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POLAROGRAPHIC DETERMINATION OF Pb AND Zn IN CARBONATE ROCKS

by

Ron Hartree

A thesis submitted to the School of Graduate Studies in partial fulfillment of the requirements for the degree of M.Sc. in Geology

UNIVERSITY OF OTTAWA

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...He said that all he had learned by his travels was that science only needed a spoonful of supposition to build a mountain of demonstrated fact out of; and that for the future he meant to be content with the knowledge that nature had made free to all creatures and not to go prying into the august secrets of the Deity.

From, Some Learned Fables for Good Old Boys and Girls.

Mark Twain.

ABSTRACT

Polarographic technique is proposed as a very sensitive and reasonably accurate method for the determination of trace concentrations of Pb and Zn in the carbonate portion of limestones and dolostones. The studied samples, mostly from Australia, cover the time span of 110 to 2700 Ma.

In order to avoid large contaminations from the non-carbonate portion of the rock, the samples were leached in weak (8% v/v) HCl and agitated continuously for 4 hours. The polarographic analysis was performed using "differential pulse" polarography in .2M ammonium citrate at pH 3 ± 0.1.

The geometric mean value of lead for both limestone and dolostone was found to be 3.1 ppm, and for zinc it was 4.2 ppm and 6.1 ppm respectively. These values are similar to published results. The main factor controlling Zn distribution in carbonates is mineralogy; dolostones have higher zinc concentrations than limestones. In limestones, the main controlling factor of Pb and Zn distribution is not understood but some secondary control is exercised by a weak secular trend for Zn and by insoluble residue for both Pb and Zn. In contrast, Zn in dolostones appears to be correlated with the presence of illite/muscovite and/or K-feldspar and Pb may be concentrated in reef-bank rather than lagoonal environments.

RESUME

La polarographie est une méthode d'analyse très sensible et raisonnablement précise pour déterminer des concentrations en trace de Pb and Zn dans la partie carbonate des calcaires et dolomies. Les échantillons proviennent surtout de l'Australie et couvrent la période de 110 à 2700 Ma.

Pour éviter d'importantes contamination par la partie non carbonate des roches, les échantillons furent dissous dans une solution diluée (8% v/v) de HCl et continuellement agités pendant 4 heures. La polarographie a pulsation différentielle dans une solution de citrate d'ammonium .2M et un pH de 3 ± 0.1 fût employer pour les analyses.

La concentration géométrique moyenne de plomb dans le calcaire et la dolomie est de 3.1 ppm, et la concentration moyenne de zinc est de 4.2 ppm et 6.1 ppm respectivement. Ces valeurs sont en accord avec les résultats publiés. La minéralogie est le facteur principal controllant la distribution de Zn dans les carbonates; les dolomies ont une concentration de zinc supérieure aux calcaires. Le facteur controllant la distribution de plomb et de zinc dans les calcaires n'est pas bien compris mais un control secondaire est excercé par une tendence séculaire du zinc et par le résidu insoluble pour le plomb et le zinc. En contraste, le zinc présent dans le dolomies semble être en correlation avec la présence d'illite/muscovite et/ou de felspath potassique et le plomb pourrait être concentrer dans les environments de cécifs plutôt que dans les lagons.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Aims of the Study

Typically composed of skeletal remains of marine organisms, most carbonate rocks are lithified by exposure to fresh water. The transition from carbonate sediment to carbonate rock is accomplished by changes in texture and mineralogy of the sedimentary particles. This mineralogic and textural stabilization is accompanied by changes in minor and trace element distributions.

The study of trace amounts of Pb and Zn in the soluble portion of carbonate rocks was undertaken because both Pb and Zn are divalent cations with ionic radii such that they can substitute for Ca and for Mg in lattice positions of calcite and dolomite. Specifically, it was hoped that the results may help to shed light on the following problems:

- the levels of Pb and Zn concentrations in average unmineralized limestones and dolostones in order to evaluate their suitability as possible source rock for carbonate hosted Pb/Zn deposits;

- to investigate whether any secular trends for Pb and Zn in carbonate rocks is displayed;

- to investigate whether factors such as the environment of deposition, textures and mineralogy control the distribution of Pb and Zn.

The samples utilized in this study cover a time span of 110 Ma (ie. 10^6 years) to 2700 Ma and their petrological description, geological setting and location, as well as chemical and isotopic composition have been previously reported (Veizer and Compston,

1974, 1976; Veizer and Hoefs, 1976; Veizer, 1977; Veizer and Garrett, 1978; Veizer, 1978).

Previous Work

The average published Zn concentrations for carbonate rocks vary with the method used for extraction of Zn from the rock and to some extent with location of samples. Wedepohl (1972), using analysis of total carbonate rock by XRF, calculated that the mean of Zn in marine limestones should be ~ 20 ppm, with approximately 10-15 ppm associated with their silicate portion. Graf (1960) estimated an average of 26 ppm Zn in total carbonate from evaluation of published data. Warren and Delavault (1961) found 18 ppm Zn using an "aqua regia" extract of 104 carbonates of Devonian, Silurian and Ordovician age from southern Ontario, Canada. These authors do not list the silicate component of their samples but, when obvious "shaly" carbonates are excluded, their mean (70 samples) is lowered to 12 ppm. This is still higher than results found by others, possibly due to the aqua regia attack, which may be leaching zinc from the insoluble portion of the rock. Renard (1975) in his study of Eocene hypersaline carbonates of the Paris Basin utilized 1N acetic acid on 10 g of sample at 55°C for 2 hours (a dilute attack similar in strength to the one described in this work) and determined Zn by A.A.S. His mean value for zinc, excluding samples which contain > 50% insoluble residue, is 4.7 ppm, which is comparable with present findings. Honjo and Tabuchi (1970) in their study of mostly Permian aged carbonate samples from Japan utilized 6 ml of 5.7N HCl on 1 gm of sample

acting overnight and determined Zn by A.A.S. Their mean value for Zn on 201 samples is 5.7 ppm. They also analysed carbonate samples of Permian age from Japan and of Pleistocene to Holocene age from Indonesia, south Taiwan and Japan. Their mean values for Zn are 8.2 (N = 10), 6.5 ppm (N = 4) and 2.5 ppm (N = 41) respectively. Pingitore (1978) extracted Zn from Pleistocene calcite corals of Barbados with 35 ml of 5% (v/v) HCl on 1 g of sample. His mean Zn value on 43 A.A.S. determinations is 19.6 ppm.

The average concentrations of Pb in carbonate rocks is 5 ppm (Wedepohl, 1974) and of this, 2 to 3 ppm would be contributed by the insoluble portion. Warren & Delavault (1961) found 3.8 ppm Pb using the above mentioned aqua regia attack. This lower sensitivity of Pb than Zn to non-carbonate contamination is due to the fact that an average shale or sandstone contains about 4 times less Pb than Zn (~ 25 vs ~ 100 ppm respectively; Wedepohl, 1972, 1974).

A polarographic technique was utilized in the present study because it was suspected that lead and perhaps zinc will be present in concentrations too low for reliable determination by flame A.A.S. Polarography was first developed by Heyrovsky (1926). Since then it has been developed into a powerful electro-chemical technique, which can routinely measure concentrations in the 10^{-12}M region for a number of ions in solution. Geological applications of polarographic technique include determination of uranium in various ores (Bond et al,

1974; Martres and Burastero, 1971; Batly, 1970); simultaneous determination of ferrous, ferric and total iron in silicate rock standards (Beyer et al, 1975), and determination of copper, nickel and cobalt in cobalt mineral concentrates and mine tailings (Hitchen, 1954).

The technique discussed in the present work was developed by the author for the simultaneous determination of Pb and Zn in the carbonate portion of carbonate rocks.

Acknowledgements

I would like to thank my research supervisor, Dr. Ján Veizer, for his patient guidance, particularly during the write-up of this thesis; Mr. A. Hitchen for his advice in setting up and instruction on the use of the polarograph; Dr. B. E. Conway and Dr. G. Armbrust for serving on my research committee; Estelle Forgues for excellent typing of the manuscript; and finally to my wife Mary, for her encouragement during the research as well as the write-up of the manuscript.

ANALYTICAL PROCEDURES AND TECHNIQUES

Sample Preparation

The studied samples are outcrop specimens, cleaned of all weathered surfaces, and powdered to ≤ 200 mesh in a tungsten carbide dish (Veizer, personal communication, 1977).

The powdered samples were dried for 1 hour at 110°C and cooled in a desiccator for ~30 minutes. Approximately 2 g of sample was accurately weighed then placed in a 125 ml Erlenmeyer flask (all glassware was cleaned overnight in 6M HNO_3 to remove adhering metals; PAR Technical note TN 109A), to which 50 mls of 8% HCl was added. The sample was slowly agitated on a sample shaker for 4 hours (see the following sections). Then the samples were filtered through Whatman 40 paper and rinsed with 50 mls of deionized-distilled water into 250 ml beakers.

The insoluble residue (I.R.) was ashed at ~ 950°C for 3 hours in a muffle furnace and determined gravimetrically.

Selection of Leaching Conditions

A diagenetically stabilized carbonate rock is composed from ≤ 50% of carbonate minerals (Folk, 1974, p. 168); with calcite and/or dolomite as the dominant and ankerite ($Ca(MgFe)(CO_3)_2$) and siderite ($FeCO_3$) as the most frequent subordinate phases (Pettijohn, 1975, p. 323-324). Strontianite ($SrCO_3$), cerussite ($PbCO_3$), witherite ($BaCO_3$), rhodochrosite

($MnCO_3$), smithsonite ($ZnCO_3$), and others can be present in trace amounts (Ellingboe and Wilson, 1964). The non-carbonate fraction, comprising up to 50% of the total rock, is composed of clay minerals (~10% in an average limestone; Wedepohl, 1971, p. 152), silica, aluminosilicates, gypsum, anhydrite, some sulfides (generally pyrite), glauconite and collophane (Pettijohn, 1975, p. 325-326). In order to study trace elements in the carbonate minerals, it is necessary to separate the carbonate from the non-carbonate portion. The separation procedure utilized in this study is a weak acid leach of the carbonate minerals because mechanical separation, due to the extremely fine-grained nature of the samples, would be very difficult if not impossible.

In a previous study of dissolution of possible mineral constituents of carbonate rocks, Ellingboe and Wilson (1964), using a 100% excess of 10% v/v HCl, demonstrated the following relationships: a) calcite, strontianite, cerrusite and witherite are completely dissolved in 2 hours; b) 72% of siderite is in solution after 4 hours and 98% after 24 hours; c) 98% of dolomite, rhodochrosite and ankerite is also dissolved in 24 hours; d) 50% of montmorillonite is in solution after 24 hours; e) pyrite, illite and kaolinite are insoluble at this HCl concentration. Dreimanis (1962) has shown, using 20% HCl with continuous agitation, that 95% of dolomite is dissolved within 15 to 45 minutes.

Chemical separation of the carbonate minerals will cause some leaching of elements from the non-carbonate fraction but the selection of a dilute acid leach should minimize this effect. Furthermore, consideration of the covariance of Pb and Zn with Al, the latter derived clearly by leaching from the insoluble residue, enables us to estimate the relative amount of aluminosilicate leaching that has taken place.

Since the aim of the present study is to measure Pb and Zn distribution in Ca-Mg carbonate phases, a 4% excess of 8% v/v HCl (calculated for total sample as $CaCO_3$) was utilized for leaching purposes. Figure 1 shows that, under constant agitation, both limestone and dolostone reach a plateau for Zn as well as Pb within 1 hour. The absence of further increase in Pb or Zn concentrations with increasing leaching period is due to a) weak acid, which is apparently not dissolving Fe carbonate and aluminosilicate constituents; b) utilization of most of the acid for dissolution of Ca-Mg carbonates (and sulfates if present) with only small excess left for reaction with Fe carbonate and aluminosilicates; c) general absence of reactive montmorillonite, which is not known to be a common constituent in carbonate rocks (Robbins and Keller, 1952; Pettijohn, 1975, p. 325); d) combination of the above.

On the basis of these experiments and from consideration of the results of Ellingboe and Wilson (1964) and Dreimanis (1962) a 4 hour leaching time was chosen. This appears sufficient for dissolution of Ca-Mg carbonates while leaving the

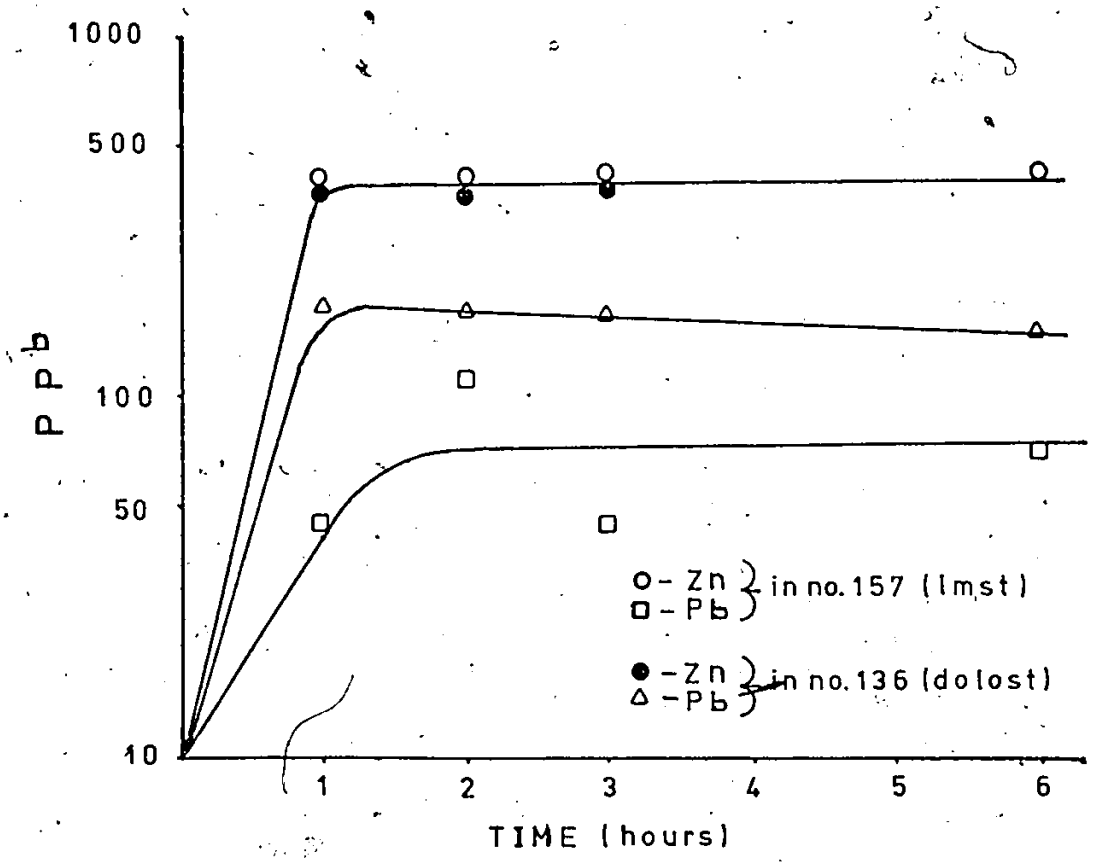

Figure 1 - Dependence of Pb and Zn concentration on leaching conditions.

aluminosilicate fraction and siderite relatively intact, ie. without undue leaching.

Polarography

A PAR model 174 polarograph in differential pulse mode and an H-type Sargent-Welch polarographic cell were employed. One arm of the cell contained a saturated calomel reference electrode (SCE) prepared after Meites (1955, p. 21-22) and the whole cell was submerged in a constant temperature bath set at $25^{o}C \pm 1^{o}C$

The supporting electrolyte was a 0.2M ammonium citrate solution adjusted with ammonium hydroxide to pH 3.0 $\pm$ .1 (PAR application brief W-1). The peak potential ($E_{\frac{1}{2}}$) of lead (II) is -0.43V and of zinc(II), -1.03V vs SCE.

A cursory investigation of possible interfering elements revealed that Fe(III), Fe(II), Co(II), Mn(II) were not reduced between -0.1 and -1.15V. V(V), V(IV), Mo(II), U(IV), Cr(V), Ti(II), although reduced between these potentials, will not interfere with the lead peak unless present in much greater amounts than normally found in calcite or dolomite. Similarly, Ni(II) and Cr(III) will not interfere with the zinc peak unless present in amounts 2 or 3 times that of zinc. This rarely occurs in carbonate minerals. Co(II), the element which interferes most with Zn(II), is not reduced in this supporting electrolyte.

Concentrations (in ppm) of lead and zinc in the sample solutions were calculated from peak heights at $E_{\frac{1}{2}}$ using standard curves prepared by spiking a 'typical' rock solution with known amounts of lead and zinc. To convert ppm in solution to ppm in the rock the following formula was used:

$$\frac{\text{ppm in solution} \times 25 \text{ (dilution in mls)}}{\text{weight of sample (g)}} = \text{ppm in rock}$$

Transfer of Sample to Supporting Electrolyte

The filtrate was transferred to a warm (~75°C) hot plate and evaporated to near dryness. This drying procedure was crucial. If the sample was allowed to dry too much it became brown colored, almost burnt looking, and would not dissolve properly in the supporting electrolyte. The proper looking product, requiring generally 14-16 hours evaporation, was a yellow gelatinous residue with a thin white crust which, in most cases, had an almost "pearly" luster. The yellow gelatinous residue, after cooling to room temperature, was dissolved in 10 mls of supporting electrolyte (.2M ammonium citrate pH = 3.0 ± .1) forming a clear (sometimes slightly cloudy) yellow liquid which was transferred into a 25 ml volumetric flask. The beaker was rinsed thoroughly with small (2 to 5 ml) portions of ammonium citrate and this was added to the volumetric flask. The pH of this solution was adjusted back to 3.0 ± .1 with concentrated ammonium hydroxide and the flask filled to the mark with supporting electrolyte.

Since the sample-ammonium citrate mixture degrades with time forming, in some cases, a white precipate after approximately an hour; ammonium citrate was added to the sample just prior to polarographic measurement. After pipeting 10 mls of sample-ammonium citrate solution and 10 minutes of deoxygenated N_2 aeration, the sample was polarographed.

Because of the relative instability of the sample-supporting electrolyte mixture the samples were analysed in batches of 12 (e.g. 10 specimens, 1 duplicate and 1 blank).

Recovery and Precision

Due to the absence of data for the soluble carbonate portion of geological reference rocks, an estimate of accuracy of the analytical technique was derived by spiking six sample powders, two dolostones and four limestones, with known amounts of Pb and Zn. The unspiked and spiked samples were digested and analysed as described in 'Sample Preparation' and 'Transfer of Sample to Supporting Electrolyte' sections. The measured concentrations of the spike, calculated as a difference between the spiked and unspiked aliquots and marked "recovery" are given in Table 1. The recovery for lead was 100±10%; for zinc 100±5% of the amount used to spike the sample powders. The precision of the technique, based on 58 replicate results is: ± .2 ppm in the 0-6 ppm range and ± .7 ppm in the 6-30 ppm range for Zn; and ± .2 ppm in the 0-6 ppm range and ± .4 ppm in the 6-12 ppm range for Pb (for calculation of precision see Crow et al., 1960).

Table 1- Recovery of Pb and Zn

Sample No.	Rock Type	Lead			Zinc		
		Conc. of spike added (ppb)	Recovery (ppb)	% Difference	Conc. of spike added (ppb)	Recovery (ppb)	% Difference
31	Dolomitic-Limestone	400	486	+21	400	415	+4
60	Limestone	300	329	+10	200	197	-2
14	Limestone	200	223	+11	400	424	+6
116	Limestone	400	422	+ 6	600	623	+4
82	Limestone	100	97	- 3	200	187	-7
168	Dolostone	200	221	+10	600	623	+4
			Average:	±10%			±5%

SAMPLE DESCRIPTION AND PREVIOUS ANALYTICAL DATA

The present study concentrates on lead and zinc distribution in the soluble portion of carbonate rocks. The samples cover the time range from 110 Ma to ~2800 Ma and are predominantly from Australia. Petrological descriptions (following Folk, 1959, 1962), geological information and location for all samples, taken from Veizer and Compston (1974, 1976) and Veizer and Hoefs (1976), are listed in Appendix 1. These publications also describe the secular trends of the $^{87}Sr/^{86}Sr$, $^{18}O/^{16}O$ and $^{13}C/^{12}C$. Sr elemental data are discussed in Veizer (1977). Major element composition of the samples studied is on file at the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2 (Veizer and Garret, 1978). These data are discussed in Veizer and Garrett (1978) (alkali metals) and Veizer (1978) (Ca, Mg, Fe, Mn, Si, P and Ti). In addition, Cambrian and Precambrian samples were analysed for C (organic) and S (Gustafson, L. B. and Veizer, J., unpublished). These measurements were available to the present author for evaluation of the possible role of C_{org} and S on the distribution of Pb and Zn in carbonate rocks.

DISTRIBUTION OF LEAD AND ZINC IN CARBONATE ROCKS

Average Concentrations

The concentration of Pb and Zn in the soluble portion of carbonate rocks (recalculated to 100% carbonate) as well as the insoluble residue content are summarized in Appendix 2. Evaluation of the recalculated results suggests that their concentrations are lognormally distributed. In order to test this assertion a χ^2 (goodness of fit) test (Crow et al, 1960, p. 87) was applied to the log transformed data. It was found, at the 95% level of significance, that for both Pb and Zn in limestone and dolostone the log transformed data satisfy the Gaussian distribution (cf. Figure 2a and b). The lognormal distribution of trace elements in geological specimens is apparently a rule rather than an exception and the matter was discussed in Ahrens (1954). These histograms include all analysed limestones and dolostones. However, two samples with very high Zn concentrations (No 161 with 113 ppm and No. D107 with >400 ppm Zn respectively) and two samples with exceptionally low lead values (No D139 and No D181 with <0.1 ppm Pb) were eliminated from further consideration by Chouvenet's criterion that their probability of occurence was less than $\frac{1}{2}$ N, where N is the number of observations in the population (Worthing and Geffner, 1943, p. 170). The geometric means of Zn concentration for these corrected limestone and dolostone populations

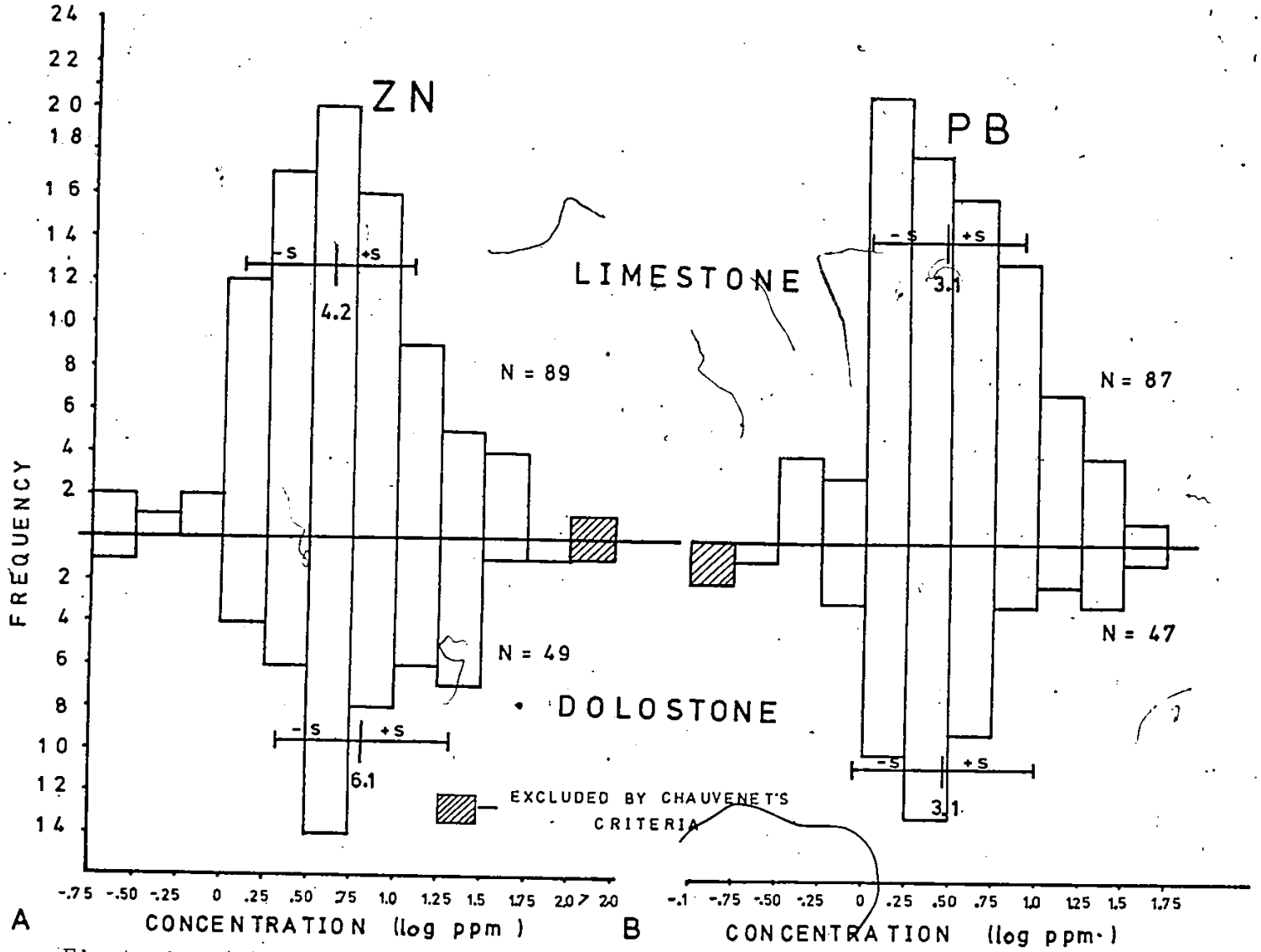

Figure 2 - (A) Zn distribution in the soluble portion of carbonate rocks. Zn values recalculated on 100% carbonate basis.

(B) Pb distribution in the soluble portion of carbonate rocks. Pb values recalculated on 100% carbonate basis.

are 4.2 ppm and 6.1 ppm respectively; and for Pb, they are 3.1 ppm and 3.1 ppm respectively (cf. Figures 2a and 2b). Subsequent statistical evaluation was based on the corrected populations utilizing the SPSS (Nie et al, 1975) version H, release 8A, August 1978, for an IBM 360/65 computer.

The Role of Mineralogy

Pb^{2+} and Zn^{2+} can substitute for either Mg^{2+} or Ca^{2+} in the lattice of calcite or dolomite (Graf, 1960; Deer, Howie and Zussman, 1967, p. 478, p. 489; Berry and Mason, 1959, p. 405, p. 411). Consideration of the rules of ionic substitution (Krauskopf, 1967, p. 463) suggests that, due to their divalent positive charge and ionic radii ($Pb^{2+} = 1.20 \times 10^{-8}$cm, $Zn^{2+} = .74 \times 10^{-8}$cm, $Ca^{2+} = .99 \times 10^{-8}$cm, $Mg^{2+} = .66 \times 10^{-8}$cm), it would be expected that limestone should contain higher Pb^{2+} and lower Zn^{2+} concentration than dolostone and vice versa; other things, such as availability of these ions, being equal.

The above inference appears to be in accord with the observed Zn data (cf. Figure 2a, Table 2). The F-test and t-test (cf. Nie et al, 1975, chapter 17) show that both mineralogical groups have similar variance, but their geometric means are different at the 95% confidence level (Table 2). This statistical difference notwithstanding, the observed difference in mean concentrations is less than expected. Contrary to expectations, Pb distribution in limestones and dolostones has similar variance as well as mean concentrations. Due to the

discussed difference in Zn concentrations of limestones and dolostones, the log of Pb/Zn ratio shows a distribution pattern similar to that of Zn (Table 2).

The relative mineralogical insensitivity of Pb and Zn concentrations is difficult to reconcile with crystallochemical considerations. If correct, it may suggest that a considerable proportion of the measured Pb and Zn are associated with the non-carbonate portions of the rocks and incorporated into the soluble fraction either during acid digestion of the samples or by their release during diagenetic breakdown of detrital minerals. Alternatively, it may be that limestones and dolostones are, by themselves, very heterogeneous groups, each containing many facies as well as samples of vastly different ages. To avoid possible underestimation of the role of mineralogy it is necessary to evaluate the influence of a) insoluble residue, (I.R.), b) facies, and c) petrographic types on Pb and Zn distributions. Furthermore, d) the role of secular variations and e) the effect of organic C and of S will be discussed.

Table 2- F and t-test of Zn, Pb and Pb/Zn in dolostones and limestones. Variables are in log units.

Variable		Number of Cases	Mean	Standard Deviation	F Value	2-Tail Prob.	t Value	Degrees of Freedom	2-Tail Prob.
Zn									
	Group 1	48	0.7866	0.431	1.24	0.427	1.99	134	0.048
	Group 2	88	0.6208	0.480					
Pb									
	Group 1	45	0.4928	0.447	1.09	0.709	-0.04	130	0.968
	Group 2	87	0.4960	0.427					
Pb/Zn									
	Group 1	43	-0.3122	0.422	1.23	0.466	-2.27	127	0.025
	Group 2	86	-0.1196	0.468					

Group 1 = dolostones

Group 2 = limestones

CONTROL OF LEAD AND ZINC DISTRIBUTION IN CARBONATE ROCKS

Introduction

In order to evaluate the role of the insoluble residue, facies and secular variation on the distribution of Pb and Zn, the measured concentrations were combined with reported petrographic (Veizer, 1971), chemical (Veizer, 1977, 1978; Veizer and Garrett, 1978) and isotopic (Veizer and Compston, 1974, 1976; Veizer and Hoefs, 1976) data on the same samples and subjected to R-mode factor analysis with PA2 procedure (ie. principle factoring with iteration) and Varimax rotation (Nie, et al, 1975; chapter 24). The effect of petrography and facies were further evaluated using Student t-tests and the effect of secular variation as well as S and organic C were evaluated using interelement correlation coefficients (r).

The purpose of factor analysis is to interpret the structure within the variance-covariance matrix of a multivariate data set. First developed in the 1930's and 1940's by experimental psychologists, factor analysis is now used commonly in geological and biological applications (Davis, 1973, p. 475). Cameron (1968, 1969) used factor analysis to interpret the genesis of the Swan Hill Reef and Slave Point carbonates in west central Alberta. He found that the use of factors with low eigenvalues, which are generally unique (ie. heavily weighted on a specific variable), aided greatly in the interpretation of the data. Miesch et al (1966) used

factor analysis to interpret the genesis of tektites from east central Texas. In order to alleviate the restraints imposed on the data by the fact that constituents within each specimen sum to 100% (Chayes, 1960), Miesch et al used correlations among the ratios of constituent/SiO_2 for extration of factors.

Pingitore (1978) used factor analysis in his study of the behavior of Zn^{2+} and Mn^{2+} during carbonate diagenesis.

The problem of closed arrays of data with each row representing a specimen and having a constant sum of 100% (Chayes, 1960) is not considered to be dominant in the present study because of the following considerations:

1) the sum is not 100%, because of the addition of isotopic ratios and because of inaccuracies inherent in any analytical data set;

2) Pb and Zn are normalized to 100% carbonate basis, thus removing them from a closed array for the major and minor elements;

3) the aim of this study is to investigate which phase (in carbonate or non-carbonate portion) controls the distribution of Pb and Zn and not the genetic implications in the formation of various phases.

The results will be discussed separately for limestones and dolostones and proceed through the following sequence of variables: (i) insoluble residue, (ii) facies, (iii) petrography, (iv) secular variations, and (v) effect of C and S.

Limestones

The total combined variation in limestones can be explained by 5 factors, with the first one explaining 65.1% of the variation (Table 3). The factors can be identified as:

Factor 1: non-carbonate fraction of the rocks (quartz and undifferentiated aluminosilicates);

Factor 2: Pb^{2+} and Zn^{2+};

Factor 3: secular variations in chemical composition of carbonates exemplified by $\delta^{18}O$ (cf. Veizer and Hoefs, 1976);

Factor 4: carbonate facies (hypersaline versus normal marine); and

Factor 5: dolomitization.

The factor analysis presented here is a very good indicator of the distribution of Zn in limestones because 98% of the variance in Zn is explained by the varimax rotated factor matrix (cf. communality, Table 3). On the other hand only 37% of the variance in Pb is explained by these factors; this means that 63% of the variance is explained by something else, perhaps a unique factor. By lowering the eigenvalue (Cameron, 1967) to .2; thirteen factors were extracted, none of which was a unique Pb factor. Attempts to extract more factors, by the PA2 procedure, were unsuccessful because after the first iteration the communality of one or more of the variables exceeded 1.0 and PA2 factoring can not be done under this circumstance.

The importance of this factor identification for the distribution of Pb and Zn (in view of the variables (i) to (v) above) will be discussed in the subsequent sections.

(i) Insoluble Residue

The prime factor controlling 65.1% of the total chemical and isotopic variation in limestones (Table 3) is the non-carbonate fraction of the rocks. The loading on factor 1 suggests that detrital quartz (cf. Veizer, 1978) and clay minerals explain a larger part of this factor. The loading of Pb and Zn on this factor is small. This is borne out by examination of the correlation matrix (Table 4), which shows that although Zn correlates positively and significantly, at the 99% confidence level, with TiO_2 (r = .405), P_2O_5 (r = .303), Al_2O_3 (r = .370), Na_2O (r = .378), and Rb (r = .293), the observed correlations are weak. Similarly Pb correlates weakly with TiO_2 (r = .330) and Na_2O (r = .389) only. This suggests that some components in the insoluble residue may exert a secondary control on Zn and Pb distribution in limestones, but the primary control must be exerted by other phenomena. This observations is consistent with the somewhat higher correlation of Pb with Zn (r = .475; Table 4) and with the fact that the major loadings on factor 2, which controls 13.1% of the total variation, are by Zn and Pb with lesser contribution by P_2O_5 and Na_2O (cf. Table 3). It cannot be excluded that factor 2 could be related to the analytical technique used to separate Pb and Zn from the insoluble residue, although the author is not able to find a reason why this should be the case.

Table 3-

Varimax rotated factor matrix for limestones. Variables (except $^{87}Sr/^{86}Sr$, $\delta^{18}O$ and $\delta^{13}C$) are in log units.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
Zn	0.167	0.934	-0.244	0.028	0.158	.98
Pb	0.153	0.524	0.246	-0.076	0.040	.37
FeO	0.682	0.147	0.369	0.187	0.400	.81
Fe_2O_3	0.587	0.294	0.415	-0.045	-0.128	.62
MnO	0.329	0.140	0.466	0.010	-0.023	.34
TiO_2	0.843	0.286	0.153	0.169	0.201	.88
K_2O	0.866	0.023	0.145	-0.052	0.070	.78
P_2O_5	0.193	0.317	0.030	-0.124	-0.026	.17
SiO_2	0.870	0.149	0.251	-0.173	0.015	.87
Al_2O_3	0.895	0.267	0.109	0.156	0.059	.91
MgO	0.094	-0.025	-0.171	0.081	0.604	.41
CaO	-0.675	-0.200	-0.044	0.223	-0.609	.92
Na_2O	0.576	0.310	0.222	0.320	0.404	.74
CO_2	-0.770	-0.281	-0.073	0.147	-0.255	.76
Rb	0.942	0.110	0.060	0.134	0.088	.93
Sr	0.177	-0.037	-0.037	0.847	0.151	.76
$^{87}Sr/^{86}Sr$	0.240	0.177	0.232	-0.458	0.094	.36
$\delta^{18}O$	-0.168	0.151	-0.744	0.028	0.042	.61
$\delta^{13}C$	-0.057	-0.076	-0.498	0.159	0.202	.32
IR	0.903	0.100	0.273	-0.171	0.033	.93
% of variation	65.1	13.1	10.1	6.6	5.1	

Table 4-

Correlation coefficients (r) for Pb and Zn with major, minor and trace elements in limestones. Variables (except $^{87}Sr/^{86}Sr$, $\delta^{18}O$ and $\delta^{13}C$) are in log units.

	Zn	Pb
Zn	1.000	0.475
Pb	0.475	1.000
FeO	0.224	0.237
Fe_2O_3	0.261	0.235
MnO	0.112	0.239
TiO_2	0.405	0.330
K_2O	0.140	0.259
P_2O_5	0.303	0.190
SiO_2	0.223	0.269
Al_2O_3	0.370	0.260
MgO	0.144	-0.102
CaO	-0.374	-0.232
Na_2O	0.378	0.389
CO_2	-0.384	-0.341
Rb	0.292	0.239
Sr	0.065	-0.081
$^{87}Sr/^{86}Sr$	0.185	0.261
$\delta^{18}O$	0.287	-0.179
$\delta^{13}C$	0.127	-0.150
IR	o.170	0.235

(ii) Facies

High Na and Sr concentrations are generally typical of hypersaline facies (Veizer et al, 1977, 1978; Veizer and Garrett, 1978). This suggests that the weak factor 4 (Table 3), explaining 6.6% of the total variation in limestones, is related to facies. Neither Pb nor Zn are highly weighted on this factor suggesting that distribution of these elements is not facies controlled.

To verify this assertion limestones from the two main environmental groups studied, lagoonal and reef-bank were tested for differences in mean concentration of Pb and Zn. Table 5 shows that the means of Pb and Zn are not significantly different at the 95% confidence level.

(iii) Petrography

Samples of micrite and sparite (cf. Appendix 1) from comparable depositional and diagenetic environments were tested for differences in their mean concentrations of Pb and Zn. Tables 6 and 7 show that in both lagoonal and reef-bank facies the means for micritic and sparitic types are not statistically different at the 95% confidence level.

(iv) Secular variation in Zn and Pb concentrations in limestones

Factor 3 is interpreted as secular variation in the chemical composition of limestones, particularly because of the high $\delta^{18}O$ loading (Veizer, 1978; Veizer and Hoefs, 1976). The loading of Zn on this factor is small, however zinc in limestone does

Table 5- F and t-test of Zn and Pb in lagoonal and reef-bank limestones. Variables are in log units.

Variable	Number of Cases	Mean	Standard Deviation	F Value	2-Tail Prob.	t Value	Degrees of Freedom	2-Tail Prob.
Zn								
Group 1	37	0.6097	0.439	1.17	0.641	-0.14	79	0.892
Group 2	44	0.6236	0.474					
Pb								
Group 1	36	0.5686	0.366	1.70	0.107	1.04	78	0.302
Group 2	44	0.4679	0.477					

Group 1 = lagoonal limestones

Group 2 = reef-bank limestones

Table 6- F and t-test of Zn and Pb in micritic lagoonal and sparitic lagoonal limestones. Variables are in log units.

Variable		Number of Cases	Mean	Standard Deviation	F Value	2-Tail Prob.	t Value	Degrees of Freedom	2-Tail Prob.
Zn									
	Group 1	26	0.6748	0.424	1.15	0.731	1.40	35	0.169
	Group 2	11	0.4559	0.456					
Pb									
	Group 1	25	0.5574	0.297	2.88	0.033	-0.27	34	0.787
	Group 2	11	0.5939	0.505					

Group 1 = lagoonal limestones -micritic

Group 2 = lagoonal limestones -sparitic

Table 7- F and t-test of Zn and Pb in micritic reef-bank and sparitic reef-bank limestones. Variables are in log units.

Variable	Number of Cases	Mean	Standard Deviation	F Value	2-Tail Prob.	t Value	Degrees of Freedom	2-Tail Prob.
Zn								
Group 1	27	0.6111	0.517	1.59	0.339	-0.22	42	0.829
Group 2	17	0.6434	0.411					
Pb								
Group 1	27	0.4051	0.431	1.58	0.293	-1.10	42	0.277
Group 2	17	0.5676	0.542					

Group 1 = reef-bank limestones - micritic

Group 2 = reef-bank limestones - sparitic

show a weak, but significant at the 99.9% confidence level, negative correlation with age ($r = -0.342$, Figure 3). The weak secular trend for Zn is evident whether the normal or log-normal time scale is utilized. In contrast Pb does not show any secular variations with age ($r = .004$). This evaluation suggests that age related phenomena may exercise weak secondary control on Zn concentrations and no control at all on Pb concentrations in limestones.

(v) S and organic Carbon

The Cambrian and Precambrian limestone samples ($N = 36$), for which S and organic C data were available, were evaluated for the possible control of these variables on Pb and Zn distribution. The correlations of Pb and Zn with sulfur are not significant at the 95% confidence level, suggesting that sulfur content is probably not exercising any control on Pb and Zn distribution in limestones older than 600 Ma.

Organic carbon, on the other hand, does show negative correlation, at the 95% confidence level, with Pb ($r = -.322$). The meaning of this weak negative correlation is not understood. Zinc and organic carbon do not correlate significantly.

Dolostones

The total combined variation in dolostones can be explained by six factors (Table 8). These factors are interpreted as:

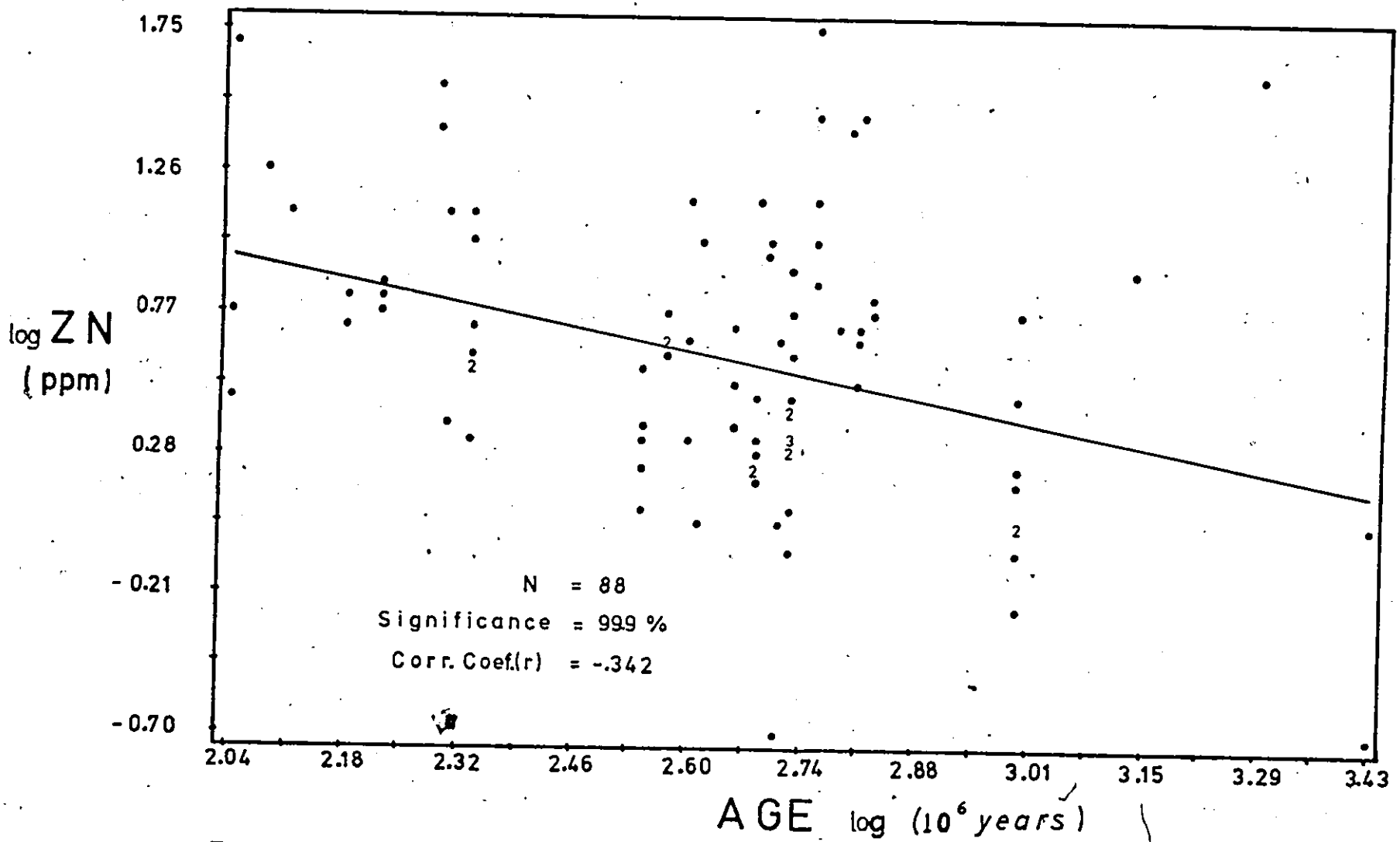

Figure 3 - Secular variation of zinc in limestones. The linear least square fit regression line is defined by equation log Zn = -.571 log (10^6 years) - 2.127. 2,3 indicates number of samples at 1 point.

Factor 1: aluminosilicate constituents;

Factor 2: quartz and chert;

Factor 3: secular variations in isotopic ($\delta^{18}O$) and particularly chemical (Fe^{2+}, Mn^{2+}) composition of dolostones;

Factor 4: facies;

Factor 5: Pb^{2+} and Zn^{2+};

Factor 6: stoichiometry of dolomite.

More than 50% of the variance in Pb and Zn is explained by the 6 factors in the varimax rotated factor matrix and this is generally considered satisfactory (cf. communality, Table 8). In an effort to extract information on the residual 45% of Pb variance and 36% of Zn variance, factors with lower eigenvalues were attempted. However, after the first iteration the communality of one or more variables exceeded 1.0 and PA2 factoring can not be done under such circumstance.

In contrast to limestones, where the first factor is "insoluble residue", in dolostones this factor is split into two factors (1 and 2), accounting together for 67.5% of the total chemical and isotopic variation. The third factor, explaining 12.9% of the variation is interpreted as substitution of Fe^{2+} and Mn^{2+} in lattice positions of dolomite. This effect is age related, due to the presence of Mn^{2+} and/or Fe^{2+} enriched dolostones in progressively older sequences (Veizer, 1978), causing Sr exclusion from the dolomite lattice (Veizer, 1977) and thus easy contamination of the residual

carbonate bound Sr by radiogenic Sr from silicates (Veizer and Compston, 1974, 1976). Similarly $\delta^{18}O$ shows clear secular variation (Veizer and Hoef, 1976). The importance of these agents in evaluating the controlling factors for Pb and Zn distribution in dolostones will be discussed with respect to variables (i) to (v) above.

(i) Insoluble Residue

Factors 1 and 2 (Table 8), explaining 47.8% and 19.5% respectively of the total chemical and isotopic variation in dolostones, are related to the insoluble portion of the rock. Factor 1 is heavily influenced by K_2O (.913), Rb(.899) and Al_2O_3 (.809) and moderately by TiO_2 (.641) and Na_2O (.464). From this factor it may be inferred that illite/muscovite and/or K-feldspar as well as ilmenite, which is usually enriched in the coarser fraction of the insoluble residue, are contributing greatly to the total chemical variation. The relatively high loading of zinc on this factor indicates that possibly zinc has been released from these constituents of the insoluble residue either during acid digestion of the samples or, more likely, during diagenetic reconstitution of these minerals. The released zinc could have been sequestered into carbonate during dolomitization of the original carbonate phase. Factor 2, heavily influenced by SiO_2 (.977) and I.R. (.948) loading, is chert (Veizer, 1978).

Table 8-

Varimax rotated factor matrix for dolostones. Variables (except $^{87}Sr/^{86}Sr$, $\delta^{18}O$ and $\delta^{13}C$) are in log units

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communality
Zn	0.452	0.178	0.166	0.096	0.620	0.058	.66
Pb	0.044	0.265	-0.194	-0.128	0.618	-0.209	.55
FeO	0.254	0.101	0.744	-0.062	-0.023	0.152	.66
Fe_2O_3	0.264	0.280	0.420	0.198	0.421	-0.277	.61
MnO	0.110	0.029	0.773	-0.304	0.164	-0.031	.73
TiO_2	0.641	0.261	0.402	0.206	0.282	-0.122	.78
K_2O	0.913	0.150	0.223	-0.126	0.082	0.009	.91
P_2O_5	0.309	0.052	0.311	0.067	-0.041	-0.089	.21
SiO_2	0.190	0.844	0.142	0.153	0.225	-0.158	.87
Al_2O_3	0.809	0.388	0.194	0.304	-0.005	-0.233	.99
MgO	-0.091	-0.156	0.014	0.033	-0.070	0.701	.53
CaO	-0.118	-0.729	-0.105	-0.032	-0.074	-0.466	.78
Na_2O	0.464	0.188	0.136	0.579	0.173	-0.053	.64
CO_2	-0.254	-0.864	-0.080	0.016	-0.159	0.179	.87
Rb	0.900	0.174	0.113	0.126	0.203	0.023	.91
Sr	0.113	0.147	-0.243	0.843	-0.012	-0.000	.81
$^{87}Sr/^{86}Sr$	0.196	0.185	0.454	-0.184	-0.185	-0.029	.35
$\delta^{18}O$	0.057	0.096	-0.418	0.671	-0.079	0.356	.77
$\delta^{13}C$	-0.056	-0.031	-0.037	0.368	-0.310	0.433	.42
IR	0.198	0.865	0.093	0.208	0.083	-0.167	.87
% of variation	47.8	19.5	12.9	9.7	5.5	4.6	

Table 9-

Correlation coefficients (r) for Pb and Zn with major, minor and trace elements in dolostones. Variables (except $^{87}Sr/^{86}Sr$, $\delta^{18}O$ and $\delta^{13}C$) are in log units

	Zn	Pb
Zn	1.000	0.444
Pb	0.444	1.000
FeO	0.307	-0.191
Fe_2O_3	0.447	0.341
MnO	0.242	-0.025
TiO_2	0.648	0.187
K_2O	0.582	0.090
P_2O_5	0.083	0.011
SiO_2	0.454	0.358
Al_2O_3	0.364	0.106
MgO	-0.075	-0.236
CaO	-0.179	-0.179
Na_2O	0.403	0.082
CO_2	-0.323	-0.396
Rb	0.613	0.154
Sr	0.146	-0.013
$^{87}Sr/^{86}Sr$	0.144	-0.144
$\delta^{18}O$	0.146	-0.133
$\delta^{13}C$	-0.148	-0.392
IR	0.401	0.225

Pb, on the other hand, is not highly loaded on any of the insoluble residue factors but it does correlate positively with Zn (r = .44), SiO_2 (r = .358)and Fe_2O_3 (r = .341) suggesting some weak second order association with these elements (cf. Table 9).

Zinc (.620) and lead (.618) are loaded on factor 5, which explains 5.5% of the total variation. This is the most important factor for Pb and Zn but its geologic meaning is not understood. As already mentioned, the possibility that it is a consequence of the analytical technique cannot be unequivocally discounted.

(ii) Facies

Statistical evaluation (t-test) of lagoonal versus reef and bank dolostones showed no difference in the mean concentrations of Zn (Table 10). In contrast the mean of Pb in reef-bank facies (5.5 ppm) may be higher than that of the lagoonal facies (2.7 ppm). Due to the small sample size of the reef-bank group (N = 9) the means are statistically different at the 95% confidence level only in a one-tailed test (Nie et al, 1975, p. 271; cf. Table 10).

(iii). Petrography

In order to determine whether the grain size of the studied dolostone samples rather than facies is the controlling variable of Pb distribution, the samples were divided into fine and coarse grained. Since the reef-bank group was too small for further subdivision only the lagoonal group was

Table 10- F and t-test of Zn and Pb in lagoonal and reef-bank dolostones. Variables are in log units.

Variable	Number of Cases	Mean	Standard Deviation	F Value	2-Tail Prob.	Pooled Variance Estimate t Value	Degrees of Freedom	2-Tail Prob.
Zn								
Group 1	40	0.7801	0.418	1.55	0.357	-0.23	46	0.819
Group 2	8	0.8189	0.521					
Pb								
Group 1	36	0.4318	0.421	1.34	0.515	-1.88	43	0.066*
Group 2	9	0.7370	0.488					

Group 1 = lagoonal dolostones

Group 2 = reef-bank dolostones

* One-tailed probability for Pb is .066/2 = .033. The null hypothesis in the one-tailed test states that the mean of reef-bank dolostones is larger than the mean of lagoonal dolostones.

tested for differences in their mean Pb and Zn concentrations. Neither Pb nor Zn showed any statistically significant difference (Table 11). This shows that it may be environment (facies) rather than petrography, which is important for Pb distribution.

(iv) Secular variations of Pb and Zn in dolostones

Secular variations due to substitution of Fe^{2+} and Mn^{2+} for Mg^{2+} in lattice positions in dolomite have been discussed in the introductory part of this section. Neither Pb nor Zn in dolostones vary with age.

(v) Sulphur and organic carbon

Cambrian and Precambrian dolostone samples, for which S and organic C data were available (N = 35 for Zn; and 32 for Pb), were correlated with Pb and Zn and do not show any significant relationship to these variables.

Summary

The above review of controlling factors of Pb and Zn distribution in dolostones and limestones enables the following conclusions to be drawn:

Zinc in dolostones is inferred to correlate with the illite/muscovite and/or K-feldspar component of the rocks. This suggests that it was either leached from these minerals during acid digestion of the carbonate portion, or released during diagenetic reconstitution of these minerals (Pingitore, 1978) and sequestered into the diagenetically formed dolomite.

Table 11- F and t-test of Zn and Pb in fine-grained lagoonal and coarse-grained lagoonal dolostones . Variables are in log units.

Variable	Number of Cases	Mean	Standard Deviation	F Value	2-Tail Prob.	Pooled Variance Estimate t Value	Degrees of Freedom	2-Tail Prob.
Zn								
Group 1	30	0.7867	0.373					
Group 2	10	0.7603	0.555	2.21	0.102	0.17	38	0.865
Pb								
Group 1	28	0.4447	0.400					
Group 2	8	0.3867	0.516	1.66	0.322	0.34	34	0.737

Group 1 = lagoonal dolostones - fine grained

Group 2 = lagoonal dolostones - coarse grained

In limestones Zn is loaded on a separate factor (factor 2, with a very weak affinity to Fe^{3+}, Ti^{2+} and P). The meaning of this factor is not understood. Weak second order controls are exercised by: (a) insoluble residue (either through laboratory leaching or diagenetic release into carbonate), and (b) secular variations in limestone composition, causing Zn decrease with increasing age.

Lead in dolostones may be associated more with the "late" diagenetic hyposaline reef-bank dolostones than with the penecontemporaneous and early diagenetic, frequently hypersaline, lagoonal varieties. Additional data are required to verify this assertion. The weak correlation of Pb with SiO_2 and Fe_2O_3 indicates a second order control by insoluble residue (perhaps in iron oxide coatings). It may also be released from aluminosilicates during experimental treatment of the samples or be released by aluminosilicates into the carbonate phases during diagenesis. In limestones, Pb - together with Zn - is loaded on factor 2. The meaning of this factor is not understood. A very weak second order control by aluminosilicate phases is also possible.

CONCLUSIONS

A polarographic technique was developed for the analysis of trace amounts of Pb and Zn in carbonate rocks. These elements, extracted from the soluble portion with weak HCl, were analysed in a .2M ammonium citrate (pH 3.0 ± 0.1) supporting electrolyte utilizing a dropping mercury electrode and differential pulse polarography.

The recovery of the analytical technique was 100 ± 10% (of the amount added) for Pb and 100 ± 5% for Zn. The precision for zinc based on 58 replicate analysis, is ±0.2 ppm and ± 0.7 ppm at the 0-6 and the 6-30 ppm Zn level respectively. For Pb it is ± 0.2 ppm and ± 0.4 ppm at the 0-6 and the 6-12 ppm levels. The mean (geometric) concentration of Pb in both limestones and dolostones was 3.1 ppm, and for zinc it was 4.2 and 6.1 respectively.

The dominant control for zinc distribution in carbonate rocks is exercised by mineralogy since zinc concentration in dolostones are higher than in limestones. This statistical difference notwithstanding, the observed difference in the mean concentrations is less than expected. The primary control of zinc distribution within the dolostone group is exercised by constituents of the insoluble residue such as illite/muscovite and/or K-feldspar. Control of zinc distribution within the limestone group is not understood, but a weak negative correlation with age is observed. Another secondary

influence may be exerted by the insoluble residue.

The primary control for Pb in dolostone may be facies, with the "late" diagenetic hyposaline reef-bank dolostones having higher lead concentrations than the penecontemporaneous to early diagenetic, frequently hypersaline and lagoonal, dolostones. However additional sampling of the reef-bank group is required to verify this assertion. A weak secondary control is probably exerted by the insoluble residue. In limestone the primary control of Pb distribution is not understood but a weak secondary control is probably exercised by the insoluble residue.

Due to the low concentration of lead and zinc in unmineralized limestone and dolostones, the author feels that the present study does little to refute the belief that carbonate hosted Pb/Zn ores are carried into the carbonate rock and are deposited by heated formation waters which leached elements from underlying shales or silicate material (cf. Jackson and Beales, 1967; Hitchon, 1975; Carpenter, Trout, and Pickett, 1974; Roedder, 1967; Hall and Heyl, 1968; Wedepohl, 1972).

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APPENDIX 1

No.	Age	Locality	Description
5	Barremian-Aptian	Bobrovecká Valley, High Tatra Mts.	Dark organodetrital limestone-packed biomicrite
6	Barremian-Aptian	Kýčera, High Tatra Mts.	Dark organodetrital limestone-packed biomicrite
7	Barremian-Aptian	Bobrovecká Valley, High Tatra Mts.	Dark crinoidal limestone- crinoidal biomicrite
8	Late Neocomian	Zázrivá Valley, Križna Nappe	Dark-grey marly pelagic limestones (Biancone type)-biomicrite
9	Neocomian	Zázrivá Valley, Križna Nappe	Dark-grey marly pelagic limestones (Biancone type)-biomicrite
11	Oxfordian-Tithonian	Bobrovee, High Tatra Mts.	Pink muddy limestones-biomicrite
12	Oxfordian-Kimmeridgian	Osobitá, High Tatra Mts.	Pink muddy limestones-biomicrite
14	Bathonian	Bobrovecká Valley, High Tatra Mts.	Pink crinoidal limestone-crinoidal biosparite
15	Bajocian Bathonian	Rozpadlý Gruň, High Tatra Mts.	Pink crinoidal limestone-crinoidal biosparite
16	Bajocian	Bobrovecká Valley, High Tatra Mts.	Grey crinoidal limestone-crinoidal biosparite
17	Rhaetian	Zázrivá Valley, Križna Nappe	Dark-grey coquina-crinoidal limestone-crinoidal biosparite to oosparite
18	Norian	Silická Brezová, Gemeridy Unit	Red muddy limestone (Hallstat Limestone)-biomicrite
19	Norian	Kvačianska Valley, Choč Nappe	Light-grey late diagenetic dolomite (Hauptdolomite)-dolsparite to dolmicrite
21	(Anisian?)-Karnian-Norian	Osobitá, High Trata Mts.	Grey sheet marly early diagenetic dolomite-dolmicrite

APPENDIX 1 (contd)

No.	Age	Locality	Description
22	Karnian-Norian	Spiš-Michalová Valley, High Tatra Mts.	Variegated sheet marly early diagenetic dolomite-dolmicrite
23	(Ladinian?)-Karnian-Norian	Kýčera, High Tatra Mts.	Grey sheet marly early diagenetic dolomite-dolmicrite
24	Karnian	Silická Brezová, Gemeridy Unit	Light-grey organodetrital, mainly crinoidal, limestone-biosparite-biomicrite
26	Ladinian	Kvačianska Valley, Choč Nappe	Grey massive late diagenetic dolomite (Choe Dolomite)-dolsparite
28	Ladinian	Plešivec Plateau, Gemeridy Unit	Light-grey organodetrital limestone-coral biomicrite
31	Late Anisian	Plešivec Plateau, Gemeridy Unit	Light-grey fine-grained dolomitic limestone-micrite
32	Late Anisian	Plešivec Plateau, Gemeridy Unit	Light-grey fine-grained limestone-micrite
33	Late Anisian	Rozpadlý Grúň, High Tatra Mts.	Brown-grey massive limestone-micrite
34	Late Anisian	Osobitá, High Tatra Mts.	Brown-grey massive limestone-micrite
35	Late Anisian	Osobitá, High Tatra Mts.	Brown-grey massive limestone-micrite
36	Late Anisian	Osobitá, High Tatra Mts.	Brown-grey massive limestone-micrite
38	Early Anisian	Rozpadlý Grúň, High Tatra Mts.	Grey muddy limestones (Würmlikalk)-micrite
41	Late Campilian -Early Anisian	Plešivec Plateau, Gemeridy Unit	Yellow porous limestone with rhombs of early diagenetic dolomite (Rauhwacken)-sparite
53	Tournaisian	Ningbing Homestead (Bonaparte Gulf Basin), W.A.	Skeletal sparry silty lump limestone
54	Famenian	Surprise Creek Gorge(Bonaparte Gulf Basin), W.A.	Sparry lump limestone (Ningbing Limestone)
55	Famenian	Surprise Creek Gorge(Bonaparte Gulf Basin), W.A.	Skeletal sparry algal micrite (Ningbing Limestone)
56	Famenian	S. tip of Ningbing Range (do), W.A.	Sparry algal micrite limestone (do)

APPENDIX 1 (contd)

No.	Age	Locality	Description
57	Famenian	S. tip of Ningbing Range (do), W.A.	Sparry lump limestone (do)
59	Late Emsian	Cavan Station, N.S.W.	Grey laminated stromatolitic silty limestone (Cavan Bluff Limestone)-aranaceous micrite
60	Late Emsian	Cavan Station, N.S.W.	Grey laminated stromatolitic silty limestone (Cavan Bluff Limestone)-aranaceous micrite
61	Late Emsian	Cavan Station, N.S.W.	Grey laminated stromatolitic silty limestone (Cavan Bluff Limestone)-aranaceous micrite
62	Late Emsian	Cavan Station, N.S.W.	Grey laminated stromatolitic silty limestone (Cavan Bluff Limestone)-aranaceous micrite
63	Middle Ludlovian	Rainbow Hill near Yass, N.S.W.	Dark-grey fine-grained limestone-aranaceous micrite
64	Middle Ludlovian	Yass River near Rainbow Hill, N.S.W.	Light-grey coral (Favosites) limestone (Hume Limestone)-coral biolithite
66	Middle Ludlovian	Derengolong Creek near Yass, N.S.W.	Grey coarse-grained crinoidal limestone (Barrandella Shale)-crinoidal biomicrite
68	Early Ludlovian	Derengolong Creek near Yass, N.S.W.	Light-grey organodetrital limestone-algal and crinoidal biosparite
69	Early Ludlovian	Derengolong Creek near Yass, N.S.W.	Dark-grey organodetrital limestone-biomicrite
70	Late Ordovician	Crossing of Lord and Lawrence Creek Roads, Tas.	Black fine-grained bedded marly limestone (Gordon Limestone)-micrite
71	Late Ordovician	Lord Road, Tas.	Dark-grey to black muddy limestone (Gordon Limestone)-crinoidal micrite
72	Late Ordovician	Lord Road, Tas.	Dark-grey to black muddy limestone (Gordon Limestone)-crinoidal micrite

APPENDIX 1 (contd)

No.	Age	Locality	Description
73	Middle Ordovician	Crossing of Lawrence Creek and Eden Creek Roads, Tas.	Dark-grey to black massive muddy limestone(Gordon Limestone)-biomicrite
74	Middle Ordovician	Crossing of Lawrence Creek and Eden Creek Roads, Tas.	Dark-grey to black massive muddy limestone (Gordon Limestone)-biomicrite
75	Middle Ordovician	Crossing of Lawrence Creek and Eden Creek Roads, Tas.	Dark-grey to black massive muddy limestone (Gordon Limestone)-biomicrite
76	Middle Ordovician	Junction of Lords and Westfield Roads, Tas.	Dark-grey fine-grained limestone (Gordon Limestone)-crinoidal biomicrite
77	Middle Ordovician	Junction of Lords and Westfield Roads, Tas.	Dark-grey fine-grained limestone (Gordon Limestone)-crinoidal biomicrite
78	Middle Ordovician	Florentine Valley, Tas.	Dark-grey fine-grained organodetrital limestone (Gordon Limestone)-biomicrite
79	Middle Ordovician	Mole Creek, Tas.	Dark-grey fine-grained organodetrital limestone (Gordon Limestone)-biomicrite
80	Early Ordovician	Crossing of Florence Road and Road No. 9, Tas.	Dark-grey to black massive muddy and nodular clayey limestone (Gordon Limestone)-micrite
81	Early Ordovician	Crossing of Florence Road and Road No. 9, Tas.	Dark-grey to black massive muddy and nodular clayey limestone (Gordon Limestone)-micrite
82	Early Late Cambrian	Ellery Creek W. of Alice Springs, N.T.	Brown-grey fine-grained partly recrystallized limestone (Goyder Limestone)-recrystallized micrite
83	Early Late Cambrian	Ellery Creek W. of Alice Springs, N.T.	Grey fine-grained colitic and organodetrital limestone (Goyder Limestone)-biomicrite and oomicrite

APPENDIX 1 (contd)

No.	Age	Locality	Description
84	Early Late Cambrian	Ellery Creek W. of Alice Springs, N.T.	Yellow-grey medium-grained limestone (Goyder Limestone)-intrasparite
85	Late Middle Cambrian	Ellery Creek W. of Alice Springs, N.T.	Dark-grey oolitic limestone (Jay Creek Limestone)-oointrasparite
86	Late Middle Cambrian	Ellery Creek W. of Alice Springs, N.T.	Dark-grey fine-grained laminated limestone (Jay Creek Limestone)-intramicrite
88	Late Middle Cambrian	Jay Creek W. of Alice Springs, N.T.	Yellow-grey fine-grained laminated limestone (Jay Creek Limestone)-oointrasparite
89	Late Middle Cambrian	Jay Creek W. of Alice Springs, N.T.	Grey fine-grained oolitic limestone (Jay Creek Limestone)-oosparite
90	Middle Cambrian	Ellery Creek W. of Alice Springs, N.T.	Light-grey fine-grained sheet early diagenetic dolomite (Hugh River Shale)-dolmicrite
91	Middle Cambrian	Ellery Creek W. of Alice Springs, N.T.	Grey fine-grained arenaceous algal limestone (Hugh River Shale)-arenaceous algal micrite
92	Middle Cambrian	50 miles E. of the Urandangi, Qld, 139°00', 22°00'.	Grey fine-grained organodetrital limestone (Quita Formation)
93	Middle Cambrian	50 miles E. of the Urandangi, Qld, 139°00', 22°00'.	Yellow fine-grained laminated (algal?) limestone (Quita Formation)
94	Middle Cambrian	35 miles E. of the Lawn Hill Homestead, Qld, 138°00', 18°30'	Light-grey medium-grained late diagenetic dolomite (Currant Bush Limestone)
95	Middle Cambrian	35 miles E. of the Lawn Hill Homestead, Qld, 138°00', 18°30'	Yellow-grey coarse-grained arenaceous late diagenetic dolomite (Currant Bush Limestone)
96	Middle Cambrian	50 miles ESE from Urudangi, Qld, 139°00', 21°45'	Yellow fine-grained early diagenetic dolomite (Thorntonia Limestone)-microcrystalline dolomite

APPENDIX 1 (contd)

No.	Age	Locality	Description
97	Middle Cambrian	50 miles ESE from Urandangi, Qld, 139°00',21°45'	Yellow fine-grained late diagenetic? dolomite (Thorntonia Limestone)-dolsparite
98	Middle Cambrian	Victoria River Downs, N.T.	Grey fine-grained microcrystalline dolomitic limestone (Montejinni Limestone)
99	Middle Cambrian	Wave Hill, N.T.	Yellow-grey massive dolomitic limestone (Montejinni Limestone)
100	Middle Cambrian	Brachina Gorge, S.A.	Grey nodular and laminated claye limestone (Wirrealpa Limestone)-stromatolitic? micrite
101	Middle Cambrian	Wirrealpa Creek, S.A.	Grey fine-grained organodetrital limestone (Wirrealpa Limestone)-archaeocyathid micritic biolithite
102	Middle Cambrian	Wirrealpa Creek, S.A.	Creamy-red fine-grained organogenic, partly recrystallized limestone (Wirrealpa Limestone)-archaeocyathid biolithite
103	Middle Cambrian	Wirrealpa Creek, S.A.	Variegated medium-grained organogenic limestone (Wirrealpa Limestone)-archaeocyathid biolithite
104	Early Cambrian	Old Wirrealpa Springs, S.A.	Creamy-grey clayey limestone (Parrarra Limestone)-micrite
105	Early Cambrian	Old Wirrealpa Springs, S.A.	Red fine-grained silty limestone (Parrarra Limestone)-arenaceous intramicrite
106	Early Cambrian	Old Wirrealpa Springs, S.A.	Black fine-grained arenaceous detrital limestone (Parrarra Limestone)-arenaceous intramicrite
107	Early Cambrian	Brachina Gorge, S.A.	Red fine-grained laminated arenaceous late diagenetic dolomite (Wilkawillina Limestone)-arenaceous dolsparite

APPENDIX 1 (contd)

No	Age	Locality	Description
108	Early Cambrian	Brachina Gorge, S.A.	Dark-grey massive late diagenetic calcitic dolomite (Wilkawillina Limestone)-predominantly dolsparite
109	Early Cambrian	S. of Warragee Bore, S.A.	Grey fine-grained recrystallized limestone (Wilkawillina Limestone)-crystalline limestone
110	Early Cambrian	S. of Warragee Bore, S.A.	Grey fine-grained recrystallized limestone (Wilkawillina Limestone)-crystalline limestone
PROTEROZOIC			
ADELAIDE GEOSYNCLINE (South Australia)			
111	Marinoan	Brachina Gorge, S.A.	Greamy-grey muddy laminated limestone (Wonoka Formation)-micrite
112	do	do	Red massive fine-grained early? diagenetic dolomite (Nuccaleena Formation)-dolomicrite
114	do	do	Green arenaceous fine-grained dolomitic limestone with stromatolites (Willochra Formation)-dolomitic micrite
116	do	do	Grey medium-grained silicified stromatolitic limestone (Trezona Formation)-predominantly sparite
117	do	do	Red fine-grained algal and oolitic limestone (Trezona Formation)-algal biooomicrite
118	do	do	Dark fine-grained arenaceous oolitic limestone (Etina Limestone) -arenaceous oosparite
119	do	do	do

APPENDIX 1 (contd)

No.	Age	Locality	Description
120	Sturtian	Depot Creek, S.A.	Green and grey fine-grained laminated modular dolomitic limestone, partly silicified (Brighton Limestone eq.)-alteration of algal micrite and sparite laminae
122	do	do	Red modular fine-grained oolitic limestone (Brighton Limestone eq.) -algal oobiosparite
130	do	do	Black laminated muddy early diagenetic dolomite with cherts (Tindelpina Shale Member)-siliceous dolpelmicrite
136	do	do	Black muddy early diagenetic dolomite with cherts (Skillogalee Dolomite)-dolomicrite
137	do	do	do
139	do	do	Grey creamy cavernous dolomite (Rauhwacken) (Skillogalee Dolomite) -dolomicrite
140	do	do	Variegated and red fine-grained early diagenetic dolomite with stromatolites and cherts (Skillogalee Dolomite)-stromatolitic siliceous micrite
141	Willouran	Carrieton, S.A.	Black muddy sheet early diagenetic dolomite with sporadic cherts (River Wakefield Group)-dolomicrite
142	do	do	do
143	do	do	do
144	do	do	Black laminated fine-grained arenaceous early diagenetic dolomite (River Wakefield Group)-dolomicrite

APPENDIX 1 (contd)

No.	Age	Locality	Description
AMADEUS BASIN (N.T.)			
145	Marinoan	Jay Creek, N.T.	Yellow-grey sheet muddy early diagenetic dolomite (Pertatataka Formation)-algal dolomicrite, partly recrystallized
146	do	Ellery Creek, N.T.	Grey sheet muddy early diagenetic dolomite (Pertatataka Formation)-microcrystalline dolomite
147	Upper Riphaean	Jay Creek, N.T.	Fine-grained dark-grey early diagenetic sheet dolomite (Bitter Springs Formation)
148	do	do	Variegated coarse-grained calcite with stromatolites and cherts (do) -sparite
149	do	do	Creamy fine-grained calcitic dolomite with stromatolites and cherts (do)-dolosparite
150	do	do	Dark-grey muddy limestone (do)
151	do	do	Dark-grey muddy laminated stromatolitic limestone, partly recrystallized
152	do	Ellery Creek, N.T.	Black muddy sheet argillaceous early diagenetic dolomite (do)
153	do	do	Grey laminated microcrystalline sheet early diagenetic dolomite with stromatolites and cherts (do)
154	do	do	Yellow fine-grained cavernous limestone (Rauhwacken) (do)
155	do	do	Red medium-grained arenaceous partly recrystallized nodular limestone (do)
156	do	do	Grey medium-grained weakly recrystallized limestone (do)

APPENDIX 1 (contd)

No.	Age	Locality	Description
157	Upper Riphaean	Ellery Creek, N.T.	Red argillaceous stromatolitic limestone (do)-micrite
159	do	do	Grey laminated stromatolitic muddy limestone with cherts (do)-micrite
160	do	do	Variegated partly recrystallized microcrystalline stromatolitic limestone (do)
161	do	do	Black fine-grained limestone with veins of secondary calcite (do)
	HAMERSLEY BASIN (W.A.) - BANGEMALL GROUP		
162	1.0-1.1 b.y.	115°39', 22°32', W.A.	Grey partly recrystallized medium grained early diagenetic dolomite (Bangemall Group)-algal? intradolosparite
163	do	do	Grey partly recrystallized early diagenetic dolomite (do)-predominantly dolomicrite
164	do	115°41', 22°31', W.A.	Fine-grained slightly recrystallized early diagenetic dolomite with cherts (do)-dolosparite
165	do	115°42', 22°56', W.A.	Middle-grained early diagenetic dolomite with cherts (do)
166	do	115°48', 22°52', W.A.	Fine-grained slightly recrystallized early diagenetic dolomite (do)-predominantly dolomicrite
167	do	115°43', 22°56', W.A.	Middle-grained partly recrystallized early diagenetic dolomite (do)
168	do	115°38', 23°05', W.A.	Middle-grained recrystallized mosaic dolomite with cherts (do)

APPENDIX 1 (contd)

No.	Age	Locality	Description
TASMANIA			
169	Carpentarian? -Adelaidean?	Gordon River Road near Tim Shea, Tas.	Black massive nodular fine-grained limestone (Clarke Series)
McARTHUR BASIN (N.T. and QLD.)			
170	Carpentarian	11.5 miles NW of Balbirini Homestead, Bauhinia Downs sheet, Qld.	Grey fine-grained early diagenetic dolomite (Reward Dolomite)
171	do	do	Dark-grey fine-grained early diagenetic dolomite with cherts, limonitic layers and veins of secondary calcite (Reward Dolomite)
172	do	Top Crossing, Bauhinia Downs sheet, Qld.	Pink muddy early diagenetic dolomite with aragonitic? pseudomorphs (Cooley Member)
173	do	Bald Hill, Bauhinia Downs sheet, Qld.	Grey and pink muddy early diagenetic dolomite (Mitchell Yard Member)-dolomicrite
174	do	2 miles W of old McArthur River Homestead, Bauhinia Downs sheet, Qld.	Dark-grey muddy early diagenetic dolomite (Mara Dolomite)-dolomicrite
175	do	6 miles W of Leila First Crossing, Bauhinia Downs sheet, Qld.	Yellow fine-grained laminated early diagenetic arenaceous dolomite (Leila Sandstone)-dolomicrite
HAMERSLEY BASIN - Mt BRUCE SUPERGROUP			
177	do	do	Fine to middle-grained mosaic dolomite (Duck Creek Dolomite)
178	do	116° 27', 21° 51', W.A.	Middle to coarse-grained dolomite (Wittenoom Dolomite)

APPENDIX 1 (contd)

No.	Age	Locality	Description
180	Carpentarian	116° 27', 21° 51', W.A.	Banded middle-grained dolomite with cherts (do)
181	do	117° 47', 22° 45', W.A.	Middle to coarse-grained dolomite with cherts (do)
182	do	117° 48', 21° 55', W.A.	Middle to coarse-grained dolomite with cherts and ankeritic? layers (Wittenoom Dolomite)
	BULAWAYAN GROUP	(RHODESIA)	
186	Archean	Huntsman Lime Works Quarry near the Turk Mine, 33 miles NNE of Bulawayo, Rhodesia	Black fine-grained slightly recrystallized limestone with calcitic "eyes" (Bulawayan Limestone)
187	do	do	do
	CORONATION GEOSYNCLINE (CANADA)		
189	1.7 - 2.0 b.y.		Creamy and red laminated fine-grained limestone (Utsingi Fm.)
190	do		Dark grey fine-grained slightly recrystallized dolomite (Rocknest Fm.)
191	do		do

APPENDIX 2

Pb, Zn and Insoluble Residue in Limestones and Dolostones.

Sample No.	Pb (ppm)	Pb* (ppm)	Zn (ppm)	Zn* (ppm)	Insoluble Residue (%)
5	1.3	1.3	47.9	49.1	2.4
6	1.9	1.9	5.7	5.8	2.2
7	1.8	1.9	3.1	3.2	2.4
8	2.7	4.6	10.8	18.3	41.0
9	3.5	4.6	9.7	12.6	23.1
11	2.1	2.1	5.0	5.0	.6
12	2.8	2.8	6.2	6.3	1.3
14	3.8	5.1	6.2	7.2	13.7
15	1.7	1.7	6.1	6.1	.4
16	2.1	2.7	5.2	6.7	22.6
17	22.4	22.5	35.7	35.9	.5
18	1.7	1.8	24.9	26.5	5.9
D 19	1.1	1.1	1.3	1.3	.4
D 21	2.6	2.7	8.3	8.6	3.9
D 22	1.6	1.8	8.4	9.4	10.7
D 23	2.0	2.1	3.5	3.7	4.5
24	1.3	1.3	2.4	2.4	.7
D 26	3.6	3.8	19.9	21.0	5.4
28	19.5	19.6	13.0	13.0	.3
31	7.3	7.3	10.5	10.5	.1
32	14.3	14.3	13.0	13.0	.2
33	2.2	2.2	5.0	5.0	.5
34	2.2	2.2	3.8	3.9	1.7
35	1.0	1.0	2.0	2.0	2.2
36	2.5	2.6	3.7	3.8	2.1
38	1.4	1.4	4.1	4.1	.3

* recalculated on 100% soluble (insoluble residue free basis)

D = Dolostones

APPENDIX 2 (contd)

Sample No.	Pb (ppm)	Pb* (ppm)	Zn (ppm)	Zn* (ppm)	Insoluble Residue (%)
D 41	6.7	7.3	10.9	11.8	8.0
53	1.1	1.1	3.8	3.9	3.9
54	1.2	1.2	1.2	1.2	1.7
55	2.1	2.2	1.6	1.6	2.5
56	1.0	1.0	2.2	2.2	1.1
57	1.5	1.6	2.4	2.5	3.5
59	5.4	6.7	4.6	5.7	19.9
60	2.9	4.0	3.6	5.0	27.4
61	1.6	2.0	3.3	4.2	21.5
62	2.2	3.2	3.3	4.8	31.4
63	N.D	N.D	10.3	14.8	30.2
64	.5	.5	4.7	4.7	.7
66	.5	.5	2.1	2.2	5.3
68	1.6	1.7	1.1	1.1	3.3
69	9.6	11.4	8.8	10.4	15.3
70	1.4	1.6	4.5	5.1	12.2
71	1.0	1.0	3.1	3.2	3.3
72	1.6	1.7	2.2	2.4	8.0
73	1.3	1.4	2.0	2.2	7.7
74	2.1	2.3	13.2	14.2	6.8
75	.9	1.0	2.7	2.9	6.4
76	2.0	2.1	1.6	1.7	3.3
77	1.4	1.4	1.5	1.6	3.4
78	1.1	1.1	1.8	1.9	2.8
79	.4	.4	1.6	1.7	4.6
80	6.2	9.6	6.1	9.5	35.6
81	5.2	8.0	6.5	10.0	35.2
82	3.5	3.7	.2	.2	5.7
83	3.3	3.8	.9	1.0	12.9
84	9.0	10.4	4.0	4.6	13.1
85	11.3	12.7	4.1	4.4	7.1

APPENDIX 2 (contd)

Sample No.	Pb (ppm)	Pb* (ppm)	Zn (ppm)	Zn* (ppm)	Insoluble Residue (%)
86	7.4	8.0	2.1	2.3	7.0
88	1.4	1.6	1.7	1.9	12.5
89	7.6	8.1	.8	.8	5.7
D 90	1.5	1.6	3.5	3.6	4.1
91	5.6	5.8	2.8	2.8	1.7
92	1.3	1.4	2.0	2.2	9.8
93	1.7	1.9	5.6	6.1	9.8
D 94	2.2	2.2	3.1	3.1	.7
D 95	3.8	5.1	3.5	4.7	25.8
D 96	7.1	8.2	3.2	3.3	3.4
D 97	4.6	4.7	1.6	1.6	1.4
98	5.7	5.8	2.8	2.8	1.7
99	4.4	4.5	1.2	1.2	2.0
100	8.2	10.0	6.8	8.3	18.3
101	2.3	2.4	2.5	2.6	3.9
102	1.1	1.2	1.8	1.9	4.6
103	3.5	3.8	2.4	2.6	6.8
104	3.5	4.0	12.4	14.1	12.3
105	10.1	14.1	40.1	56.2	28.6
106	2.7	3.5	5.7	7.5	23.9
D 107	27.7	45.3	> 400	> 655	38.9
D 108	21.8	22.1	14.4	14.5	1.1
109	53.3	55.8	28.1	29.4	4.4
110	19.8	10.8	9.8	10.3	4.7
111	8.5	10.3	4.2	5.1	17.1
D 112	.9	1.0	16.2	18.7	13.5
114	1.7	2.7	15.4	24.1	36.2
116	10.9	13.4	2.8	3.4	18.7
117	7.5	8.2	4.7	5.2	9.1
118	8.4	9.5	25.6	29.0	11.6

APPENDIX 2 (contd)

Sample No.	Pb (ppm)	Pb* (ppm)	Zn (ppm)	Zn* (ppm)	Insoluble Residue (%)
119	18.0	21.0	4.2	4.9	14.5
120	2.5	3.3	4.5	6.0	24.9
122	7.6	8.1	6.1	6.5	5.9
D 130	11.2	15.0	15.8	21.2	25.5
D 136	2.2	2.5	4.6	4.9	11.6
D 137	1.3	1.4	2.4	2.6	7.0
D 139	.1	.1	3.2	3.4	5.2
D 140	2.2	2.7	4.3	5.3	19.1
D 141	1.9	2.3	7.9	9.4	15.8
D 142	1.6	2.4	3.4	5.0	36.3
D 143	2.3	2.6	5.1	5.9	13.2
D 144	N.D.	N.D.	13.9	20.7	32.9
D 145	2.6	2.7	10.9	11.4	4.7
D 146	1.4	1.5	4.3	4.5	5.2
D 147	2.0	2.2	3.6	3.9	9.7
D 148	3.2	3.5	2.1	2.3	7.4
D 149	N.D.	N.D.	13.1	16.0	18.1
150	3.0	3.3	1.6	1.7	7.3
151	1.1	1.1	1.5	1.5	1.3
D 152	1.4	1.7	2.5	3.0	17.2
D 153	.9	1.3	2.0	3.0	32.7
154	3.2	3.3	1.1	1.1	3.4
155	1.4	1.7	.7	.8	16.1
156	3.4	3.9	2.5	2.9	13.6
157	N.D.	N.D.	5.1	6.2	17.7
159	1.4	1.5	.5	.5	5.7
160	1.2	1.2	1.0	1.0	3.9
161	5.7	5.9	113.0	116.4	2.0
D 162	2.9	3.0	3.7	3.8	2.2
D 163	1.4	1.4	3.0	3.1	3.3

APPENDIX 2 (contd)

Sample No.	Pb (ppm)	Pb* (ppm)	Zn (ppm)	Zn* (ppm)	Insoluble Residue (%)
D 164	15.5	17.7	4.5	5.1	12.6
D 165	3.5	4.7	5.2	7.1	26.3
D 166	2.2	2.2	1.6	1.6	1.2
D 167	4.4	4.5	9.7	10.0	3.1
D 168	3.2	3.3	6.9	7.2	4.3
169	3.7	5.7	5.1	7.9	35.5
D 170	1.1	1.1	1.3	1.3	2.3
D 171	6.2	8.1	3.3	4.3	23.5
D 172	.6	.7	3.1	3.4	9.7
D 173	19.5	20.5	62.8	66.2	5.1
D 174	1.3	1.3	10.3	10.5	2.0
D 175	20.0	28.0	14.5	20.3	28.5
D 177	1.3	1.4	22.4	24.2	7.4
D 178	.3	.3	5.3	5.4	2.8
D 180	N.D.	N.D.	16.4	20.0	16.7
D 181	.1	.1	.1	.1	.9
D 182	.8	1.0	N.D.	N.D.	22.9
186	1.1	1.1	.2	.2	.7
187	.5	.5	1.1	1.1	.4
189	2.9	3.1	39.5	41.6	5.0
D 190	3.9	4.0	11.3	11.5	2.0
D 191	4.5	4.8	30.1	32.4	7.2