$ massive; dominant quartz, lesser dolomite, significant plagioclase and minor k-spar, chlorite and calcite.

- D2-79-74 Calc-dolomitic siltstone to arenite:
medium to dark grey laminated, very fine grained siltstone to arenite, lighter laminae calcitic; quartz dominant with important plagioclase and lesser dolomite and calcite; minor k-spar, chlorite and mica.
- D2-80-74 Calc-dolomitic arenite:
medium to grey, (upper) bedded medium and (lower) fine grained arenite ($< .6$ mm), including $\approx 15\%$ (≤ 1 mm) black dolomudstone grains, quartz dominant, dolomite ($< 250\ \mu$) $\approx$ as grains with significant calcite ($\leq 400\ \mu$) as grains & cement, plagioclase and minor k-spar, mica ($< 100\ \mu$) and chlorite; clastics $\approx$ subrounded-subangular ($< 600\ \mu$).
- D2-81-74 Impure limemudstone:
medium grey, massive; calcite dominant, significant plagioclase and minor quartz.
- D2-83-74 Impure limemudstone:
medium to dark grey, $\approx$ massive with minor black (organic ?) streaks; calcite dominant, with lesser quartz and minor dolomite, plagioclase and micas.
- D2-85-74 Silty calcarenite:
dark grey, finely laminated to cross-laminated, very fine grained (arenite?); calcite dominates, with important quartz and plagioclase and minor dolomite (and possibly chlorite and k-spar ?).
- D2-87-74 Calc-dolomitic siltshale:
medium-dark grey and black bands of siltshale; quartz and dolomite dominate with lesser calcite, chlorite and minor plagioclase, mica and K-spar.
- D2-89-74 Silty dolomudstone & dolomitic siltshale:
medium-dark grey and black bands of massive and poorly laminated (to streaky) impure dolomudstone and siltshale; dolomite and quartz dominate with lesser plagioclase, calcite and micas (?).
- D2-91-74 Silty calc-dolomudstone & dolomitic siltshale:
medium and dark grey, banded dolomudstone and very fine grained (arenite?), with black and lighter colored streaks respectively; dolomite and quartz dominate with lesser calcite and plagioclase and minor k-spar and micas.

- D2-93-74 Dolomitic siltshale:
dark grey and black bands of siltshale with black streaks; quartz dominates, important dolomite, plagioclase, significant calcite, minor k-spar, micas and pyrite (as streaks and disseminations).

Lower Black Shale Complex

- D2-95-74 Siltshale to mudshale:
medium-dark grey and black laminated siltshale to mudshale; quartz dominant important proportion of illite, lesser calcite and plagioclase and minor k-spar, chlorite and dolomite; pyrite occurs as laminations and crystals.
- D2-97-74 Dolomitic siltshale to mudshale:
light, medium and dark grey laminated siltshale, with local discontinuous laminations (streaks); quartz dominant with lesser dolomite and illite and minor plagioclase, k-spar, calcite and chlorite.
- D2-133-74 Silty calc-dolomudstone:
medium to dark grey, massive (* weakly mottled); dolomite dominates, with lesser quartz and calcite and minor k-spar, plagioclase and chlorite.
- D2-134-74 Silty dolomitic limemudstone:
light and dark grey, bedded ; calcite dominates, lesser quartz and dolomite and minor plagioclase (and possibly mica ?).
- D2-135-74 Silty dolomitic limemudstone:
light and dark grey; weakly laminated to massive; slickensides present; calcite dominates with lesser dolomite and quartz and minor plagioclase, k-spar, chlorite (and possible mica ?).
- D2-136-74 Silty calc-dolomudstone:
dark grey irregularly laminated to massive; dominant dolomite with lesser quartz and calcite and minor plagioclase, k-spar and micas.
- D2-137-74 Sandy dolomudstone & dolomitic siltshale:
medium-dark grey and black laminated impure dolomudstone with local black siltshale laminae and fine sandy laminae; dolomite dominates with lesser quartz and minor plagioclase, k-spar, calcite and possibly micas (?).
- D2-138-74 Sandy calc-dolomudstone:
medium and dark grey, laminated; lighter laminae more

calcitic and sandy; dolomite dominates with lesser quartz and calcite and minor k-spar, plagioclase, chlorite and possibly mica (?).

- D2-139-74 Silty calc-dolomudstone:
light and dark grey, laminated; dolomite dominates with lesser quartz and calcite and minor plagioclase, k-spar, chlorite (and mica ?).
- D2-99-74 Silty dolomitic limemudstone:
light and dark grey, laminated; pale laminations appear more calcitic; calcite and dolomite dominate with lesser quartz and minor k-spar, plagioclase (?) and micas.
- D2-140-74 Silty dolomitic limemudstone & calc-dolomudstone:
light and medium grey bedded (and laminated) dolomitic limemudstone and calc-dolomudstone; dolomite and calcite dominate with lesser quartz and minor plagioclase, k-spar, chlorite (and mica ?).
- D2-141-74 Impure calc-dolomudstone:
medium and dark grey laminated dolomudstone; darker laminae are more calcitic; dolomite dominant with lesser quartz and calcite and minor plagioclase, k-spar, chlorite and mica (?).
- D2-142-74 Impure calc-dolomudstone:
light to dark grey and black laminated dolomudstone; darker laminae more calcitic; quartz and dolomite dominate with lesser calcite, k-spar, mica and minor chlorite.
- D2-143-74 Dolomitic siltstone to fine arenite:
medium to dark grey and black laminated (with lensoidal texture) very fine grained arenite; dolomite and quartz dominate with lesser plagioclase and k-spar and minor calcite and micas.
- D2-144-74 Impure calc-dolomudstone:
medium to dark grey laminated calc-dolomudstone with darker siltshale laminae; dolomite and quartz dominate with lesser calcite and minor k-spar, plagioclase and possibly chlorite and mica (?).
- D2-145-74 Impure calc-dolomudstone:
light-medium grey and dark grey laminated dolomudstone; darker bands more calcitic; dolomite and quartz dominant with lesser calcite and minor k-spar, plagioclase, pyrite and possibly micas.
- D2-146-74 Dolomitic siltstone:
m. grey and black beds of dolomitic siltstone; quartz

occurs as detrital and authigenic (≤ 1 mm) varieties and calcite crystals (≤ 500 μ) are poikilotopic and secondary; quartz and dolomite (≤ 80 μ , hypidiotopic) dominate with lesser plagioclase; calcite, chlorite and mica; minor $\approx$ euhedral pseudomorphic & poikilotopic quartz (< 1 mm).

- D2-147-74 Dolomitic siltstone:
light grey, laminated siltstone; vertical calcite fracture; quartz and dolomite dominate with lesser plagioclase and k-spar, calcite and minor mica and possibly chlorite (?).
- D2-148-74 Silty calc-dolomudstone:
light grey, laminated dolomitic to limestone-rich and pyrite-rich laminae; dolomite dominates with quartz and lesser plagioclase, k-spar, calcite, pyrite and minor chlorite and mica.
- D2-101-74 Impure dolomitic limemudstone:
light to medium grey, massive except for pyrite laminae and a few stylolites; calcite dominates with lesser quartz and dolomite and minor pyrite, plagioclase, k-spar and possible micas (?).
- D2-103-74 Impure calc-dolomudstone:
light-medium grey, weakly laminated to massive dolomudstone with minor (≤ 1 mm) calcite patches (secondary ?); dolomite and quartz dominate with lesser calcite and minor k-spar, chlorite and possibly mica (?) and plagioclase (?).
- D2-105-74 Impure dolomitic limemudstone:
medium and dark grey bedded limemudstone; calcite and dolomite dominate with lesser quartz and minor mica and possible k-spar (?) and plagioclase (?).
- D2-107-74 Impure dolomitic limemudstone:
dark grey laminated limemudstone with pyritiferous laminae; minor local darker patches (≤ 1 mm); calcite and dolomite dominate with lesser quartz and minor k-spar and chlorite.
- D2-109-74 Impure dolomudstone:
dark grey weakly laminated (calcitic) to massive dolomudstone; dolomite dominant with lesser quartz and minor k-spar.
- D2-111-74 Impure dolomudstone:
dark grey, massive dolomudstone with minor siltshale? grains (≤ 1 mm); dolomite dominates with lesser quartz and minor mica and k-spar.

DESCRIPTION OF PYRITE SAMPLES ANALYZED FOR ISOTOPIC SULFURUPPER ALBANELL FORMATION

- A-2-85: (1-2 mm) pyrite cube at contact between an algal dolowackestone and dolopackstone; since cold finger was required for sample, $\delta^{34}\text{S}$ is only an approximation. Plate 10.

LOWER ALBANELL FORMATIONUpper Black Shale Complex

- D2-156-74: Pyritized crenulated algal layer; anhedral to euhedral crystals ($\leq 800\ \mu$) coalescing into larger masses; calcite fracture appears to fracture pyrite (earlier), although some sulfides are in the fracture; probably early post-compaction pyritization.
- D2-115-74: Sandy stylonodular dolomudstone with local pyritiferous lenses ($\leq 5\ \text{mm}$);
- D2-118-74: Pyritized cross-bedded (organic-rich) arenaceous dolostone; 20-30% pyritized mass composed of anhedral to euhedral crystals ($\leq 250\ \mu$) coalescing from interparticle cavities, forming a branching network which transects the structure yet preserves it; pyritization related to a redox front. Plate 47.
- D2-8-74: Light to medium grey stylonodular dolomudstone with subangular to subrounded ($\leq 1\ \text{mm}$) pyritiferous lenses and fine laminae; calcite may be associated with the latter; probably early post compaction (?) pyrite.

Upper Banded Dolostone Unit

- D2-15-74: Silty dolomudstone with subrounded to subangular pyrite lenses ($\leq 1\ \text{mm}$) associated with dark (organic?) matter; probably early diagenetic post compaction (?).
- D2-29-74: Laminated silty to sandy dolomudstone $\pm$ cross-laminated with a large ($\leq 6\ \text{mm}$) and smaller

poikilotopic cube associated with the sedimentary structure and cross-cutting the laminations; late diagenetic pyrite with chlorite pressure shadows. Plate 48.

- D2-33-74: Dolomitic arenite & quartz arenite with a (3-4 mm) pyrite cube; late diagenetic pyrite with pressure shadows.
- D2-38-74: Laminated ($\pm$ cross-laminated) sandy dolomudstone to dolomitic arenite with pyrite lense (≤ 1 cm) composed of coalescing cubes and trapped silicate and carbonate matrix; associated with sedimentary structure; cubes are largest in the center, suggesting earlier growth; early to later diagenetic post compaction pyrite with chlorite pressure shadows.
- D2-44-74: Silty stylolaminar dolomudstone with a subrounded (≤ 5 mm) pyritiferous mass composed of coalescing cubes trapping little host material; sediment is displaced around pyrite; pre-compaction early diagenetic sulfide with chlorite pressure shadows. Plate 43.

Lower Banded Dolostone Unit

- D2-53-74: Sandy dolomitic-lime-wackestone with finely disseminated pyrite; kiba separation; early (?) diagenetic pyrite.
- D2-60-74: Silty-sandy lime-dolomudstone with thin (≤ 4 mm) disseminated pyrite band with a decreasing proportion of pyrite downward; sharp upper contact + gradational base; possibly early diagenetic pyrite (?); kiba separation.
- D2-90-74: Sandy, organic-rich dolomudstone to siltshale with disseminated pyrite (& organic) streaks and isolated radiating crystals ($\approx < 500 \mu$) surrounded by calcite and associated with organics; early diagenetic (?); kiba separation. Plate 46.

Lower Black Shale Complex

- D2-94-74: Dolomitic siltshale with discontinuous pyrite laminae (1-2 mm thick) of cubic crystals trailing and coalescing toward each other; possibly early diagenetic pyrite.

- D2-151-74: Silty dolomudstone to dolomitic siltshale hosting a 2 cm thick pyrite lense; sediment displaced by growth of lense; crystalline size & coalescence of pyritization and $\delta^{34}\text{S}$ increases toward center (isotopic evidence contrary to textural evidence); the crystals are free of inclusions; early diagenetic and pre-compaction. Plate 44.
- D2-152-74: Dolomitic ($\approx$ black) organic-rich siltshale hosting 1 cm thick pyrite band displacing sediment; matrix fills the intercrystalline cubic areas; horizontal fractures filled by secondary quartz and carbonate; believed to be early diagenetic pre-compaction pyrite; $\delta^{34}\text{S}$ increases with vertical thickness.
- D2-98-74: Impure laminated dolomudstone with pyrite cubes ($\leq 700 \mu$) and discontinuous laminae of variable thickness ($\leq 1-2 \text{ mm}$) associated with black organic laminae (cubes $\leq 100 \mu$); larger isolated cubes appear to replace authigenic quartz, suggesting ≥ 2 generations of pyrite; (latter is probably early diagenetic). A = lower pyrite laminae; B = (later diagenetic?) upper pyrite cubes. Plate 45.
- D2-153-74: impure interlaminated limemudstone and dolomudstone with 1-2 cm thick pyrite band displacing sediment; white crystalline calcite associated near the base of the pyrite; several oblique fractures healed by coarsely crystalline calcite; associated stromatolitic(?) structure or a compaction feature; pyrite is early diagenetic and pre-compaction; (white calcite is probably a vein, suggested by broken pyrite cubes and fragment of dark carbonate inclusions); calcite, quartz & chlorite pressure shadows; $\delta^{34}\text{S}$ increases towards base. Plate 42.
- D2-145-74: Impure calc-dolomudstone with a 2 mm pyrite lense; early diagenetic (?)
- D2-148-74: Silty calc-dolomudstone with alternating pyrite and limestone-rich laminae; pyrite consist of ($\leq 500 \mu$) tiny cubes and coalesced streaks; probably early diagenetic.
- D2-154-74: Impure laminated limemudstone and dolomudstone displaced by a pyrite layer ($\leq 5 \text{ mm}$ thick); growth by coalescence; occasional isolated cubes associated with authigenic quartz suggesting two generations; early diagenetic pre-compaction pyrite; $\delta^{34}\text{S}$

heaviest towards base.

- D2-101-74: Impure dolomitic limemudstone with discontinuous pyrite cubes and subrounded masses (1 $\approx$ mm) forming streaks; kiba separation on fine grained pyrite also performed, with similar isotopic composition ; probably early diagenetic.
- D2-102-74: Impure laminated dolomitic limemudstone hosting a discontinuous flat 1-2 mm thick pyrite lense composed of fine grained cubes; probably early diagenetic; although $\delta^{34}\text{S}$ heaviest in center, limited sampling (3) precludes further interpretation.
- D2-106-74: Impure limemudstone hosting disseminated pyrite and a thin aggregate of pyrite cubes (2-3 mm); probably early diagenetic.
- D2-155-74: Brecciated dolostone from the Icon Sullivan Mine, hosting secondary cubes of various sizes; probably related to faulting and ore emplacement.
- NOTE: grab sample from Icon Sullivan Mine; stratigraphically correlates with the base of the Black Shale Complex (Lehmann, 1974).
- D12-A-77: Basal stromatolitic dolostone with a slightly discordant irregular laminae (2-3 mm thick); somewhat discordant nature suggests fault-related origin.
- D12-B-77: Dark grey basal stromatolitic dolostone with concentric cherty laminae within a fine grained matrix, is intruded by a white dolomitic vein with pyrite lining the margins; definitely late and fault-related pyrite. Plate 49.

PETROGRAPHIC DESCRIPTION OF ADDITIONAL SAMPLESUPPER ALBANELL FORMATIONBanded Dolostone Unit

- A-9-84 Stromatolitic dolomudstone and sandy dolopackstone:
Pink dolostone, alternating finer ($\leq 10 \mu$) and coarser ($\approx 70 \mu$) stromatolitic laminae $\pm$ quartz grains (≤ 1 mm) and rare intercolumn K-feldspar in stylolitic and erosional (?) contact with overlying dolopackstone; attempted algal re-establishment overwhelmed by clastics.
- A-40-85 Pebble-sized oncolitic-intraclastic dolostone to dolopackstone and dolomudstone:
Grey dolostone, subrounded oncolites (≤ 3 cm) and laminae with alternating coarser (centimicron) and finer (decimicron) laminae; intraclasts (≤ 3 mm; ripped up algal layers?) in fine grained $\pm$ micritic matrix; latter is dark brown and pseudomorphs of quartz (after evaporites?); abundant shelter porosity $\pm$ fenestrae; $\pm$ oncolitic truncated surfaces.
- A-33b-85 Interlaminated intraclastic dolowackestone and dolomudstone:
Grey dolostone; interlaminated dolowackestone ($\leq 500 \mu$) intraclasts in dark brown ($\leq 15 \mu$) matrix, dark brown dolomudstone and dolospar veins with ≥ 3 dolospar generations and magnetite? in center; dark brown dolostone hosts cubic pseudomorphs of quartz (after evaporites?) and elongate dolomite-filled cavities; stylolites; associated with intraformational breccia.
- A-54d-85 Sandy dolopackstone to dolowackestone:
Beige to pinkish dolostone; $< 40\%$ mature quartz (< 1.5 mm) $\pm$ chert and intraclasts (< 2 mm), brownish radial-fibrous (< 2 mm; acicular crystals $\approx 50 \mu$) and dark brown micritic ($\leq 15 \mu$) clasts; matrix ($< 200 \mu$); several generations of bladed spar ($\pm$ prismatic) and Fe-oxides; $\pm$ laminae and stylolites.
- A-52e-85 Sandy dolowackestone and dolomudstone:
Grey dolostone; $\approx 30\%$ (< 1 mm) mature quartz and $\approx 15\%$ intraclasts in hypidiotopic matrix ($\approx 60 \mu$); micritic ($\leq 15 \mu$) band and quartz grain lamina displaced by force of crystallization; ≥ 3 spar generations with coarsest dolospar and quartz in center; stylolitization of quartz grains.

- A-8-84 Algal(?) dolomudstone:
Grey, alternating darker ($\leq 25 \mu$) and lighter ($\leq 100 \mu$) laminae and veins ($\leq 1000 \mu$); laminae may form bulbs ($< 3 \text{ mm}$); minor ($\leq 150 \mu$) quartz grains and intraclasts; common stylolitic boundaries.
- A-65b-85 Interlaminated dolopackstone and dolomudstone:
Grey dolostone; alternating layers of intraclastic ($\leq 5 \text{ mm}$) dolomudstone to dolowackestone and dark brown ($\leq 20 \mu$) coarser and finer (algal?) laminae $\pm$ intraclasts; ≥ 3 spar generations in cavities (shelter porosity?); stylolites.
- A-66b-85 $\pm$ Irregularly laminated (algal?) dolomudstone-dolowackestone:
Grey dolostone; dark brown distorted ($\leq 15 \mu$) laminae and fenestrae(?); ≥ 2 generations of spar; local Fe-oxides; $\approx 15\%$ quartz ($\leq 400 \mu$) $\pm$ intraclastic dolowackestone clasts.
- A-11b-85 Disrupted dolomudstone to $\pm$ sandy dolopackstone:
Grey dolostone; dark brown ($\leq 15 \mu$) laminated disrupted layers $\pm$ with quartz (as pseudomorphs?); intraclasts and sandy dolopackstone near base; quartz ($\leq .5 \text{ mm}$); $\pm$ thin (algal?) laminae contouring surface; stylolites; fenestrae and veins filled by dolomite $\pm$ rare micaceous mineral.
- A-20-85 Pebble-sized oncolitic-intraclastic dolostone to dolopackstone:
Grey dolostone; $\approx 25\%$ ($< .5 \text{ mm}$) subrounded quartz, $\approx 35\%$ coated intraclasts and oncolites ($< 1 \text{ cm}$) $\pm$ ooids in sparry ($< 200 \mu$) matrix; rare radiating fibrous clasts and micaceous mineral (?); algal intraclasts show evidence of detrital binding; veins have several generations of spar: finely crystalline $\rightarrow$ brownish bladed $\rightarrow$ limpid $\pm$ subhedral-euhedral $\rightarrow$ cherty $\rightarrow$ megaquartz. Stromatolites observed $\approx 25 \text{ m}$ SE along shore.
- A-6-85 Intraclastic dolopackstone-dolograinstone:
Beige and red dolostone; ($\leq 80 \mu$) intraclasts ($< 6 \text{ mm}$) surrounded by reddish ($\leq 20 \mu$; hematitic?) matrix; shelter porosity with ≥ 2 spar generations and sheet cracks abundant; stylolites. Intraformational breccia (Plate 11) nearby.
- A-2-85 Interbedded fenestral dolomudstone and sandy dolowackestone to dolopackstone:
Light and dark grey dolostone; 20% subrounded quartz ($\leq 1 \text{ mm}$) and locally adhering to discrete (algal?) laminae ($< 500 \mu$); $\approx 20\%$ intraclasts ($\leq 2 \text{ mm}$), rare chert and

brown fibrous clasts in fine matrix; local shelter porosity; erosional surface with microtopography separates underlying dark grey fenestral dolomudstone ($\leq 25 \mu$) from overlying clastics; early dolospar generations ($\pm$ bladed) in fenestrae and truncated by erosion; insitu radial fibrous cements appear to surround fenestrae; rare pyrite cube and micaceous mineral. Intraformational breccia nearby. Plate 10.

- A-13-85 Algal dolomudstone and dolopackstone:
Grey dolostone; $\approx 20\%$ subrounded quartz ($\leq 1 \text{ mm}$), $\approx 25\%$ allochems, intraclasts ($\leq 2 \text{ mm}$) including fibrous clasts; peloids with dark cortex, rare micritic ooids (> 10 concentric laminae); locally alternating clastics and (algal?) laminae; stylolitic contact between dolopackstone and underlying dark brown dolomudstone bands ($\leq 10 \mu$); spar filled cavities $\approx$ surrounded by several fine (algal?) laminae.
- A-23-84 Very coarse-grained oncolitic dolostone in a fine-grained to dolospar matrix:
Grey and black (cherty) dolostone; ($< 2 \text{ cm}$) $\approx 30\%$ oncolites with irregular concentric ($\pm$ cherty) laminations; idiotopic-hypidiotopic ($\leq 25 \mu$; max $\approx 100 \mu$); 30% intraclasts; ≥ 2 generations of interparticle cement with megaquartz last; oncolites characterized by local radiating acicular fabric. Plate 23.
- A-71c-85 Oncolitic dolomudstone:
Grey dolomite; $\approx 30\%$ oncolites ($\pm$ capped by acicular fabrics); alternating lighter ($\leq 150 \mu$) and finer hypidiotopic laminae; matrix ($\leq 20 \mu$, max $\approx 50 \mu$) hypidio-idiotopic and massive; dolomite, quartz and downward radiating blades (cut by cherty laminae-gravity cements?) in cavities; $\pm$ truncated oncolitic surfaces). Plate 37.
- A-78b-85 Dolowackestone and coarser-grained dolomitic fabric:
Grey dolomite; lower brecciated dolowackestone (matrix $\approx < 15 \mu$) overlain by an intraclastic layer (with shelter porosity) and hosting a circular ($< 2 \text{ cm}$) allochem (oncolite?) with upward radiating divergent fibers ($< 3 \text{ mm}$) of aragonite(?); $\pm$ cherty concentric laminae; minor detrital quartz; dark brown matrix infills inter-ray cavities. Plate 25.
- A-82c-85 Medium crystalline dolostone:
Beige dolomite; $\approx 70\%$ xenotopic to hypidiotopic ($\leq 75\text{--}300 \mu$) brownish crystals; $10\text{--}20\%$ darker ($\leq 50\text{--}75 \mu$) cavity margin dolospar; $5\text{--}10\%$ cherty patches; later euhedral and zoned dolomite versus xeno-hypidiotopic $\pm$ bladed margins; Fe-oxides line cavities; megaquartz in

center. Plate 39.

- A-83-85 Oolitic ironstone:
Red to grey; $\approx$ 60% magnetite ($\pm$ hematite) often as flattened ooids (< 1.5 mm) in $\approx$ 40% cherty and quartz matrix; rhombohedral opaque and translucent (hematitic) replaced carbonates. Plate 41.
- A-17h-85 Fenestral dolowackestone:
Grey dolomite; $\approx$ 40-50 % allochems (ooids?, caliche pisoids?, oncolites?, peloids and intraclasts) 2-3 mm maximum with alternating coarser (200 - 300 μ) and finer (≤ 15 μ) concentric laminae. ($\pm$ circumgranular cracking ?); $\pm$ cherty cores; $\approx$ 30 - 40 % dark brown (≤ 15 μ) matrix; $\approx$ 10 % quartz and dolomite in fenestrae; "insitu" formation of allochems suggested. Plate 24.
- A-17b-85 Intraclastic dolopackstone-dolowackestone ($\approx$ undelies A-17h-85):
Grey dolomite; $\pm$ laminated (≤ 60 μ) matrix; 50 -65 % intraclasts (< 5 mm), ooids (micritic cortex), peloids $\pm$ quartz, chert and radiating fibrous grains; rare downward radiating fibrous to bladed cement with chert laminae; stylolites. Plate 36.
- A-58b-85 Interbedded intraclastic algal dolomudstone and pebble-sized oncolitic dolostone:
Red-beige dolomite; $\approx$ 50% rounded and ellipsoidal (large intraclastic cores) oncolites (< 1 cm) and algal (< 2 cm) intraclasts ($\pm$ radial fibrous clasts); $\approx$ 25% (< 1 mm) mature quartz in dark brown (≤ 10 μ) hematitic? matrix and abundant shelter porosity (≥ 3 spar generations: micritic (10-20 μ) $\pm$ gravity cements--> bladed--> prismatic $\pm$ coarse dolomite and quartz $\pm$ Fe-oxides; pendant vadose cements. Plate 35.

Sandy Dolostone Unit

- A-38a-85 Interlaminated dolomudstone and oolitic dolopackstone:
Grey dolomite; $\approx$ 60 % (≤ 3 mm) ooids and intraclasts; ooids are recrystallized, dissolved ($\pm$ broken) with geopetal sediment and sparry roofs; micritic ($\pm$ hematitic) vadose cements; dolomudstone laminae $\approx$ 50 μ ; cavity dolospar ($\approx$ 200 μ) and late quartz. Plate 33.
- A-16-84 Interbedded dolowackestone and dolomudstone:
Grey dolomite; overlying dolowackestone $\approx$ 15% mature ($\leq .5$ mm) quartz, $\approx$ 25% micritic ooids, intraclasts ($\leq .5$ mm) of hypidiotopic (≤ 20 μ) fabric and $\approx$ 60% matrix dolomite (< 100 μ); the underlying dolomudstone (≤ 20 -

30 μ) bed is in stylolitic contact.

- A-49b-85 Sandy intraclastic dolopackstone:
Grey dolomite; $\approx 65\%$ allochems including subrounded ($\leq 1-2$ mm) quartz, intraclasts (≤ 2 mm), (normal, compound and micritic (> 10 laminae)) ooids (≤ 1.5 mm); minor chert and radial fibrous clasts; $\approx 25\%$ (≤ 10 μ) matrix and laminae; $\approx 10\%$ (≤ 50 μ) cavity dolospar (≤ 800 μ); rare geopetal sediment and sparry roofs occupying leached intraclasts; stylolites; (algal?) laminae with adhering quartz. Plate 32.
- A-48h-85 Imbricated intraclastic (pebble-sized) oolitic dolograinstone layer:
Red dolomite; $\approx 75\%$ 1-2 cm oolitic and leached intraclasts; compound, superficial $\pm$ dissolved ooids present; $\approx 25\%$ dark brown micritic (hematitic?) meniscus $\pm$ interparticle cement and shelter porosity spar (≤ 150 μ); micaceous(?) mineral; stylolites. Plate 31.
- A-48b-85 Interbedded oolitic dolopackstone to dolomudstone (underlies A-48h-85):
Red dolomite; $\approx 25\%$ superficial compound ooids (1-2 mm) $\pm$ quartz or dolomitic cores, quartz, intraclasts; $\approx 60\%$ dark brown ($\pm$ hematitic?) matrix and laminae (≤ 50 μ) $\pm$ meniscus cements; shelter porosity and fenestral dolospar; $\pm$ silicified ooid laminae; mold of evaporite? mineral cluster with chlorite traces. Plate 19.
- A-32c-85 Silicified oolitic dolograinstone and dolomudstone:
Light grey silicified ooid lenses overlying dolomudstone; $\approx 30\%$ (≤ 7 mm) ooids and intraclastics (< 3 mm) showing various degrees of silicification with idiotope (≤ 200 μ) secondary $\pm$ zone dolomite; lower dolomudstone and remnant dolomite $\approx$ hypidiotope (< 500 μ). Occur as ooid lenses lying in shallow depressions on cryptogalaminates (Sample A-32b-85).
- A-14d-85 Coarsely crystalline oolitic dolograinstone:
Grey dolomite; coarsely (≤ 500 μ) crystalline xenotopic-hypidiotope crystals; $\approx 10\%$ detrital (≤ 1 mm) quartz along base, showing sutured and replaced margins. Plate 30.
- A-35-85 Oncolitic dolowackestone to pebble-sized oncolitic dolostone:
Beige to yellow dolomite; $\approx 30\%$ rounded to subrounded oncolites (< 2 cm) with abundant alternating dark hypidiotope (≤ 20 μ) and lighter (≤ 80 μ) laminae; $\approx 10\%$ algal laminae; and $\approx 60\%$ matrix of intraclasts, $\pm$ ooids, quartz and shelter ($\pm$ fenestral) porosity with quartz and dolomite (≤ 300 μ). Plate 5.

LOWER ALBANEL FORMATIONUpper Black Shale Complex

- D2-157-74 Organic-rich (algal? intraclastic) dolomudstone:
Dark grey to black, $\approx 25\%$ calcite-rich algal? clasts (≤ 2 cm) in hypidiotopic ($\leq 50 \mu$) dolomitic and organic-rich matrix; xenotopic calcite ($\leq 80 \mu$) concentrated in algal clasts; minor silicates; low amplitude stylolites; DEPTH = 1908.25 m. Plate 1.
- D2-156-74 Cryptalgal dolomudstone:
Dark grey pyritized and crenulated algal mats in an idio-hypidiotopic ($\leq 80 \mu$) dolomite matrix; calcite-filled fractures cut pyrite band, suggesting earlier formation. DEPTH = 1921.52 m.

Upper Banded Dolostone Unit

- D2-38-74 Sandy dolomudstone to dolomitic arenite:
Grey laminated $\pm$ cross-laminated; idio-hypidiotopic ($\leq 25 \mu$) dolomite and xenotopic calcite; subangular (80 – 200μ) quartz, plagioclase and feldspar; bent micas ($< 250 \mu$); poikilotopic pyrite lense associated with sedimentary boundary. DEPTH = 2090.22 m.
- D2-44-74 Silty stylolaminar dolomudstone:
Dark grey; idio-hypidiotopic ($\leq 50 \mu$) dolomite; subangular ($\leq 80 \mu$) quartz, plagioclase and feldspar; minor (bent) micas ($\leq 200 \mu$); early diagenetic pyrite sphere displacing sediment; minor secondary calcite patches up to ≈ 6 mm, composed of xenotopic ($\approx \leq 100 \mu$) crystals. DEPTH = 2121.31 m. Plate 43.

Lower Banded Dolostone Unit

- D2-66-74 Sandy fine limegrainstone to limemudstone:
Grey laminated to weakly cross-laminated sandy grainstone; subrounded ($\leq 80 \mu$) calcite (and as cement); minor idiopathic ($\leq 50 \mu$) dolomite; subrounded-subangular ($\leq 100 \mu$) quartz, plagioclase and micas ($\pm$ bent). DEPTH = 2230.28 m.
- D2-90-74 Sandy organic-rich dolomudstone to siltshale:
Dark grey with black laminae and streaks; idio-hypidiotopic ($\leq 30 \mu$, max $\approx 100 \mu$) dolomite; minor calcite, surrounding pyrite cluster; subangular quartz, feldspar

($\pm$ plagioclase), all $\leq 100 \mu$; minor micas ($\leq 110 \mu$).
DEPTH = 2378.57 m. Plate 46.

Lower Black Shale Complex

- D2-151-74 Silty dolomudstone to dolomitic siltshale:
Dark grey, organic-rich (with clastics) dolostone ($\pm$ pyrite streaks) with $\approx$ hypidiotopic ($\leq 25 \mu$) dolomite, hosts a ≈ 2 cm pyrite lense displacing sediment; darker pyrite margins contrast with increasing coalescence and crystal size towards the center; crystalline quartz and carbonate ($\leq 500 \mu$) inclusions in pyrite; detrital clastics ($\leq 80 \mu$) include quartz, plagioclase and micas. DEPTH = 2421.85 m. Plate 44.
- D2-152-74 Organic-rich dolomitic siltshale:
Dark grey to black; hypidiotopic(?) dolomite ($\leq 25 \mu$), quartz ($\leq 60 \mu$), plagioclase and micas; organics as laminae, lenses and streaks; 1 cm thick pyrite layer with healed fractures and inclusions of crystalline quartz ($\leq 300 \mu$) and carbonate; stylolites. DEPTH = 2422.08 m.
- D2-98-74 Impure laminated dolomudstone:
Light grey, finer and coarser, organic and pyrite-rich laminae; idio-hypidiotopic dolomite ($\leq 80 \mu$); subangular detrital quartz ($\leq 75 \mu$), plagioclase and mica; authigenic, twinned and poikilotopic ($\leq 600 \mu$) quartz; pyrite occurs as laminae and lenses ($\leq 50 \mu$ cubes) associated with organics; also as coarser crystals $\pm$ associated with authigenic quartz. DEPTH = 2423.37 m. Plate 45.
- D2-153-74 Impure interlaminated dolomudstone and limestone:
Pyrite and grey and black carbonate bands; a ≈ 2 cm pyrite band exhibits a pre-compaction structure, is fractured and healed by calcite; associated with organics; pyrite formed by coalescence of cubes ($\approx 500 \mu$ max.); pressure shadows of chlorite, quartz and calcite; subadjacent black limestone-rich and below more dolomite-rich bands; $\approx$ hypidiotopic ($\leq 25 \mu$) carbonate; subangular quartz, micas ($\leq 50 \mu$); stylolites. DEPTH = 2425.81 m. Plate 42.
- D2-154-74 Impure laminated limemudstone and dolomudstone:
Light and dark grey-black and pyrite interlaminations; precompaction pyrite band (≤ 1 cm) within coarser ($\leq 100 \mu$, more clastic) and finer ($\leq 15 \mu$) hypidiotopic dolomite laminae; detrital quartz, plagioclase and (bent) micas; authigenic and poikilotopic quartz (≤ 2 mm) cuts across laminations; pressure shadow around

pyrite; pyrite also as cubes and $\pm$ associated with authigenic quartz; stylolites. DEPTH = 2440.74 m.

D2-104-74 Impure limemudstone and dolomudstone:

Interaminated grey, xeno-hypidiotopic calcite-rich ($\approx \leq 400 \mu$ and $\approx \leq 200 \mu$) laminae & beds, $\pm$ darker ($\approx \leq 20 \mu$) dolomititic matrix, and darker ($\approx$ idiopathic) dolomite layer ($\approx \leq 25 \mu$) near base; minor subangular quartz, plagioclase, feldspar ($\leq 130 \mu$) and micas; limestone to dolostone transition is $\approx$ gradational; early dolomitization is suggested. DEPTH = 2458.57 m. Plate 18.

D2-106-74 Impure limemudstone:

Laminated grey, hypidiotopic (max. $\leq 150 \mu$) calcite (individual and crystal aggregates) and idio-hypidiotopic dolomite (often $\leq 30 \mu$); subangular quartz, plagioclase, feldspar, mica and chlorite; pyrite cubes ($\leq 500 \mu$) coalesce into masses with pressure shadows; stylolites; silicate versus carbonate-rich laminae; dolomitization of calcite suggested by fine euhedral rhombs. DEPTH = 2468.48 m.

APPENDIX 3

SUMMARY OF CHEMICAL (XRF & AAS) AND OXYGEN AND CARBON
ISOTOPIC DATA FOR THE UPPER & LOWER ALBANEL FORMATION CARBONATES

(OXYGEN & CARBON ISOTOPES: in permil PDB)

(XRF: oxides in percent, trace elements in ppm)

(AAS: Ca, Mg, Fe and IR in percent; Sr, Na, Al and Mn in ppm)

XRF DATA

UNDER 1% AL2O3

SAMPLE	SiO2	AL2O3	FE2O3	MGO	CAO	NA2O	K2O	TiO2	P2O5	MNO	S	BA	CR	ZR	SR	RB	Y	NB	ZN	NI	TOTAL
A-4M-84	1.85	0.27	0.84	20.31	30.26	0.00	0.06	0.00	0.00	0.11	0.01	52	25	0	29	0	11	0	7	3	53.733
A-7B-84	0.53	0.07	0.30	21.02	30.86	0.00	0.01	0.00	0.00	0.04	0.05	48	13	0	21	0	3	0	13	0	52.892
A-7R-84	1.50	0.29	0.76	20.36	30.17	0.00	0.09	0.01	0.00	0.08	0.01	49	13	1	24	0	6	0	2	0	53.289
A-25A-85	19.18	0.01	0.28	17.14	24.83	0.00	0.00	0.00	0.00	0.04	0.00	7	18	0	20	0	4	2	15	0	61.492
A-30A-85	21.49	0.02	0.36	16.80	23.98	0.00	0.00	0.00	0.00	0.05	0.00	76	13	0	20	0	12	3	11	0	62.713
A-32B-85	0.10	0.01	0.24	21.45	30.57	0.00	0.00	0.00	0.00	0.04	0.01	29	13	0	16	0	5	0	0	0	52.430
A-36B-85	19.70	0.08	0.31	17.17	24.62	0.00	0.00	0.00	0.00	0.04	0.00	50	15	0	26	0	3	0	10	0	61.499
A-43BG-85	7.53	0.03	0.31	19.69	28.18	0.01	0.00	0.00	0.00	0.04	0.00	49	13	0	16	0	0	0	14	0	55.823
A-44-85	3.08	0.04	0.49	20.74	29.80	0.00	0.00	0.00	0.00	0.07	0.00	32	9	0	28	0	5	0	8	0	54.213
A-47B-85	15.47	0.03	0.27	18.25	25.82	0.00	0.00	0.00	0.00	0.04	0.00	55	8	0	18	0	6	0	8	0	59.889
A-48G-85	2.73	0.22	0.39	20.91	29.85	0.00	0.06	0.01	0.00	0.05	0.00	55	12	0	23	0	7	0	0	0	54.227
A-52A-85	2.25	0.12	0.25	20.87	30.15	0.00	0.03	0.01	0.00	0.03	0.00	58	10	0	28	0	7	0	12	0	53.711
A-54A-85	7.51	0.55	0.36	19.40	28.35	0.00	0.18	0.02	0.00	0.05	0.01	48	9	8	30	1	10	0	17	0	56.444
A-55A-85	3.90	0.56	0.33	20.34	29.18	0.00	0.24	0.02	0.00	0.05	0.01	108	13	12	30	1	5	0	4	0	54.638
A-56A-85	0.83	0.18	0.16	21.37	30.58	0.00	0.05	0.00	0.00	0.02	0.00	58	13	0	23	0	7	0	10	0	53.207
A-59A-85	0.85	0.22	0.30	21.50	30.64	0.00	0.06	0.01	0.00	0.03	0.01	75	13	0	27	0	10	0	8	8	53.641
A-62B-85	2.79	0.18	0.22	20.60	29.88	0.00	0.05	0.01	0.00	0.03	0.01	58	11	0	27	0	7	0	4	0	53.773
A-72B-85	1.36	0.12	1.40	20.02	30.29	0.00	0.03	0.01	0.00	0.18	0.00	50	6	0	36	0	7	0	5	0	53.416
A-79B-85	1.64	0.24	0.34	21.11	30.52	0.00	0.07	0.01	0.00	0.05	0.01	53	19	0	28	0	8	0	9	0	53.985
M-1-84	1.44	0.10	0.25	21.23	30.18	0.00	0.02	0.00	0.00	0.02	0.03	62	6	0	44	0	12	0	7	5	53.294
M-2-84	0.53	0.09	0.22	21.73	30.41	0.06	0.04	0.00	0.00	0.01	0.04	69	2	0	28	0	8	0	4	5	53.131
M-4-84	0.54	0.07	0.19	21.65	30.44	0.03	0.05	0.00	0.00	0.01	0.01	72	0	0	14	0	9	1	0	0	52.990
M-5-84	1.44	0.18	1.20	19.83	29.22	0.01	0.13	0.01	0.00	0.04	0.04	17	8	2	21	0	13	0	2	0	52.109
M-7A-84	0.11	0.05	0.49	21.62	30.64	0.07	0.00	0.00	0.00	0.03	0.01	16	2	0	23	0	8	0	5	13	53.019
M-7B-84	0.96	0.15	0.56	21.15	30.32	0.08	0.05	0.00	0.00	0.03	0.02	54	5	4	42	0	14	0	8	13	53.349
M-8A-84	0.70	0.19	0.46	21.21	30.33	0.01	0.06	0.00	0.00	0.04	0.01	48	3	3	22	0	14	0	0	3	53.011

UNDER 1% AL2O3

SAMPLE	SiO2	AL2O3	FE2O3	MGO	CAO	NA2O	K2O	TiO2	P2O5	MNO	S	BA	CR	ZR	SR	RB	Y	NB	ZN	NI	TOTAL
M-9-84	0.41	0.02	1.68	20.47	30.44	0.00	0.00	0.00	0.00	0.18	0.01	39	5	0	61	0	12	0	0	3	53.224
M-10A-84	2.80	0.07	0.48	20.78	29.60	0.00	0.01	0.00	0.00	0.06	0.00	37	0	0	24	0	6	0	0	7	53.808
M-11-84	0.55	0.07	0.14	21.46	30.35	0.02	0.05	0.00	0.00	0.01	0.01	91	5	0	10	0	6	0	0	0	52.683
M-12-84	0.87	0.14	0.30	21.24	30.13	0.06	0.08	0.00	0.00	0.03	0.02	158	5	2	18	0	11	3	11	2	52.887
A-1-84	1.67	0.34	1.35	20.20	30.09	0.02	0.11	0.01	0.00	0.17	0.01	48	9	7	36	0	12	0	6	1	53.989
A-2A-84	0.87	0.26	0.30	20.90	27.92	0.00	0.08	0.01	0.00	0.03	0.00	27	3	11	26	0	13	5	14	0	50.387
A-3A-84	4.52	0.20	0.31	20.34	28.12	0.02	0.06	0.01	0.00	0.04	0.00	55	13	6	25	0	6	3	10	0	52.464
A-4A-84	14.89	0.41	0.59	17.82	24.64	0.02	0.15	0.01	0.00	0.07	0.00	67	6	14	24	0	10	5	7	0	58.615
A-5A-84	19.29	0.11	0.25	17.01	24.56	0.00	0.02	0.00	0.00	0.03	0.01	27	9	9	20	0	10	3	0	0	61.289
A-5B-84	17.98	0.11	0.26	17.44	25.15	0.05	0.02	0.00	0.00	0.03	0.01	44	7	7	23	0	8	0	0	0	61.064
A-6-84	2.29	0.27	0.25	20.78	29.94	0.00	0.09	0.01	0.00	0.03	0.01	14	4	5	29	0	5	0	4	0	53.672
A-7-84	1.51	0.29	0.78	20.63	30.19	0.04	0.09	0.01	0.00	0.07	0.01	57	7	4	24	0	6	0	4	0	53.638
A-8-84	2.47	0.27	0.36	20.72	30.01	0.05	0.08	0.01	0.00	0.04	0.00	37	4	5	25	0	7	0	7	0	54.006
A-9A-84	17.47	0.11	0.62	17.25	25.31	0.09	0.02	0.00	0.00	0.07	0.01	35	7	6	20	0	8	0	0	0	60.958
A-10-84	2.73	0.34	0.29	20.72	29.94	0.10	0.10	0.01	0.00	0.03	0.01	51	5	17	26	0	8	1	6	0	54.289
A-12B-84	1.33	0.25	0.35	21.01	30.34	0.00	0.08	0.01	0.00	0.04	0.00	30	2	0	28	0	6	0	4	0	53.421
A-13A-1-84	5.52	0.08	0.30	20.30	28.86	0.01	0.01	0.00	0.00	0.03	0.00	26	8	4	12	0	9	0	10	0	55.124
A-13A-2-84	3.83	0.04	0.21	20.65	29.51	0.02	0.00	0.00	0.00	0.03	0.00	33	6	0	12	0	5	0	0	0	54.307
A-13A-3-84	0.91	0.03	0.22	21.47	30.39	0.00	0.00	0.00	0.00	0.03	0.00	56	4	0	14	0	7	0	2	0	53.064
A-13A-4-84	12.12	0.14	0.42	18.78	26.67	0.01	0.03	0.00	0.00	0.05	0.01	46	7	6	15	0	7	0	10	0	58.239
A-13A-5-84	5.38	0.04	0.28	20.53	29.09	0.10	0.00	0.00	0.00	0.03	0.00	25	4	1	13	0	4	0	9	0	55.455
A-13B-84	4.51	0.04	0.38	20.61	29.27	0.03	0.00	0.00	0.00	0.04	0.01	24	7	2	19	0	5	0	0	0	54.907
A-13C-84	4.85	0.56	0.25	20.09	29.05	0.00	0.25	0.02	0.00	0.03	0.00	60	6	23	36	2	9	1	3	0	55.112
A-14A-84	23.20	0.88	0.46	15.78	23.09	0.00	0.46	0.03	0.00	0.05	0.01	58	7	89	38	9	8	1	4	0	63.976
A-15-84	9.89	0.04	0.29	19.30	27.51	0.01	0.00	0.00	0.00	0.03	0.01	48	2	3	20	0	9	0	7	0	57.083
A-16-84	7.06	0.84	0.60	19.58	27.91	0.00	0.31	0.02	0.00	0.07	0.01	60	10	20	31	5	9	3	2	0	56.408

UNDER 1% AL2O3

SAMPLE	SiO2	AL2O3	FE2O3	MGO	CAO	NA2O	K2O	TiO2	P2O5	MNO	S	BA	CR	ZR	SR	RB	Y	NB	ZN	NI	TOTAL
D2-3-74	8.36	0.70	0.51	18.70	26.94	0.00	0.40	0.04	0.00	0.03	0.01	47	18	10	44	1	58	0	0	8	55.715
A-17-84	13.33	0.13	0.45	18.38	26.54	0.00	0.03	0.00	0.00	0.05	0.00	23	7	10	34	0	7	1	10	0	58.944
A-18-84	13.57	0.12	0.39	18.30	26.35	0.00	0.03	0.00	0.00	0.05	0.00	40	10	5	21	0	6	2	0	0	58.824
A-19-84	6.48	0.02	0.29	19.61	28.32	0.05	0.00	0.00	0.00	0.04	0.01	35	3	0	23	0	8	0	39	0	54.820
A-20-84	10.28	0.02	0.19	19.15	27.48	0.00	0.00	0.00	0.00	0.02	0.00	29	9	0	21	0	3	0	35	0	57.158
A-21-84	1.96	0.02	0.20	20.88	30.13	0.02	0.00	0.00	0.00	0.02	0.01	19	7	0	29	0	10	0	7	0	53.253
A-22-84	2.58	0.04	0.21	20.92	30.11	0.02	0.00	0.00	0.00	0.02	0.01	33	3	0	20	0	9	1	4	0	53.927
A-23-84	25.39	0.10	0.36	15.60	22.80	0.01	0.02	0.00	0.00	0.05	0.00	47	0	2	41	0	5	0	7	0	64.340
A-24-84	1.15	0.21	1.28	20.48	30.15	0.00	0.03	0.01	0.00	0.15	0.01	49	7	0	33	0	4	2	1	0	53.473
A-25A-84	3.66	0.40	0.87	19.98	29.50	0.07	0.13	0.01	0.00	0.11	0.00	58	5	3	48	0	7	0	12	0	54.744
A-26A-84	1.39	0.11	0.33	21.04	30.38	0.00	0.02	0.00	0.00	0.04	0.00	45	7	0	24	0	3	2	7	0	53.341
A-27-84	1.65	0.14	0.65	20.58	30.09	0.06	0.04	0.00	0.00	0.08	0.00	40	8	0	37	0	7	2	9	0	53.294
A-28-84	0.89	0.36	0.29	20.82	30.36	0.01	0.11	0.02	0.00	0.03	0.00	29	3	2	30	0	8	2	8	0	52.906
A-29-84	0.50	0.12	0.20	21.56	30.74	0.01	0.02	0.00	0.00	0.02	0.00	45	5	0	23	0	10	1	5	0	53.193
A-30-84	0.84	0.07	0.48	20.81	30.42	0.01	0.01	0.01	0.00	0.06	0.00	16	8	0	25	0	9	0	20	0	52.708
A-31-84	18.30	0.03	0.18	17.25	25.09	0.01	0.00	0.00	0.00	0.02	0.00	47	6	0	21	0	6	0	12	0	60.889
D2-113-74	28.74	0.63	0.87	14.63	21.33	0.00	0.40	0.04	0.00	0.03	0.03	73	2	82	55	1	20	0	15	0	66.720
D2-114-74	24.90	0.58	0.92	15.53	22.56	0.00	0.38	0.03	0.00	0.03	0.08	85	4	17	58	4	19	0	2	2	65.019
D2-115-74	29.10	0.66	0.84	14.48	21.36	0.00	0.41	0.04	0.00	0.03	0.05	111	8	10	66	5	19	0	7	0	67.002
D2-116-74	15.97	0.91	0.82	17.11	25.28	0.00	0.59	0.03	0.00	0.04	0.03	129	16	4	69	7	23	0	250	34	60.844
D2-117-74	4.25	0.34	1.64	19.82	28.77	0.00	0.23	0.01	0.00	0.04	0.15	77	2	3	46	1	25	1	0	0	55.269
D2-118-74	7.81	0.30	1.89	18.83	27.41	0.00	0.19	0.01	0.00	0.06	0.05	105	0	4	49	0	20	0	23	0	56.571
D2-119-74	13.56	0.68	0.86	17.68	25.41	0.00	0.45	0.02	0.00	0.06	0.04	264	7	4	56	0	27	0	75	0	58.802
D2-120-74	11.84	0.76	0.69	18.39	25.93	0.00	0.46	0.03	0.00	0.07	0.00	214	1	6	64	2	25	0	20	4	58.200
D2-122-74	17.20	0.52	1.27	16.73	24.51	0.00	0.34	0.02	0.00	0.09	0.00	203	4	7	51	0	20	3	11	0	60.717
D2-125-74	8.64	0.50	1.13	19.02	27.67	0.00	0.30	0.03	0.00	0.10	0.05	313	13	8	51	1	19	0	20	0	57.331

UNDER 1% AL2O3

SAMPLE	SiO2	AL2O3	FE2O3	MGO	CAO	NA2O	K2O	TiO2	P2O5	MNO	S	BA	CR	ZR	SR	RB	Y	NB	ZN	NI	TOTAL
D2-126-74	13.08	0.32	1.33	18.10	26.34	0.00	0.20	0.02	0.00	0.09	0.04	273	0	6	66	0	18	1	45	0	59.563
D2-127-74	15.59	0.62	1.27	17.44	25.35	0.00	0.38	0.03	0.00	0.11	0.02	520	0	7	64	0	20	1	30	0	60.879
D2-128-74	41.69	0.24	1.14	11.87	17.34	0.00	0.12	0.01	0.00	0.09	0.14	165	6	3	60	0	15	0	59	4	72.668
D2-129-74	8.37	0.70	1.66	18.82	27.47	0.00	0.38	0.04	0.00	0.13	0.01	503	4	6	59	3	20	0	21	0	57.651
D2-1-74	12.04	0.78	0.27	19.11	26.00	0.00	0.38	0.03	0.00	0.04	0.09	47	5	7	58	10	29	0	12	0	58.770
D2-5-74	11.43	0.59	0.39	18.37	26.49	0.00	0.41	0.02	0.00	0.03	0.01	64	43	3	57	0	30	0	16	0	57.770
D2-11-74	13.97	0.71	0.76	17.92	25.40	0.00	0.45	0.03	0.00	0.05	0.14	247	22	9	58	1	18	0	0	0	59.470
D2-17-74	2.97	0.35	0.38	20.74	29.42	0.00	0.21	0.01	0.00	0.02	0.02	105	40	1	34	0	12	3	0	0	54.140

OVER 1% AL2O3

SAMPLE	SiO2	AL2O3	FE2O3	MGO	CAO	NA2O	K2O	TiO2	P2O5	MNO	S	BA	CR	ZR	SR	RB	Y	NB	ZN	NI	TOTAL
M-3-84	9.96	1.50	0.89	18.59	26.62	0.00	1.15	0.07	0.00	0.06	0.01	977	15	29	28	10	14	0	17	11	59,308
M-6-84	47.73	11.09	4.81	6.66	8.15	0.04	6.56	0.48	0.00	0.06	0.01	229	81	190	35	132	16	8	27	40	85,674
D2-35-74	43.23	8.40	3.36	8.79	12.91	0.90	3.28	0.29	0.00	0.05	0.01	765	99	90	167	72	23	4	38	14	81,370
D2-37-74	44.69	9.04	3.09	8.89	11.68	1.44	2.88	0.32	0.00	0.04	0.01	631	52	104	153	81	22	5	48	16	82,220
D2-39-74	35.56	4.44	2.81	11.01	16.99	0.56	1.55	0.15	0.00	0.07	0.01	343	16	51	194	31	22	2	28	8	73,235
D2-41-74	43.17	5.50	2.47	10.99	13.81	0.80	1.38	0.21	0.00	0.05	0.01	284	27	72	136	34	18	2	36	9	78,453
D2-43-74	38.79	7.39	2.62	11.86	13.49	1.00	2.15	0.27	0.00	0.05	0.01	358	1504	100	146	52	27	2	33	26	77,945
D2-45-74	43.37	7.11	2.42	9.86	12.84	1.19	2.10	0.24	0.00	0.06	0.07	319	27	93	143	60	22	7	27	12	79,332
D2-47-74	49.01	5.97	1.81	6.90	14.15	1.16	1.91	0.18	0.00	0.05	0.02	408	48	131	198	46	18	1	25	2	81,658
D2-49-74	38.19	8.80	2.83	11.28	12.86	1.11	2.69	0.37	0.00	0.06	0.05	450	56	59	137	80	21	2	54	17	78,341
D2-61-74	51.85	8.04	2.48	6.80	11.05	1.45	2.07	0.27	0.00	0.06	0.02	408	124	127	176	49	18	3	28	110	84,222
D2-65-74	8.30	2.27	0.82	1.74	46.28	0.58	0.41	0.08	0.00	0.06	0.01	129	90	18	299	8	26	2	0	0	60,606
D2-67-74	17.93	3.21	1.06	2.86	38.30	1.24	0.59	0.09	0.00	0.07	0.02	220	41	47	296	8	28	2	4	0	65,432
D2-71-74	39.67	7.87	1.06	2.76	22.91	2.99	1.50	0.25	0.00	0.04	0.02	460	26	222	251	28	23	0	18	14	79,198
D2-73-74	44.20	6.40	1.56	5.42	18.22	2.14	1.24	0.20	0.00	0.05	0.05	369	30	184	194	29	18	2	12	0	79,563
D2-77-74	42.43	8.34	3.29	10.89	11.62	1.51	1.73	0.30	0.00	0.05	0.14	374	435	102	131	42	23	2	32	13	80,446
D2-79-74	48.91	5.96	1.34	5.39	15.98	1.97	1.20	0.16	0.00	0.03	0.07	269	118	209	204	32	19	0	17	9	81,110
D2-80-74	51.60	5.79	1.16	5.44	14.58	2.01	1.09	0.16	0.00	0.04	0.00	260	22	268	155	22	18	0	13	5	81,956
D2-83-74	5.26	1.20	0.67	1.62	48.78	0.30	0.19	0.04	0.00	0.05	0.03	101	25	12	274	0	28	0	0	0	58,207
D2-85-74	41.94	7.10	3.23	7.38	16.25	1.38	1.45	0.26	0.00	0.04	0.34	332	38	99	188	37	24	0	34	8	79,467
D2-89-74	36.82	7.31	2.42	10.71	15.34	1.55	2.03	0.27	0.00	0.08	0.01	445	53	100	144	52	27	1	31	6	76,645
D2-91-74	36.30	6.00	3.49	9.53	17.37	1.00	1.39	0.20	0.00	0.10	0.37	314	88	76	210	34	26	0	28	10	75,843
D2-95-74	65.61	16.96	2.96	2.45	0.23	0.37	6.41	0.56	0.04	0.01	0.26	1040	121	71	14	206	5	10	33	19	96,042
D2-97-74	59.20	14.97	1.67	3.77	3.70	1.38	5.85	0.81	0.06	0.07	0.02	1303	98	172	51	162	22	13	12	7	91,708
D2-101-74	34.15	6.02	2.70	6.92	20.85	0.39	2.77	0.67	0.00	0.21	0.01	464	640	142	103	49	24	8	31	7	74,870
D2-103-74	34.56	3.94	5.11	16.99	30.58	0.10	1.36	0.20	0.00	0.54	0.01	256	77	42	240	27	20	0	22	4	93,467

OVER 1% AL2O3

SAMPLE	SiO2	AL2O3	FE2O3	MgO	CAO	NA2O	K2O	TiO2	P2O5	MNO	S	BA	CR	ZR	SR	RB	Y	NB	ZN	NI	TOTAL
D2-121-74	14.40	1.17	1.55	16.94	25.09	0.00	0.76	0.06	0.00	0.08	0.01	633	7	12	67	8	22	2	11	4	60.144
D2-123-74	33.95	4.33	1.34	12.74	17.01	0.03	2.67	0.18	0.00	0.07	0.08	2323	11	31	53	37	23	2	16	111	72.695
D2-124-74	21.35	2.36	1.09	15.89	22.37	0.21	1.24	0.11	0.00	0.09	0.09	709	14	21	57	18	25	2	23	0	64.911
D2-130-74	24.30	1.99	1.44	15.07	21.69	0.00	1.15	0.11	0.00	0.11	0.12	741	6	17	69	15	26	2	19	3	66.077
D2-131-74	34.54	2.79	1.07	12.75	18.06	0.00	1.65	0.16	0.00	0.06	0.02	1124	11	23	71	20	20	3	140	3	71.256
D2-132-74	22.83	1.62	1.59	15.20	21.88	0.03	0.92	0.05	0.00	0.09	0.29	831	11	9	60	11	16	0	172	0	64.632
D2-133-74	32.74	4.78	3.36	9.43	18.33	0.44	2.36	0.31	0.00	0.35	0.01	431	19	78	103	47	20	6	4	3	72.179
D2-134-74	24.57	5.05	1.17	2.99	32.26	1.50	1.82	0.20	0.00	0.19	0.04	326	14	47	134	28	18	4	9	20	69.863
D2-135-74	23.73	4.48	1.56	4.31	31.72	1.15	1.66	0.22	0.00	0.21	0.01	305	8	46	149	28	20	2	22	0	69.127
D2-136-74	28.35	5.57	3.12	8.10	23.20	0.69	2.13	0.36	0.00	0.29	0.04	501	15	112	175	42	23	6	47	5	71.967
D2-137-74	34.68	6.53	4.44	11.07	15.53	0.64	2.28	0.39	0.00	0.30	0.02	487	15	94	107	48	27	6	87	10	75.984
D2-138-74	29.56	4.69	3.86	9.75	21.25	0.46	1.69	0.28	0.00	0.32	0.09	368	16	62	160	34	23	2	50	10	72.024
D2-139-74	27.63	5.04	4.11	10.29	22.40	0.39	1.40	0.23	0.00	0.31	0.01	323	15	55	168	32	21	3	26	15	71.886
D2-140-74	33.55	6.09	3.80	9.23	19.02	0.69	1.99	0.39	0.00	0.28	0.03	408	26	94	133	48	23	7	100	21	75.172
D2-141-74	36.10	5.84	3.92	10.18	16.66	0.51	2.10	0.41	0.00	0.35	0.01	420	25	92	123	49	22	7	0	6	76.166
D2-142-74	37.87	6.52	3.64	9.40	15.55	0.69	2.45	0.42	0.00	0.35	0.01	490	34	114	112	57	24	5	9	6	76.993
D2-143-74	39.23	8.80	4.64	10.19	12.34	0.93	2.74	0.48	0.00	0.30	0.05	584	42	135	91	65	21	6	0	22	79.825
D2-144-74	30.20	5.57	3.82	9.89	19.68	0.54	2.11	0.74	0.00	0.38	0.00	486	26	112	159	43	27	8	6	4	73.041
D2-145-74	29.89	6.81	5.72	12.63	16.13	0.56	1.89	0.47	0.00	0.38	0.01	380	38	90	107	52	23	7	49	44	74.598
D2-146-74	47.31	9.96	4.63	9.45	8.82	1.22	2.85	0.41	0.00	0.26	0.01	548	35	90	61	84	18	4	55	65	85.029
D2-147-74	46.49	10.09	3.81	8.52	9.62	1.16	3.20	0.61	0.00	0.27	0.01	608	50	142	66	87	26	10	39	22	83.903
D2-148-74	39.86	8.69	3.72	9.38	13.03	0.80	3.07	0.54	0.00	0.34	0.01	529	29	113	78	84	24	5	55	16	79.541
D2-51-74	53.07	7.92	1.97	6.66	10.49	2.01	2.06	0.17	0.00	0.04	0.14	379	43	160	143	48	17	0	30	18	84.640
D2-53-74	37.45	5.66	1.27	2.57	25.75	2.02	1.33	0.12	0.00	0.05	0.05	294	237	175	213	24	23	1	15	5	76.370
D2-55-74	50.50	7.67	2.29	6.46	12.56	1.79	1.81	0.22	0.00	0.05	0.09	325	291	105	182	44	21	2	54	19	83.560
D2-57-74	38.82	5.41	0.98	2.87	24.20	1.88	1.25	0.13	0.00	0.05	0.13	259	86	209	201	21	20	1	10	2	75.820

OVER 1% AL2O3

SAMPLE	SiO2	AL2O3	FE2O3	MGO	CAO	NA2O	K2O	TiO2	P2O5	MNO	S	BA	CR	ZR	SR	RB	Y	NB	ZN	NI	TOTAL
D2-59-74	44.55	9.77	4.49	8.26	11.36	1.05	2.74	0.38	0.00	0.06	0.05	388	69	71	152	86	20	3	58	31	82.820
D2-63-74	63.90	8.15	1.24	4.04	7.50	2.58	1.89	0.25	0.00	0.03	0.02	353	29	415	137	47	14	3	71	15	89.730
D2-69-74	15.83	4.27	1.64	3.53	37.75	1.23	0.64	0.12	0.00	0.06	0.02	180	947	45	336	10	32	0	6	5	65.310
D2-75-74	57.70	7.70	1.73	5.70	9.17	2.45	1.64	0.21	0.00	0.04	0.00	395	18	188	146	35	16	0	8	8	86.450
D2-81-74	8.82	2.45	0.84	1.93	45.63	0.77	0.33	0.05	0.00	0.05	0.04	163	1	15	298	6	24	0	5	0	60.980
D2-87-74	43.53	6.59	2.94	9.65	14.10	1.01	1.52	0.23	0.00	0.06	0.01	267	40	81	148	41	20	2	40	13	79.700
D2-93-74	38.25	10.40	4.41	7.39	15.44	1.17	2.61	0.43	0.00	0.09	0.33	493	43	109	305	65	25	5	149	26	80.650
D2-99-74	20.20	4.47	2.44	6.16	31.80	0.83	1.20	0.21	0.00	0.25	0.03	238	13	46	212	25	21	2	15	3	67.660
D2-105-74	10.54	1.70	1.17	5.53	40.51	0.02	0.98	0.09	0.00	0.20	0.01	163	34	26	48	14	14	3	2	0	60.770
D2-107-74	10.17	1.60	1.48	8.35	37.54	0.00	0.98	0.12	0.00	0.14	0.00	189	23	27	45	13	15	0	4	0	60.400
D2-109-74	12.94	1.28	2.37	15.58	26.25	0.00	0.89	0.08	0.00	0.15	0.04	347	5	22	40	15	14	3	9	0	59.650
D2-111-74	7.69	1.00	2.21	17.86	27.78	0.00	0.49	0.06	0.00	0.30	0.01	181	4	13	37	8	17	1	8	0	57.430
D2-7-74	16.71	1.64	1.02	16.57	23.58	0.00	1.14	0.06	0.00	0.03	0.01	223	20	13	59	8	32	0	0	11	60.810
D2-9-74	13.37	1.45	1.28	17.73	25.40	0.00	0.84	0.09	0.00	0.14	0.07	658	27	14	54	9	31	0	19	5	60.450
D2-13-74	18.43	1.67	0.82	16.40	23.35	0.00	1.17	0.08	0.00	0.02	0.23	584	23	17	58	10	19	0	7	4	62.240
D2-15-74	9.72	1.45	0.56	18.80	26.66	0.00	1.06	0.05	0.00	0.02	0.04	367	149	18	55	7	19	0	3	0	58.450
D2-19-74	26.49	6.10	1.18	13.12	18.40	0.12	4.22	0.27	0.00	0.02	0.04	1706	40	59	31	45	22	5	9	7	70.170
D2-21-74	18.01	2.49	2.41	15.85	22.97	0.07	1.64	0.13	0.00	0.04	0.02	459	15	434	47	27	32	1	16	3	63.750
D2-23-74	51.41	9.46	1.86	6.38	8.98	0.81	6.42	0.31	0.00	0.04	0.01	956	90	123	63	87	17	2	25	6	85.850
D2-27-74	37.38	5.71	2.71	12.65	15.62	0.48	1.84	0.22	0.00	0.04	0.01	709	226	66	144	49	28	3	45	25	76.800
D2-29-74	50.41	7.14	2.83	14.52	18.25	0.96	2.57	0.26	0.00	0.05	0.01	1069	61	105	198	60	32	2	45	7	97.180
D2-25-74	40.33	6.05	2.78	11.00	13.98	1.24	2.10	0.19	0.00	0.05	0.07	585	152	76	122	43	19	0	19	17	77.910
D2-31-74	44.54	8.08	3.62	10.54	11.45	1.06	2.66	0.28	0.00	0.05	0.02	1250	36	92	124	49	23	3	59	5	82.470
D2-33-74	52.39	10.98	1.71	5.62	7.70	1.17	7.06	0.45	0.00	0.05	0.07	1343	53	217	122	119	17	6	23	16	87.400

AAS DATA

LIMESTONES

SAMPLE	LEVEL	UNIT	DEPTH	SR	NA	AL	MN	CA	MG	FE	IR	O18DOL	C13DOL	O18CAL	C13CAL
D2-27-74	L	3	2032.65	398	73	1123	391	33.9817	2.9581	0.5995	29.5	-8.86	3.01	-11.16	2.04
D2-53-74	L	4	2165.58	341	159	626	609	35.6312	2.6980	0.7276	47.6	.	.	-12.26	-1.47
D2-57-74	L	4	2184.17	340	352	989	684	33.8911	3.2111	0.6568	49.1	.	.	-12.53	-1.28
D2-65-74	L	4	2225.64	349	75	249	461	38.0311	0.9606	0.3870	12.7	.	.	-13.08	0.21
D2-67-74	L	4	2235.29	386	82	417	578	35.0194	1.8648	0.7385	24.3	.	.	-13.10	0.59
D2-69-74	L	4	2245.76	525	89	1413	542	39.8467	1.9861	0.6648	23.0	.	.	-13.13	1.45
D2-71-74	L	4	2256.73	434	457	1249	515	33.0061	2.5373	0.8676	51.6	-10.09	2.99	-13.08	2.22
D2-81-74	L	4	2334.78	379	61	306	267	39.0988	1.0262	0.3099	10.3	.	.	-11.51	1.46
D2-83-74	L	4	2344.54	316	47	265	358	38.9122	0.9203	0.3271	7.9	-10.93	1.23	.	.
D2-85-74	L	4	2354.60	306	142	936	374	38.5059	1.3780	0.5463	27.5	.	.	-11.39	-1.30
D2-93-74	L	4	2393.37	675	368	5108	1607	26.4519	4.7924	1.4138	69.6	-6.99	-3.27	-10.75	-4.79
* D2-95-74	L	5	2409.48	54	1113	29776	332	5.4787	1.5205	0.9123	94.3	.	.	-11.56	-8.22
D2-134-74	L	5	2426.19	234	128	433	2772	33.8432	2.5311	1.1817	34.8	-9.69	-2.08	-11.17	-0.43
D2-135-74	L	5	2426.80	240	137	956	2629	31.6160	3.6443	1.4504	30.8	.	.	.	.
D2-99-74	L	5	2429.45	304	80	2021	3095	28.2439	4.6852	1.7711	30.4	-9.49	-1.63	-11.18	-0.77
D2-101-74	L	5	2440.88	230	69	1452	1924	33.8567	2.2088	0.8934	32.9	-9.70	-3.29	-11.36	-1.27
D2-105-74	L	5	2463.44	77	62	659	2431	31.0009	6.0475	1.2608	17.3	-9.01	3.53	-10.43	2.85

* Sample D2-95-74 is siltshale to mudshale.

HIGH SR DOLOSTONES

SAMPLE	LEVEL	UNIT	DEPTH	SR	NA	AL	MN	CA	MG	FE	IR	O18DOL	C13DOL	O18CAL	C13CAL
D2-25-74	L	3	2022.59	250	245	2783	738	21.2035	15.1221	2.4532	50.2	-8.69	2.08	.	.
D2-29-74	L	3	2043.02	367	157	2814	574	22.5853	11.0741	1.9440	47.5	-8.62	3.81	-9.06	3.40
D2-31-74	L	3	2053.08	357	294	5586	796	23.3767	9.4666	2.5550	61.7	-7.50	3.99	-9.37	3.50
D2-33-74	L	3	2062.53	369	535	5332	1061	19.4457	10.5010	2.7360	76.2	-9.29	3.37	-9.37	3.08
D2-35-74	L	3	2074.72	328	327	.	994	21.0431	10.4775	3.2583	60.4	-9.74	3.67	.	.
D2-37-74	L	3	2083.87	327	335	3270	769	20.7934	10.3341	2.4766	62.0	-8.45	3.68	.	.
D2-39-74	L	3	2095.46	363	159	1365	870	21.5891	10.9437	2.4865	46.1	-9.49	3.36	.	.
D2-41-74	L	3	2105.21	309	245	2327	792	21.8395	11.3114	2.2804	56.5	-9.22	3.32	.	.
D2-43-74	L	3	2116.49	313	308	5255	735	20.7090	11.4299	2.0206	54.4	-8.06	2.99	.	.
D2-45-74	L	3	2126.25	329	325	2816	1002	20.6556	10.6342	2.1481	57.7	-8.63	2.74	.	.
D2-47-74	L	4	2136.61	451	323	2438	870	24.4083	7.9872	2.0812	60.9	-10.03	1.38	.	.
D2-49-74	L	4	2146.37	299	325	4419	992	21.0517	11.1231	2.0583	57.0	-8.85	0.20	.	.
D2-51-74	L	4	2154.60	375	524	3034	829	22.8434	8.9024	1.6544	64.2	-8.31	-0.09	-10.39	-0.59
D2-55-74	L	4	2175.03	456	336	2569	789	23.5400	7.5807	1.9057	65.2	-8.99	0.04	-11.59	-0.85
D2-59-74	L	4	2194.23	434	332	3937	1167	25.0211	7.7934	1.7628	61.6	-8.74	-0.12	-11.22	-0.91
D2-61-74	L	4	2204.60	432	607	4874	1063	20.3461	7.3679	2.1083	62.4	-9.18	0.35	-11.52	-0.66
D2-63-74	L	4	2215.58	490	647	2259	972	23.4593	8.1463	1.9736	77.8	-9.23	0.67	-11.51	-0.13
D2-73-74	L	4	2267.10	421	428	1592	848	24.8642	8.1790	2.0783	68.9	-10.31	3.41	-11.86	3.40
D2-75-74	L	4	2277.47	437	758	5580	790	20.9428	9.1716	2.3287	68.3	-9.55	3.78	-10.88	3.28
D2-77-74	L	4	2287.53	305	288	2320	760	21.0664	10.9968	2.1179	58.8	-9.87	3.17	.	.
D2-79-74	L	4	2297.28	485	305	1385	601	28.4601	7.5400	1.3655	62.8	-8.92	2.81	.	.
D2-80-74	L	4	2302.47	358	762	1900	581	17.2368	6.9475	1.1947	59.5	-8.88	2.26	.	.
D2-87-74	L	4	2364.66	381	219	2859	819	23.3452	8.6056	1.9321	53.5	-9.08	-1.13	.	.
D2-89-74	L	4	2374.72	282	306	2033	1151	22.8086	11.2454	2.1549	50.0	-7.82	-3.85	-8.80	-4.87
D2-91-74	L	4	2384.48	352	415	3157	1246	24.9403	8.6222	1.8560	46.9	-8.75	-4.62	.	.
D2-97-74	L	5	2419.94	191	1096	.	3135	12.7515	8.7280	3.4786	88.5	-8.71	-2.80	.	.

HIGH SR DOLOSTONES

SAMPLE	LEVEL	UNIT	DEPTH	SR	NA	AL	MN	CA	MG	FE	IR	O18DOL	C13DOL	O18CAL	C13CAL
D2-133-74	L	5	2425.43	192	163	1478	4566	26.8678	11.0711	3.6336	41.0	.	.	.	.
D2-136-74	L	5	2427.33	257	134	.	4263	20.3584	7.5726	3.3595	38.4	-9.22	-2.30	-10.39	-1.74
D2-137-74	L	5	2428.02	213	144	2447	4856	20.4850	10.5386	4.2607	48.4	.	.	.	.
D2-138-74	L	5	2428.50	281	104	2120	4097	26.3812	8.4782	3.1968	40.0	-9.41	-2.20	-10.17	-2.09
D2-139-74	L	5	2428.99	291	107	3264	3999	27.0149	8.0527	2.7609	37.4	.	.	.	.
D2-140-74	L	5	2429.59	265	241	3578	4189	27.3899	7.7836	3.6148	45.3	-9.38	-2.74	-10.51	-1.88
D2-141-74	L	5	2430.33	240	175	3185	2518	20.9893	9.5089	3.8366	45.7	.	.	.	.
D2-142-74	L	5	2430.94	184	244	.	6281	20.2303	10.2816	4.2081	49.2	-9.91	-2.71	.	.
D2-143-74	L	5	2431.78	231	199	4626	5523	22.6710	9.7982	4.6725	57.7	.	.	.	.
D2-144-74	L	5	2432.29	276	176	3668	4773	25.6114	8.5212	3.5178	40.8	-9.17	-2.40	-10.06	-2.83
D2-145-74	L	5	2433.05	217	138	4296	5467	20.6601	9.6458	4.1857	44.1	.	.	.	.
D2-146-74	L	5	2434.34	239	186	4862	5632	23.2332	9.5350	5.6470	63.5	-9.42	-2.97	.	.
D2-147-74	L	5	2434.96	183	440	7671	6282	20.0155	7.0855	3.8595	65.7	.	.	.	.
D2-148-74	L	5	2435.46	166	237	8684	5064	20.4302	8.3623	3.5045	48.3	-9.68	-4.37	.	.
D2-103-74	L	5	2453.69	279	78	1757	4565	25.1945	10.0104	2.9872	31.8	-10.01	-6.08	.	.

LOW SR DOLOSTONES

SAMPLE	LEVEL	UNIT	DEPTH	SR	NA	AL	MN	CA	MG	FE	IR	O18DOL	Cl3DOL	O18CAL	Cl3CAL
A-1A-84	U	1	55	50	80	145	1454	19.6422	12.3343	1.0062	4.5	-6.32	0.87	.	.
A-31-84	U	1	210	38	83	31	180	21.9462	13.8802	0.1197	19.0	-5.66	0.63	.	.
A-30MI-84	U	1	220	37	148	163	2618	22.3772	13.3264	0.8061	1.1	-6.21	0.84	.	.
A-30MA-84	U	1	220	39	103	75	504	20.6401	11.9455	0.3366	4.3	-5.85	0.90	.	.
A-28A-84	U	1	240	40	156	63	223	21.0381	12.9960	0.1409	4.4	-5.84	0.73	.	.
A-27A-84	U	1	275	49	98	52	553	20.8941	12.8293	0.4545	5.1	-6.17	0.82	.	.
A-24A-84	U	1	290	51	63	209	1271	21.1722	12.6020	0.9282	6.3	-6.64	0.65	.	.
A-72BG-85	U	1	300	47	92	8	1496	21.7052	10.8396	1.0429	8.0	-6.55	0.79	.	.
A-79B-85	U	1	305	41	114	104	323	21.5177	13.2782	0.2259	3.8	-5.82	0.70	.	.
A-26A-84	U	1	325	39	95	112	347	25.3793	13.8147	0.2079	3.6	-5.62	0.74	.	.
A-2A-84	U	1	430	38	108	157	215	20.7952	13.2351	0.1505	3.3	-5.83	1.52	.	.
A-59A-85	U	1	500	35	91	178	197	19.9092	13.4643	0.1581	3.7	.	.	.	.
A-3A-84	U	1	510	40	114	136	276	21.6126	13.7568	0.2467	5.5	-6.25	1.29	.	.
A-4MI-84	U	1	535	39	133	240	856	21.8387	11.9711	0.5817	3.9	-6.02	1.19	.	.
A-4MA-84	U	1	535	41	112	259	567	23.8380	12.8870	0.5101	16.1	-6.01	1.59	.	.
A-52A-85	U	1	550	39	122	110	191	21.6210	13.2424	0.1718	4.3	-5.55	1.67	.	.
A-54A-85	U	1	615	42	128	228	365	16.8026	12.8129	0.2939	10.0	-5.44	1.29	.	.
A-7BMI-84	U	1	620	33	121	85	225	20.1884	13.8171	0.1939	2.6	-5.07	1.38	.	.
A-7RMI-84	U	1	620	33	137	111	454	20.0741	13.6842	0.5347	5.3	-5.94	1.19	.	.
A-55A-85	U	1	650	44	73	151	328	22.7648	13.5002	0.2947	5.7	-6.70	1.30	.	.
A-56A-85	U	1	700	22	140	103	129	21.3059	11.8543	0.0869	5.6	-6.01	1.58	.	.
A-10-84	U	1	730	39	115	201	220	19.6038	12.5421	0.1667	4.4	-6.92	1.13	.	.
A-62B-85	U	2	760	39	101	138	209	21.3388	13.1545	0.1673	4.2	-6.33	1.13	.	.
A-48G-85	U	2	795	56	99	96	645	20.6072	13.7052	0.3258	6.0	-6.17	1.16	.	.
A-36B-85	U	2	810	35	121	64	336	23.0551	13.2533	0.2416	20.3	-7.40	0.90	.	.
A-32B-85	U	2	820	22	56	0	232	22.1146	13.0827	0.1516	5.5	-5.91	0.90	.	.

LOW SR DOLOSTONES

SAMPLE	LEVEL	UNIT	DEPTH	SR	NA	AL	MN	CA	MG	FE	IR	O18DOL	C13DOL	O18CAL	C13CAL
A-12B-84	U	2	840.00	34	115	61	291	20.3936	13.4322	0.2409	5.5	-6.32	1.19	.	.
A13A-1-84	U	2	935.00	24	71	63	259	23.8393	13.9887	0.1150	6.9	-6.98	1.08	.	.
A13A-2-84	U	2	935.00	20	64	33	195	20.2079	13.6166	0.0886	4.3	-6.33	1.32	.	.
A13A-3-84	U	2	935.00	21	86	11	204	20.6553	13.1966	0.1020	4.2	-6.50	1.31	.	.
A13A-4-84	U	2	935.00	29	99	100	402	18.6519	13.3735	0.1900	12.7	-7.46	1.10	.	.
A13A-5-84	U	2	935.00	23	98	98	243	20.0676	13.5387	0.1185	6.3	-6.92	1.30	.	.
A-13C-84	U	2	935.00	49	90	97	212	19.6453	13.3082	0.1663	6.5	.	.	.	.
A-30A-85	U	2	965.00	19	85	119	427	23.1600	13.3692	0.3087	22.0	-7.28	0.61	.	.
A-15-84	U	2	975.00	30	108	129	272	21.6835	13.3570	0.1795	9.1	-5.43	1.66	.	.
A-43B-85	U	2	1000.00	24	62	2	281	19.6125	13.3987	0.1675	6.3	-6.05	1.21	.	.
A-44B-85	U	2	1025.00	30	68	74	494	22.8577	13.3085	0.3254	4.8	-7.97	0.58	.	.
A-20-84	U	2	1065.00	33	103	11	182	20.9340	14.2086	0.0954	11.0	-5.11	1.27	.	.
A-21-84	U	2	1070.00	38	118	21	189	21.1062	13.2681	0.1155	4.7	-5.21	1.26	.	.
A-47B-85	U	2	1075.00	34	56	11	300	23.2887	13.1911	0.2015	16.1	-7.46	0.59	.	.
A-22-84	U	2	1085.00	28	117	5	178	20.0044	13.3158	0.0774	5.5	-4.55	1.34	.	.
A-25A-85	U	2	1120.00	38	100	3	318	19.9582	13.1835	0.2568	19.5	-6.95	1.17	.	.
M-7B-84	L	1	1130.00	57	130	48	271	21.2891	12.9547	0.2632	6.3	-4.40	0.80	.	.
M-6-84	L	1	1150.00	63	145	7559	1395	18.8334	8.9431	4.3137	68.0	-6.15	0.27	.	.
M-5-84	L	1	1165.00	32	134	185	386	19.6931	13.1529	0.8090	3.3	-5.81	0.54	.	.
M-11-84	L	1	1225.00	18	125	0	52	22.1445	13.7096	0.0531	2.8	-6.06	-0.59	.	.
M-3-84	L	1	1320.00	39	112	321	535	20.3994	13.2152	0.5754	11.3	-3.11	1.72	.	.
M-12-84	L	1	1350.00	34	119	0	216	20.8097	13.1518	0.1303	5.1	-4.19	0.58	.	.
M-1-84	L	1	1715.00	58	160	144	127	20.4356	13.1864	0.0431	3.9	-4.61	1.83	.	.
M-2-84	L	1	1880.00	42	150	61	46	22.4997	13.9418	0.0066	3.8	-1.90	0.31	.	.
D2-1-74	L	2	1895.00	78	159	466	314	20.4143	11.9630	0.0486	14.6	-3.81	-3.26	.	.
D2-3-74	L	2	1906.73	62	182	107	231	19.7960	12.6916	0.0499	10.7	-3.55	-2.47	.	.

LOW SR DOLOSTONES

SAMPLE	LEVEL	UNIT	DEPTH	SR	NA	AL	MN	CA	MG	FE	IR	O18DOL	CI13DOL	O18CAL	CI13CAL
D2-5-74	L	2	1916.50	84	140	132	209	21.9002	13.0341	0.0408	20.0	-3.70	-2.73	.	.
D2-113-74	L	2	1922.89	102	123	288	276	21.3910	12.5819	0.4688	30.9	.	.	.	.
D2-114-74	L	2	1923.63	77	141	.	321	20.3464	12.7379	0.7477	27.0	-4.50	-2.72	.	.
D2-115-74	L	2	1924.41	117	128	537	301	24.0364	12.7808	0.5684	30.9	.	.	.	.
D2-116-74	L	2	1927.46	84	143	.	306	24.3113	12.6171	0.3381	19.4	-4.57	-2.55	.	.
D2-7-74	L	2	1928.08	98	133	687	266	21.2324	12.4397	0.3416	25.1	-4.54	-2.60	.	.
D2-117-74	L	2	1928.43	62	161	148	342	20.8669	12.9915	0.8526	5.8	.	.	.	.
D2-118-74	L	2	1929.21	55	167	.	425	22.3317	12.1371	1.4080	9.6	-3.79	-0.01	.	.
D2-119-74	L	2	1930.03	73	142	303	577	23.3404	12.8340	0.6197	15.9	.	.	.	.
D2-120-74	L	2	1930.87	72	139	.	574	22.3557	11.6841	0.7562	13.6	-4.19	-0.36	.	.
D2-121-74	L	2	1931.60	98	121	343	740	20.4502	12.1248	0.6075	17.8	.	.	.	.
D2-122-74	L	2	1932.69	65	159	.	959	22.1538	11.6169	0.9548	18.7	-4.39	-0.19	.	.
D2-123-74	L	2	1933.56	85	170	.	951	20.8638	12.9767	1.1046	43.6	.	.	.	.
D2-124-74	L	2	1934.47	89	164	808	958	23.3267	12.8302	0.7077	26.4	-3.42	0.45	.	.
D2-125-74	L	2	1935.44	70	154	136	828	22.9879	13.1759	0.7837	10.5	.	.	.	.
D2-127-74	L	3	1936.86	94	117	216	1007	19.1007	12.4769	0.9271	17.5	.	.	.	.
D2-128-74	L	3	1937.65	131	110	147	1006	21.0624	12.9284	1.0584	41.0	-3.28	1.27	.	.
D2-129-74	L	3	1938.46	83	103	173	1199	22.8070	13.0131	1.1190	11.3	.	.	.	.
D2-9-74	L	3	1938.75	63	165	351	1133	22.2303	12.6169	0.8956	16.2	-2.66	2.50	.	.
D2-130-74	L	3	1939.35	130	145	.	1006	25.0076	14.1121	1.1328	27.4	-3.69	1.87	.	.
D2-131-74	L	3	1940.26	143	172	939	750	22.6718	12.6676	0.8594	39.8	.	.	.	.
D2-132-74	L	3	1941.18	80	152	.	1525	19.8453	11.4121	1.0339	26.9	-3.52	1.91	.	.
D2-11-74	L	3	1952.47	77	112	204	438	21.3442	12.9862	0.4674	15.9	-8.09	3.81	.	.
D2-13-74	L	3	1961.00	97	150	206	191	22.1294	14.5831	0.2823	23.9	-3.09	2.52	.	.
D2-15-74	L	3	1971.06	75	146	420	140	20.8650	13.2044	0.3029	13.2	-4.23	2.67	.	.
D2-17-74	L	3	1981.23	43	153	135	73	20.0163	14.2001	0.1562	6.2	-5.30	1.87	.	.

LOW SR DOLOSTONES

SAMPLE	LEVEL	UNIT	DEPTH	SR	NA	AL	MN	CA	MG	FE	IR	O18DOL	C13DOL	O18CAL	C13CAL
D2-19-74	L	3	1991.80	43	252	775	234	21.5546	12.4882	1.0244	34.8	-5.65	0.81	.	.
D2-21-74	L	3	2001.25	77	154	551	379	21.9342	13.1250	1.9323	30.1	-6.80	0.54	.	.
D2-23-74	L	3	2012.22	126	274	2090	1011	19.9969	10.2801	2.7558	67.0	-8.27	1.06	.	.
D2-107-74	L	5	2472.89	63	65	600	1379	28.2860	6.5914	1.2596	12.8	-9.28	3.37	-10.37	2.7
D2-109-74	L	5	2482.95	60	123	201	1524	21.3290	10.0283	1.8092	16.5	-8.02	4.70	.	.
D2-111-74	L	5	2493.02	56	142	384	2766	22.8719	12.1538	1.6152	12.6	-8.91	3.46	.	.

APPENDIX 4

SUMMARY OF ELECTRON MICROPROBE RESULTS
FOR SELECTED DOLOMITE FABRICS

RESULTS OF ELECTRON MICROPROBE ANALYSES OF DOLOMITE FABRICS

SAMPLE	# OF ANALYSES	%FeO	%MnO	%SrO	%CaO	%MgO	COMMENT
A6985	3	.30	.08	0	30.70	20.64	ACICULAR FABRIC (PLATE 21)
A78B85	3	.30	.05	0	30.81	20.54	RADIATING FANS (PLATE 25)
"	1	0	0	0	30.64	21.01	INTER-FAN COAR- -SER DOLOSPAR
A58B85	3	.84	.14	0	31.19	20.40	GRAVITY CEMENT (PLATE 35)
"	3	.70	.05	0	29.49	21.11	PEBBLE + ACIC- -ULAR LAMINAE
A2984	4	.09	.003	0	30.85	21.40	COARSELY CRYST- -ALLINE DOLOSTONE (PLATE 28)
A17B85	3	.61	.11	.003	30.33	20.19	BLADED CEMENT (PLATE 36)
"	2	.46	.15	0	30.70	20.36	MICRITE MATRIX
A71C85	3	.07	.003	0	31.26	20.95	BLADED DOLOSPAR
"	2	.85	.12	0	31.25	20.50	ACICULAR CROWN (PLATE 37)
"	2	1.04	.15	.005	31.12	20.44	COARSER ACICUL- -AR DOLOMITE

ANALYTICAL METHOD

Dolomite samples were analyzed by the wavelength dispersive method with a Cambridge Microscan 5 electron probe at the University of Carleton in Ottawa. The instrument is operated with a 15 kv accelerating potential and a specimen (absorbed) current of 30 nanoamperes measured on a dolomite standard.

Dolomite (Ca and Mg), Rhodochrosite (Mn), Celestite (Sr) and Arenal Horneblende U.S.N.M. 111356 (Fe) standards were used. Carbon was calculated from stoichiometry. Major elements have an analytical error of $\pm 1\%$; minor elements have a relative error of up to $\pm 25\%$. The detection limit of SrO is 0.02 wt. %.

APPENDIX 5

SUMMARY OF SULFUR ISOTOPIC RESULTS FOR PYRITE
SAMPLES OF THE UPPER & LOWER ALBANEL FORMATIONS

SULFUR ISOTOPES OF PYRITE

Sample	Depth (meters)	# of analyses	Range $\delta^{34}\text{S}$ ‰	$\delta^{34}\text{S}$ aver‰	Comment
A-2-5	-	1	-	26.9	cube (cold finger)
<u>U. Black Shale Unit</u>					
D2-156-74	1921.50	2	10.55 - 11.96	11.26	pyritized algal mat
D2-115-74	1924.42	1	-	21.42	lenses ($5 \leq \text{mm}$)
D2-118-74	1929.29	3	14.83 - 15.16	14.99	pyritized cross-bedded dolostone
D2-8-74	1934.17	1	-	19.13	small lenses ($\leq 1 \text{ mm}$)
<u>U. Banded Dolostone Unit</u>					
D2-15-74	1971.06	1	-	7.19	small lenses ($\leq 1 \text{ mm}$)
D2-29-74	2043.02	4	38.70 - 39.56	39.09	large ($\leq 6 \text{ mm}$) and smaller cubes
D2-33-74	2062.53	1	-	39.30	cube
D2-38-74	2090.27	1	-	28.90	lense ($\leq 1 \text{ cm}$)
D2-44-74	2121.37	1	-	18.61	early diagenetic lense
<u>L. Banded Dolostone Unit</u>					
D2-53-74	2165.58	1	-	21.76	Kiba separation
D2-60-74	2199.42	1	-	4.63	Kiba separation
D2-90-74	2378.69	1	-	25.15	Kiba separation
<u>L. Black Shale Unit</u>					
D2-94-74	2400.03	1	-	25.41	laminae
D2-151-74	2421.82	5	-7.12 to +2.70	-2.82	early diagenetic lense
D2-152-74	2122.05	4	14.14 to 53.92	29.07	early diagenetic (?) 1 cm layer
D2-98-74	2423.50	2	11.92 - 12.68	12.30	cube and laminae
D2-153-74	2425.81	8	48.05 - 60.15	53.93	early diagenetic (?) lense
D2-145-74	2433.05	1	-	31.58	lense
D2-148-74	2435.46	1	-	25.65	cubes
D2-154-74	2440.80	3	32.10 - 37.30	34.20	layer ($\leq 5 \text{ mm}$ thick)
D2-101-74	2440.88	1	-	36.52	cube
D2-101-74	2440.88	1	-	36.91	Kiba separation
D2-102-74	2444.84	3	11.85 - 36.36	25.57	laminae
D2-106-74	2468.63	1	-	33.63	lense (2-3 mm thick)
D2-155-74	2495 ?	1	-	26.42	Icon Sullivan cube
<u>Basal Stromatolitic Dolostone Unit</u>					
D12-A-77	284.07	1	-	19.93	discordant lamina
D12-B-77	287.91	1	-	18.22	pyrite vein lining ca- vity margins

APPENDIX 6

SUMMARY OF STRONTIUM, OXYGEN AND CARBON ISOTOPIC RESULTS OF
SELECTED UPPER & LOWER ALBANEL FORMATION CARBONATES

SUMMARY OF STRONTIUM ISOTOPES

SAMPLE	Mn	Sr	DEPTH	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$^{87}\text{Sr} / ^{86}\text{Sr}$	$10^3(\text{Sr}/\text{Ca})$
	(ppm)		(meters)	(‰ PDB)			
A1584	272	30	975	1.66	-5.43	0.7112	0.12
M7b84	271	57	1130	0.80	-4.40	0.7060	0.27
M1084*	69	115	~980	0.85	-6.41	0.7101	0.52
D21074*	665	73	1946	2.68	-3.56	0.7127	0.32
D21274*	202	373	1957	2.98	-9.76	0.7065	1.54
D23974	870	363	2095	3.69	-8.24	0.7152	1.68
D25374	609	341	2166	-1.49	-12.26	0.7126	0.96
D25974	1167	434	2194	-0.12	-8.74	0.7140	1.73
D26574	461	349	2226	0.21	-13.08	0.7112	0.92
D28074	267	379	2335	2.26	-8.88	0.7117	1.71
D210274*	3378	602	2445	-2.77	-10.19	0.7274	2.55
D211274*	30452	270	2501	---	---	0.7254	1.18

* = Veizer's unpublished electron microprobe and isotopic data.

ANALYSES OF CALCITE VEINS & ADDITIONAL SAMPLES

SAMPLE	CORE DEPTH (m)	$\delta^{18}\text{O}$ ‰ (PDB)	$\delta^{13}\text{C}$ ‰ (PDB)	COMMENT
D2774	1928.08	-6.99	-8.61	en échelon
D212574	1935.44	-7.85	-4.65	"
D24974	2146.37	-12.50	-1.63	"
D214774	2434.96	-11.61	-4.98	"
D215374	2425.81	-11.08	+2.02	(PLATE 42)
D12B77	287.91	-9.96	-0.55	(PLATE 49)
D2153A74	2425.82	-11.72	-3.77	(PLATE 42)
D2153B74	2425.83	-9.96	-4.53	"

¹ Mean of 2 analyses from fault-dolomite vein in the Basal Stromatolitic Dolostone Unit

² Analysis of organic-rich limestone layer immediately below the calcite vein (PLATE 42)

³ Analysis of subjacent light grey dolomitic layer (PLATE 42)

APPENDIX 7

PHOTOGRAPHS OF SELECTED SAMPLES FROM
THE MISTASSINI BASIN

(Stratigraphic tops of photographs are as illustrated unless indicated otherwise. The scale for the hand specimens illustrated is in centimeters; photomicrograph bar scale represents 1mm unless indicated otherwise.)

LOWER ALBANEL FORMATION

UPPER BLACK SHALE COMPLEX

Plate 1 - Sample D2-157-74: Organic-rich (algal?) calcitic clasts set in a fine dolomitic matrix. Algal mats, deformed pyritized algal layers and intraclastic breccias, stratigraphically underly the calcitic clasts. The unit is interpreted as a tidal flat and lagoon. The preservation of calcite may be due to the dolomitization-inhibiting effects of organic matter and/or lower permeability. Depth=28.04 meters

UPPER ALBANEL FORMATION

SANDY DOLOSTONE UNIT

Plate 2 - Sample A-47c-85: Oxidized fenestral dolomudstone with well developed laminoid quartz and dolomite-filled fenestrae. Sample near contact with Lower Albanel Formation.

Plate 3 - Sample A-14d-85: Sample collected from apparent herring bone cross-bedded oolitic and sandy dolostone, interpreted as tidal channel or bar. Height of outcrop $\approx$ 1.5m.

Plate 4 - Sample A-48f-85: Oxidized columnar stromatolite with abundant algal fragments, fenestrae, shelter cavities and dolomudstone intercolumn matrix. Interpreted as a shallow subtidal-intertidal environment.

Plate 5 - Sample A-35-85: Oxidized oncolitic dolostone showing irregular to rounded oncoids of various sizes, algal laminations and cement-filled fenestrae and shelter cavities. Peritidal deposition suggested.

BANDED DOLOSTONE UNIT

Plate 6 - Specimen near A-1-84: Conophyton-like stromatolite, at least one meter in height. Note abundant high amplitude stylolites. Penny for scale in upper right. Deeper water (below wave base?) deposition suggested.

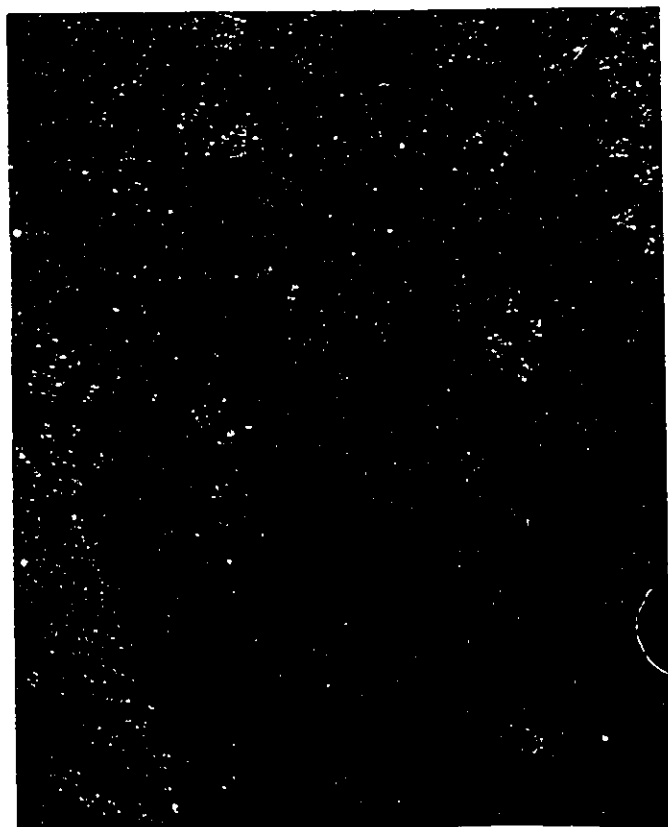


PLATE 4

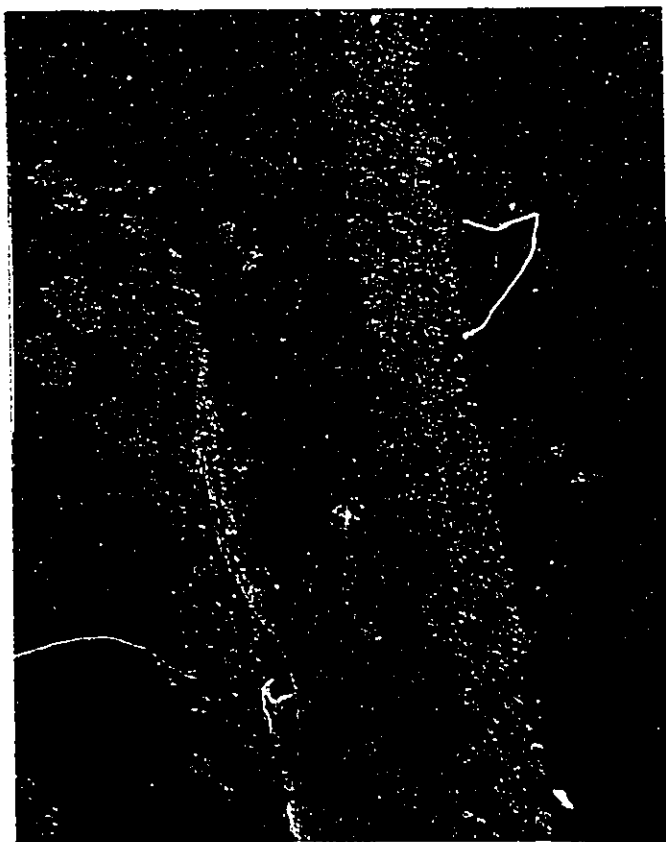


PLATE 5

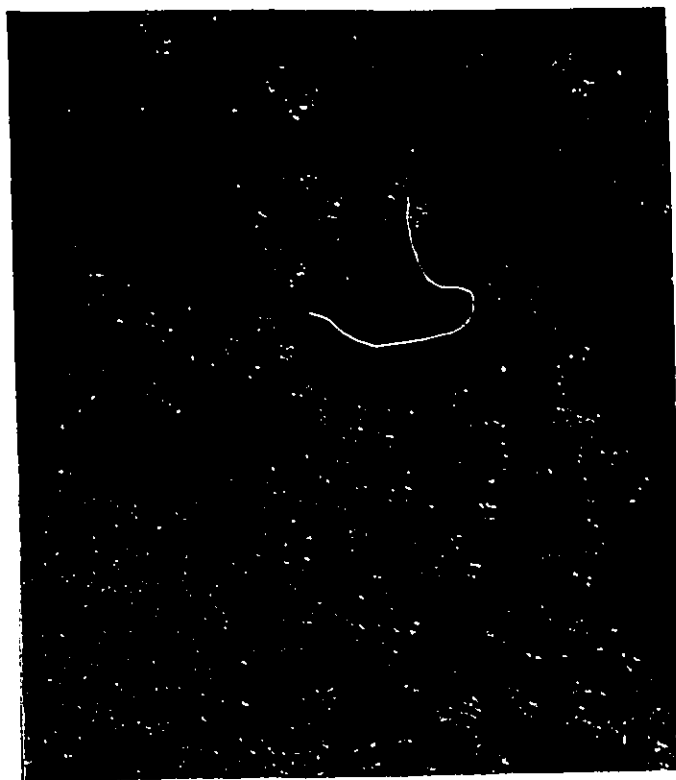


PLATE 6

Plate 7 - Sample A-1-84: Polished slab of columnar stromatolite occurrence (Plate 6) showing intense stylolitization. Intercolumn fill composed of dolomudstone and black (organic-rich?) fragments. Note the conspicuous lack of fenestrae, characteristic of most other stromatolitic occurrences.

Plate 8 - Sample A-74-85: Laterally-linked stromatolites grading upward into chertified algal laminated dolostone of a shallowing upward stromatolitic cycle. The fabric-selectivity of chert is evident along the south shore of Lake Albanel. Hammer $\approx$ 40 centimeters long.

Plate 9 - Cryptalgalaminated dolostone overlying tiny (Plate 21) and larger stromatolites. Note tepee-like structure (A) in lower left of photograph. Interpreted as the upper portion of a shallowing-upward stromatolitic cycle. Hammer visible $\approx$ 15 centimeters.



PLATE 7

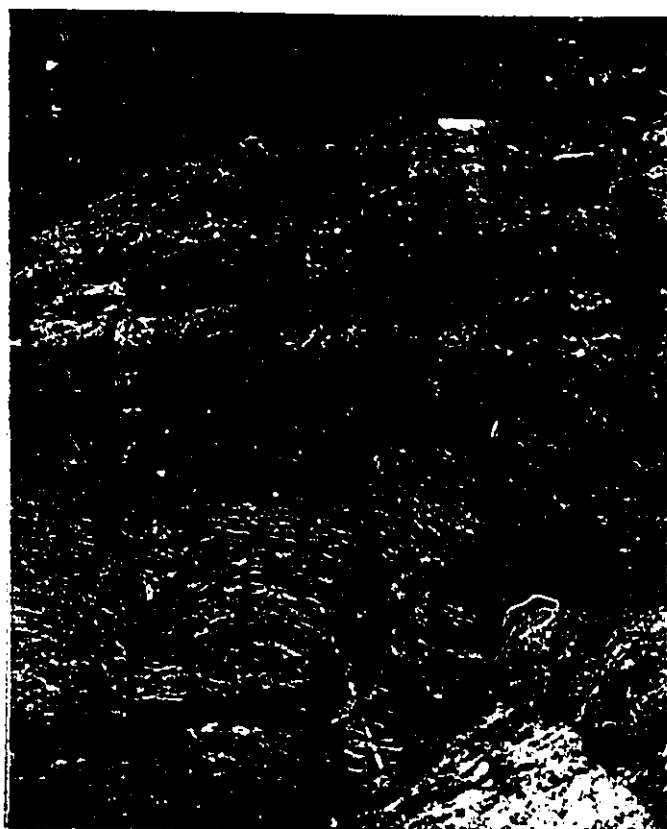


PLATE 8



PLATE 9

Plate 10- Sample A-2-85: Fenestral dolomudstone overlain by dolowackestone to dolopackstone. Cemented surface is indicated a by sharp, straight erosional boundary and almost vertical form and clastic accumulation on lee-side of dolowackestone depression. Early pore cementation is suggested by erosion of the dolospar-filled fenestrae. Note presence of tiny pyrite cube (A) near contact. Supratidal.

Plate 11- Sample A-5-85: Oxidized dolomudstone possessing fenestral (curled) cryptalgalamine and overlain by intraformational breccia of similar texture. Note high amplitude stylolites along base. Supratidal.

Plate 12- Sample A-8-85: Distorted cryptalgalamine showing early distortion (water saturated) by compaction. Preservation of distorted fenestrae suggests early precipitation of quartz. Note several oblique stylolites, suggesting tectonic stress oblique to the normal axis. Vertical sample width = 8 centimeters.

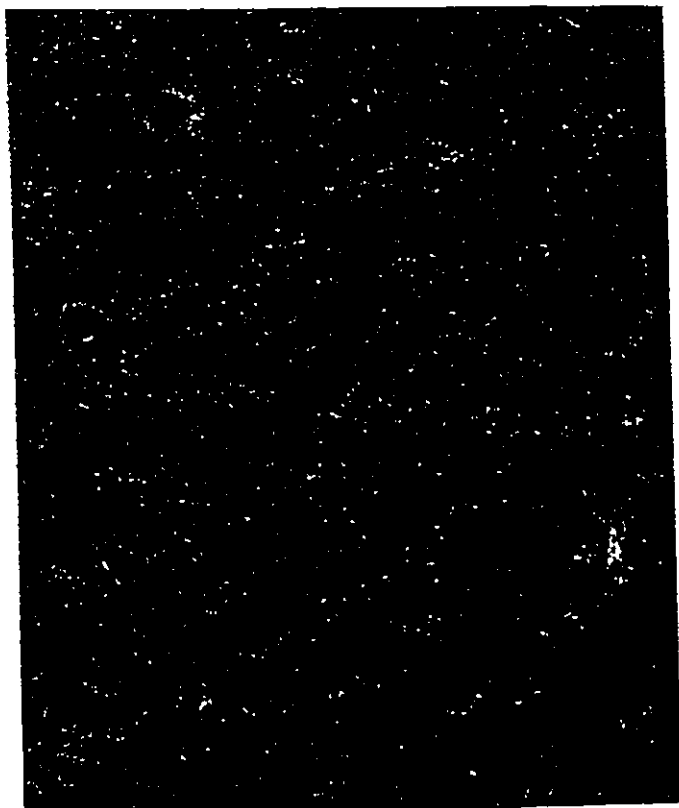


PLATE 10

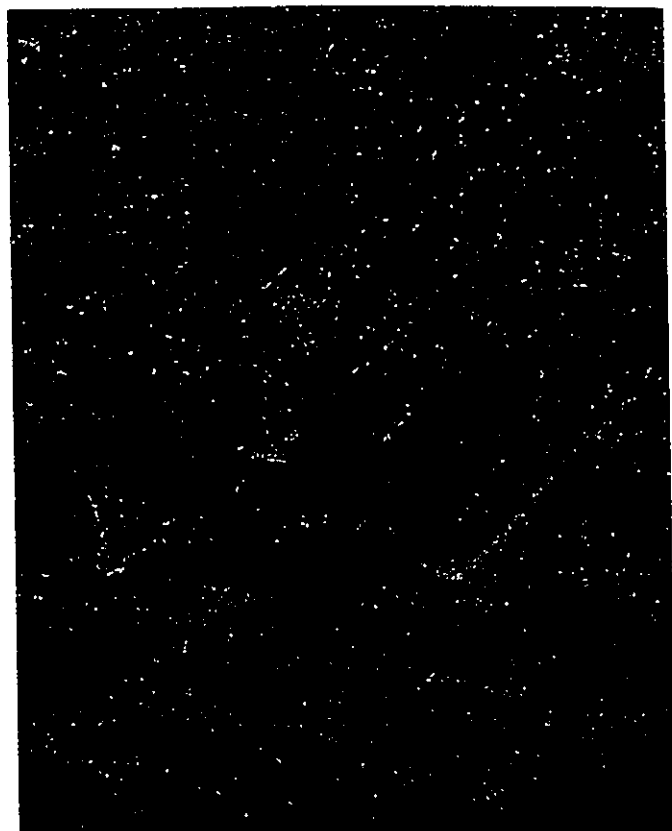


PLATE 11

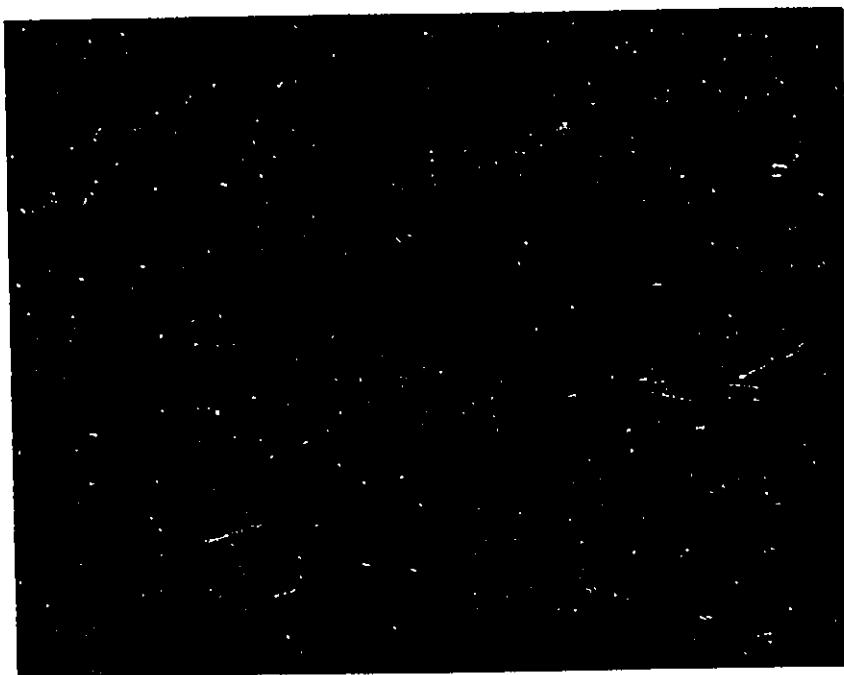


PLATE 12

Plate 13- Sample A-7-84: Fenestral cryptalgal dolomudstone showing both rigid and fluid textures; associated with tepee breccia. The oxidized red and beige dolomudstones formed in the supratidal zone. Horizontal width of sample = 7 centimeters.

Plate 14- Sample A-31-84: Laminoid-fenestral-rich cryptalgalaminated dolostone. Note the abundant "blister-like" forms filled by quartz and dolospar. The fabric may represent pustular-like mats in the upper portions of the intertidal zone. Sampled from the upper portion of the Upper Albanel Formation, near the Temiscamie Formation contact. Vertical scale is in millimeters.

Plate 15- Sample A-60-85: Peritidal tepee-structure illustrating successive brecciation; older tepees are more inclined. The sample represents the upper portion of a shallowing-upward stromatolitic sequence, underlain by cryptalgalaminations and stromatolites.

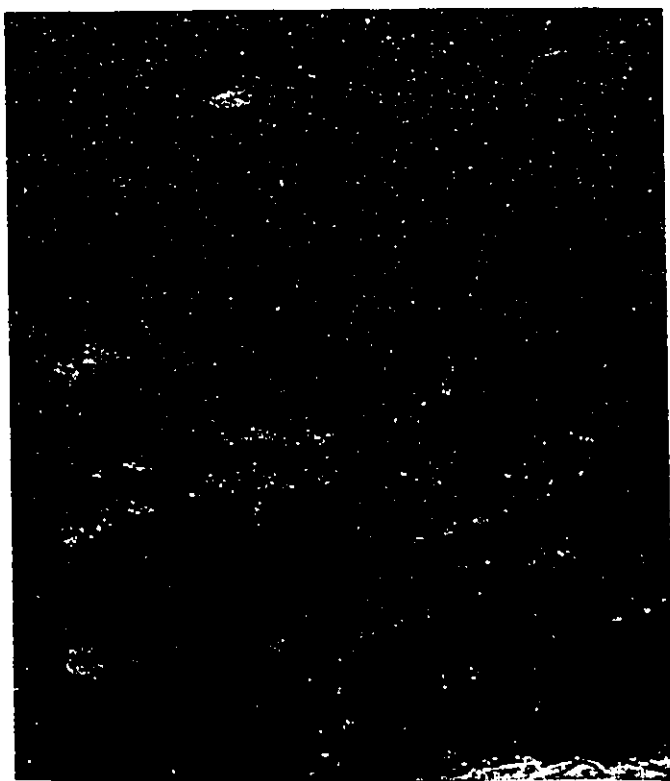


PLATE 13

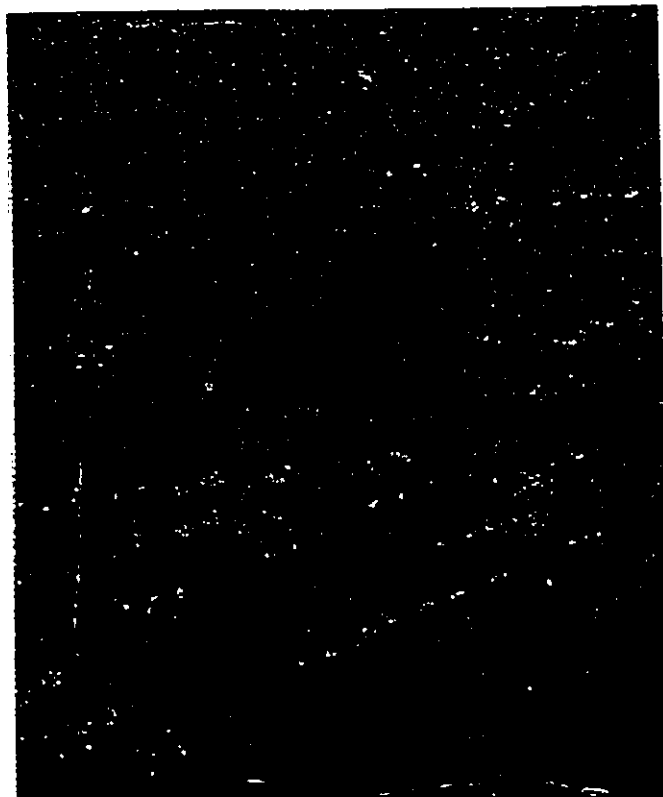


PLATE 14



PLATE 15

Plate 16- Sample A-29-84: Severely fractured (& recrystallized), coarsely crystalline dolostone. Bladed ($\pm$) radiating crystal bundle (A), may reach 1 centimeter in length (see photomicrograph in Plate 28). Possibly a vestige of an aragonitic(?) fan after a fault-related recrystallization. Scale is in millimeters. (No stratigraphic orientation).

PHOTOMICROGRAPHS

LOWER ALBANEL FORMATION

LOWER BLACK SHALE COMPLEX

Plate 17- Sample D2-146-74: Dolomitic siltstone with secondary calcite and quartz. Calcite (stained) is poikilotopic and patchy. Note the form of replacive quartz crystal and its crosscutting nature, confirming its secondary origin. Horizontal scale bar = 1mm. Uncrossed polars.

Plate 18- Sample D2-104-74: Interbedded (impure) limemudstone and dolomudstone. Coarser crystalline calcite (white) contrasts with the finely crystalline, early diagenetic dolomite (dark). Note the microscopically gradational boundary. Horizontal scale bar = 1mm. Crossed polars.



PLATE 16

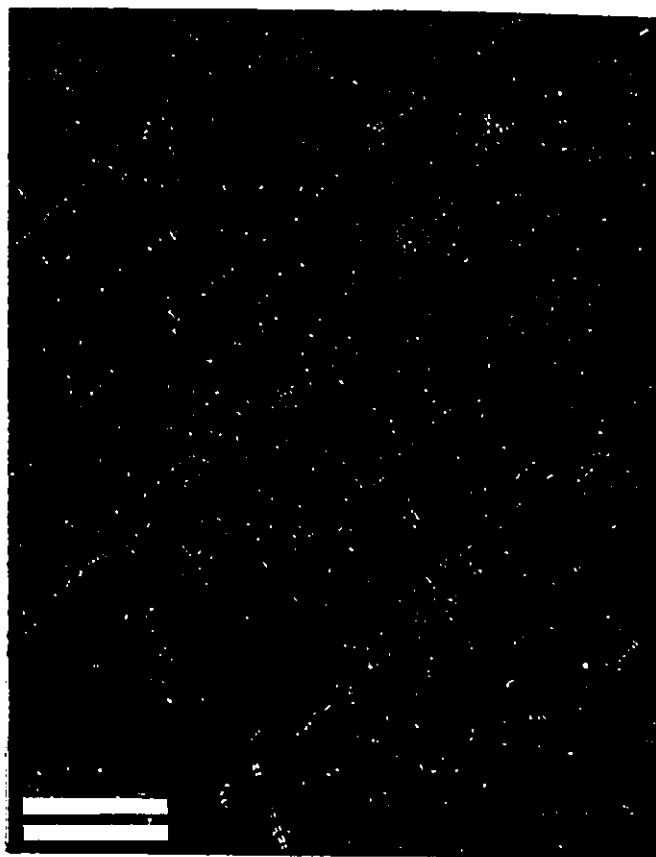


PLATE 17



PLATE 18

UPPER ALBANEL FORMATION

SANDY DOLOSTONE UNIT

Plate 19- Sample A-48b-85: Interlaminated (red) oolitic dolomudstone. Note the inferred presence of evaporite molds (1) with apparent traces of chlorite, fenestrae (2), compound ooids (3) and dissolved ooids (4). Sample underlies stromatolites of Plate 4. Horizontal scale bar = 1mm. Uncrossed polars.

Plate 20- Oncolitic dolostone (see Plate 5) possessing a dolopackstone-grainstone to coarser-grained fabric. Note the crystalline quartz and dolomite occluding both fenestrae (1) and shelter porosity (2). Oncolites vary from irregular to rounded, with abundant (alternating) finer and coarser laminae. Horizontal scale bar = 1mm. Crossed polars.

BANDED DOLOSTONE UNIT

Plate 21- Sample A-69-85 :Digitate stromatolitic dolomudstone underlying cryptalgalaminates (Plate 9). Note the fine grained (dark) intercolumn detritus, dolospar filled roofs (1) and faint radially arranged elongate crystalline (aragonitic?) fabric (2). Deposition in a protected subtidal (tidal pool?) environment is indicated. Horizontal scale bar = 1mm. Uncrossed polars.

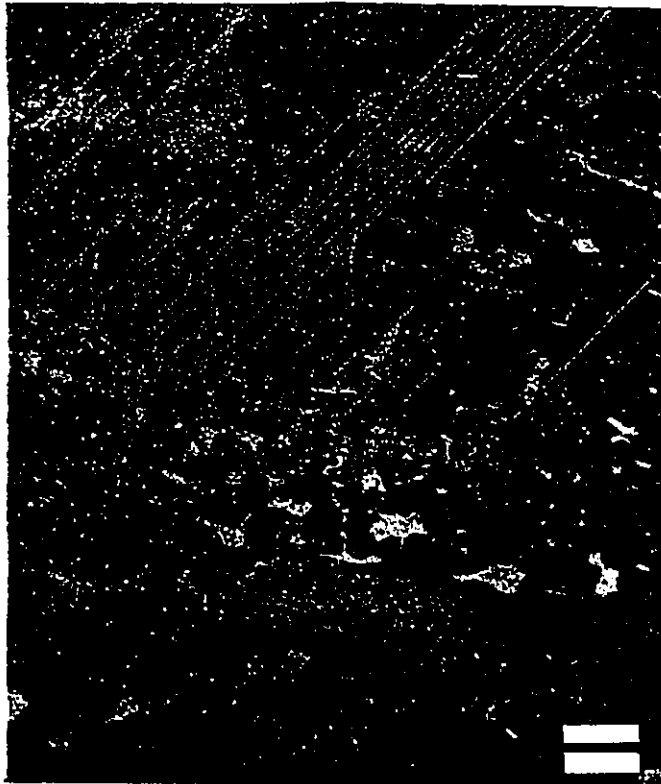


PLATE 19

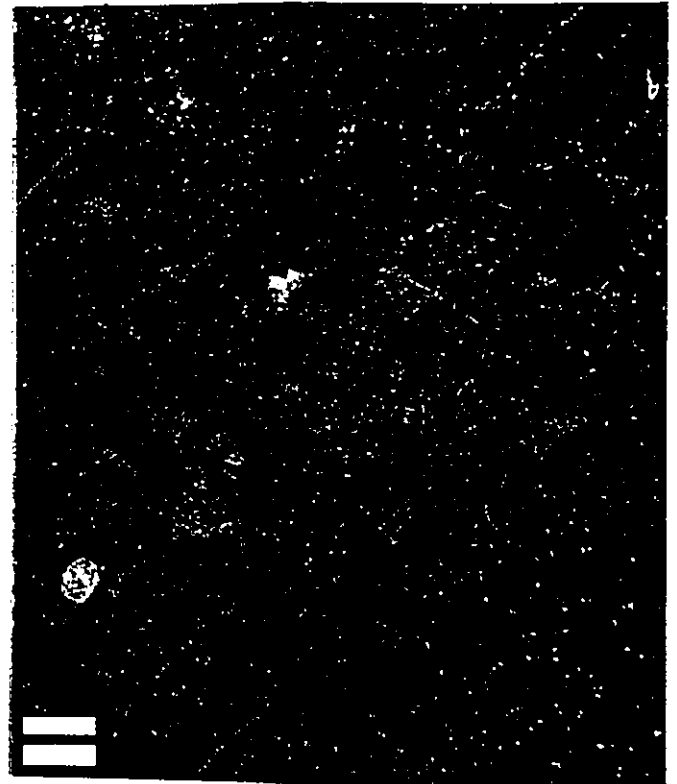


PLATE 20

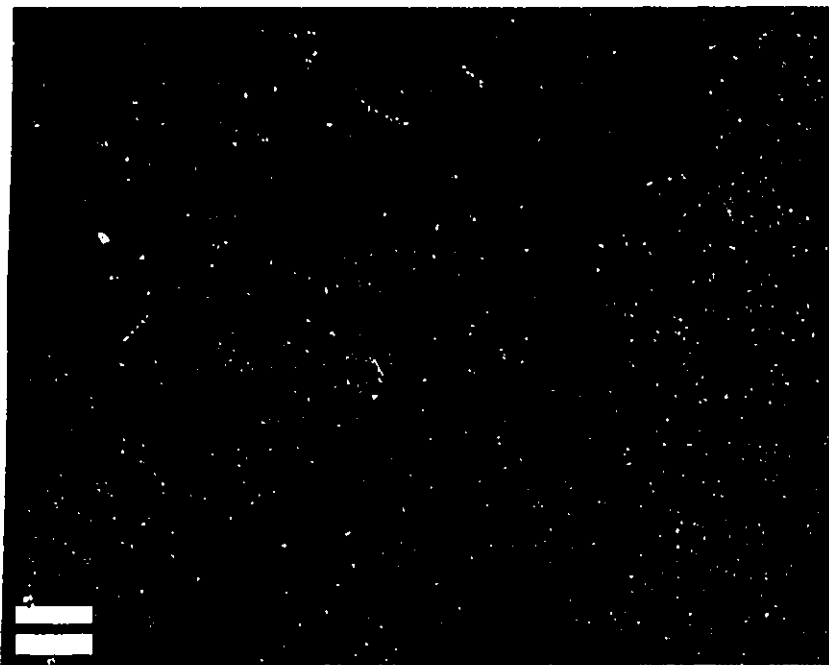


PLATE 21

Plate 22- Magnification of fenestral dolostone (Plate 10). Note the fine, irregular and "folded" laminae comprised of acicular dolomite aligned perpendicular to the latter. Precipitation of high magnesium calcite (aragonite?) within or on an algal mat is suggested. The upper and lower coarsely crystalline zones represent fenestral. Horizontal scale bar = 1mm. Uncrossed polars.

(SOUTH SHORE OF LAKE ALBANEL)

Plate 23- Sample A-23-84: Partly silicified very coarse-grained oncolitic dolostone in a cement-supported matrix. Observe the radially-arranged acicular fabric (1), suggestive of aragonite. Interoncoloid cavities are filled with dolomite and later, coarsely crystalline (central) quartz. Horizontal scale bar = 1mm. (No stratigraphic orientation.) Uncrossed polars.

Plate 24- Sample A-17h-85: Oolitic(?) - pisolitic layer possessing a dark dolomicritic texture for both pisoids and matrix. The apparent "in situ" formation as well as the circum-granular-like fabrics are suggestive of caliche pisoids. Horizontal scale bar = 1mm. Crossed polars.

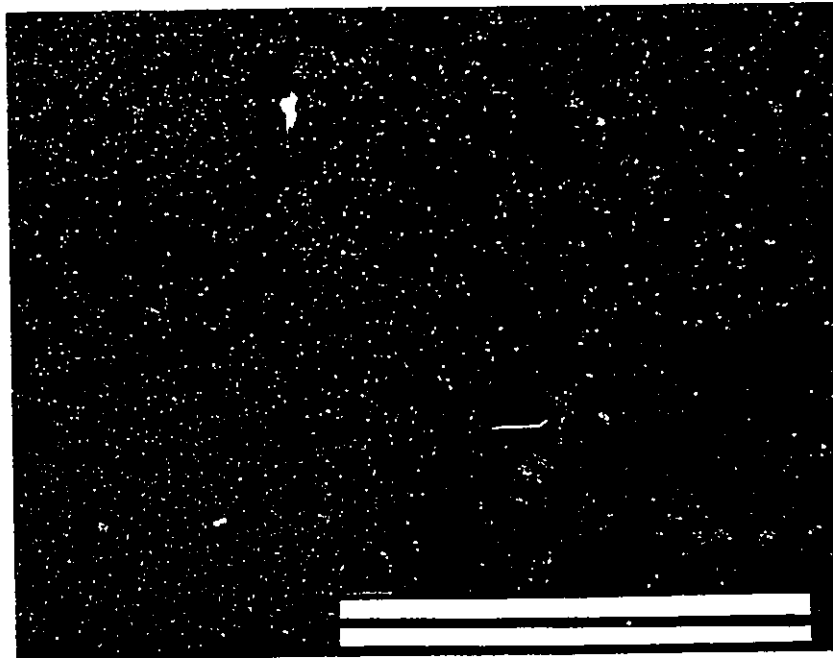


PLATE 22

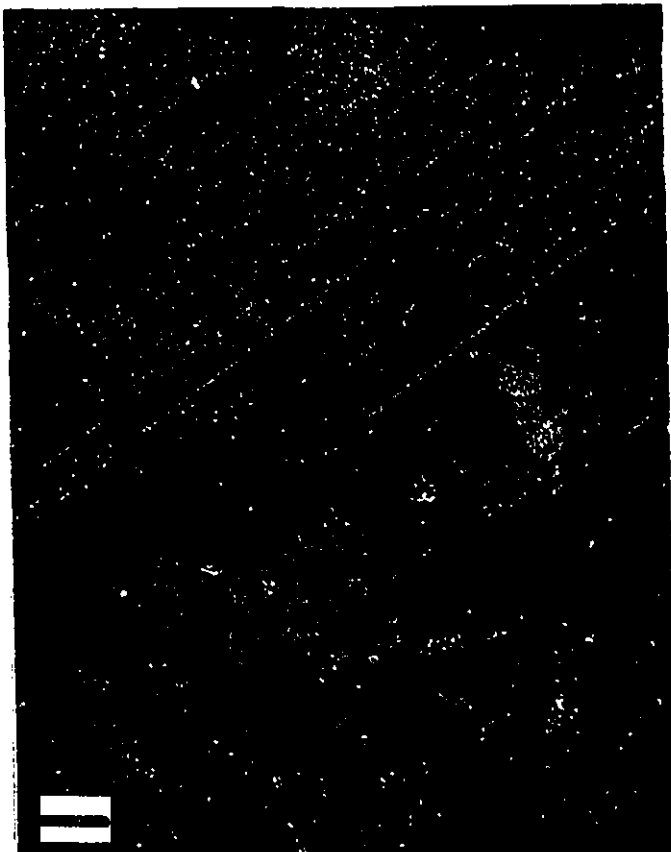


PLATE 23



PLATE 24

Plate 25- Sample A-78b-85: Dolowackestone to coarser-grained dolomitic fabric hosting (on an oncolitic host?) upward-radiating divergent aragonitic(?) fans. The acicular crystals are now composed of a finely crystalline dolomitic mosaic. The divergent acicular bundles are believed to have been deposited subtidally. Fine detrital quartz, interstitial and overlying the fabric, implies a detrital nature for the dark dolomicrite. Horizontal scale bar = 1mm. Crossed polars.

Plate 26- Sample A-30-84: Cryptalgal dolomudstone with stylolite seams and apparent evaporite (gypsum?) molds (A). Locally, opaques were observed within the molds. Horizontal scale bar = 1mm. Crossed polars.

Plate 27- Sample A-24-84: Dolomudstone hosting presumed evaporite molds (A). Note the rectangular re-entrants in many of the molds. A stylolite is visible near the bottom. Sample collected from upper portion of shallowing upward stromatolitic sequence. Horizontal scale bar = 1mm. Crossed polars.

Plate 28- Photomicrograph of Plate 16 illustrating the coarsest dolomitic crystalline texture found. The crystals appear to form divergent bundles; individual serrated laths attain several millimeters in length. A relict aragonitic(?) precursor after fault recrystallization is suggested. Horizontal scale bar = 1mm. Crossed polars.

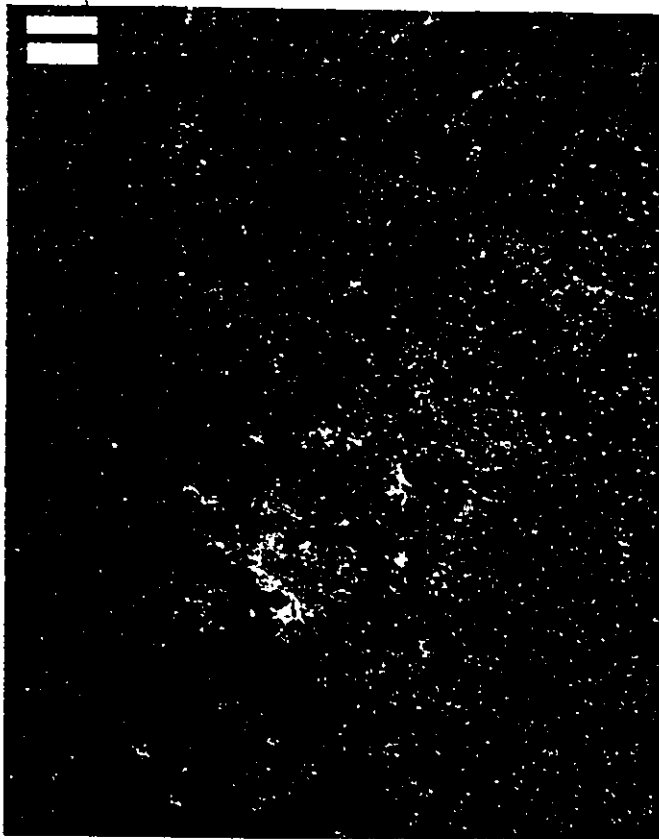


PLATE 25

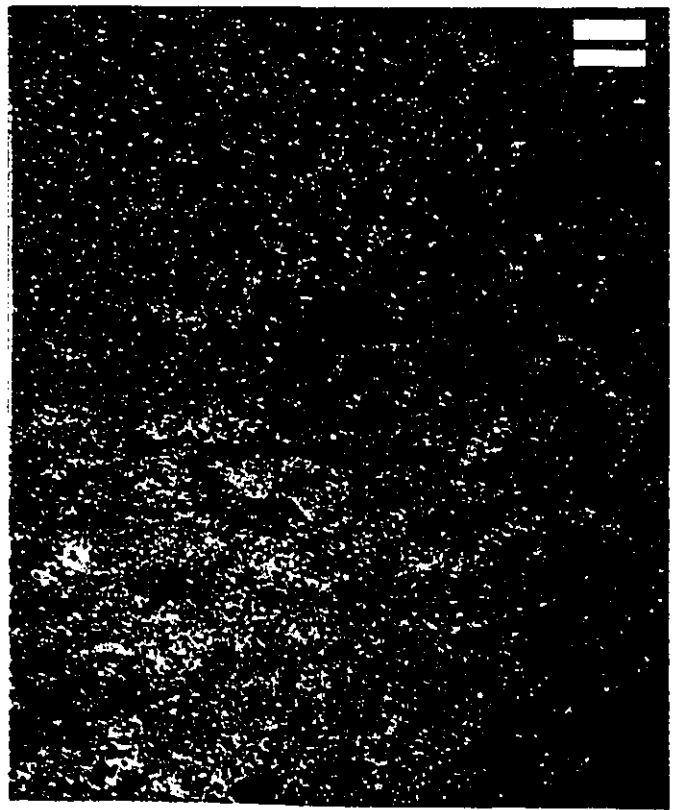


PLATE 26

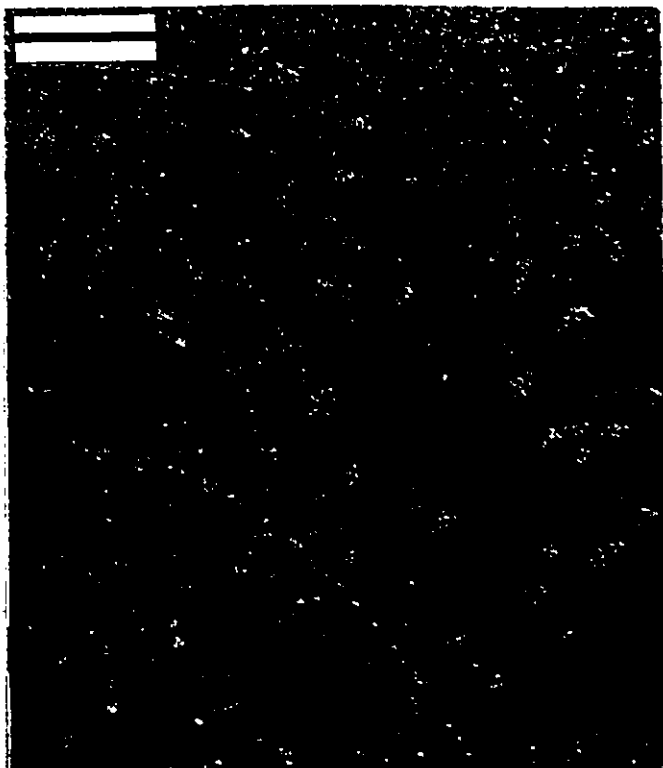


PLATE 27

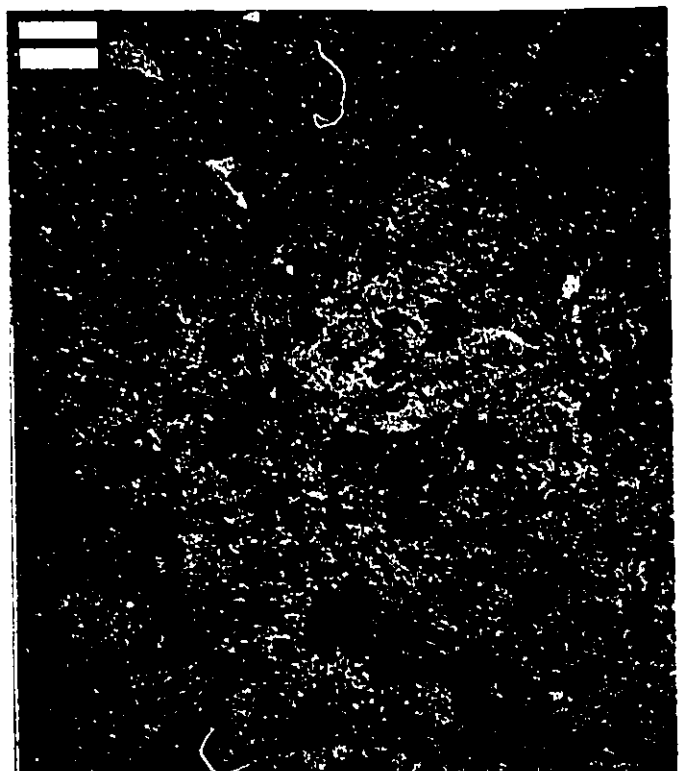


PLATE 28

DIAGENESIS

Plate 29- Sample A-30a-85: Lower portion of dolograinstone thin section displaying intense silicification of pores and ooids. Preservation of the upper portion (not visible) is attributed to early cementation. Horizontal scale bar = 1mm. Uncrossed polars.

Plate 30- Sample A-14d-85: Coarsely crystalline oolitic dolograinstone hosting detrital quartz laminae. Note the serrated quartz boundaries indicative of dissolution and carbonate replacement (increased pH). Horizontal scale bar = 1mm. Crossed polars.

Plate 31- Sample A-48h-85: Imbricated intraformational breccia composed of an oolitic dolograinstone, suggesting early cementation and later disruption. Note the variety of oolitic allochems: compound ooids (1), coarsely crystalline ooids (2) and dissolved ooids (3). The increase in crystalline size toward the center of certain ooids and intraclasts suggests total dissolution of a metastable (aragonite?) precursor, followed by later precipitation and dolomitization. Evidence of marine vadose diagenesis is suggested by meniscus cement (4); meteoric diagenesis is suggested by the presence of dissolved ooids. Horizontal scale bar = 1mm. (Stratigraphic top = ↖). Crossed polars.

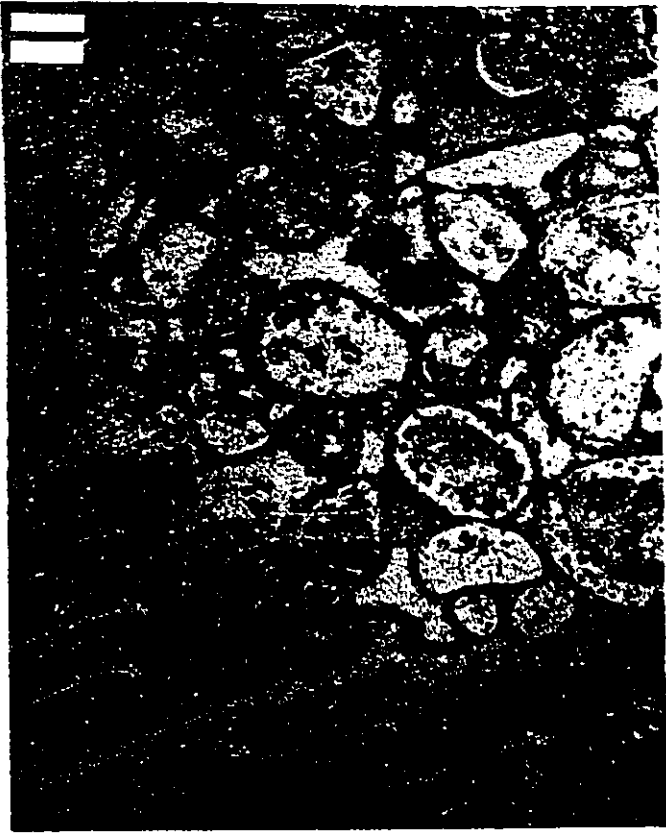


PLATE 29



PLATE 31

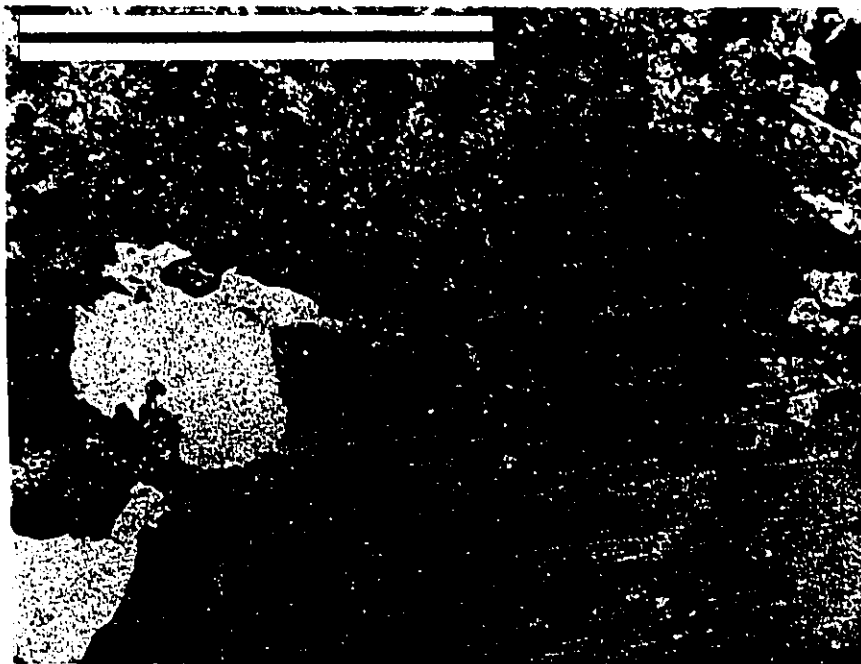


PLATE 30

Plate 32- Sample A-49b-85: Dolopackstone hosting various allochems, detrital quartz and chert. Note the radial fibrous grain (A) composed of irregular and curved laminae hosting finely crystalline acicular dolomite. Textural evidence suggests a precursor high magnesium calcite (aragonite?). Its detrital origin indicates a penecontemporaneous cement, probably as a surface crust. This is supported by the incorporation of detrital quartz. The allochem is overlain by fine irregular (algally precipitated?) laminae. Horizontal scale bar = 1mm. Crossed polars.

Plate 33- Sample A-38a-85: Interlaminated oolite and dolomudstone showing dissolved ooids filled with micritic dolomite and overlain by coarse dolospar, typical of geopetal fabrics. Certain ooids also appear to be cemented by a micritic meniscus-like (vadose) cement. Diagenetic stabilization (of aragonite?) in the presence of meteoric water is suggested. Horizontal scale bar = 1mm. Uncrossed polars.

Plate 34- Magnification of dissolved ooid (in sample A-38a-85) displaying geopetal fabric. Preaking of dolomicritic cortex probably occurred after deposition of dolomicritic sediment and followed by precipitation of spar, based on the incorporated fragment of cortex. Rupture may be due to compaction or by "force of crystallization" of early cements. Horizontal scale bar = 1mm. Uncrossed polars.

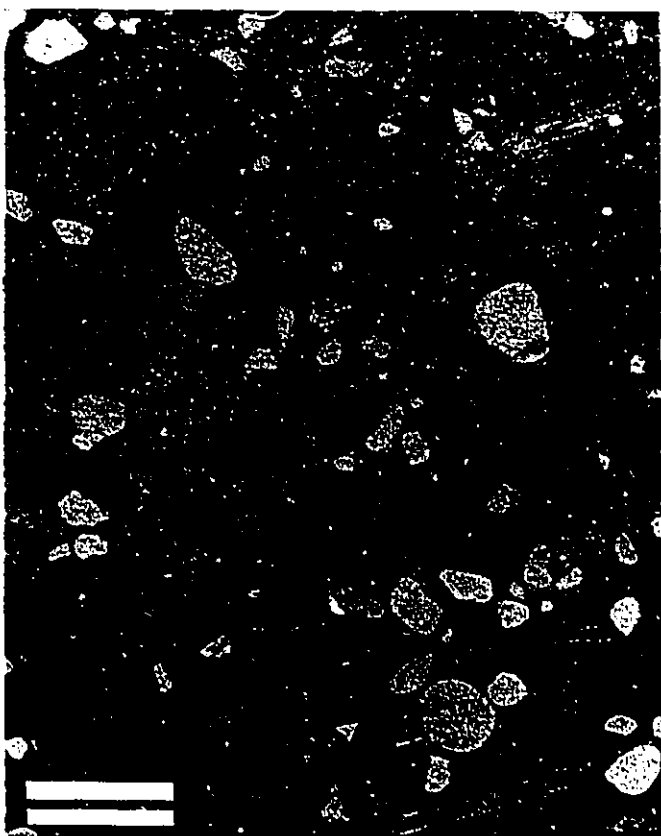


PLATE 32

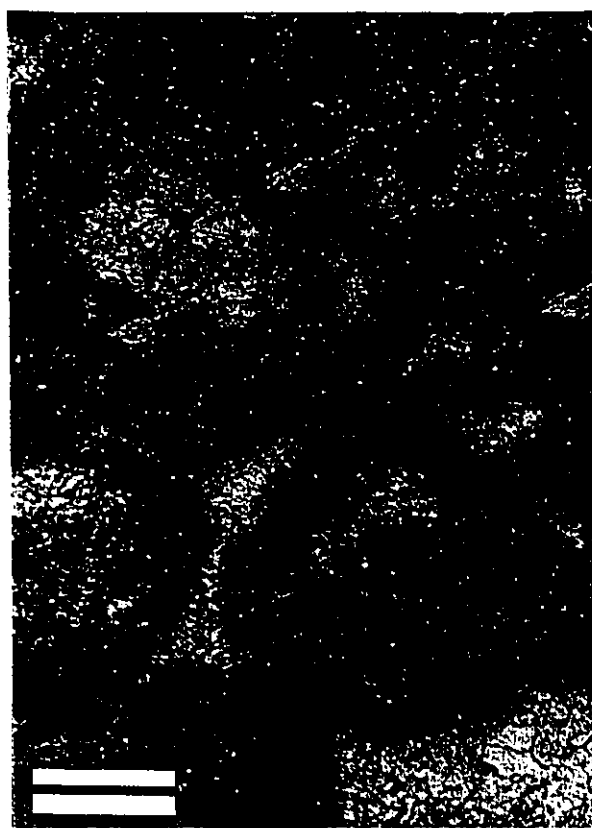


PLATE 33

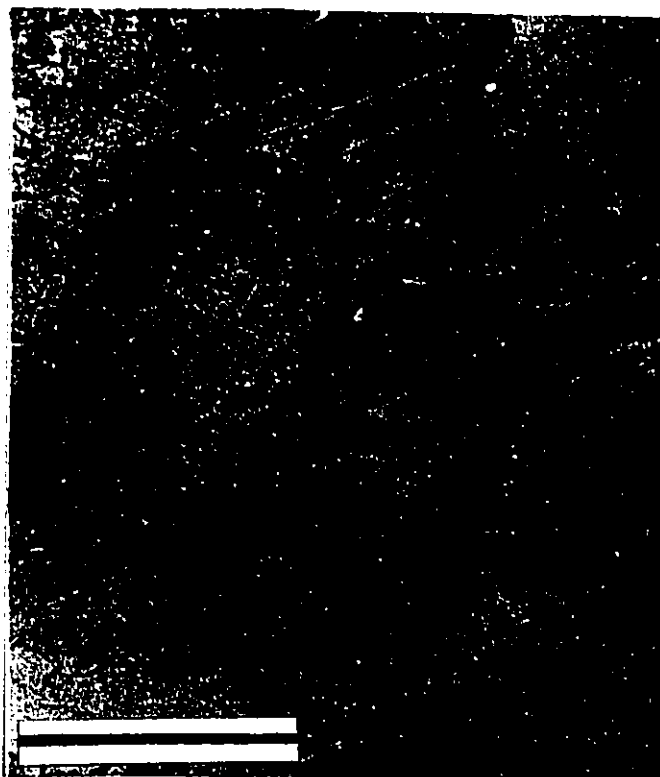


PLATE 34

Plate 35- Sample A-58b-85: Oncolitic and intraclastic dolostone layer underlain by numerous generations of cavity-filled dolospar and iron oxides. Observe the gravity (aragonitic?) cements now composed of radiating dolomite bundles enhanced by Fe-oxide coatings. Marine vadose diagenesis is suggested. Latest prismatic crystals in cavity possibly of deeper burial (or meteoric phreatic?) origin. Horizontal scale bar = 4.5mm. Uncrossed polars.

Plate 36- Sample A-17b-85: Radial fibrous to bladed dolomitic fans are associated with and stratigraphically underly oncolitic (Plate 23) and pisolitic? (Plate 24) occurrences. An early precipitative origin (of precursor high magnesium calcite?) is indicated by the erosion and deposition of the cement allochem (observed in the same thin section). Horizontal scale bar = 1mm. Crossed polars.

Plate 37- Sample A-71c-85: Oncolitic dolostone displaying the concentric nature of alternating coarser and finer dolomitic crystalline laminae. Note the "crown" fabric (A) composed of acicular-like (previously aragonitic?) dolomite crystals. Underlying the oncolite (just out of the field of view) is a dolomitic cement fan, hosting horizontal, early diagenetic chert laminae. Horizontal scale bar = 1mm. Uncrossed polars.



PLATE 35

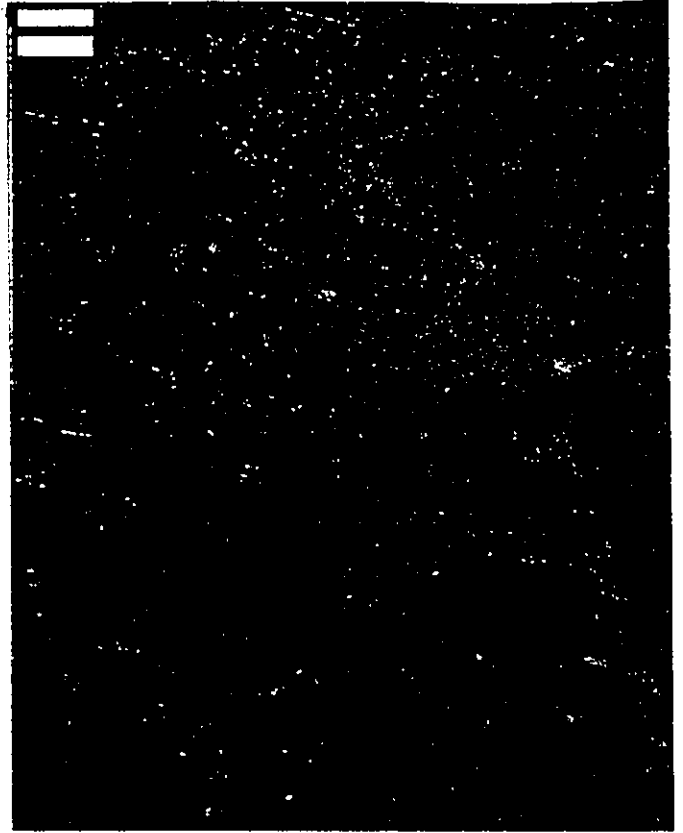


PLATE 37



PLATE 36

Plate 38- Magnification of silicified ooids in Plate 29. Compare the euhedral dolomite crystals within the silicified cortex with the subhedral ones in the center. This suggests a later dolomitization (post-silicification) episode for the former. Horizontal scale bar = 1mm. Uncrossed polars.

Plate 39- Sample A-82c-85: A medium coarser-crystalline dolostone hosting later dolomite within cavities. Idiomatic form, large size and zoned nature suggest later growth. Zoning reflects fluctuating pore water chemistry. Horizontal scale bar = 1mm. Uncrossed polars.

Plate 40- Sample A-30d-85: Photomicrograph of a reddish oolitic dolograinstone characterized by a recrystallized texture. Note the coarser crystalline nucleus versus the darker, finer cortex. Paragenetic sequence of cement as follows: (1) bladed dolospar, (2) iron oxides, (3) subhedral-euhedral dolospar and (4) central, late quartz precipitate. Horizontal scale bar = 1mm. Uncrossed polars.

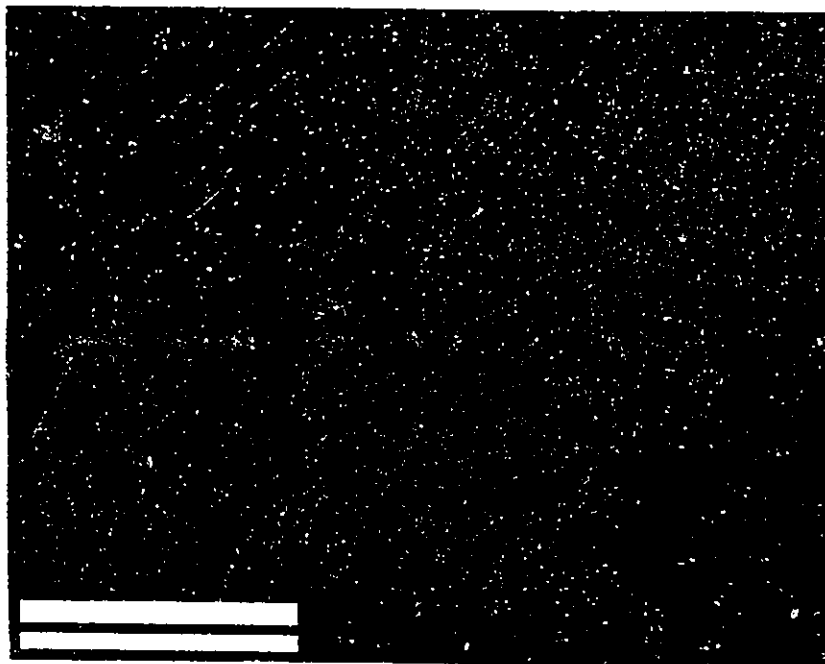


PLATE 38

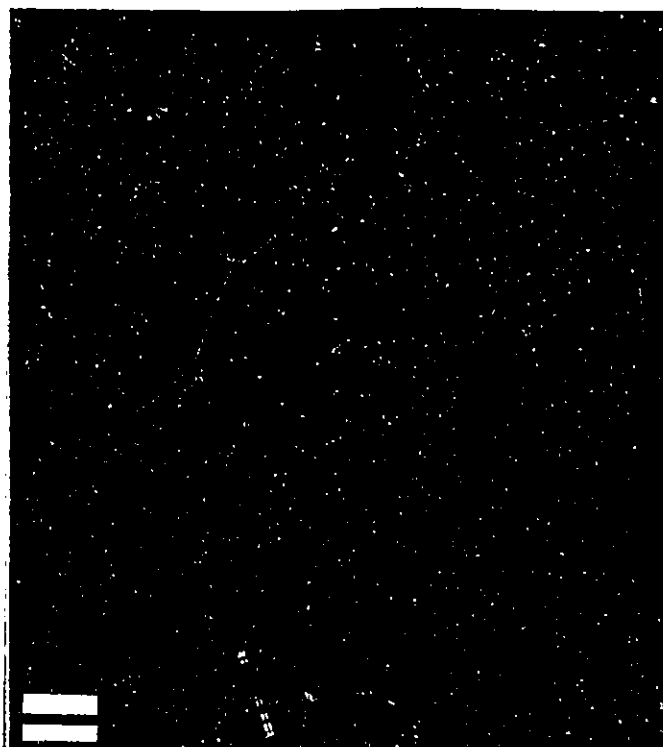


PLATE 39

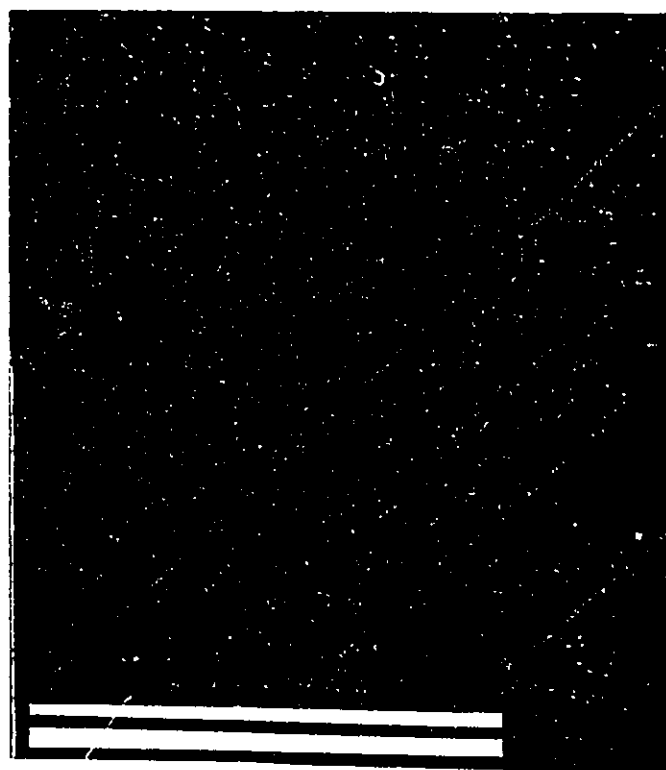


PLATE 40

Plate 41- Sample A-83-85: Oolitic-textured iron formation, stratigraphically overlying and near the Upper Albanel Formation contact. Ooids are composed of magnetite and minor hematite, set in a dominantly quartz matrix. Note the flattened nature of the ooids and the lack of concentric laminae distinguished by crystalline quartz. (1). A carbonate replacement origin is suggested by the presence of translucent rhombohedral crystals (2) partially replaced by hematite. Horizontal scale bar = 1mm. Crossed polars.

PYRITE SAMPLES

Plate 42- Sample D2-153-74: Early diagenetic pyrite nodule displacing sediment during growth. Note compaction features (stromatolite?). Fractured pyrite and secondary calcite with host inclusions are visible. Depth = 525 meters (L. Black Shale Complex).

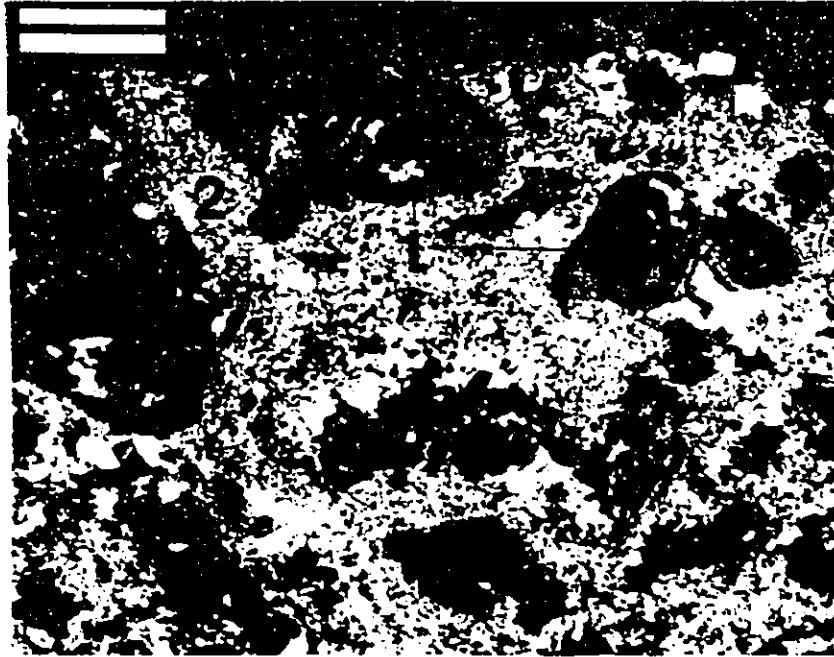


PLATE 41



PLATE 42

Plate 43- Sample D2-44-74: Early diagenetic pyrite mass, surrounded by a pressure shadow and exhibiting a pre-compaction feature. Core depth = 226.37 m (U. Banded Dolostone Unit). Horizontal scale bar = 1mm. Uncrossed polars.

Plate 44- Sample D2-151-74: Early diagenetic pyrite lense displacing sediment. Darker margins contain more host sediment, unlike the greater degree of coalescence in the center. Core depth = 526.82 m (L. Black Shale Complex). Scale is in millimeters.

Plate 45- Sample D2-98-74: Specimen hosting two apparent pyrite generations: (A) a fine-grained laminae associated with organics and (B) later (?) cubes $\pm$ associated with authigenic quartz. Core depth = 528.50 m (L. Black Shale Complex).

Plate 46- Sample D2-90-74: Radiating pyrite clusters (primary? or replacement?) surrounded by calcite and locally associated with organic streaks. Possible evidence of SO_4 -reduction? Core depth = 483.69 m (L. Black Shale Complex). Horizontal scale bar = 1mm.

PLATE 43

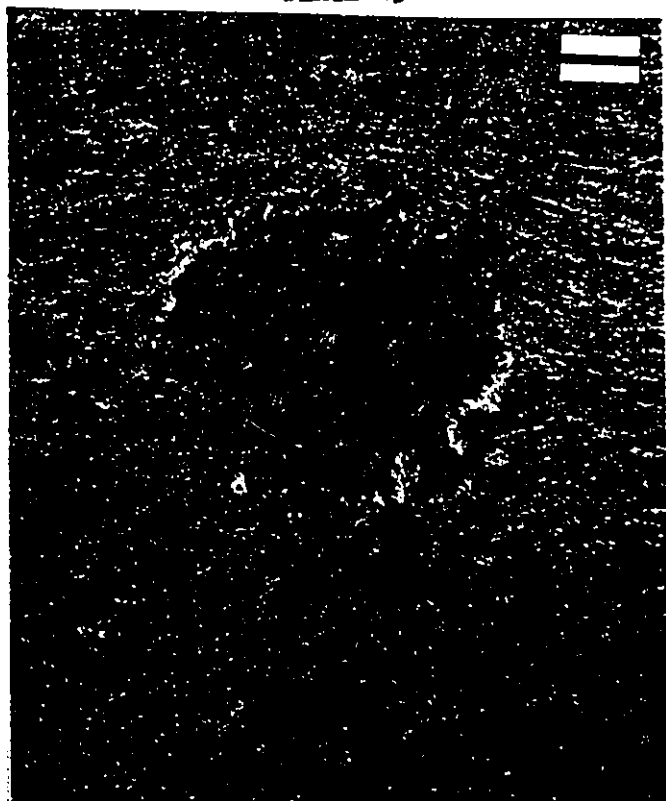


PLATE 44

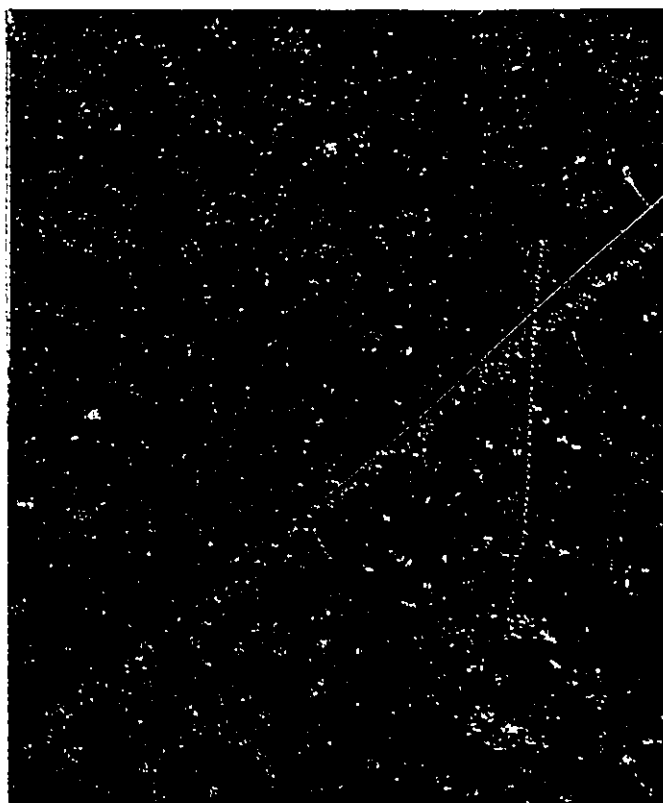


PLATE 45



PLATE 46

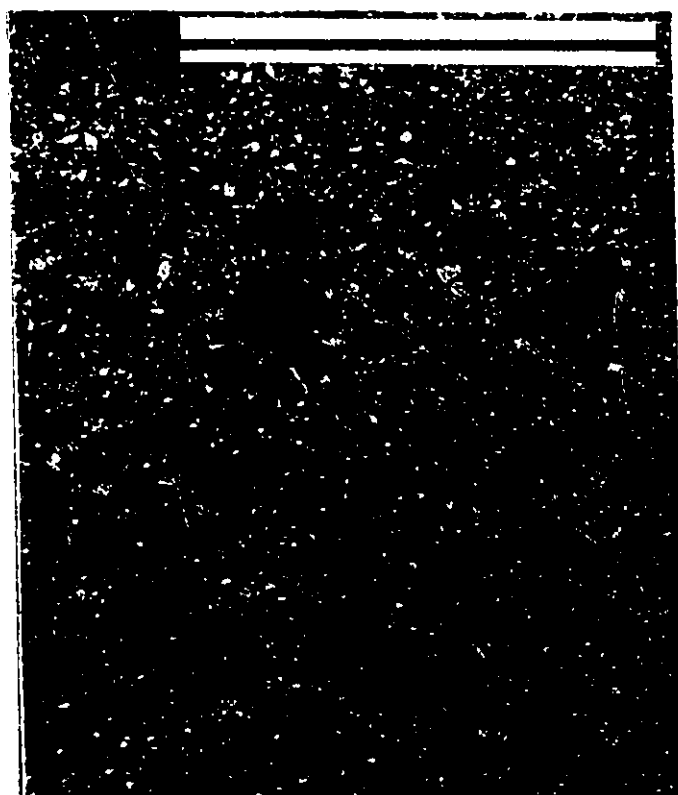


Plate 47- Sample D2-118-74: Cross-bedded pyritized dolostone showing an apparent water-escape structure. Note the sharp boundaries between pyrite and host and the excellent preservation of the sedimentary structures. Interpreted as interstitial pyrite precipitation along a redox front. Core depth = 34.29 meters (U. Black Shale Complex).

Plate 48- Sample D2-29-74: Photomicrograph of (one of two) large, later diagenetic pyrite cubes, characterized by euhedralism and incorporation of host during later growth. Core depth = 148.02 m (U. Banded Dolostone Unit). Horizontal scale bar = 1mm.

Plate 49- Sample D12-B-77: An example of paragenetically latest pyrite. Basal stromatolitic dolostone with fault-related pyrite and dolomite vein. The former precipitated first and may be related to the nature of the organic-bearing rocks. Core depth = 287.91 m. (Basal Stromatolite Dolostone Unit).

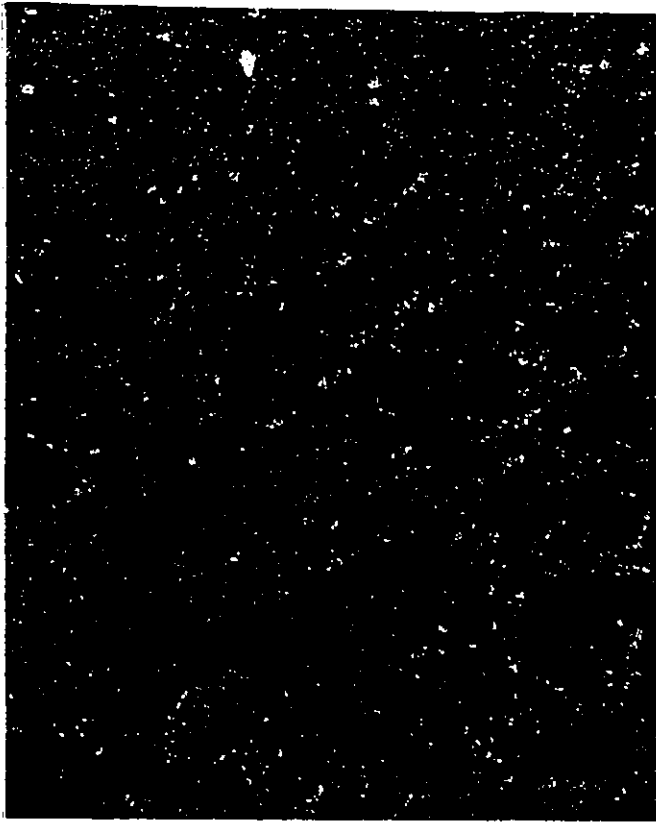


PLATE 47

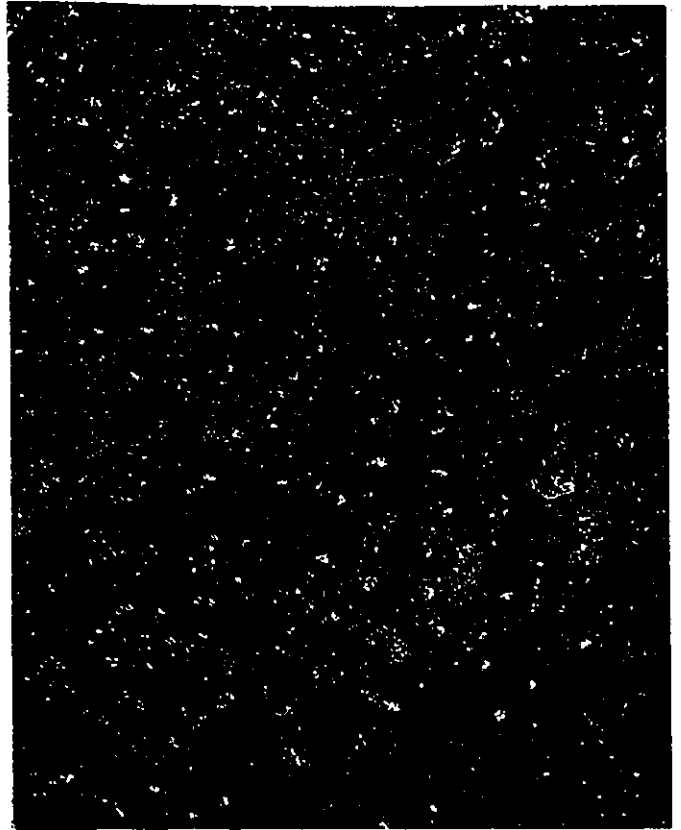


PLATE 49

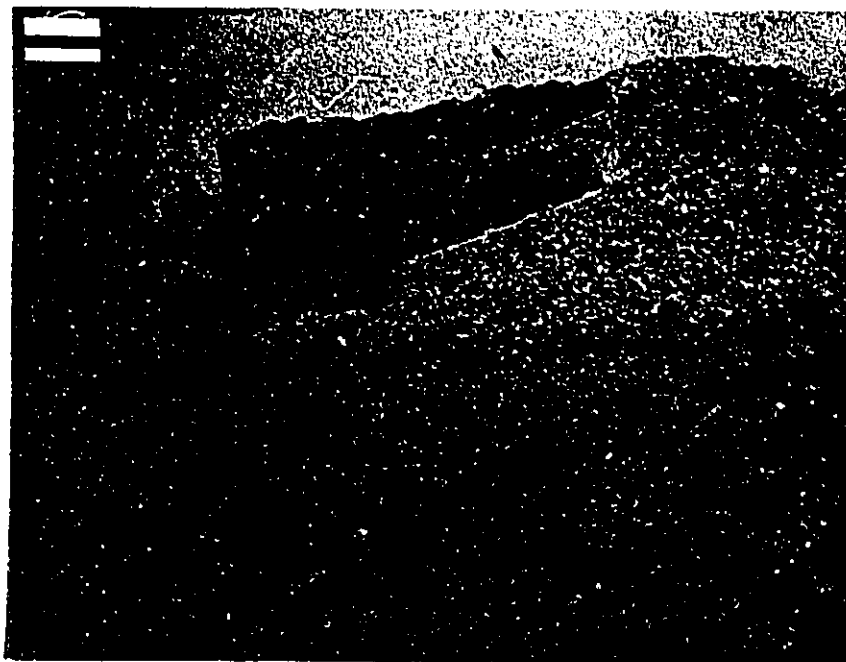


PLATE 48