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**Orbicular Diorite of Fisher Lake, California:
Reverse Zoning and Oscillatory Precipitation Mechanisms**

by Dolores G. Durant

**A thesis submitted to the Faculty of Graduate and Postdoctoral Studies in
partial fulfilment of the requirements for the degree of Ph.D. in Earth Sciences.**

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Abstract

Magmatic orbicules from Fisher Lake CA range up to 20 cm in diameter. They contain a central core surrounded by shells that number from one to over forty and alternate in composition from predominantly felsic to predominantly mafic. Comb layering has the same type of patterning but is found as long, linear, ribbon-like, strips ranging up to 10 m wide and dozens of metres long.

Detailed petrology and extensive chemical analyses using the microprobe have been done on the orbicules, comb layering and host rocks of the Fisher Lake orbicular diorite. Within the orbicules has been found crystals of gradually, reverse-zoned, branching/budding, orthopyroxene and feather plagioclase in a radiating growth pattern extending away from the core. Shells containing these crystal shapes alternate with shells containing anhedral crystals of plagioclase, orthopyroxene, Fe-Ti oxides, amphibole and minor biotite. The comb layering consists of layers of elongated, budding, oscillatory zoned hornblende that alternate with anhedral plagioclase, pyroxene and hornblende.

The comb textures within both the orbicules and the comb layering are postulated to have formed as a result of the interaction between two magmas of slightly differing chemical compositions. The comb layering formed at the boundary between a partially solidified, very warm, magma mush and a completely molten magma. The orbicules formed in the molten magma where incorporated xenoliths from the partially solidified magma acted as centres of nucleation. The comb texture crystal morphology indicates that the crystals grew under far-from-equilibrium conditions while the crystal chemistry indicates constant temperature conditions. Phase diagrams and Gibbs free energy diagrams show that reverse zoning can be achieved under these two

conditions.

Mathematical modelling based on the Volterra-Lotka equations produces the oscillatory precipitation of anhedral, hornblende-rich shells alternating with anhedral, Fe-Ti oxide-rich shells. Modification of the Volterra-Lotka equations by adding two non-linear terms, generates a curve similar to that of the modal percentage of orthopyroxene across an entire orbicule, i.e. an oscillating line that gradually decreases in amplitude (comparable to a damped pendulum).

Orbicules and comb layering are not the result of large-scale, oscillating, magmatic conditions but are formed as a newly emplaced magma attains a new equilibrium. Therefore the comb textures are a self-organizational phenomena occurring during a far-from-equilibrium stage of crystallization in a suddenly, small-undercooled magma before the onset of widespread, near-to-equilibrium precipitation.

Sommaire

Les orbes magmatiques provenant de Fisher Lake, Californie, font jusqu'à 20 cm de diamètre. Elles contiennent une partie centrale entourée de une à plus de quarante couches, alternant entre une composition grandement felsique et une grandement mafique. Les couches en herse possèdent le même genre de motif mais se présentent sous forme de longues et linéaires languettes, semblables à des rubans, pouvant aller jusqu'à 10 m de largeur et des douzaines de mètres de longueur.

Une pétrologie détaillée et des analyses chimiques approfondies de microsonde ont été faites sur les orbes, les couches en herse et les roches encaissantes de la diorite orbiculaire de Fisher Lake. Dans ces orbes les cristaux changent graduellement d'un zonage inversé à une ramification ou bourgeonnement d'orthopyroxène et de plumes de plagioclase et forment un motif rayonnant du centre des orbes. Les couches contenant ces formes cristallines alternent avec d'autres contenant des cristaux allotriomorphiques de plagioclase, d'orthopyroxène, d'oxydes de fer et titane, d'amphibole et de biotite, en moindre quantité. Les couches en herse consistent de cristaux d'hornblende allongés et bourgeonnants avec un zonage oscillatoire, alternant avec des cristaux allotriomorphiques de plagioclase, de pyroxène et d'hornblende.

Il est postulé que les textures observées sont le résultat de l'interaction entre deux magmas de compositions chimiques un tant soit peu différentes. Les couches en herse se forment à la frontière entre une bouillie magmatique partiellement solidifiée et très chaude et un magma complètement fondu. Les orbes se forment dans le magma fondu où sont incorporés des xénolites provenant du magma partiellement solidifié et qui agissent comme centres de

nucléation. La morphologie cristalline à texture d'herse indique que la croissance de ces cristaux se fait dans des conditions loin-de-l'équilibre, alors que la chimie cristalline indique des conditions de température constante. Des diagrammes de phases et d'énergie libre d'activation de Gibbs démontrent que le zonage inversé peut être obtenu sous ces deux genres de conditions.

Un modèle mathématique utilisant les équations de Volterra-Lotka génère la précipitation oscillatoire de couches riches en cristaux allotriomorphiques d'hornblende alternant avec des couches riches en cristaux allotriomorphiques d'oxydes de fer et titane. La modification de ces équations par l'addition de deux termes non-linéaires génère une courbe similaire à celle du pourcentage modal d'orthopyroxene à travers la totalité d'une orbe, c'est-à-dire une ligne oscillatoire dont l'amplitude décroît graduellement (comparable à un pendule amorti).

Les orbes et les couches en herse ne sont pas le résultat de conditions magmatiques oscillatoires à grande échelle, mais plutôt se forment lorsqu'un magma nouvellement introduit atteint un nouvel équilibre. Donc, les textures en herse sont un phénomène d'auto-organisation se produisant sous des conditions de cristallisation loin-de-l'équilibre lors d'une petite mais soudaine surfusion d'un magma et ce avant la généralisation d'une précipitation près-de-l'équilibre.

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1. Introduction

1.1 Thesis Rationale and Contributions to Science

There is no doubt that one of the highlights of working on the orbicules and comb layering at Fisher Lake is that they are so beautiful. They boggle the mind with their colour, variety, and intricate complexity. There is one particular orbicule that I picked up that has over 40 shells; thin shiny black shells alternating with thicker white or gray ones that surround a small, coarse grained, white and dark green core. It is a beautiful sight! I know that others feel this way because whenever I hand this orbicule to another person, they simply stare at it for a while, and then they just hold onto it for a while longer, and ultimately, I have a heck of a time prying it out of their hands in order to get it back! Anyone who holds it is struck with curiosity and I can see the questions on their face: How did it form? Where did I find it? How could something so detailed, so complex as this create itself in a magma? Why don't we yet know the answers?

These are the questions that drive any research – how and why – and these are the questions that I keep coming back to. We do not have a satisfactory answer for how and why orbicules and comb layering form.

Most papers on orbicular rocks are descriptive, few give bulk chemical analyses, even fewer give chemical analyses of felsic versus mafic shells and none give detailed analyses across an orbicule. My contribution to science is the recognition that magmatic orbicules contain budding, branching orthopyroxene and feather plagioclase, that are gradually reverse-zoned. I also contribute an extensive electron microprobe data set of these reverse-zoned minerals as well as whole rock chemical analyses of the orbicules. Additionally, a detailed mineral modal analysis of two orbicules with numerous shells is included.

The branching crystal habits within the comb textures are indicative of far-from-equilibrium magmatic conditions that occurred before widespread crystallization of the magma. Another of my contributions is to use this information to detail a formation mechanism for these reverse-zoned, branching crystals.

In many papers, a general, rather nebulous, formation mechanism for the comb textures is usually relegated to a paragraph at the end of the paper or else a mechanism has been formulated that is so specific to that particular occurrence that it does little to explain the fact that comb texture is found in many different igneous rock compositions. I propose a theory of autonomous growth that does not require fluctuation of intensive parameters. I also contribute a mathematical formulation that can be the basis of formation of orbicules in magma of any composition.

The orbicules provide insight to a larger phenomenon which is ubiquitous throughout geology, that of oscillating pattern formation. Fine scale repetitive layering is found in many types of rocks all over the world. Understanding the mechanism that produces orbicules and comb layering will help shed light on the formation mechanisms of some of these other fine scale, repetitive layering phenomena.

1.2 General Characteristics of Magmatic Orbicules and Comb Layering

Magmatic orbicules are extremely uncommon. A compilation of the known orbicule localities by Leveson (1966) revealed about 160 localities of orbicules of all origins (fig. 1.1). McKinney (1985) updated Leveson's list by adding about another 50 localities. Of all of these, only about half are magmatic orbicules, the rest being metamorphic. The combination of



**Fig. 1.1 World map showing the locations of orbicule outcrops
(after Leveson 1966).**

orbicules and comb layering is far more rare. McKinney (1985) found only 12 locations where both phenomena can be found with most of them occurring in the Sierra Nevada batholith.

The most common types of orbicular and comb layering host rocks are plutonic rocks such as granite, diorite and gabbro. The occurrences themselves are usually small, ranging from 200 to 300 m wide at Fisher Lake California to single, erratic boulders in Scandinavia.

Orbicules are generally spheroidal to ellipsoidal, ranging in size from a few centimetres to several decimetres (fig. 1.2). Orbicule cores may consist of host rock, country rock, fragments of earlier formed orbicules, or fragments of comb layering. The number of discrete shells of distinct mineralogy surrounding these cores varies from 1 to at least 40 (e.g. the Fisher Lake orbicules). Shell thickness varies from shell to shell and contacts may be sharp or gradational. Crystals may be elongated tangentially to the core, as in the comb texture, or be anhedral to subhedral, growing in polymineralic shells that vary in size from aphanitic to centimetre scale.

Comb layering consists of the same type of comb texture growth as seen in the orbicules but instead of spherical shells, the layers are spread laterally through the rock, like sedimentary bedding (fig. 1.3). The name comb layering is derived from the appearance of the crystals in that they are elongated and oriented perpendicular to the layering like the teeth in a comb; a texture known as comb texture (Moore & Lockwood, 1973). The layers range from millimetres to centimetres in thickness while sequences of layers can range up to as much as 19 m thick and 180 m long (Walawender, 1976).

1.3 Historical Work on Magmatic Orbicular Rocks

Orbicular rocks have been recorded in the literature as far back as 1802 by von Buch

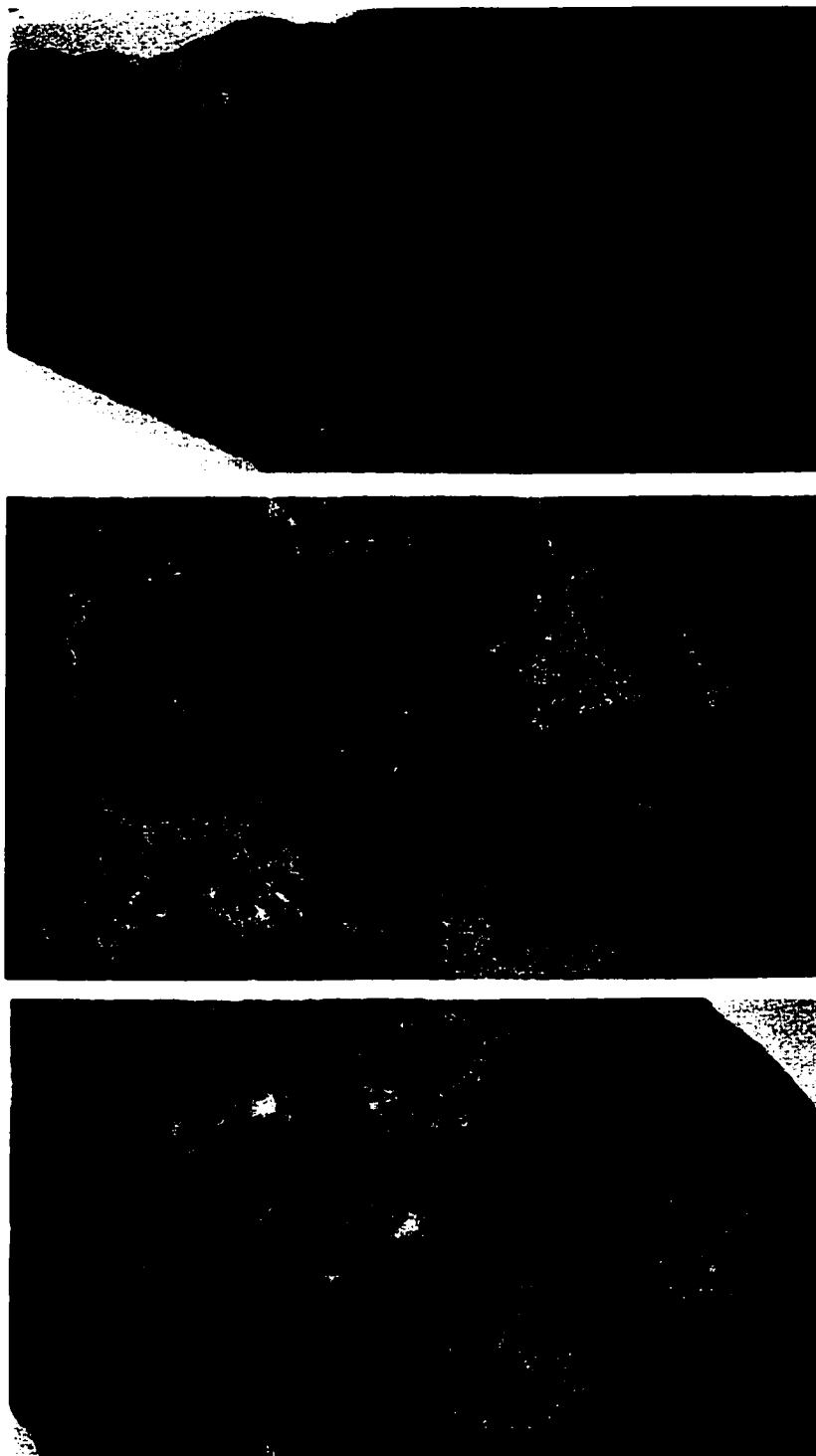


Fig. 1.2 Variety of orbicules from Scandinavia, top - 20 cm across, middle - 20 cm across, bottom- 15 cm across (samples from Johns Hopkins University Collection)

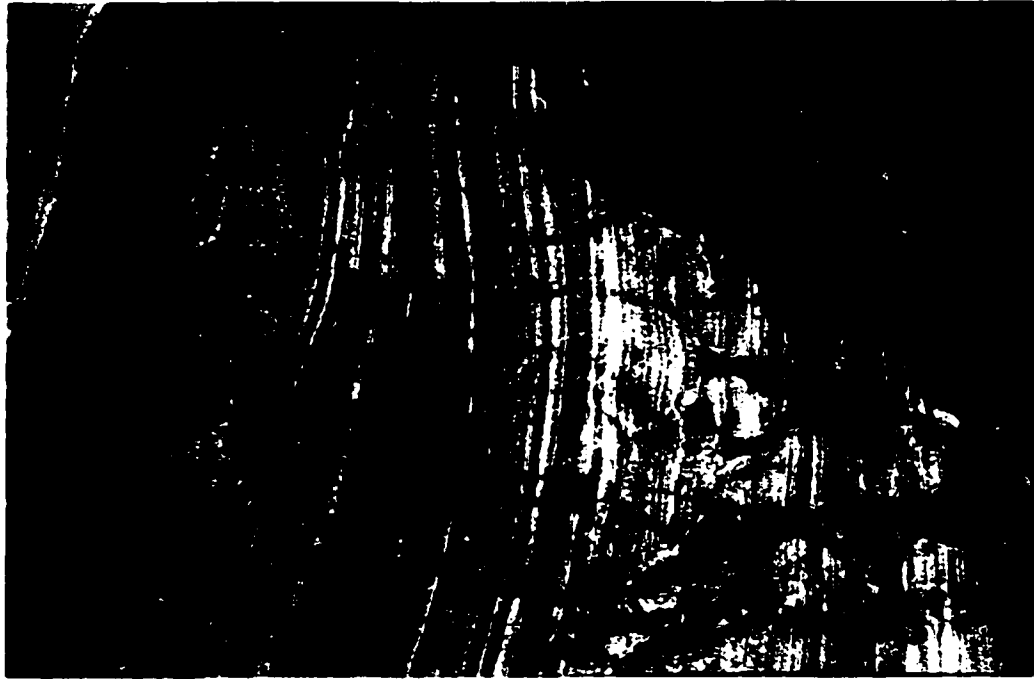


Fig. 1.3 Comb layering at Fisher Lake, CA consists of hundreds of cm scale layers with hornblende or orthopyroxene crystals oriented perpendicular to the layering (lens cap is about 7 cm diameter).

who was the first to write about “balls” from a granite in Germany which increased in mica content from the centre outwards (Hatch, 1888). During the 1800's about a dozen papers describing these curious “concretionary” spheroids were written. From these papers, Hatch (1888) developed a theory in which the spheres formed by crystallization around a core during the consolidation of a stationary granite magma and that deformation of the spheres could have been caused by subsequent flow of the surrounding magma prior to consolidation.

The formation of orbicules as crystallized pockets of immiscible fluid was suggested by Adams (1898) and Daly (1914). This was later disputed by Grieg (1927) who claimed that liquid immiscibility does not occur in eruptive magmas. Much later, Philpotts (1982) found that basalts could contain globules of immiscible fluids but these drops are on the order of 50 μm , far too small a scale for magmatic orbicules. This has not stopped others from proposing immiscibility as the mechanism for orbicule formation. Lapin and Vartiainen (1983) suggested that orbicules containing forsterite and magnetite formed from an immiscible ore-silicate melt that differentiated from a carbonatite magma. A partly crystallized granitic melt with residual, low viscosity, high potassium, pockets is postulated by Chauris *et al.* (1989) to have formed orbicules with radiating microcline crystals.

Wiik (1899) theorized that orbicules moved through various magmas in order to produce the shells of differing compositions. Vogt (1906) invoked an eutectic mixture of quartz and feldspar to produce felsic cores and shells but does not account for mafic shells while Lawson (1904) invoked eutectic mixtures along with temperature changes caused by latent heat of crystallization.

Several theories promoted a metamorphic origin for the igneous orbicules, “liquation”,

where partial melting of a rock produces pods of liquids that cool and crystallize from the outside inward (Backstrom, 1893; Belyankin & Petrov, 1939), and “granitization” which includes metasomatic replacement of pre-existing minerals by hydrothermal fluids (Eskola, 1938; Simonen, 1950; Rankama, 1963). An interesting twist to the theory of granitization was provided by Elliston (1984) who proposed that orbicules crystallized from a dense hydrosilicate gel built from clay minerals and hydrous ferromagnesian minerals that, upon dewatering, crystallized into granite. Formation from crystallized fragments that melted and differentiated while cooling, was postulated by Benedicts and Tenow (1911).

Shells around xenocrystic cores were explained by Leveson (1963, 1966) as reaction rims between the cores and magma in a diffusion process similar to Liesegang banding. Liesegang-type double-diffusion between pockets of nuclei-rich magma and nuclei-poor host magma is stressed by Moore (1984) as the mechanism that produced spherical rhythmic layering on a 2 m scale. Bryhni and Dons (1975) also suggested that orbicular shells are a result of the reaction between xenoliths and magma. They proposed that a partially solidified magma was brecciated by injection of a second magma. The breccia melted and reacted with the later magma which subsequently recrystallized around the brecciated xenoliths forming shells. Barrière (1972) postulated that shells are an interaction between a xenolithic core and the surrounding magma in a reaction that was not chemical but diffusion controlled.

Hydrous minerals are commonly present and orbicule formation in water-vapour-rich pockets of magma was suggested as long ago as 1888 by Iddings but there is still disagreement on just how water becomes involved. Variation in water pressure was proposed by Yoder (1954) to explain shells around cores that have the same composition as the host rock. Periodic water-

pressure oscillations, that caused mineral stability fields to oscillate between mafic and felsic mineralogy, are the controlling mechanism postulated by Emerson (1962). Rhythmic metasomatic crystallization is invoked by Leveson (1963, 1966, 1973) in order to produce a Liesegang-type alternating mineralogy of the shells. Van Diver (1968) agrees with the Liesegang mechanism of Leveson (1963) for plagioclase and biotite orbicules that were later metasomatized to inward radiating hornblende. In a later paper, van Diver (1970) postulated a different mechanism to explain the occurrence of microfolding within orbicular shells of undeformed elongated biotite crystals. He suggested that these biotite flakes initially gathered around buoyant bubbles and that the parent magma was subsequently microfolded as succeeding shells were formed.

Streams of a water-rich fluid are invoked by Moore and Lockwood (1973) in order to produce shells of varying composition in orbicules that appear to be abraded. Several subsequent papers agreed with this mechanism, e.g. Rodda, 1976; Walawender, 1976. Thompson and Gilles (1974) proposed that xenoliths reacting with hydrothermal fluids during the crystallization of a granitic melt formed orbicules with alternating hydrous and anhydrous mineral shells. Alternating hydrous and anhydrous mineral shells are postulated by van Diver and Maggetti (1975) to be the result of fluctuating P_{H_2O} through oscillating release and containment of volatiles which seemed to affect the precipitating shells but not the simultaneously precipitating matrix. Maggetti *et al.* (1978) formed orbicules with secondary mineralization in the shells by having the orbicules carried up into higher P_{H_2O} magma while anhydrous shells form when the orbicules drop into drier magma. A water enriched crystallizing granodiorite was suggested by Enz *et al.* (1979) in order to produce biotite and plagioclase orbicules surrounded by a biotite monzonitic matrix. Symes *et al.* (1987) postulated a locally oscillating P_{H_2O} during crystallization to generate

oscillating anhydrous/hydrous shells. Owen (1991) suggested H₂O flash inputs that produced water-rich globules that interacted with the magma to produce hydrous shells. Sinclair and Richardson (1992) and Samson and Sinclair (1992) proposed that quartz-tourmaline orbicules in the Yukon formed from a hydrous B-, F- and Fe-bearing fluid that was trapped in a crystallizing granitic magma. Some of these orbicules appear to have miarolitic cavities that contain quartz, tourmaline or topaz crystals.

Supersaturation has been suggested by Poldervaart and Taubeneck (1959) who hypothesized that shell deposition took place in oversaturated regions located near the walls of plutons where convection currents, caused by disturbances such as stoping, would bring in fresh magma that allowed new shells to precipitate.

Viscosity is thought to be an important factor in producing alternating shell compositions though there is little agreement on how. Sederholm (1928) stressed the importance of high magma viscosity in causing low diffusion rates that would, in turn, allow magma crystallizing around the orbicules to become enriched in components of minerals that would then precipitate. High viscosity is also espoused by Hildebrand (1950) to explain flow lines in the matrix and orbicules that are elongated in the direction of flow. Low viscosity is advocated by Moore and Lockwood (1973) in order to create the elongated, delicate, curved branching crystals found in the comb layering next to the orbicules.

Recent studies are beginning to show some consensus on at least one step in orbicule formation; that the magma was initially superheated destroying nuclei, and later supercooled and thus limiting crystal growth to the cores (Barrière, 1972; McKinney, 1985; Symes *et al.*, 1987; Yazgan & Mason, 1988; Owen, 1991; Ort, 1992; Shackleton, 1994).

A small group of authors have begun looking at orbicules as a self-organizational phenomenon. McBirney *et al.* (1990) found concentric, orbicular-like, layering in a fault zone in a rhyolite dike. They postulated that the layering “resulted from late-stage crystallization and self-organization during devitrification in a warm hydrous environment” (p. 321). Ortoleva *et al.* (1994) have suggested that orbicular granites form from the interaction of Liesegang banding (or the Ostwald/Prager supersaturation-nucleation-depletion cycle) and the instability of the uniform host fluid.

1.4 Historical Studies on Comb Layering

The term comb layering was first suggested by Moore and Lockwood (1973) as a generic, more descriptive, term for ‘Willow Lake type layering’ as suggested by Poldervaart and Taubeneck (1959). Willow Lake is a composite intrusion in the Elkhorn Mountains in Oregon where Poldervaart and Taubeneck found elongated crystals that had formed at high angles (60° to 90°) to the layering within rhythmically banded gabbro. They were the first to distinguish this type of layering from the Skaergaard-type rhythmic layering where the long axes of minerals are oriented parallel to the banding and form from gravity stratification.

McKinney (1985) lists seventeen localities of comb layering, twelve of which are in California in Mesozoic aged plutons. There are two vastly different theories as to the formation of comb layering within these California plutons. The original theory suggested by Poldervaart and Taubeneck (1959) and Taubeneck and Poldervaart (1960) postulated that comb layers formed from undercooling and crystallization in an oversaturated magma. This magma was subjected to vigorous disturbances such as turbulent currents due to emplacement or stoping, etc.

that brought fresh magma to the oversaturated region. Crystallization took place on the walls of the chamber where undercooling was most efficient, heat being removed through the cooler country rock by rapid water migration. Undercooling resulted in rapid crystallization of elongated, branching and/or feathery crystals that were oriented perpendicular to the cooler wall. Influx of fresh magma produced plagioclase and pyroxene while older unrefreshed magma, with its higher water content, crystallized plagioclase and amphibole. Thus the chemical composition of the parent magma would have been near the pyroxene-amphibole phase boundary and precipitation could easily, and repeatedly, change from pyroxene to amphibole. When the influxes ceased, the remaining magma, which had moved well into the plagioclase field, crystallized. This theory is partly supported by McKinney (1985) in that he postulated undercooling and rapid growth in supersaturated magma on a cooler wall, but his “cooler” wall is a high temperature, partially crystallized magma.

The second theory is from Moore and Lockwood (1973) who described a supercritical aqueous fluid that had high velocity, low density, low viscosity, was free of suspended crystals, and supersaturated in Ca plagioclase, hornblende and clinopyroxene. This fluid originated from various parts of the pluton and streamed up the contact between magma and wall rock along furrows, precipitating curved, branching, unbroken crystals while transporting broken chunks of comb layering. This theory is supported by Walawender (1976) who found comb layering 19 m thick consisting of plagioclase and hornblende between two gabbro intrusions in the Los Pinos pluton, Peninsula Range batholith, Southern CA.

Morton (1969) mentions comb layered plagioclase in the Lakeview Mountains pluton of California but does not speculate on how it formed.

Just as McKinney (1985) postulated that comb layering formed between two magmas, Berg (1980) had suggested that comb layers of olivine alternating with plagioclase in a snowflake troctolite formed after fast injection of a picritic magma above a slightly cooler one near the base of a magma chamber. The cooler, older magma helped supercool, and thus supersaturate, the later picritic magma. Bryhni and Dons (1975) also suggested that comb layering formed at the boundary of two magmas but that the actual crystals formed from the recrystallization of the older rock. Superheating and supersaturation from increasing P_{CO_2} at a chill margin was proposed by Barrière (1972) to have caused the rapid crystal growth of comb layering. He suggested that the oscillating shells could have formed from a cotectic magma which produced plagioclase and hornblende crystals, or that the shells formed by small variations of pressure and temperature in the magma.

Symes *et al.* (1987) modelled comb layering in a supercooled norite by oscillating the P_{H_2O} in order to create layers that oscillated in amphibole content. Webber *et al.* (1997) also invoked oscillating P_{H_2O} , via volatile escape, in dike “line rock” to produce oscillatory supersaturation, nucleation and growth of garnet in a background of albite, muscovite and perpendicular quartz.

Comb layered rocks should be distinguished from comb textured rocks in that comb layering indicates organization of the comb texture into multiple, rhythmically precipitated layers. Examples of comb texture that are not layered include: (1) the branching harrisitic olivines of Rhum (Brown, 1956; Wadsworth, 1961; Donaldson, 1977) and Centre Hill, Ontario (Thériault & Fowler, 1996) where olivine crystals, oriented perpendicular to the magma chamber floor, grew during lulls in cumulate settling, (2) feather norites of Sudbury (Bain, 1926), (3) plagioclase in

Skaergaard (Wager & Deer, 1939; McBirney & Noyes, 1979), (4) vein “fringe” of olivine and plagioclase crystals in Ireland documented by Preston (1963) who proposed that the perpendicular crystal growth was not due to a high crystal growth velocity but to the direction of maximum heat conductivity between the vein material and the host rock, and (5) hornblende/plagioclase appinites in Nova Scotia (Murphy *et al.*, 1991) which includes both rhythmically banded dike rocks and comb textured, intrafasciculate plagioclase and hornblende crystals. All of the rocks listed above contain elongate crystals likely formed by rapid crystallization but lack the distinctive rhythmic layering in mineralogy and colouration as seen in comb layered rocks.

1.5 Geology of the Sierra Nevada Region

The oldest basement rocks in the Sierra Nevada area range from 2,500 to 1,450 Ma and consist of granite, greenstone, marble, quartzite, schist, and gneiss. These are covered by a nearly 31 km thick sequence of sedimentary and volcanic rocks from an epicratonic trough environment, and topped by volcanic rocks produced by continental rifting at a spreading centre aged 1,450 to 850 Ma (Poole *et al.*, 1992). By 850 Ma, ocean crust was forming in the rift and by 500 Ma, a continental shelf sequence > 6 km thick had been deposited (Poole *et al.*, 1992). During the Middle Cambrian to Lower Ordovician, sea level rise and continental margin subsidence saw the future California in an off-shore, deep marine, environment consisting mainly of mudstones, thin carbonates, and fine siliciclastic rocks (Poole *et al.*, 1992). In the early Middle Ordovician, the deep marine sediments were covered by carbonate rocks deposited in gradually shallowing water but by the Mid Ordovician, due to marine incursion, the sedimentation of the area was dominated

by deep water shales (Poole *et al.*, 1992). In the Upper Ordovician much of the western U.S. was a submerged continental shelf, during which time the future California received lime mud deposits as it lay further westward off the continental slope (Poole *et al.*, 1992). In Lower Silurian to Middle Devonian time, limey siltstones were deposited as the area underwent several episodes of uplift and erosion (Poole *et al.*, 1992).

The Upper Devonian marked the beginning of the Antler orogeny with uplift and erosion in the western United States, mainly Nevada, Utah and Wyoming, as arches rose and fell providing source materials for the western deposits (Poole *et al.*, 1992). During this time, the Northern Sierra Nevada exotic terrain accreted onto the North American plate. This terrain contains four stacked allochthons of Cambrian to Middle Devonian deep oceanic rocks overlain by Upper Devonian to Upper Paleozoic island arc deposits called the Shoo Fly complex (Poole *et al.*, 1992). These deposits underwent greenschist metamorphism and are now located along the northwestern side of the Sierra Nevada batholith (SNB) (Poole *et al.*, 1992).

The California area experienced renewed subsidence and ocean transgression along with andesitic island-arc volcanism in the Late Devonian (Miller *et al.*, 1992). Rocks of this suite were overlain by Early Mississippian calc-alkalic volcanic arc rocks and intra-arc sedimentary rocks (Miller *et al.*, 1992). In the Late Mississippian, the thrusting associated with the Antler orogeny ceased, and deep water cherts and shales were deposited until the Early Pennsylvanian (Miller *et al.*, 1992). These were covered in the late Early Permian to early Late Permian by mafic to intermediate volcanic rocks that may represent extension to the east of the Sierra Nevada region and were then overlain by upper Lower Permian calc-alkalic volcanic rocks (Miller *et al.*, 1992). Subduction to the west of the Sierra Nevada region caused uplift, as well as the emplacement of,

the Calaveras complex, a part of the Cache Creek terrain of metamorphosed accretionary wedge deposits (Miller *et al.*, 1992) while to the west, the metamorphosed ophiolites of the Fiddle Creek complex were emplaced (Saleeby & Busby-Spera, 1992). Both of these complexes now lie just west of the Sierra Nevada batholith. The whole area, was subsequently overlain by Upper Triassic limestone reef deposits (Miller *et al.*, 1992).

During the Early to Middle Jurassic, deposition of andesitic submarine volcanic-arc magmatism from a west lying subduction zone alternated with deposition of intra-arc basinal, deep marine turbidites (Saleeby & Busby-Spera, 1992). This was followed by the Late Jurassic Nevadan orogeny, which resulted in deposition of more turbidites from the previous volcanic arcs and created major east dipping thrust faults (Saleeby & Busby-Spera, 1992).

An Andean-type subduction zone to the west, between the Lower and Upper Cretaceous, (150 to 80 Ma) resulted in the intrusion of the Sierra Nevada batholith (fig. 1.4) (Miller *et al.*, 1992), first in the west and south and then gradually to the east and north (Cowan & Bruhn, 1992). The Sierra Nevada batholith was intruded as a collection of plutons that became more felsic in composition with time (Cowan & Bruhn, 1992). Lower Cretaceous magmas (>110 Ma) were mainly tonalitic in composition and the plutons were generally concentrically zoned to granodioritic or trondhjemite cores (Cowan & Bruhn, 1992). By the Upper Cretaceous (110 to 80 Ma), the magmas were mainly granodiorites with some quartz monzonites and granites in concentrically zoned plutons with mafic margins and felsic cores (Cowan & Bruhn, 1992). Chemical trends from west to east across the Sierra Nevada batholith include increasing SiO₂, K₂O and ⁸⁷/86Sr_i (0.704 to 0.706). These are due to the change in wall rock composition from western volcanic arc sediments to eastern continental interior, miogeoclinal rocks (Cowan &

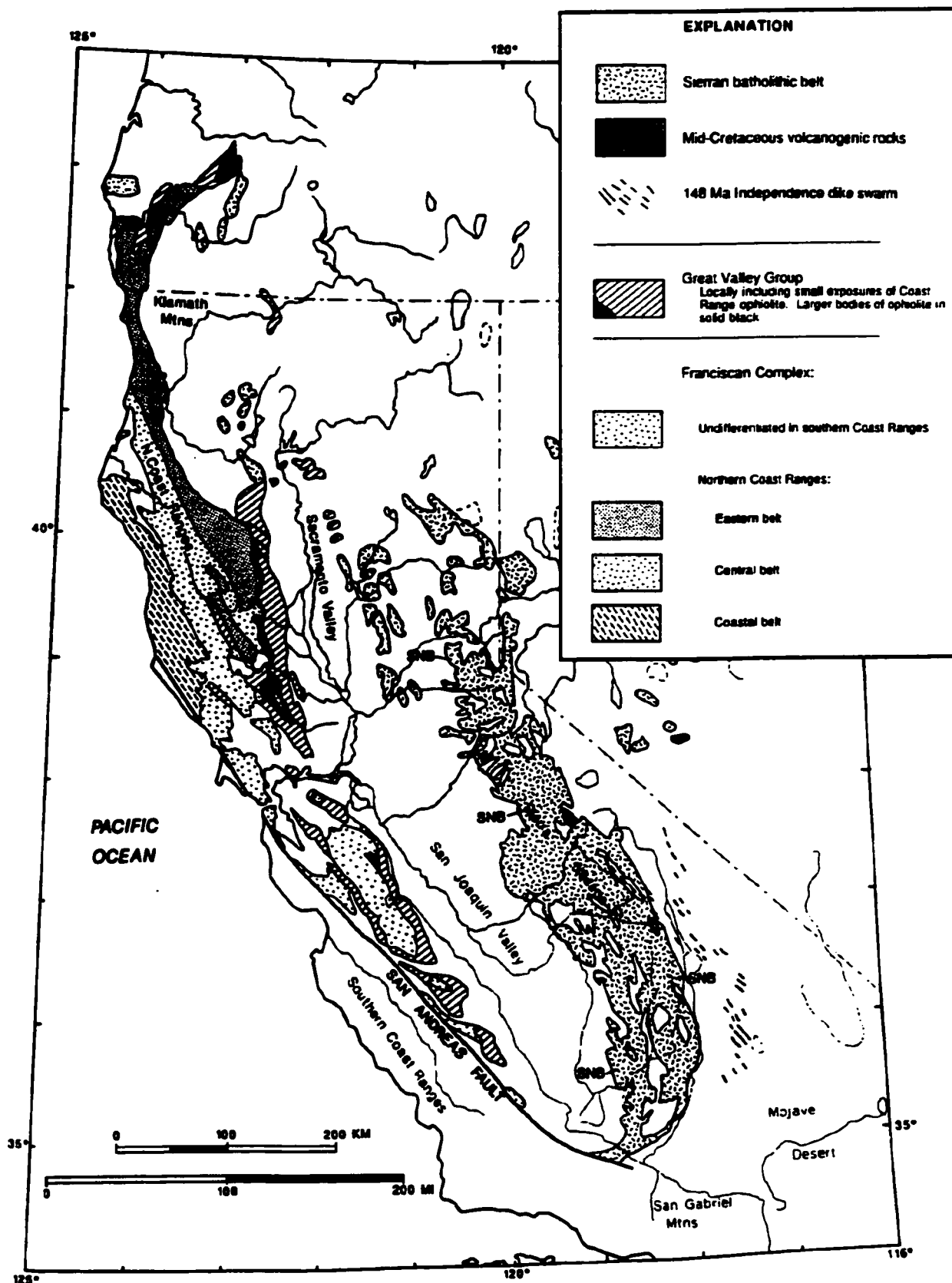


Fig. 1.4 Map of the western U.S. showing the active zones during the Jurassic and Cretaceous (after Cowan and Bruhn 1992).

Bruhn, 1992). Andalusite in the contact aureoles indicates emplacement of the Sierra Nevada batholith plutons at <10 km depth.

At 80 Ma, the Laramide orogeny began and the Sierra Nevada region was uplifted as the volcanic cover eroded away (Miller *et al.*, 1992). There was magmatism slightly to the east of the Sierra Nevada batholith in Nevada at 75 Ma (Miller *et al.*, 1992). Shallow subduction of the Farallon plate during the Laramide resulted in the uplift of the Rocky Mountains east of the North America plate edge (Christiansen & Yeats, 1992). In the early Eocene, there was attachment of accretionary terrains along the continental margin and deposition of auriferous gravels in the Sierra Nevada Range (fig. 1.5) (Christiansen & Yeats, 1992).

The end of the Laramide, at 50 Ma (mid Eocene), was signalled by the northward movement of the subduction zone, continued continental extension in the east, and strike-slip faulting in California (Christiansen & Yeats, 1992). The Great Valley basin was filled with sediments from the fore-arc basin as was the subduction zone to the west (Christiansen & Yeats, 1992). The northward moving subduction zone resulted in the Early Cascades Volcanic Arc in Washington and Oregon (Christiansen & Yeats, 1992). This magmatism reached down into northern California between 31 and 20 Ma, and Sacramento from 24 to 22 Ma (Oligocene) (Christiansen & Yeats, 1992). Also during the mid Tertiary, another magmatic belt extended from the Sierras to the Wasatch Range and reached the Tahoe area (<28 Ma) where andesite and rhyolite were deposited (Christiansen & Yeats, 1992). This generally marks the end of deposition in the Sierra Nevada region. Magmatic activity continues today in the Basin and Range of Nevada and in the Cascades to the north, while rotation of accretionary terrains continues in the Great Basin along the San Andreas fault system.

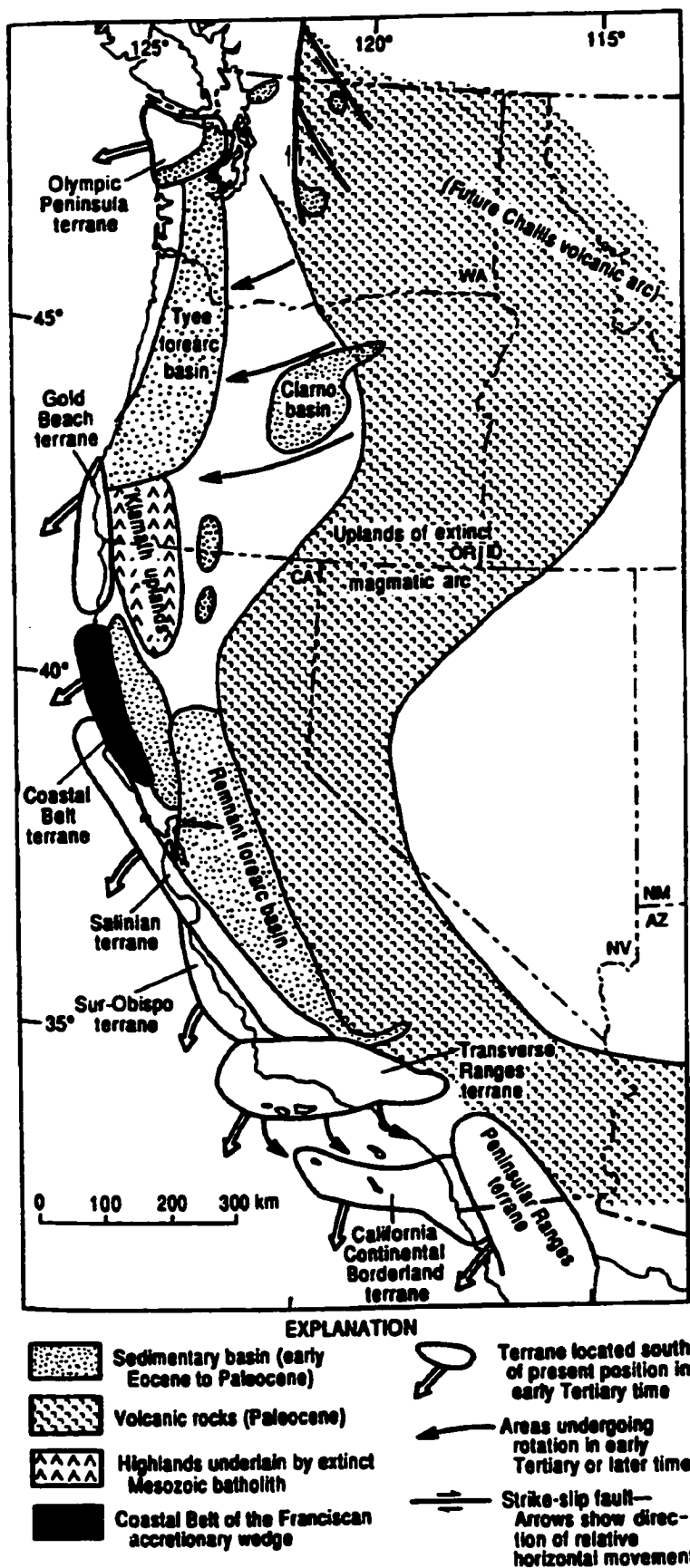


Fig. 1.5 Tectonic map of the western U.S. during the Paleocene and Eocene (Miller et al 1992).

1.6 Regional Geology of Fisher Lake

The Fisher Lake area is located less than an hour west of Truckee, CA about 6 km south of interstate highway 80. Access is from a 3 km long dirt road going south from Donner Trail School and then by foot along a ski trail (fig. 1.6). The scenery is quite beautiful with beige mountains, occasional evergreen trees, tiny blue/green lakes and a deep blue sky. Fisher Lake is at an elevation of ~2100 m, about 100 m above the main outcrops of interest. Orbicules and comb layering occur in small areas, usually less than 0.5 km² dispersed over ~ 4 km² of a Jurassic multiphase, composite, diorite pluton (McKinney, 1985; Moore & Lockwood, 1973).

The Fisher Lake area has been extensively mapped by McKinney (1985) at 1:24000 scale (fig. 1.7). He found three phases in the diorite whose cross cutting relationships revealed that the porphyritic phase was oldest, followed by the hornblende-rich phase, and then the orbicule and comb layering host phase. These were followed by granodiorite and then granite to make up the bulk of the composite pluton (McKinney, 1985). The comb texture host phase is heterogeneous containing dikes, hornblende clots, and xenoliths along with the orbicules and comb layering.

Field work was done during the summers of 1995 and 1996. In 1995, camp was set up at a nearby campground for one week with daily hiking in and out of the area in order to bring out as many samples as possible. A back-pack camp was established at a large pond just north of Fisher Lake in 1996 with observations, mapping, and sampling being carried out over a period of three days.

Samples taken during this study within a metre of either side of several comb layering units in the comb layering host phase were analysed and shown to be diorite but samples from amongst the orbicules appear to be gabbro (ch. 2.1). The gabbro is extremely localized while the

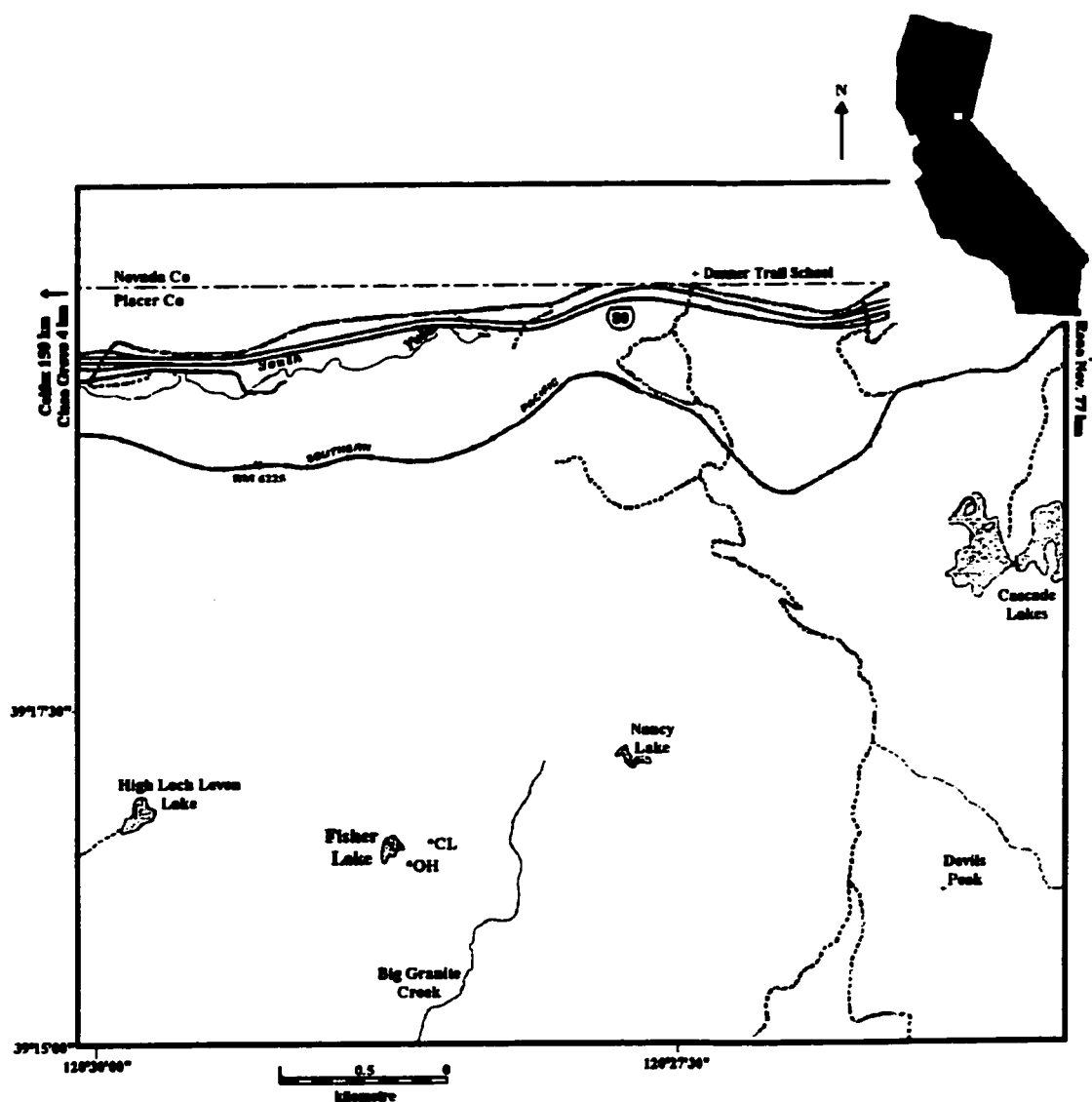


Figure 1.6 Location map of Fisher Lake CA showing the locations of Orb Hill (OH) and Comb Ledge (CL). Access to the area is via Interstate 80, through Cisco Grove to a secondary road to Donner Trail School and then a dirt road (dashed lines) to the Southern Pacific Railway. Ski trails allow hiking about 3 km to the outcrops.

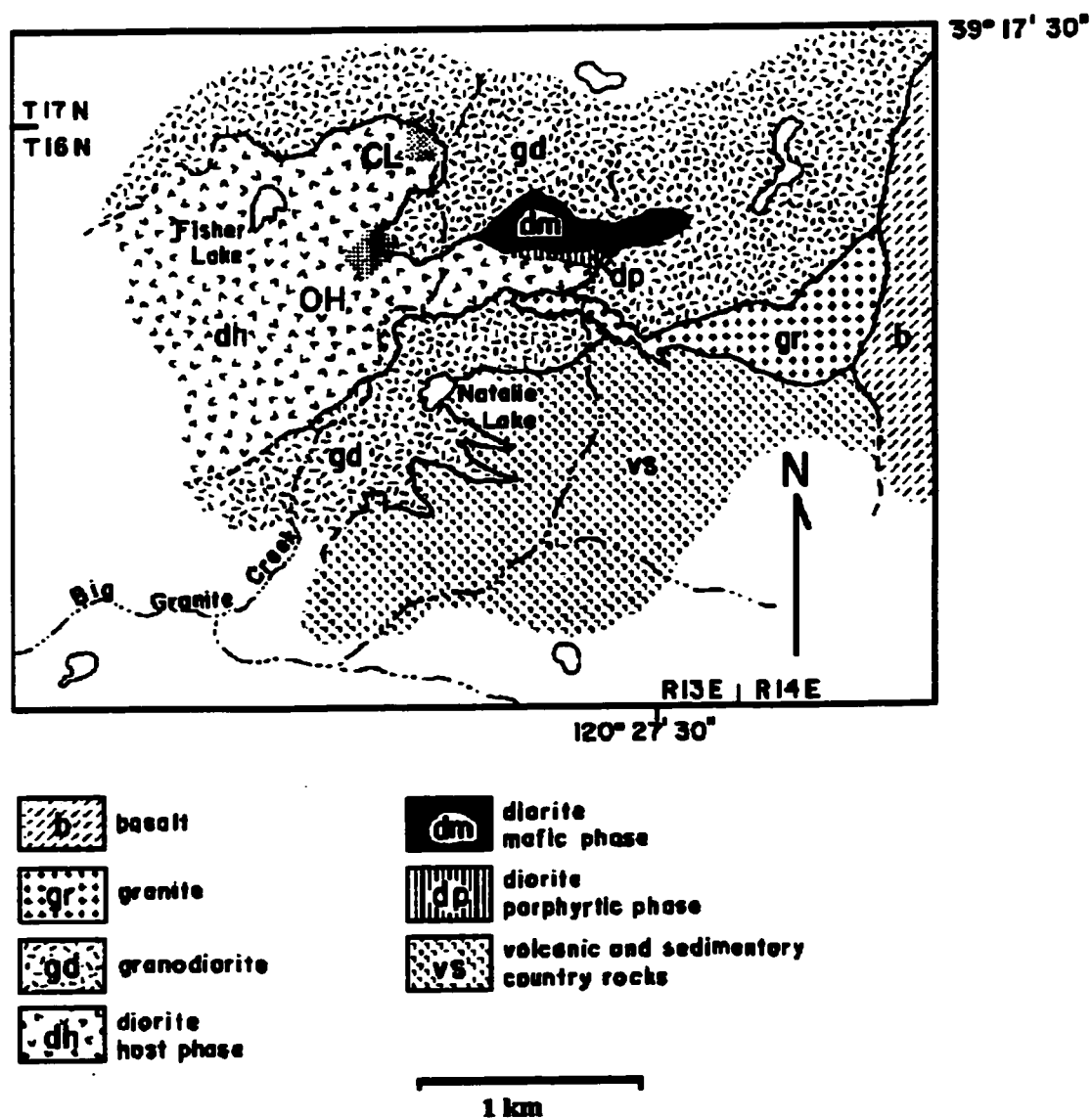


Fig. 1.7 Geology map of the Fisher Lake area showing the Orb Hill (OH) and Comb Ledge (CL) outcrops as stippled areas (after McKinney 1985).

diorite is far more extensive, thus, the naming of the outcrop as orbicular diorite by previous authors. However, for this study, the orbicular host rock will be called gabbro while the comb layering host rock will be designated diorite since there are important differences between the two comb textured phenomena.

The orbicules are found mainly in one small outcrop while the comb layering predominates in another small outcrop about 0.5 km north. McKinney (1985) named these two outcrops Orb Hill and Comb Ledge, a reflection of the major phenomena found there and the shape of the outcrops. Orb Hill is indeed a small hill near the base of a near-by steep rock face and Comb Ledge is a ledge on the side of this steep face. These names will be kept for this thesis.

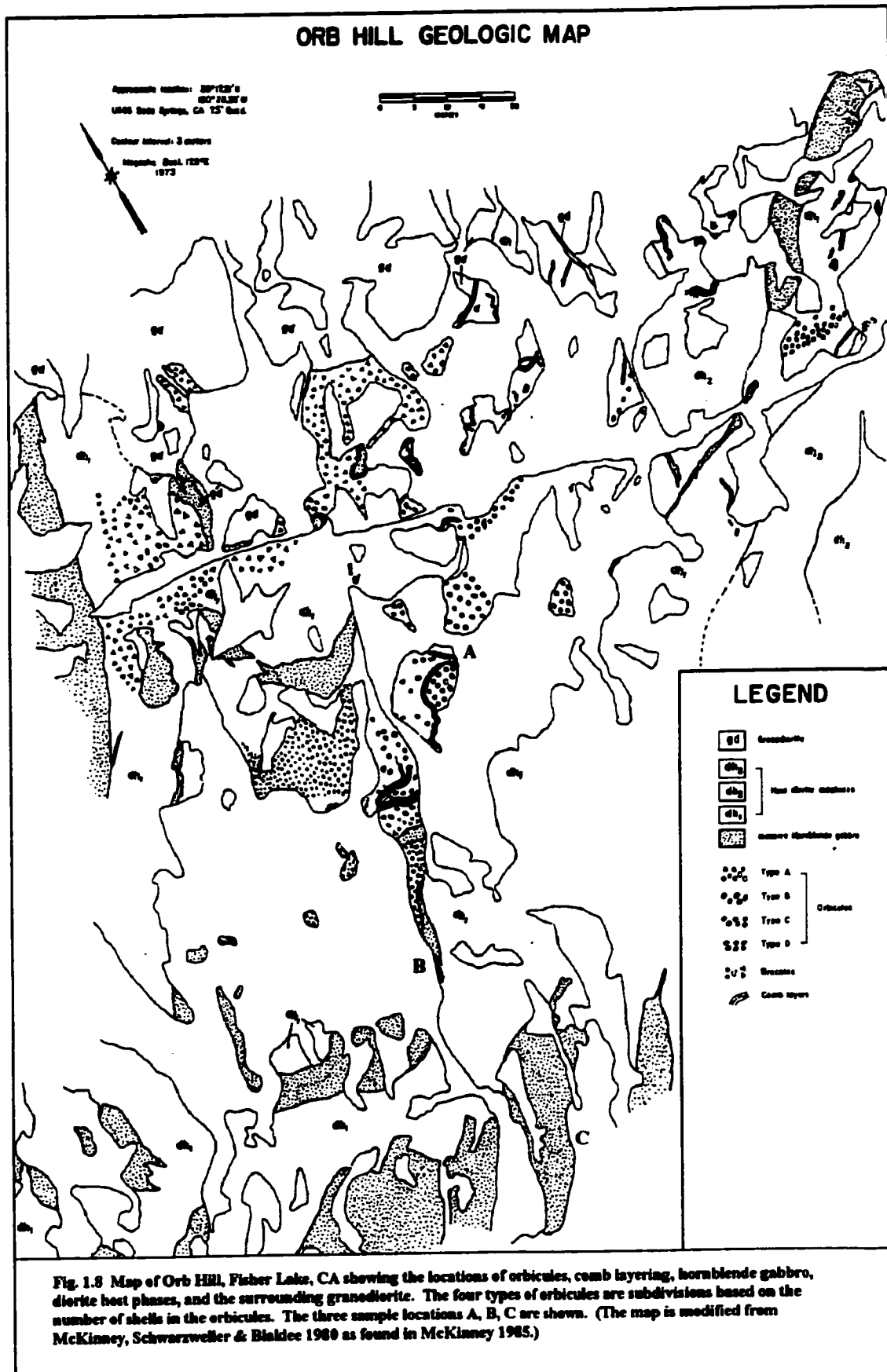
1.7 Geology of Orb Hill

Orb Hill is a small hill, roughly circular in plan, about 100 m in diameter and about 40 m high. The orbicules are the same overall colour as the surrounding rock and thus they are very difficult to spot until one is very close to them.

The orbicular host rock consists of two types of rocks, one more melanocratic than the other. Although both contain orbicules, the multi-shelled orbicules are more abundant in the darker gabbro while the small amount of comb layering found at Orb Hill is predominantly in the lighter diorite.

The orbicules are found scattered over the hill, concentrated in pockets from densely packed, separated by a few millimetres, to medium packing with up to decimetre separations.

Site B (fig. 1.8) has the highest concentration of orbicules ranging in complexity from uni- to multi-shelled, and in size, from a few cm up to 50 cm, the average being approximately 15 to



20 cm. The different types (based on the number of shells) of orbicules are often mixed together but at Site B they are segregated into pockets of the same type, i.e. angular breccia surrounded by a single shell, uni-shelled orbicules, or multi-shelled orbicules. There is a very prominent white and black banding in many of the multi-shelled orbicules, wherein felsic mineral layers alternate with mafic mineral layers around coarser-grained, white and dark green, cores (fig. 1.9). Smaller orbicules are only slightly less colourful with some brown (orthopyroxene) overtones. The orbicular shells do not appear to be correlative between adjacent orbicules. There are pockets over 20 cm long of very coarse grained plagioclase and hornblende crystals up to 3 cm long that are similar in appearance to the Greendale complex appinites from Nova Scotia (Murphy *et al.*, 1991). The Greendale appinites (visited by Durant in 1996) formed from pockets of water-rich gabbroic melt found near the tops of small stocks. The “appinites” at Fisher Lake (fig. 1.10) are found in the melanocratic host rock with no visible reaction rim between them and the host rock. Orbicules in the same area as the “appinites” are found in a coarse grained hornblende matrix (fig. 1.11) that weathers faster than the finer grained orbicules, resulting in the orbicules falling out of the host rock onto a scree slope. The orbicules are not perfectly spherical but ellipsoidal, and in outcrop, are usually crowded together with only a thin veneer of host rock between them. Many of the orbicules are greenish due to weathering of orthopyroxene to hornblende.

A sharp contact between the lighter brown diorite and the darker (nearly black) gabbro (fig. 1.12) is located at Site C (fig 1.8). The brown diorite looks similar to the diorite host rock of Comb Ledge including the black amphibole clots (clusters of subhedral, cm size, crystals) that are clustered at the contact. The brown colouration is due to weathering of orthopyroxene.

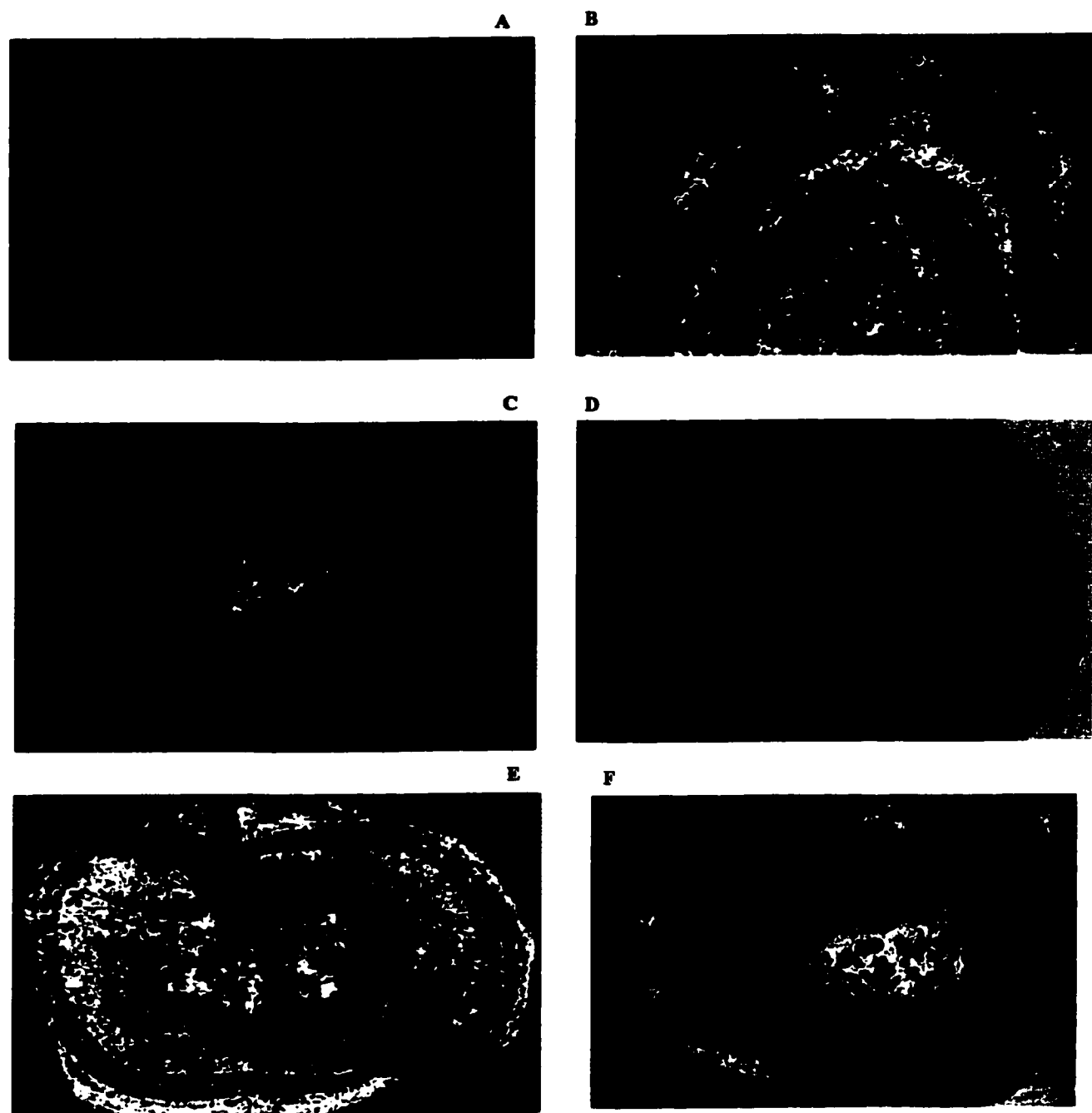


Fig. 1.9 Photos of the wide variety of orbicules found at Orb Hill. Horizontal field of view; A) 9 cm, B) 11 cm, C) 9 cm, D) 6 cm, E) 9 cm, F) 12 cm.



Fig. 1.10 In-situ pocket of elongated amphibole crystals found within the gabbro. Note the absence of a reaction rim with the host rock. (knife handle is 8.3 cm long) Photo taken by A.E.Lalonde.



Fig.1.11 Outcrop of multi-shelled orbicules in the gabbro. The matrix is mainly large amphibole crystals. (knife is 8.3 cm long) Photo taken by A.E. Lalonde.



Fig. 1.12 Photo showing the sharp contact between the hornblende gabbro on the left and the diorite on the right. Clots of hornblende crystals can be seen along the contact in the diorite. (Fully open Brunton compass is 22 cm long) Photo taken by A.E. Lalonde.

A large splay of comb layering (about 2 m by 1 m) is present at Site A (fig. 1.8) with orbicules between the splayed layers (fig. 1.13). The splay composition is mainly brown orthopyroxene, and plagioclase. Development of the orbicules within the layers ranges from one shell around a piece of angular breccia to many shells around a coarse grained centre (fig. 1.14). The host rock surrounding the splay appears to be the same brown diorite as seen at Site C. The crystals in the host rock are largely unoriented and the rock has a heterogeneous texture seen as varying amounts of black hornblende (fig. 1.14) among the orthopyroxene and plagioclase.

1.8 Geology of Comb Ledge

Comb Ledge is about 60 m wide by about 100 m long and is located on a fairly steep rock face. The comb layering is found only on the ledge and does not extend up the side of the rock face. The ledge ends in a vertical drop of more than 100 m down to a river valley and thus it is unknown if the comb layering continues in this direction.

Spectacular comb layering is found throughout Comb Ledge in a multitude of colours, layer thicknesses, crystal shapes and mineral types (fig. 1.15). The colours range through black, red, gray, brown, and white while the layers range from mainly mm up to approximately 2 cm in thickness. Sequences of layers range from a few 10's of cm to about 10 m (fig 1.16) The comb layering is straight in some spots but often has gentle curves that occasionally turn into fairly sharp corners. Packages of comb layers tend to end under brush or broken rocks. One site of splayed comb layering (less spectacular than the one at Orb Hill) shows the layers splitting apart and fading into the diorite host rock.

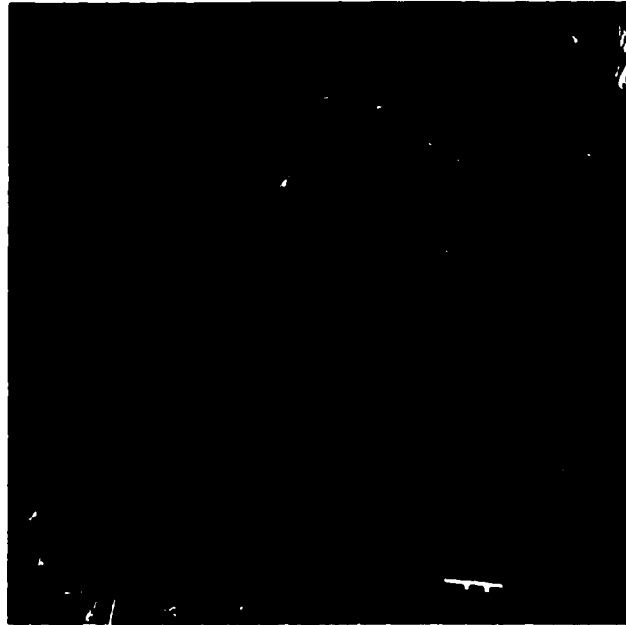


Fig 1.13 Large splay of comb layering at Orb Hill in diorite. There are orbicules within the the splay that range from pieces of breccia to multi-shelled. The crystal growth direction of the comb layering on the left side is towards the bottom left corner. (scale is a colour control patch 20 cm long) Photo taken by A.E. Lalonde.

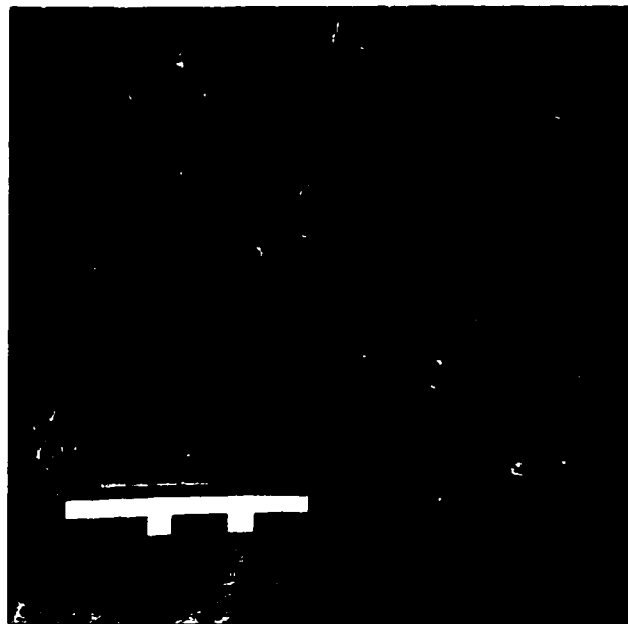


Fig. 1.14 Close up of an orbicule from within the comb layering splay shown above, towards the top right hand corner. The heterogeneous texture of the host diorite is visible via the black amphibole crystals. (scale is same as above) Photo by A.E. Lalonde.

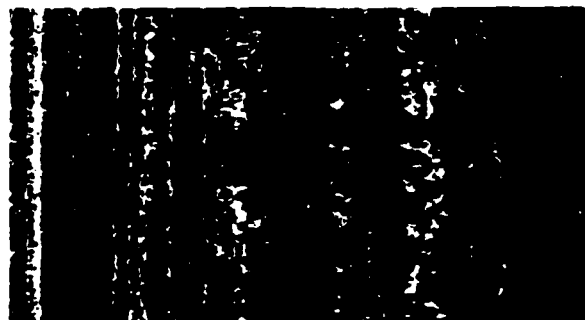
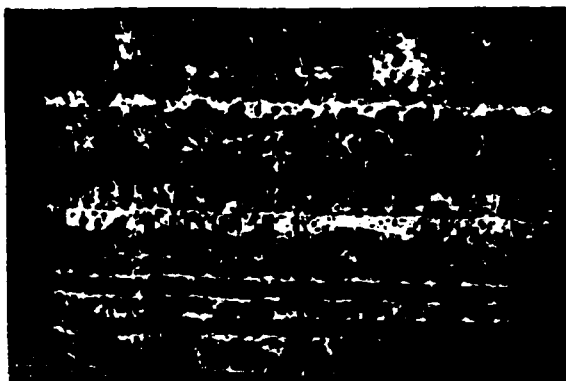
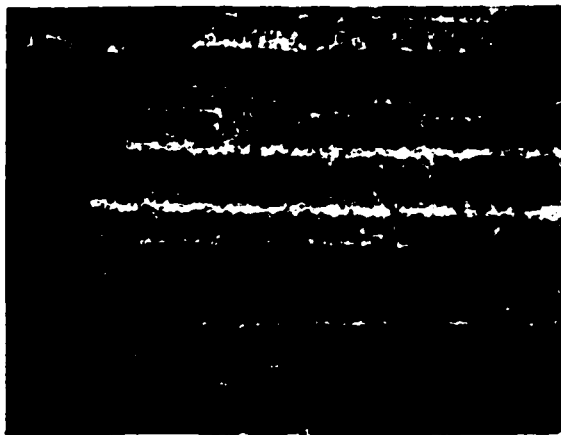


Fig. 1.15 Photos showing the diversity in the comb layering found at Fisher Lake (horizontal field of view for each photo is ~10 cm).

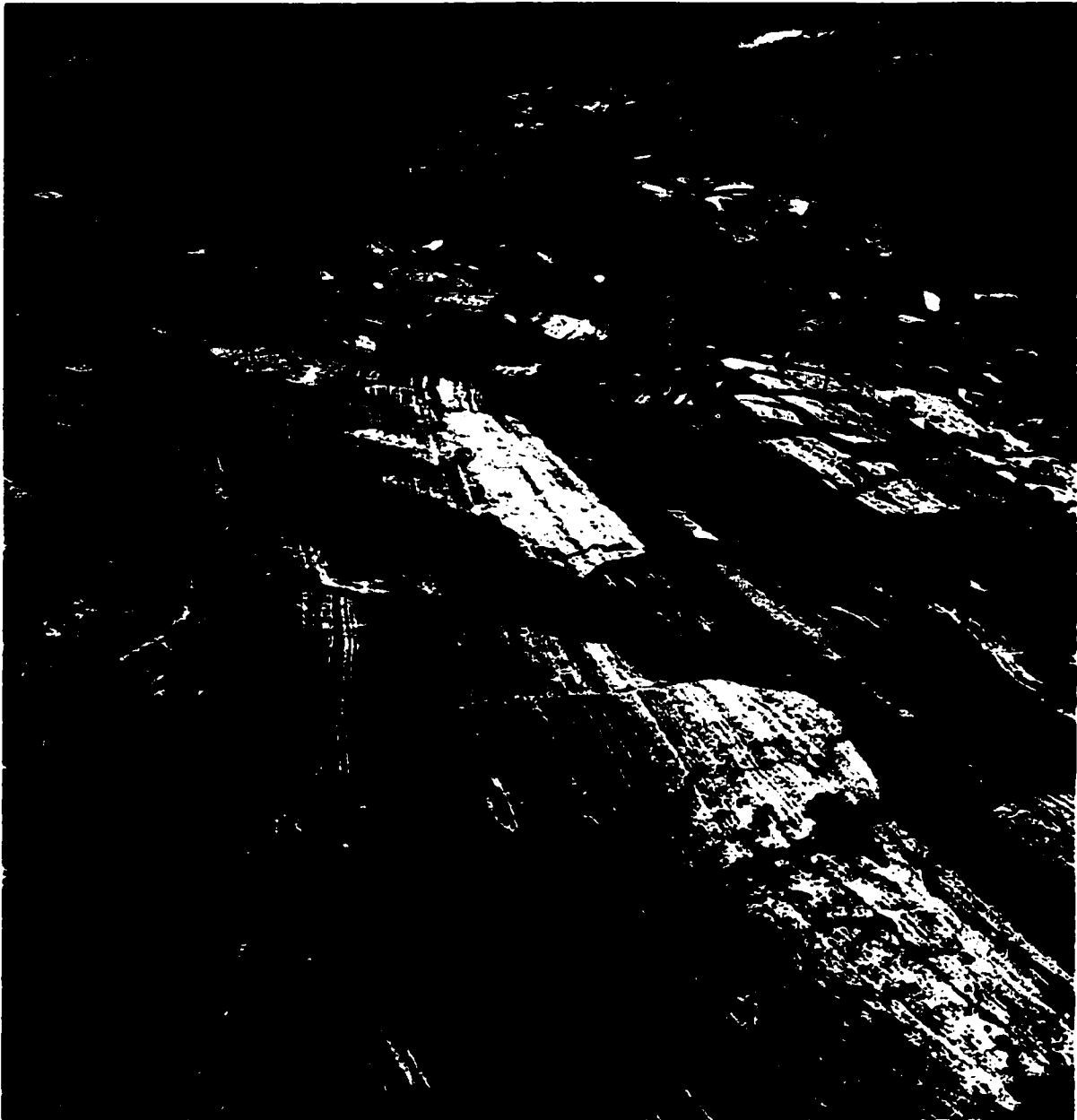


Fig. 1.16 Spectacular example of the comb layering found at Comb Ledge. This package of layers is more than 10 m wide . The mineralogy consists mainly of plagioclase, amphibole and pyroxene that create brown, white and black layers all set in a brownish diorite. (scale is a 22 cm fully open Brunton compass) Photo by A.E. Lalonde.

Since each comb layering sequence is different from any other and since there were so many of these sequences, it is not feasible to describe them all here. Therefore only a few sites, each fairly representative of a number of sequences, were observed in detail. The comb layering package seen in figure 1.16 was too big to analyse in detail during the short time that we were there so we just admired it!

A close look at one sequence at Site 2 (fig. 1.17) shows comb layering that pinches and swells from 27 cm to 37 cm (fig. 1.18). The growth direction of the layers was determined by observation of the branching amphibole crystals. At the interface from which the branching crystals grew, or the “growth horizon”, both sharp and gradational contacts were found. Also, there was a small enclave of host rock within the layering. Clusters or clots of amphibole crystals were concentrated along the sides of the comb layering. The host rock on both sides of the comb layering appeared to be similar. To test how similar, samples of the host rock from both sides of the comb layering were taken and bulk chemical analyses were done (chapter 3.2). This sampling procedure was also followed for specimens collected at Sites 3 and 4.

Comb layering at Site 3 (fig. 1.17) is about 37 cm thick and has a large, mafic enclave (~1 m long) along one edge (fig. 1.19). Branching orthopyroxene crystals could not be found in order to determine growth direction. Hornblende clots were concentrated along the sides of the comb layering.

In contrast to the brown overtones of the comb layering at the previous sites, the comb layering at Site 4 (fig. 1.17) was much more colourful having black hornblende crystals alternating with white plagioclase and minor brown orthopyroxene (fig. 1.20). The host rock at the base of this package of comb layering is more melanocratic than that seen at the other sites. Here again

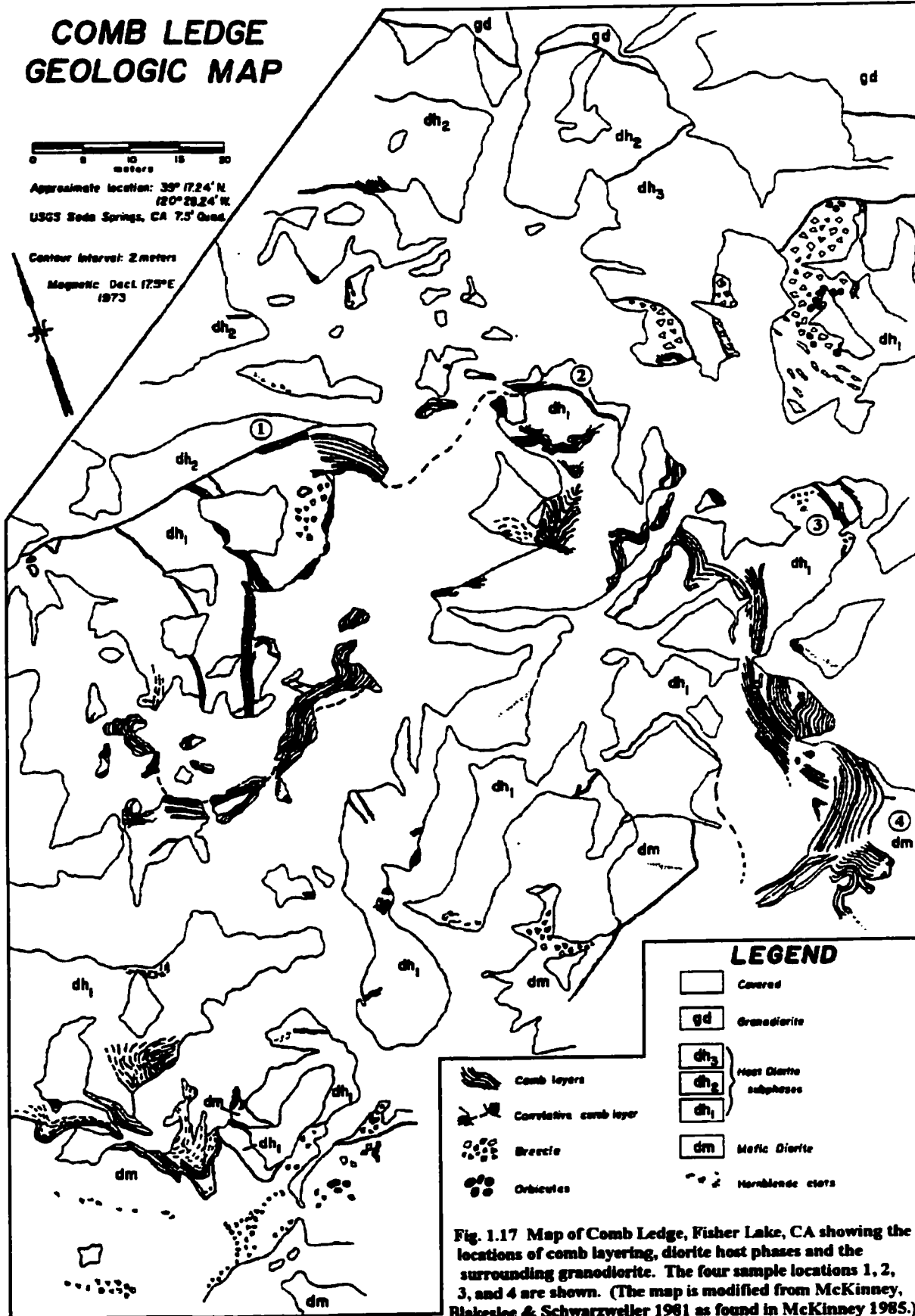
COMB LEDGE GEOLOGIC MAP



Approximate location: 39° 17.24' N
120° 28.24' W
USGS Soda Springs, CA 7.5' Quad

Contour Interval: 2 meters

Magnetic Decl: 17.3° E
1973



LEGEND

- Covered
- gd Granodiorite
- dh₃ Host Diorite subphases
- dh₂
- dh₁
- dm Mafic Diorite
- Hornblende clots

Fig. 1.17 Map of Comb Ledge, Fisher Lake, CA showing the locations of comb layering, diorite host phases and the surrounding granodiorite. The four sample locations 1, 2, 3, and 4 are shown. (The map is modified from McKinney, Blakeslee & Schwarzweller 1961 as found in McKinney 1985.)

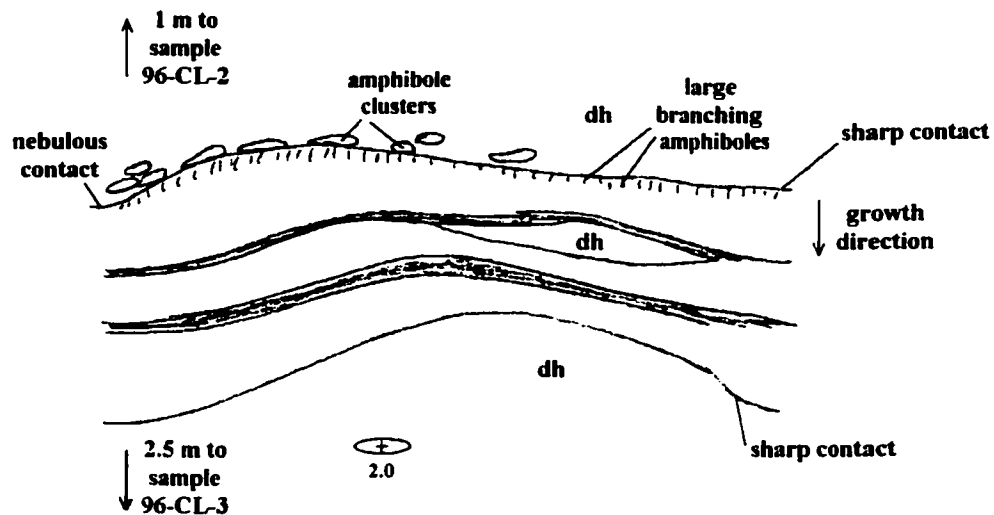
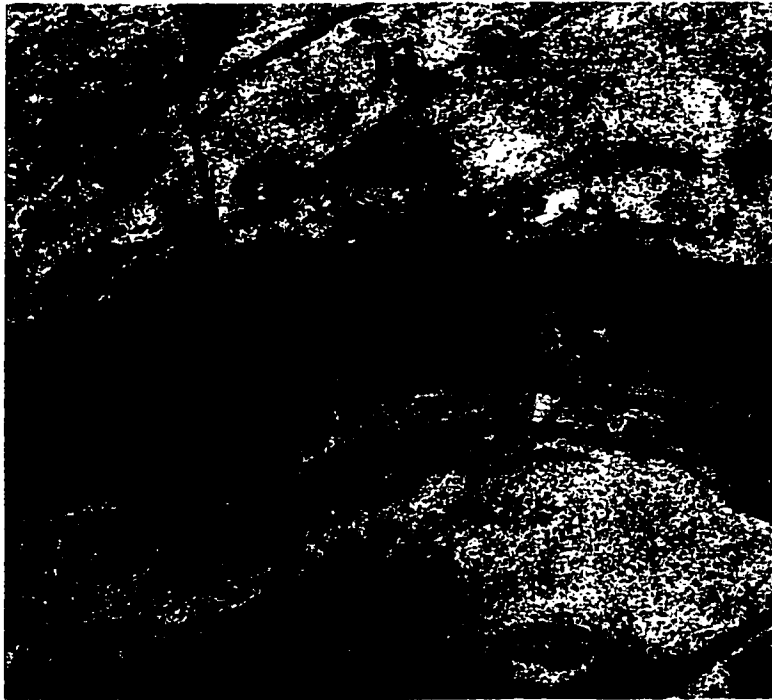


Fig. 1.18 Photo showing a segment of comb layering that pinches and swells from Comb Ledge. Below is a sketch showing details of the photo such as sharp and nebulous contacts between the comb layering and the host diorite (dh), the large branching amphibole crystals that indicated growth direction, amphibole clusters, and a pocket of diorite within the comb layering and locations of two host rock samples analysed in chapter 3. (Swiss army knife is 8.3 cm long). Photo by A.E. Lalonde.

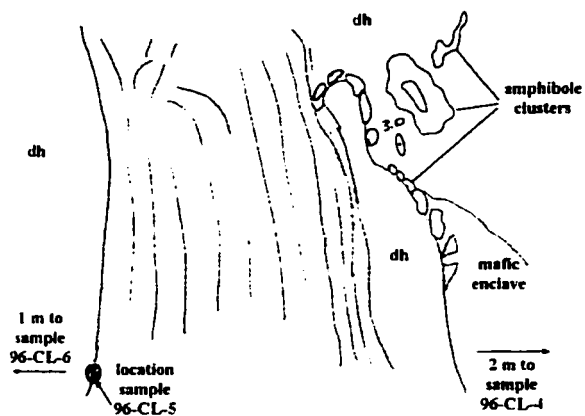


Fig. 1.19 Photo showing comb layering from Comb Ledge with very strong colour banding variations of brown, white and black. The layering (~37 cm across) is surrounded by diorite (dh), amphibole crystal clusters, and a nearby mafic enclave less than 0.5 m long. The scale is a Swiss army knife, 8.3 cm long located towards the upper right. Photo by A.E. Lalonde.

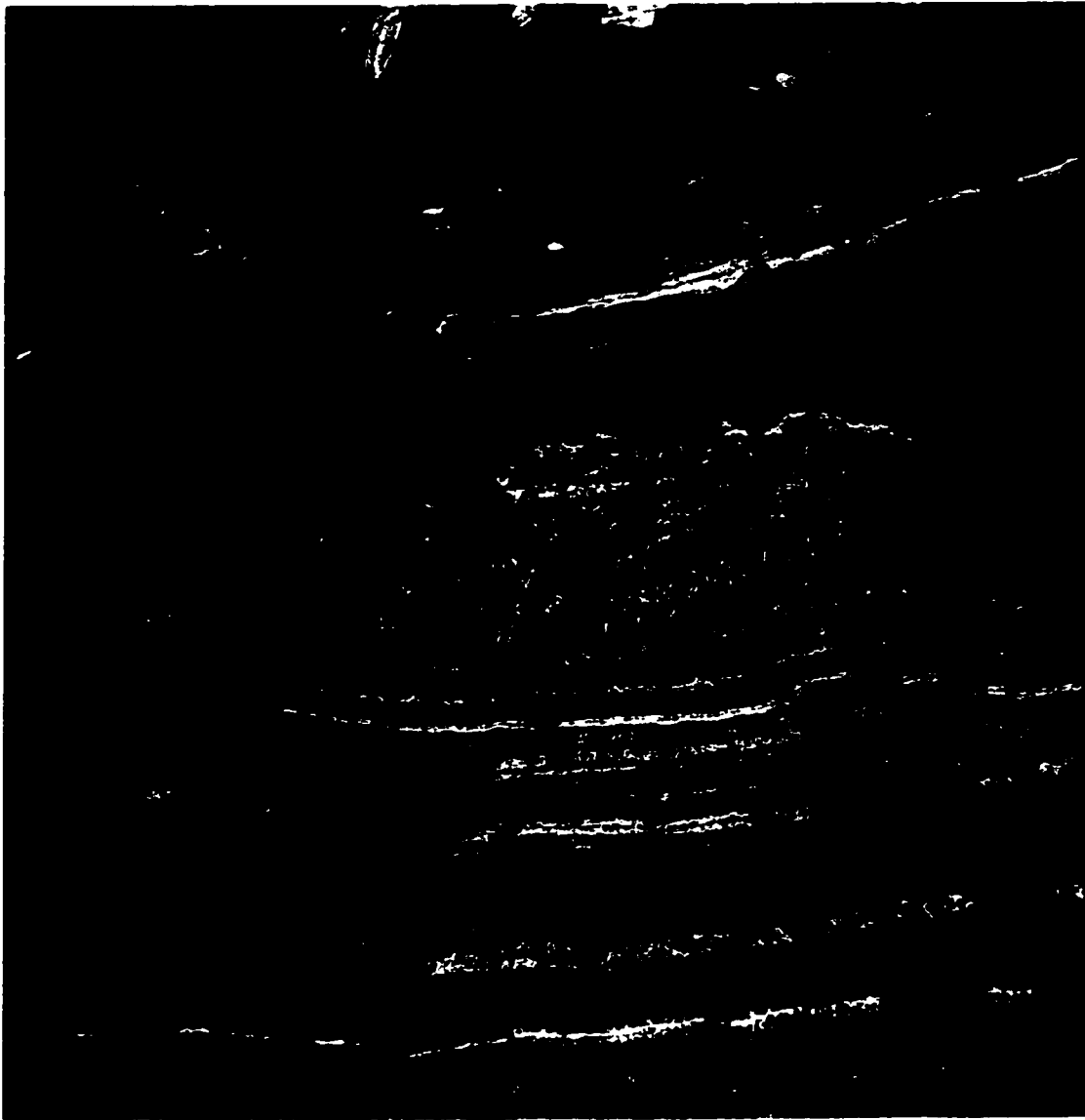


Fig. 1.20 Photo of black (hornblende) and white (plagioclase) comb layering at Comb Ledge. The brown weathered host diorite can be seen at the top. Sample 96-CL-7 (chapter 2) was collected 2.5 - 3 m below this face. In the centre can be seen elongated amphibole and plagioclase crystals up to 2 cm long that look very much like the appinites found in Nova Scotia (see text). Branching amphibole crystals in the comb layering just below the appinite bleb indicate that the growth direction is towards the bottom of the photo. (Swiss army knife upper left of centre is 8.3 cm long). Photo by A.E. Lalonde.

growth direction of the comb layering was determined by black branching hornblende crystals. There are many 'appinite' enclaves amongst the layering with crystals up to 3 cm long (fig. 1.20). The layering in figure 1.20 was gently curved like much of the rest of the comb layering on Comb Ledge but, as can be seen in figure 1.21, the layering can be tightly folded, as in this case, into an omega shape. This particular spot was the most spectacular representation of the undulating nature of many of the comb layering packages. No faults or dikes were seen to indicate that the omega curving of these layers could have formed after solidification of the magma.

The heterogeneous nature of the diorite host rock was investigated at Site 1 (fig. 1.17). This diorite is medium grained and weathered light brown due to the orthopyroxene. It contains many coarse grained hornblende clots scattered randomly over the surface which weathered out easily, leaving pits in the rock surface. Also the diorite contains small, decimetre-sized pods of coarser-grained diorite as well as pods of finer-grained diorite (fig. 1.22). There are no visible reaction rims between the pods, clots and host rock, but the pods are surrounded by a fabric composed of oriented hornblende. Only a few orbicules were found in the host diorite, ranging in size from a few cm to ~ 10 cm in diameter. Their colour was mainly black (hornblende) or brown (orthopyroxene). Closer inspection of the orbicules was needed to see the light coloured, felsic shells. There were no visible reaction rims between the orbicules and the host rock though there were again aligned hornblende grains around some orbicules (fig. 1.23).

As can be seen in several of the preceding figures (e.g. figures 1.19, 1.22, 1.23), heterogeneity in the diorite host rock is not uncommon. The lack of reaction rims between the host rock and the heterogeneities suggest that they mixed together gracefully, i.e. temperature and/or compositional differences were small.

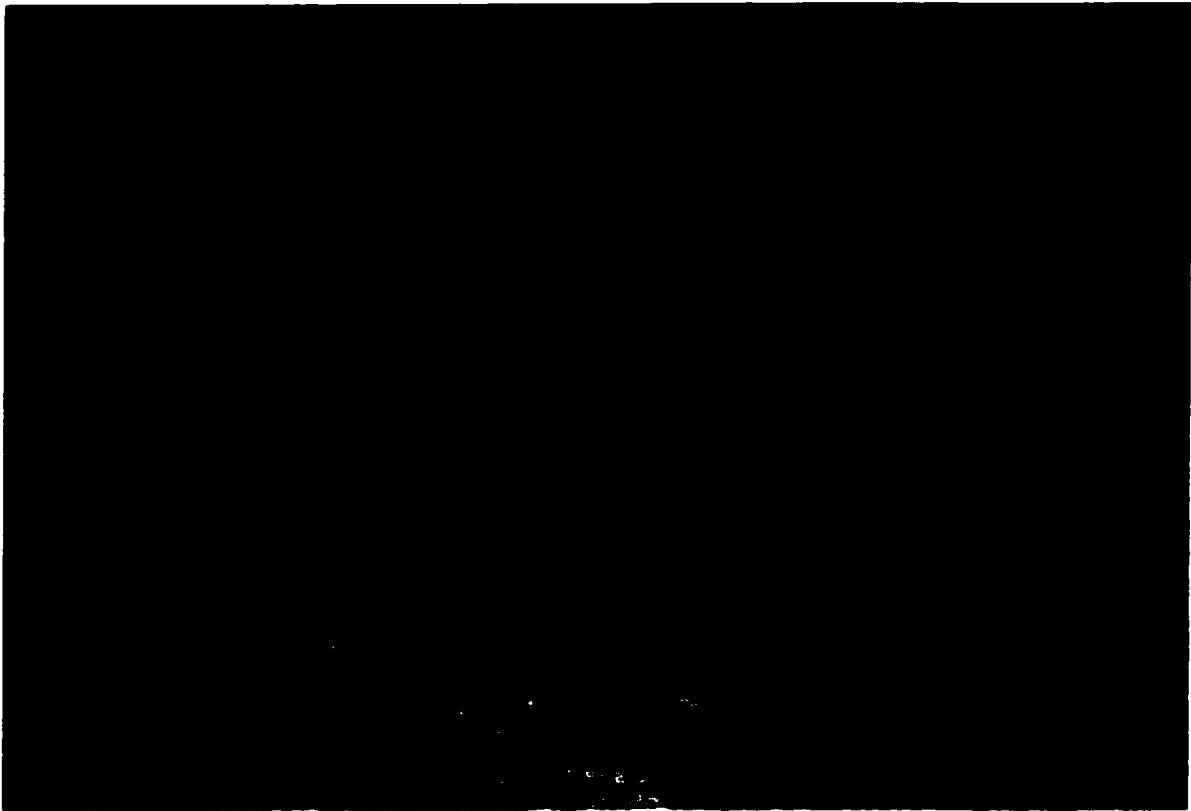


Fig. 1.21 Photo of a very colourful segment of comb layering from Comb Ledge with red, black, white and brown layers. The layers are highly curved resembling an omega shape of which one half of the omega can be seen here. The curving of the layers appears to be primary, i.e. there are no dikes or faults, etc. to indicate that movement took place after solidification of the magma. There are many appinite blebs within the comb layering containing amphibole crystals up to 3 cm long. The outcrop shown in the photo is about 3 m across. Photo taken by A.E. Lalonde.

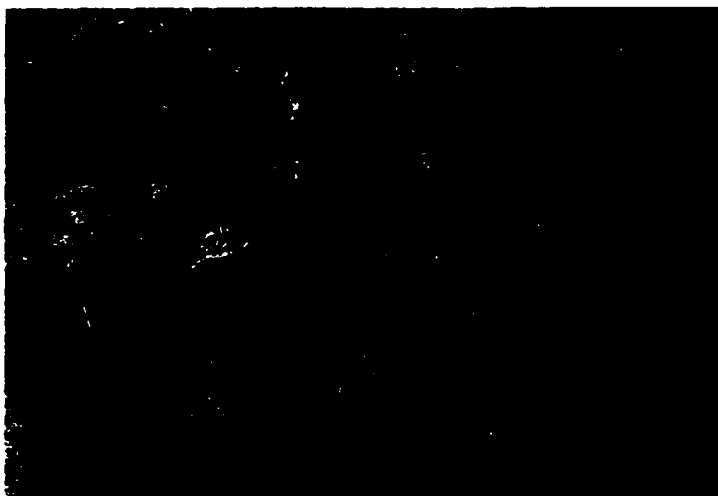


Fig. 1.22 Photo taken at Comb Ledge showing two inclusions, one coarser grained and the other finer grained, than the surrounding rock. The two inclusions appear to have approximately the same composition as the surrounding rock. They are surrounded by a fabric of oriented hornblende. There is no reaction rim around the coarser grained inclusion and only a thin, faint rim around the finer grained inclusion. (Swiss army knife is 8.3 cm long). Photo by A.E. Lalonde.

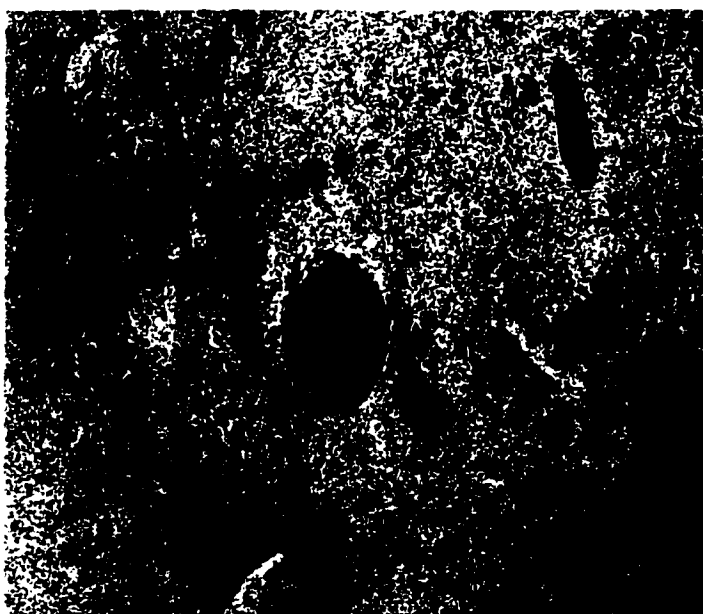
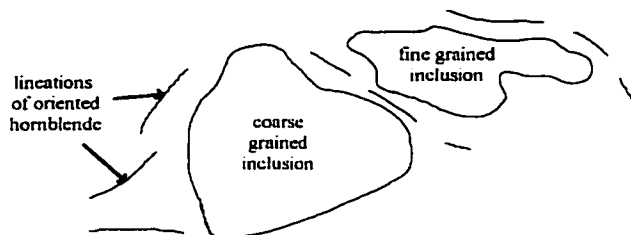
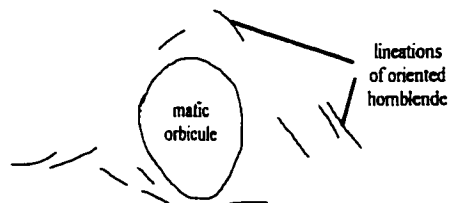


Fig. 1.23 Photo from Comb Ledge showing a mafic orbicule with a coarse grained centre surrounded by a fabric of oriented hornblende. There is no reaction rim between the orbicule and the surrounding rock. (Swiss army knife is 8.3 cm long). Photo by A.E. Lalonde.



1.9 Branching/Budding Crystal Habits

A particularly noticeable feature of the orbicules and the comb layering is the unique crystal habits that make up the comb texture. In the orbicules the comb texture consists of platy, branching/budding orthopyroxene (fig. 1.24) and feather plagioclase (fig. 1.25) while in the comb layering, platy, budding hornblende crystals make up much of the comb texture (fig. 1.26). The elongated, branching/budding morphology of these minerals is reminiscent of dendritic growth.

Generally, dendrites are indicative of high undercoolings where both diffusion and crystal growth rates are fast. When crystal growth rates are faster than chemical component diffusion through a melt, a thick boundary layer of rejected impurities builds up before the growth front. Large perturbations on the crystal face are the only ones that can reach through this thick boundary layer to get to undepleted magma. The shape of these perturbations is generally long and slender, i.e. dendritic (fig. 1.27).

Experiments done by Lofgren (1980) using basalts produced millimetre-sized, dendritic crystals of pyroxenes at cooling rates of over 10 °C/hr and of plagioclase at over 30 °C/hr. These types of high cooling rates are likely found in dikes or sills and show how chill margins of small magmatic bodies can contain dendritic growth. These crystals are also much smaller than those of the branching/budding crystals in the comb textures of Fisher Lake. This said, these experiments will help to constrain the conditions for orbicule and comb layering formation as will be discussed in future chapters.

The branching crystals found at Fisher Lake are much longer (up to 1 cm) and thicker (up to 0.5 cm wide across the ends of the branches) than typical dendrites. In the orbicules, the most spectacular branching orthopyroxenes were found in the innermost shell radiating away from the

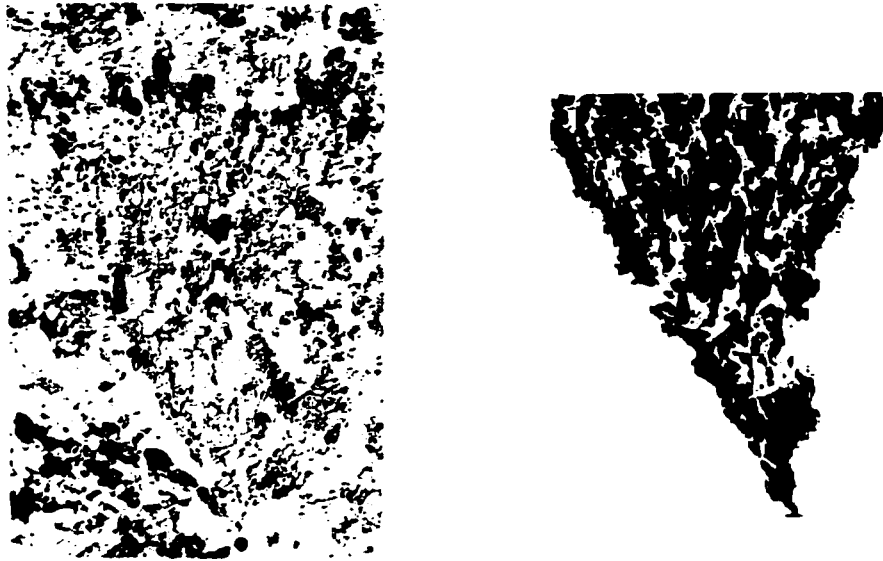


Fig. 1.24 Photomicrograph (left photo) of a branching orthopyroxene from the innermost shell of a Fisher Lake orbicule. The detail of the branching crystal is enhanced in the black/white image on the right. Crystal is 8 mm from top to bottom. Growth direction of the crystal is from bottom to top.

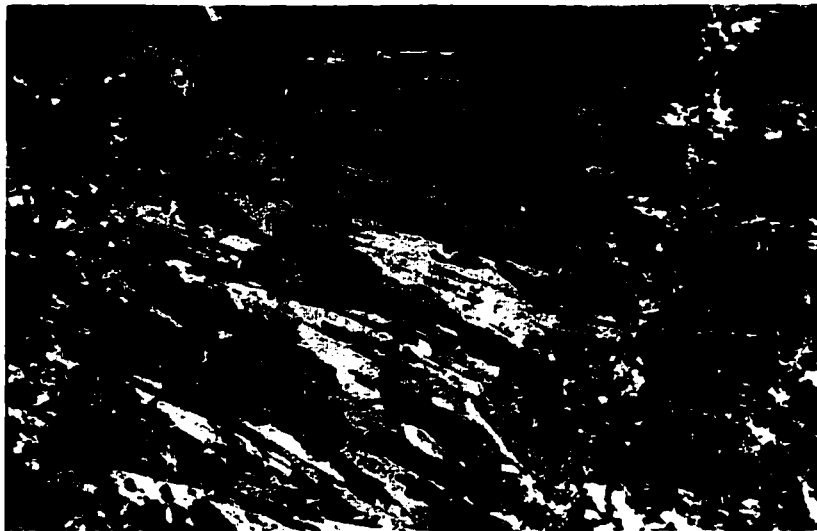


Fig. 1.25 Photomicrograph of feather plagioclase (crossed polarizers) from an orbicule. The plagioclase crystals are about 5 mm long. Growth direction of the plagioclase crystals is from the left to right away from the central core. A shell of tiny anhedral crystals cuts through the feather plagioclase. (Photo is ~ 1 cm wide)



Fig. 1.26 Photomicrograph of platy, budding, elongated hornblende in comb layering from Fisher Lake. Growth direction is from left to right. Horizontal field of view is ~1.5 cm.



Fig. 1.27 Two examples of the branching dendritic shape. The upper photo, A, is of dendritic crystals formed in impure hexachloroethane. The lower photo, B, is crystalline manganese dioxide in limestone. (photos from Kirkaldy, 1999; no scale given)

xenolithic core (e.g. fig. 1.24) where the chemical potential gradient between the xenolith and the magma would have been maximum. Subsequent radial shells contain smaller orthopyroxenes that are mainly budding with only the occasional single, side branch. The feather plagioclase are best formed in outer shells where the orthopyroxene are smaller and the plagioclase have taken up more space.

2. Petrography

Detailed petrographic and chemical (chapter 3) studies have been done on several specimens of host rock from both Orb Hill and Comb Ledge along with one sample of comb layering from Comb Ledge and two orbicules sampled from the float at Orb Hill. Both orbicules contain at least two shells each of radial/longitudinal growth and anhedral growth.

2.1 Host Rocks

At Orb Hill, samples were taken of two different host rocks, one more mafic than the other. At Comb Ledge, two different host rocks were also evident with one slightly more mafic than the other. Also, samples of the host rock from each side of three sets of comb layering were collected in order to determine if the comb layering was currently situated at the boundary between two different types of igneous rock.

All of the samples had a light brown colouration to the weathered surface due to the presence of orthopyroxene. These weathered surfaces also had variable relief with black hornblende having a higher relief than the brown orthopyroxene and light gray plagioclase.

2.1.1 Orb Hill - Felsic Host Rock 96-OH-1

The hand sample has a light gray fresh surface, along with a weathered light brown and black surface. Crystals are phaneritic, small to medium sized, ranging up to 1 mm for orthopyroxenes and up to 3 mm for plagioclase. The sample is about two thirds white to light gray plagioclase and one third mafic minerals. There are occasional anhedral clusters (up to 2 cm) of black hornblende and light brown orthopyroxene with crystals up to 3 mm long.

In thin section (fig. 2.1), plagioclase is by far the most abundant mineral (table 2.1). It is subhedral and generally clear under plane light. Overgrowths can be seen as turbid zones with fluid inclusions and in the sweeping extinction under crossed polars. Most crystals have albite twinning while a minority have both albite and Carlsbad twinning. The albite twinning is often indistinct and smeared but ten measurements of An content using the Michel-Lévy technique found An_{39-71} . A single albite-Carlsbad twinned crystal produced An_{77} . One albite twinned crystal with a distinct core and rim produced values of An_{66} and An_{37} respectively. One crystal with a core and rim was analyzed by electron microprobe producing values of approximately An_{45} and An_{65} respectively. The majority of crystals appear to have an axial ratio of about 1:1. The more calcic plagioclase, albite-Carlsbad twinned crystals are generally larger than the albite twinned

<i>mineral</i>	<i>96-OH-1 (felsic)</i>	<i>96-OH-2 (mafic)</i>
plagioclase	69	43
orthopyroxene	6	3
clinopyroxene	5	<1
amphibole	12	43
Fe-Ti oxides	6	5
biotite	2	-
alteration	<1	6
rock type (IUGS)	hornblende diorite	hornblende gabbro

Table 2.1 Mineral mode percentages for the two Orb Hill (OH) host rocks attained by point counting 1000 points per thin section per sample.



Fig. 2.1 Scanned image of the felsic host rock from Orb Hill (96-OH-1). Large black crystals are amphibole, gray are pyroxene and colourless are plagioclase. Thin section is 3 cm by 2 cm.

crystals suggesting that there may be more than one generation of plagioclase crystals (the larger, more calcic crystals and the smaller albite twinned crystals), and/or that the rock cooled through a large temperature range. The smearing of the albite twinning adds uncertainty to the optical determination of An content values.

Orthopyroxene and clinopyroxene crystals are also subhedral and have a red staining from alteration along many fractures. Often found rimming the pyroxenes are pale yellow-brown to dark green, pleochroic hornblendes, along with small, euhedral to subhedral Fe-Ti oxides and very small amounts of red-brown biotite that are found along fractures of the pyroxene crystals.

All the crystals in the thin section appear to be randomly oriented. It is likely that plagioclase and pyroxene formed first, Fe-Ti oxides next and hornblende last.

The naming of this rock as a diorite or a gabbro was based on the criterion laid out in table 2.2. The prefix "hornblende" is retained as a rock descriptor name consistent with IUGS naming conventions (Streckeisen, 1976).

<i>criterion</i>	<i>Gabbro</i>	<i>Diorite</i>
plagioclase composition ¹	An>50	An<50
associated rocks ¹	pyroxenites & anorthosites	granodiorites & quartz diorites
mafic minerals ¹	clino- or orthopyroxene ± olivine & hornblende	primary hornblende or biotite ± augite
colour index (% mafic minerals) ¹	>40	<40
plagioclase colour ¹	gray to greenish gray	white
plagioclase ²	average An ₆₅	average An ₄₀
plagioclase range ²	labradorite to anorthite	oligoclase to calcic andesine

Table 2.2 Criterion for classifying gabbros versus diorites
(1- Hyndman, 1985; 2 - Nockolds *et al.*, 1978)

Thus according to table 2.2, this host rock is classified as a diorite since the amount of mafic minerals is < 30 % and the most abundant mafic mineral is hornblende.

2.1.2 Orb Hill - Mafic Host Rock 96-OH-2

In hand sample, this host rock is dark gray, with a weathered surface that is black and light brown. The sample consists of about two thirds black hornblende and biotite and about one third light gray plagioclase. The crystals are phaneritic, medium sized, approximately 1 to 3 mm long, and are mainly equigranular except for occasional clusters, up to 1 cm long, of black biotite crystals.

The thin section (fig. 2.2) shows that this rock contains much less plagioclase than the other Orb Hill host rock (96-OH-1) (table 2.1). The plagioclase are euhedral to anhedral and range from 1 to 3 mm in length. As in sample 96-OH-1, most crystals have indistinct albite twinning while a few contain both albite and Carlsbad twinning. Anorthite content ranges from An_{36} to An_{65} , averaging An_{54} for albite twins. A value of An_{76} was found for a single albite-Carlsbad twinned crystal.

Hornblende is the most abundant mafic mineral being composed of anhedral to euhedral crystals. They have yellow-brown to olive-green pleochroism and 1st order, pale yellow, interference colours. A small percentage of the crystals have 2nd order, pink and orange, interference colours. Simple twinning is common and the crystals range up to 1 mm in length.

A very small amount of euhedral pyroxene crystals are present. The Fe-Ti oxides are anhedral, up to 1 mm long but there are numerous small crystals approximately 0.05 mm long found in, and around, the hornblende. Also a small amount of red-brown biotite is found in the

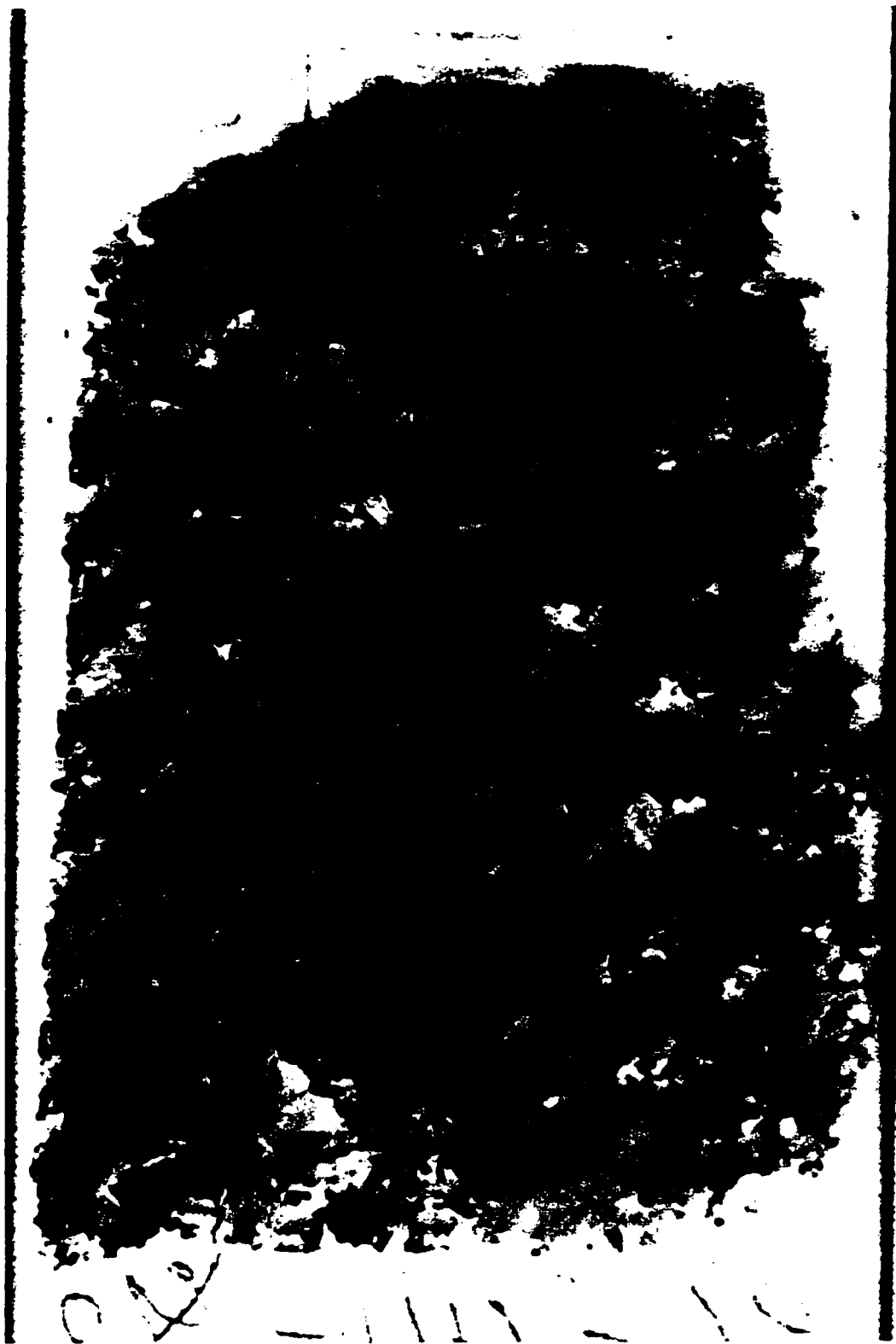


Fig. 2.2 Scanned image of the mafic host rock from Orb Hill (96-OH-2). Black crystals are amphibole, gray are pyroxene and clear are plagioclase. Thin section is 3 cm by 2 cm.

hornblende.

All the crystals in the thin section appear to be randomly oriented. Plagioclase appears to have formed slightly before, and along with, the mafic minerals whereas the Fe-Ti oxides formed last.

According to the criterion laid out in table 2.2, the mineral modes in table 2.1 and An content in table 2.3, this rock is a hornblende gabbro.

2.1.3 Comb Ledge - Felsic Host Rock 96-CL-2, 96-CL-3, and 96-CL-7

These three samples look very much alike, both in hand sample and in thin section, and are thus described together. The hand samples have a fresh, light gray surface that weathers to light brown and black. Crystal size is small to medium, ranging up to 4 mm for both plagioclase and orthopyroxene though averaging about 1 mm. The samples consist of about two thirds plagioclase and one third orthopyroxene.

In thin section, all three samples contain randomly oriented crystals. Plagioclase is mainly subhedral with Carlsbad and albite twinning that indicates a range in anorthite content from An_{32} to An_{61} (table 2.2).

Orthopyroxene crystals are subhedral to anhedral and usually surrounded by amphibole rims. Amphibole is also found as large anhedral patches up to 2.5 mm long, especially in sample 96-CL-7, where they are twinned and have inclusions of plagioclase and orthopyroxene.

<i>sample</i>	<i>rock type</i>	<i>Carlsbad-Albite twin</i>	<i>Albite twins (range, average)</i>
96-CL-2	diorite	An ₆₀	An ₃₃₋₄₄ , An ₃₇
96-CL-3	diorite	An ₇₇	An ₃₂₋₅₆ , An ₄₄
96-CL-7	diorite	none	An ₃₈₋₆₁ , An ₅₁
96-CL-4	gabbro	An ₈₀	An ₄₉₋₆₉ , An ₅₉
96-CL-6	gabbro	An ₈₈	An ₄₃₋₆₂ , An ₅₃
96-OH-1	diorite	An ₇₆	An ₃₆₋₆₅ , An ₅₄
96-OH-2	gabbro	An ₇₇	An ₃₉₋₇₁ , An ₅₄

Table 2.3 An content in plagioclase for all the host rocks from both Comb Ledge (CL) and Orb Hill (OH) for 10 albite twinned crystals using the Michel-Lévy measuring technique and a single Carlsbad-Albite twin determined after the method of Wright (from Kerr 1977, p. 297)

There is minor red-brown biotite and minor corroded olivine with serpentine along its characteristic curved fractures. Fe-Ti oxides are anhedral, up to 0.75 mm long and closely associated with both the biotite and olivine.

In section 96-CL-3 a few plagioclase crystals are euhedral and up to 4 mm long. There are also a few subhedral orthopyroxene grains up to 2 mm long.

Sample 96-CL-2 is highly altered with abundant amphibole and serpentine and only a little orthopyroxene left. The plagioclase is highly altered and many of the amphibole crystals have altered to tremolite-actinolite.

Mineral mode analyses (table 2.4) indicate that these three Comb Ledge host rock samples are diorites. Plagioclase percentages are nearly the same for all the samples as are the minor minerals such as biotite and Fe-Ti oxides. The high amount of alteration in sample 96-CL-2 is mainly serpentized hornblende.

<i>mineral</i>	96-CL-2 (f)	96-CL-3 (f)	96-CL-7 (f)	96-CL-4 (m)	96-CL-6 (m)
plagioclase	61	67	63	57	49
orthopyroxene	2	12	15	13	13
clinopyroxene	4	-	-	-	6
amphibole	11	7	12	22	25
Fe-Ti oxides	4	8	5	7	7
biotite	<1	3	2	<1	<1
alteration	18	3	4	<1	<1
<i>rock type</i>	diorite	diorite	diorite	gabbro	gabbro

Table 2.4 Mineral mode percentages for the host rocks of Comb Ledge (CL) attained by point counting (1000 grains per section per sample, f-felsic, m-mafic).

2.1.4 Comb Ledge - Mafic Host Rocks 96-CL-4 and 96-CL-6

These two hand samples are very similar having a medium gray, fresh surface and a light brown and black, weathered surface. The samples consist of about half, light gray, plagioclase and half, black hornblende. Crystals range from medium to coarse grained. Sample 96-CL-4 has plagioclase up to 5 mm long and black hornblende up to 10 mm long while 96-CL-6 has more equigranular crystals averaging 3 mm.

In thin section, the crystals are randomly oriented (fig. 2.3, sample 96-CL-4). Plagioclase is subhedral with both albite-Carlsbad and albite twins that range from An_{49} to An_{69} .

The pyroxenes are subhedral to anhedral and are usually surrounded by hornblende. Orthopyroxene crystals in sample 96-CL-6 occasionally contain clinopyroxene exsolution lamellae. Clinopyroxene crystals are small, anhedral and occasionally have simple twinning. The orthopyroxene in both samples often contain anhedral Fe-Ti oxides.



Fig. 2.3 Scanned image of mafic host rock from Comb Ledge (96-CL-4). Black crystals are amphibole, gray are pyroxene and colourless are plagioclase. Thin section is 3 cm by 2 cm.

Hornblende occurs as anhedral to subhedral crystals with well defined cleavage and as rims around the pyroxene. Fe-Ti oxides are small anhedral crystals associated with orthopyroxene and hornblende. Plagioclase and orthopyroxene appear to have formed simultaneously followed by hornblende and Fe-Ti oxides.

Mineral modes show that the two samples are much the same (table 2.4) except for the presence of a small amount of clinopyroxene and a corresponding decrease in plagioclase in sample 96-CL-6.

These host rocks are defined as gabbro according to the criteria set out in table 2.2.

2.2 Orbicule Petrography

Orbicules from Orb Hill could only be collected from the float (without the aid of a rock saw or drill and a mule or helicopter to carry them out). Most of the orbicules in the float were broken and the surfaces were altered by weathering, imparting a green tint to the otherwise medium gray orbicules. Since the orbicules were broken and the internal layering was visible, representatives of the entire range of orbicular types could be collected.

Petrographic observations have concentrated mainly on one orbicule (sample 95-OH-3) because it is essentially unaltered and is representative of the multi-shelled orbicules. Some observations are also reported on a slightly altered, multi-shelled orbicule (sample 95-OH-6).

2.2.1 Orbicule 95-OH-3

The specimen is one half of a slightly elliptical orbicule and is ~ 9 x 7 x 7 cm with a homogeneous, medium gray exterior. The exposed interior is characterized by more than ten

shells consisting of thin, millimetre-thick, light brown, fine grained shells alternating with slightly thicker white, black, and medium brown, radial shells. The orbicule has an oval, central core ~3.5 x 2 x 2 cm, that consists mainly of medium brown orthopyroxene with some white plagioclase and black hornblende. The orbicule was cut, for the thin sections, perpendicular to the broken surface to decrease the effect of weathering. The boundary between the core and the first shell is unclear in hand sample.

2.2.1.1 Orbicule Core

In thin section, (fig. 2.4) the core consists mainly of plagioclase, orthopyroxene, and amphibole. The plagioclase are unoriented, euhedral to subhedral, and have a patchy texture consisting of Na-rich areas in mainly Ca plagioclase (determined by electron microprobe). Crystals range up to 2 mm in length and may contain either albite-Carlsbad or albite twinning with the albite twins ranging from An_{42} to An_{52} . Under plane light the plagioclase is clear with no alteration.

Orthopyroxene crystals are anhedral to subhedral, have occasional plagioclase and hornblende inclusions, and are up to 2 mm in length. There are large patches of anhedral hornblende that are green in plane light and have 2nd order green, blue, and orange interference colours. The hornblende has inclusions of plagioclase, orthopyroxene and Fe-Ti oxides. Hornblende is also occasionally found as alteration rims around some of the smaller orthopyroxene and the few small crystals of clinopyroxene. Fe-Ti oxide crystals are uncommon, about 0.1 to 0.2 mm in diameter, anhedral, and are scattered throughout the core. This mineralogy and texture is similar to that of the host rocks.

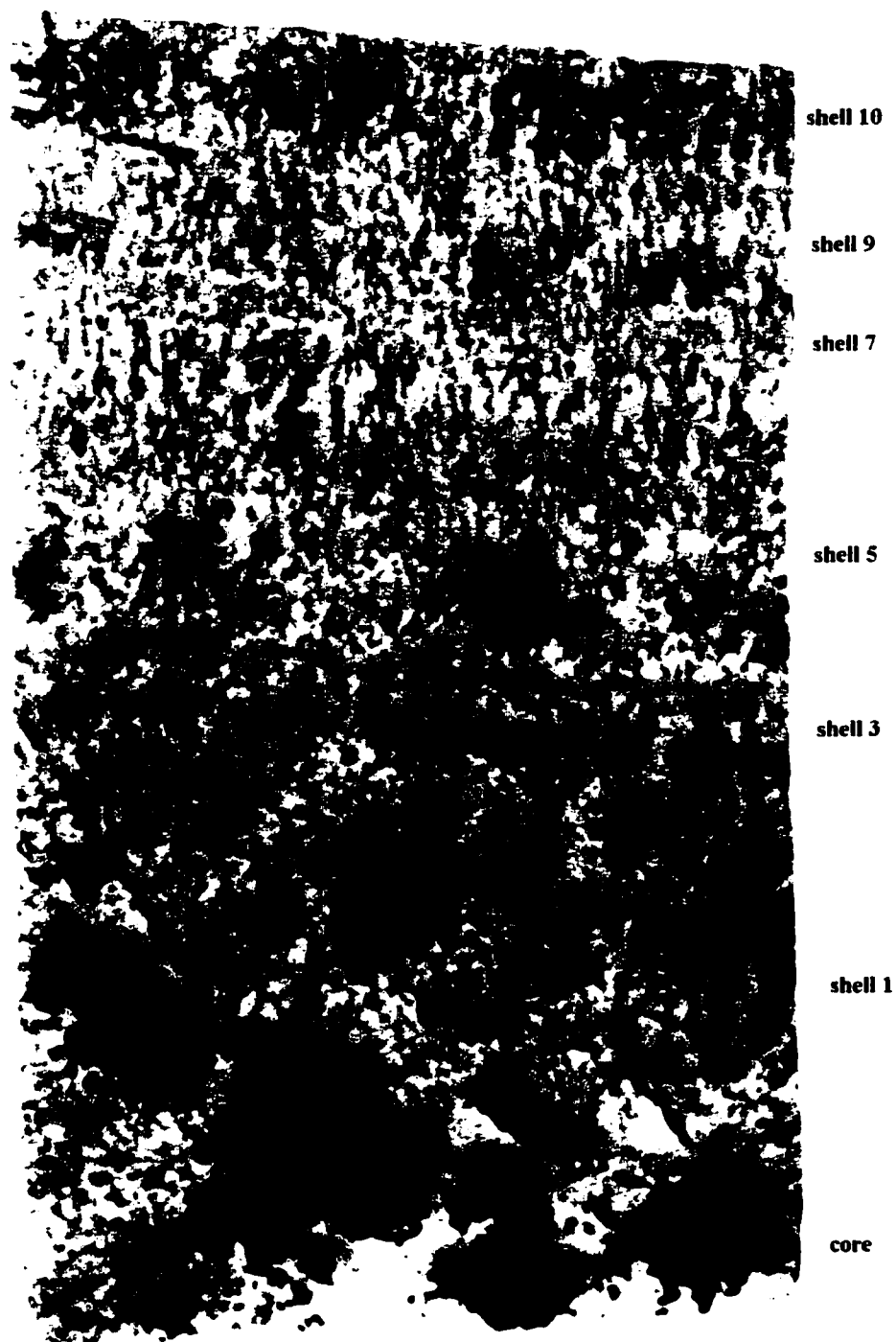


Fig. 2.4 Scanned image of multishelled orbicule from Orb Hill (95-OH-3). The core and some shells have been identified. A more detailed figure is reproduced in fig. 2.5. Black crystals are amphibole, gray are pyroxene and colourless are plagioclase. Thin section is 3 cm by 2 cm.

The order of formation in the core appears to be plagioclase first, followed by pyroxene, then hornblende, and lastly, Fe-Ti oxides.

2.2.1.2 Orbicule Shells

This orbicule has at least 11 shells as can be seen on the thin section (fig. 2.4) and matching drawing in figure 2.5. A summary of the mineralogy and morphology is found in table 2.5 and the mineral modal analyses for each shell are in table 2.6.

Shell 1 is 8 mm thick and consists of two of the three types of orthopyroxene. Type 1 orthopyroxene crystals are budding, branching and radiating outwards from the core (fig. 2.6). They are up to 8 mm long, pale green in normal light, and have 1st order, orange to yellow, interference colours. They contain inclusions of plagioclase, a few small hornblende, and Fe-Ti oxides. Type 3 orthopyroxene crystals are <0.5 mm long, anhedral, and mixed in with plagioclase crystals between the stems of the radial orthopyroxene. Plagioclase is euhedral to subhedral, up to 3 mm long, has indistinct albite-Carlsbad and albite twinning, and is mainly unoriented, however, some of the plagioclase that is lying next to the radial, branching orthopyroxene crystals are aligned with them. Hornblende occurs as anhedral patches with inclusions of plagioclase and very small amounts of brown-red biotite. Fe-Ti oxides are rare in the inner and central parts of shell 1 but increase near the outer edge of the shell where they are strongly associated with the orthopyroxene. The inner contact between shell 1 and the core is not sharp but is identifiable by a significant decrease in plagioclase in the shell along with the radial branching orthopyroxene.

Shell 2 is an anhedral shell, 0.5 to 0.75 mm thick, and is dark gray due to the high concentration of Fe-Ti oxides. This shell consists of anhedral crystals, < 0.2 mm in size, of

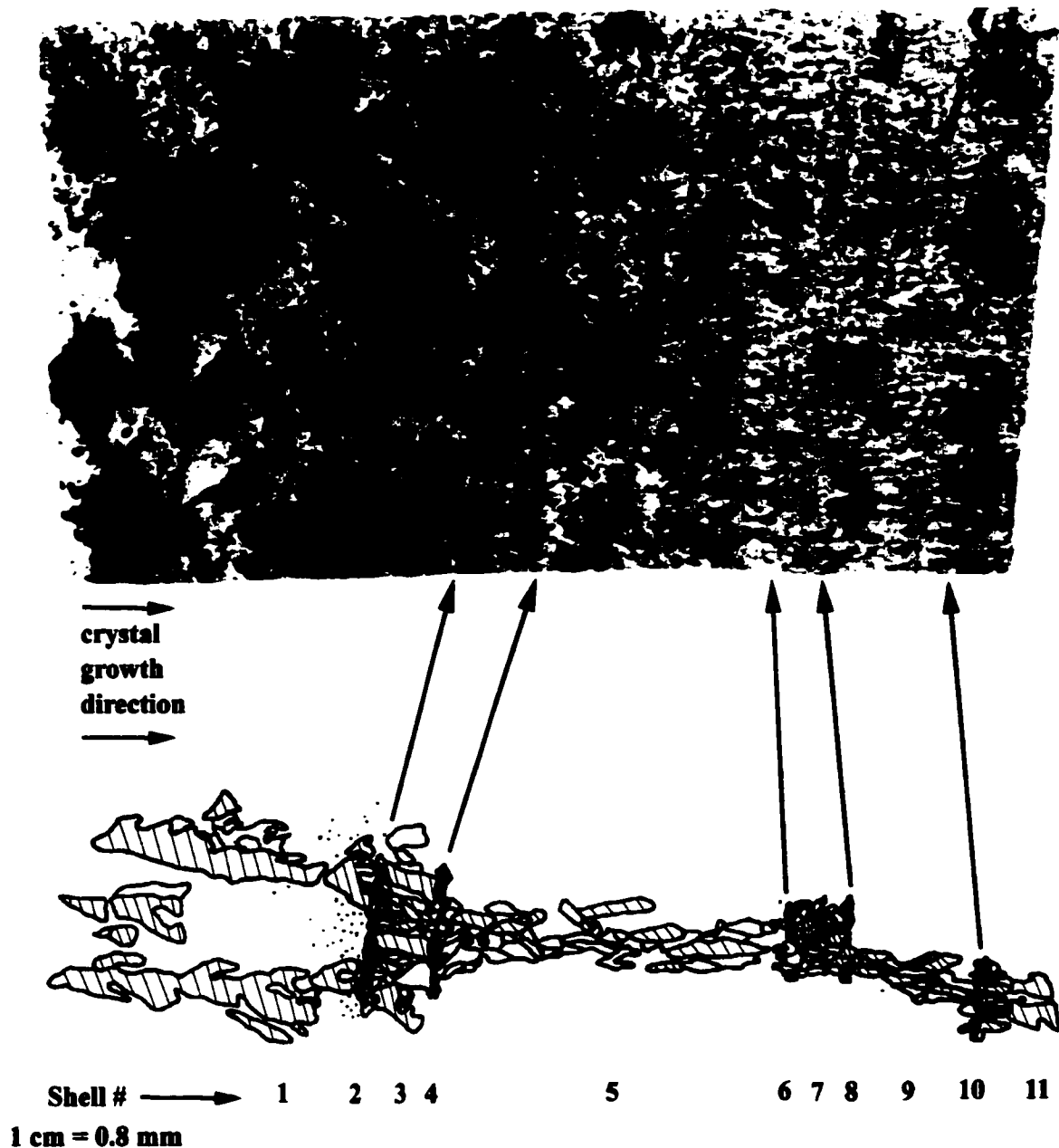


Fig. 2.5 At the top is the scanned image of the thin section of orbicule 95-OH-3 as in figure 2.4. Orthopyroxene is medium gray, plagioclase is colourless, Fe-Ti oxides are small black spots and amphibole is the large dark patches on the left. The section is 3 cm by 2 cm and growth direction is from left to right. At the bottom is a sketch detailing the morphology of orthopyroxene (striped crystals), plagioclase (colourless) and Fe-Ti oxides (small black spots) in the shells. Shell 1 emphasizes the budding, branching habit of the orthopyroxene without showing the smaller plagioclase and anhedral amphibole that is found between the orthopyroxene.

A type-1 orthopyroxene**B** type-2 orthopyroxene**C**type-1
plagioclase

Fig.2.6 There are several different crystal shapes present in the orbicules. (A) shows two examples of type-1 morphology in the branching/budding orthopyroxene found in the innermost shell (vertical length = 0.8 cm). (B) displays four examples of the wedge shaped type-2 orthopyroxene (vertical length = 0.1 cm). Type-3 are small anhedral crystals and are not shown. The two crystals in (C) are feather plagioclase (type-1) under crossed polarizing lenses. The twinning gives the appearance of feathers (vertical length = 0.4 cm). Plagioclase in the orbicules is also found as small, anhedral crystals and as larger, elongated crystals with no faces (not shown).

orthopyroxene, hornblende, Fe-Ti oxides, and a few plagioclase. The shell is not discrete but is interrupted by plagioclase from shell 1 growing into shell 2.

Shell 3 is a radial shell, 1 to 1.25 mm thick and contains two types of orthopyroxene crystals. There are about 2 to 3 dozen type-2 orthopyroxene (fig. 2.6) that stretch across the shell and are oriented perpendicular to the core boundary. These orthopyroxene crystals are wedge shaped with the narrow end abutting shell 2 and increasing in width towards shell 4. Type-3 orthopyroxene are anhedral, unoriented and smaller than the other types. Plagioclase is anhedral to subhedral averaging 0.5 mm in length, with indistinct twinning and is predominantly unoriented. Fewer than a half dozen plagioclase are radially oriented along the sides of the orthopyroxene. There is minor hornblende and no Fe-Ti oxides.

Shell 4 is quite similar to shell 2. It is an anhedral shell, 0.5 to 0.75 mm wide with more hornblende than shell 2. Two things make this shell less distinct than shell 2. First, the shell is dissected by plagioclase crystals growing through the shell from shell 3 and, second, there are fewer small crystals than in shell 2.

Shell 5 is a thick shell that is made up of about three sub-shells that are difficult to differentiate under the microscope but can be seen on the thin section photo (fig. 2.4). These sub-shells are radial growth shells wherein both plagioclase and orthopyroxene are oriented perpendicular to the core. There are two habits of plagioclase, feather (fig. 2.6) and subhedral, both with indistinct twinning. Also, all three types of orthopyroxene crystals are found here. Fe-Ti oxides are spread evenly throughout the sub-shells and mainly associated with orthopyroxene. Shell 5a is 5.5 mm thick and has an abundance of large anhedral secondary hornblende with inclusions of euhedral plagioclase and anhedral orthopyroxene. Shell 5b is 1.5 mm thick and has

less plagioclase than shells 5a and 5c but more slender, elongate, type-1 (branching/budding) and type-2 (wedge) orthopyroxene. Shell 5c is 3.3 mm thick, and has a higher abundance of large plagioclase which are predominantly the feather-shaped type-1. The orthopyroxene crystals are long and thin and not as abundant as in the rest of the shell.

Shell 6 is an anhedral shell, 1 to 1.25 mm thick with anhedral orthopyroxene and plagioclase ~ 0.25 mm across. The inner edge of the shell has an abundance of anhedral brown-red biotite and Fe-Ti oxides. Radially oriented plagioclase and approximately a half dozen orthopyroxene crystals go through this shell into shell 7.

Shell 7 is ~ 5 mm thick and consists mainly of small radially oriented, wedge shaped, plagioclase and orthopyroxene that grew through from shell 6. There is also a significant amount of anhedral plagioclase and orthopyroxene as well as scattered hornblende and Fe-Ti oxides.

Shell 8 is anhedral, 0.5 mm thick and is intermittent due to the radial plagioclase and orthopyroxene that grew through this shell from shell 6. The shell is defined by the presence of a large amount of magnetite and ilmenite. The anhedral grains consist of hornblende, Fe-Ti oxides and traces of brown-red biotite.

Shell 9 is ~ 4 mm thick and very similar in character to shell 5. There are elongated, budding orthopyroxene crystals that nucleated in shell 8 along with radially oriented type-1, feather plagioclase. Fe-Ti oxides are scattered throughout the shell in no particular pattern and are usually associated with the orthopyroxene.

Shell 10 is ~ 2 mm thick with radial orthopyroxene and plagioclase like shell 9. There is a high abundance of hornblende which is usually associated with, and surrounding, orthopyroxene. Fe-Ti oxides and biotite are small and anhedral. The biotite is red-brown and

Shell #, type	width (mm)	mineral	comments
core anhedral	2 by 3.5	orthopyroxene plagioclase hornblende	anhedral to subhedral unoriented crystals up to 2 mm long
shell 1 radial	8	orthopyroxene - type 1 plagioclase - subhedral hornblende	radially oriented branching/budding opx up to 8 mm long and elongated plagioclase up to 3 mm long
shell 2 anhedral	.5 - .75	orthopyroxene - type 3 plagioclase hornblende Fe-Ti oxides	- crystals are < 0.2 mm in size - shell is not continuous but is interrupted by plag from shell 1
shell 3 radial	1 - 1.25	orthopyroxene - type 2 & 3 plagioclase hornblende	- 2 to 3 dozen type-2 orthopyroxene stretch across shell
shell 4 anhedral	.5 - .75	orthopyroxene - type 3 plagioclase hornblende	- similar to shell 2 but with more hornblende - fewer small grains make this shell less distinct than shell 2
shell 5a shell 5b shell 5c radial	5.5 1.5 3.3	orthopyroxene - type 1 & 3 plagioclase - feather hornblende Fe-Ti oxides & biotite	- both orthopyroxene & plagioclase are oriented perpendicular to the core - oxides are spread evenly across the shells & associated with orthopyroxene
shell 6 anhedral	1 - 1.25	orthopyroxene - type 3 plagioclase Fe-Ti oxides & biotite	- oriented plag & opx from shell 5 grow through shell 6 into shell 7 - oxides and biotite concentrated at inner edge of shell
shell 7 radial	5	orthopyroxene - type 1 plagioclase - wedge	- also anhedral orthopyroxene and plagioclase - crystals originate from shell 6
shell 8 anhedral	0.5	orthopyroxene - type 2 plagioclase - subhedral hornblende Fe-Ti oxides & biotite	- shell is non-continuous due to orthopyroxene & plagioclase growing through from shell 7
shell 9 radial	4	orthopyroxene - type 1 plagioclase - feather hornblende Fe-Ti oxides & biotite	- radially oriented crystals of orthopyroxene and plagioclase originate from shell 8
shell 10 radial	2	orthopyroxene - type 1 plagioclase - feather hornblende	- hornblende associated with & surrounding orthopyroxene
shell 11 radial	1	orthopyroxene - type 1 plagioclase - subhedral	- similar to shell 7

Table 2.5 Summary table of the mineralogy and morphology of orbicule 95-OH-3

Shell # - type	Plag	Opx	Mt-II	Hbl	Bt	Cpx	# of counts
core-anhedral	40	21	2	35	1	1	285
shell 1-radial	40	46	5	7	2		501
shell 2-anhedral	30	39	20	1	10		161
shell 3-radial	39	54	3	3	1		186
shell 4-anhedral	37	28	15	-	21		134
shell 5-radial	36	40	12	10	3		188
shell 6-anhedral	43	33	5	5	14		63
shell 7-radial	38	28	15	17	3		119
shell 8-anhedral	30	30	21	12	6		66
shell 9-radial	44	33	5	18	1		166
shell 10-radial	43	27	9	21	1		195
shell 11-radial	52	40	3	1	3		126

Table 2.6 Modal analyses (percentages) per shell for orbicule 95-OH-3 attained through point counting the number of points listed in the last column.

usually associated with hornblende.

Shell 11 is very similar to shell 7 with its combination of small radial orthopyroxene and plagioclase and anhedral orthopyroxene and plagioclase. This shell is at the outside edge of the orbicule and is ~ 0.5 mm thick. Very minor amounts of hornblende, biotite and Fe-Ti oxides are scattered throughout the shell at random.

In essence, orb 95-OH-3 consists of a series of radial shells with branching, budding orthopyroxene and long feather plagioclase oriented perpendicular to the core rim that alternate with anhedral shells of fine grained plagioclase, orthopyroxene, hornblende, Fe-Ti oxides and biotite.

The order of formation of minerals found throughout the shells appears to be

orthopyroxene and plagioclase simultaneously, followed by primary hornblende and Fe-Ti oxides and then biotite and secondary hornblende.

2.2.2 Orbicule 95-OH-6

This orb is a broken half, and represents nearly one half of a sphere, ~ 8.5 cm by 9.5 cm by 4 cm in diameter with a homogeneous medium gray exterior. The exposed interior is characterized by several thick (6 mm), dark green, fine grained, shells alternating with slightly thinner white, black and green radial shells, all surrounding a small, coarse grained white, black and green core (fig. 2.7).

The core is spherical, ~ 15 mm in diameter, with unoriented, subhedral to anhedral, crystals that are > 2 mm across consisting of mainly white plagioclase, black hornblende and light green orthopyroxene with hornblende rims. The core/inner shell contact is sharp in hand sample but more difficult to discern in thin section.

Shell 1 is a 10 mm thick, radial layer of plagioclase and orthopyroxene. The orthopyroxene are long, slender, budding crystals that are more slender than those in 95-OH-3. They have the higher order interference colours of clinopyroxene but microprobe data indicate that these crystals are orthopyroxene. Plagioclase is long, slender, and wispiest than in 95-OH-3. Hornblende is mainly found as rims around the orthopyroxene crystals. There are no Fe-Ti oxides.

Shells 2 to 10 occur as a thick 7.5 mm package of anhedral shells that alternate in concentrations of Fe-Ti oxides. These opaque minerals delineate at least 5 narrow shells. The shells also consist of fine grained plagioclase, orthopyroxene and hornblende.



Fig. 2.7 Scanned image of a multishelled orbicule from Orb Hill (95-OH-6). This orbicule is much different from that shown in figure 2.4 in that between the thicker radially oriented shells are packages of anhedral shells with up to ten shells. The darker shells have a higher amount of Fe-Ti oxides than the lighter ones. Black crystals are amphibole, gray are pyroxene and colourless are plagioclase. Thin section is 3 by 2 cm.

Shell 11 is a 4.5 mm radial layer of orthopyroxene and plagioclase very similar to shell 1. Hornblende is concentrated around orthopyroxene at the centre of the shell.

Another thick package of shells consisting of anhedral crystals makes up shell 12. The Fe-Ti oxides are much less organized than in the previous anhedral shell package (shells 2 to 10), and thus this package could not be divided as easily as the first. This shell is a total of 6 mm thick and has less plagioclase and more hornblende than in shell package 2 to 10.

Shell 13 is 1 mm thick, containing anhedral plagioclase and orthopyroxene. There is no hornblende or Fe-Ti oxides.

Another anhedral shell follows, shell 14, less than 0.5 mm thick, with high concentrations of hornblende and Fe-Ti oxides as well as plagioclase and orthopyroxene.

Shell 15 is 2.5 mm thick and is a radial layer of orthopyroxene and plagioclase. Some orthopyroxene crystals have been nearly totally replaced by hornblende. Fe-Ti oxides are concentrated in the orthopyroxene.

The outer shell, 16, is ~ 0.5 mm thick and consists of anhedral grains of hornblende, plagioclase, orthopyroxene, and Fe-Ti oxides.

This orbicule essentially consists of two thick radial shells of elongated, budding orthopyroxene and plagioclase that alternate with two thick packages of anhedral shells. These thick anhedral packages have a much higher abundance of Fe-Ti oxides and hornblende where the presence or absence of the Fe-Ti oxides delineates the individual anhedral shells.

Summary

These two orbicules of Fisher Lake CA are made up of a series of shells that consist of

mainly radially oriented, elongated branching/budding orthopyroxene, feather plagioclase and large anhedral hornblende that alternates with thin anhedral shells richer in Fe-Ti oxides and biotite. Even though there are no two orbicules with the same sequence of shells, they all share the same mineralogy and alternating pattern of elongated orthopyroxene and plagioclase versus anhedral hornblende and Fe-Ti oxides.

Shell #	shell type	width (mm)	mineralogy	comments
core	a	15	Pl, Opx, Hb	unoriented subhedral crystals
1	r	10	Pl, Opx, Hb	budding elongated orthopyroxene & plagioclase
2	a	1.5	Pl, Opx, Hb, Mt	
3	a	1.5	Pl, Opx, Hb	
4	a	0.3	Pl, Opx, Hb, Mt	
5	a	1.05	Pl, Opx, Hb	
6	a	0.45	Pl, Opx, Hb, Mt	
7	a	0.9	Pl, Opx, Hb	
8	a	0.3	Pl, Opx, Hb, Mt	
9	a	0.9	Pl, Opx, Hb	
10	a	0.6	Pl, Opx, Hb, Mt	
11	r	4.5	Pl, Opx, Hb	budding elongated orthopyroxene & plagioclase
12	a	6	Pl, Opx, Hb, Mt	less Pl and more Hb than shells 2-10
13	a	1	Pl, Opx	
14	a	0.5	Pl, Opx, Hb, Mt	high concentration of Hb and Mt
15	r	2.5	Pl, Opx, Hb Mt	Mt concentrated in Opx
16	a	0.5	Pl, Opx, Hb, Mt	

Table 2.7 Summary table of orbicule 95-OH-6. Abbreviations: r = radial crystals, a = anhedral crystals, Pl = plagioclase, Opx = orthopyroxene, Hb = hornblende, Mt = Fe-Ti oxides.

2.3 Comb Layering Petrology

One sample of comb layering taken from near site 4 at Comb Ledge (location map fig. 1.17) was studied in order to compare and contrast the mineralogy of the comb texture in the comb layering to that of the shells in the orbicules, i.e. the radially oriented crystals.

2.3.1. Comb Layering 95-CL-2

The comb layering sample is 18 cm long and contains at least 60 layers of radial and anhedral growth (fig. 2.8) that range in thickness from less than 0.5 mm to nearly 2 cm. The sample is very striking, having crystals that are predominantly black or white on the cut surface and some light brown on the weathered surface.

Oversize thin sections were done of the entire sample. The area around a spectacular layer consisting of elongated, budding hornblende crystals nearly 1 cm long was chosen for detailed mineralogical analysis. This horizon of hornblende crystals can be seen as having grown from within a layer of plagioclase (fig. 2.9). The sequence of plagioclase followed by hornblende is repeated twice on the thin section.

The hornblende are long, slender, budding crystals up to 8 mm long that look very much like the type-1, budding orthopyroxene in the orbicules. They are brown and green under normal light with an interference colour of 1st order orange and yellow with some crystals containing simple twinning. They often contain anhedral patches, as well as long, thin needles, of plagioclase. There are also anhedral to euhedral shaped orthopyroxene within these budding hornblende. Between the hornblende, are small orthopyroxene crystals having nice 90° cleavage. There is no evidence that the hornblende is the result of pyroxene alteration, i.e. the grain



Fig. 2.8 Two photos of a piece of comb layering from Comb Ledge showing the intricate and variable texture surrounding sample 95-CL-2. The thin section as pictured in figure 2.9 is from the thick dark layer approximately one third down the lower photo. Black crystals are hornblende, grey are pyroxene and white are plagioclase. (vertical scale is about 4 inches)



Fig. 2.9 Photomicrograph of comb layering (sample 95-CL-2) from Comb Ledge showing elongated hornblende crystals with no alteration. Black crystals are amphibole, gray are pyroxene and colourless are plagioclase. Round, black and white spots are ink dots marking crystals for microprobe analyses. Thin section is 3 cm by 2 cm.

boundary between the euhedral orthopyroxene and the elongated hornblende is sharp and clean. The morphology and lack of evidence of alteration means that the hornblende is primary.

Plagioclase crystals located between the elongated hornblende are much smaller than the hornblende. A few elongated, feather plagioclase crystals are oriented alongside these hornblende crystals. The feather plagioclase have albite twinning but it is too smeared to do any Michel-Lévy measurements. The smaller plagioclase are mainly anhedral to subhedral with either albite-Carlsbad or albite twinning which are also usually smeared but Michel-Lévy measurements on a half dozen albite twinned crystals produced the same range in An content as seen in the Comb Ledge host rocks, i.e. An ranges from about An_{40} to An_{60} . All the plagioclase are clear under plane light and no alteration is present.

Anhedral clinopyroxene is a minor component and Fe-Ti oxides are small, anhedral, and associated with orthopyroxene.

Orthopyroxene is much less abundant in the comb layering sample than in the orbicules. The orthopyroxene are often associated with the hornblende, either around the edges of the hornblende or as inclusions. A few euhedral orthopyroxene crystals, less than 0.25 mm across, were seen at the ends of the elongated hornblende.

The order of crystallization is difficult to determine. Since the hornblende have orthopyroxene and plagioclase inclusions this would normally indicate that the hornblende formed after the orthopyroxene and plagioclase but the large size and shape of the crystals precludes them from having formed last. Therefore orthopyroxene, plagioclase and hornblende must have been forming nearly simultaneously. Given the high amount of primary hornblende over pyroxene, this rock would be classified as a diorite.

2.4 Summary

The orbicules and the comb layering have very similar mineralogy to that of the host rocks, differing slightly only in the presence of very minor amounts of clinopyroxene in the host samples (6 % or less when present).

Crystal morphology is one key difference between the orbicules and comb layering, and the host rocks. The comb textures are made up of elongated branching/budding orthopyroxene, or hornblende, and feather plagioclase alternating with anhedral plagioclase, orthopyroxene, hornblende, Fe-Ti oxides, and biotite. The host rocks contain these same essential minerals but in euhedral to anhedral morphologies randomly distributed throughout the rock.

Mineral mode analyses reveal another key difference between the comb textured phenomena and the host rocks in that the host rocks generally contain far more plagioclase and less orthopyroxene than the comb textured rocks. This suggests that either the precipitation of plagioclase was delayed or that of orthopyroxene was enhanced during the formation of the orbicules and comb layering.

3. Chemistry

The petrography, done in chapter 2, of the orbicules, comb layering and the host rocks showed that all contain essentially the same minerals though they have significant differences in modal percentages and crystal morphology. Thus, it was necessary to do chemical analyses in order to determine if the chemistry of a given mineral depended on whether it was in the comb layering, the orbicules or the host rock and if there were differences from one orbicule to the next or between layers/shells within the comb layering or the orbicule. A variation in the mineral chemistry from one setting to another will have ramifications on the formation mechanism for the orbicules and comb layering.

Given the unique nature of the orbicules and the comb layering, i.e. the oscillatory mineralogy, microprobe analyses of their individual crystals proved to be the most interesting and the most revealing, but one cannot forget the parent rocks. The seven host rock samples that were collected from Fisher Lake (five from Comb Ledge and two from Orb Hill) during the summer of 1996 were cut, chipped, powdered, weighed and analyzed by XRF (analyses done by R. Hartree at University of Ottawa) and neutron activation (INAA) (done by J. St-Pierre at École Polytechnique, l'Université de Montréal). Some of the polished thin sections (done by G. Mrazek) made from the hand samples underwent microprobe analyses (aided by G. Poirier at McGill University). Staining for potassium feldspar along with Fe titration were done in the Geochemistry lab at the University of Ottawa (aided by J. Loop). Methodologies for the XRF, INAA, microprobe, and Fe titration are detailed in appendix A.

3.1 Potassium Feldspar Staining

Petrological studies of all the samples did not reveal the presence of potassium feldspar. To ensure that indeed none was present, the two host rock samples from Orb Hill (96-OH-1 and 96-OH-2) and two from Comb Ledge (96-CL-4 and 96-CL-6) were etched with hydrofluoric acid (concentrated 37%) and then stained using a solution of 5 ml of sodium cobaltinitrite in 50 ml of distilled water. There was no characteristic bright yellow stain and thus potassium feldspar was determined not to be present in the rocks.

3.2 Host Rock Analyses

All seven host rock samples (five from Comb Ledge and two from Orb Hill) underwent XRF analyses for the determination of major oxides and selected trace elements. The resulting compositions of the oxides (table 3.1) greatly resemble those of other subduction related rocks such as the andesitic basalts found in the Aleutian Islands volcanic arc subduction zone (Marsh 1982) and the high aluminum basalt from Medicine Lake Highlands, CA (Yoder & Tilley 1962). Comparable gabbroic analyses could not be found and thus the comparison is made to volcanic rocks. The results also match the diorite host phase collected and analyzed by McKinney (1985) from the same locations at Fisher Lake.

As there is evidence in the field for magma mixing (e.g. figures 1.19 and 1.22 which show the presence of coarse and fine grained inclusions and mafic enclaves) and, since the Sierra Nevada batholith is well documented as being emplaced by magma pulses into composite plutons, this trend will be looked for in the chemical analyses.

CIPW norm calculations were performed using the NewPet software (Clarke, 1994). The

Table 3.1 Whole rock chemical compositions determined by XRF for Fisher Lake Host Rocks.

			average OH	average CL	1	2	3	4	5	6
	96-OH-1	96-OH-2	host rocks	host rocks**						
SiO ₂	50.93	43.58	47.26	47.38	48.61	49.86	41.63	49.8	48.27	47.94
TiO ₂	0.96	1.48	1.22	1.04	1.02	1.11	1.54	0.96	0.89	0.75
Al ₂ O ₃	20.65	20.26	20.46	20.16	20.99	20.63	21.49	20.12	18.28	17.45
Fe ₂ O ₃	2.72	4.51	3.62	3.69	9.87 *	9.83 *	11.70 *	4.36	1.04	1.21
FeO	6.27	6.73	6.5	6.47				5.51	8.31	8.47
MnO	0.18	0.15	0.16	0.16	0.17	0.16	0.15	0.18	0.17	0.13
MgO	4.73	7.42	6.08	6.62	4.89	4.24	7.23	4.72	8.96	10.19
CaO	9.59	12.45	11.02	11.01	9.98	9.79	13.66	9.66	11.32	11.26
Na ₂ O	3.17	1.36	2.27	1.90	3.38	3.48	1.85	3.71	2.80	2.37
K ₂ O	0.24	0.34	0.29	0.20	0.19	0.31	0.36	0.78	0.14	0.09
P ₂ O ₅	0.27	0.10	0.19	0.21	0.16	0.19	0.01	0.23	0.07	0.08
LOI	0.10	1.40	0.75	0.80					0.22	0.38
TOTAL	99.80	99.78	99.79	100.34	99.26	99.6	99.62	100.03	100.47	100.32

OH = Orb Hill

CL = Comb Ledge

1. diorite host phase, Orb Hill area, Fisher Lake (McKinney, 1985, table 3.1 sample CA/SS-80-140)
2. diorite host phase, Comb Ledge area, Fisher Lake (McKinney, 1985, table 3.1, sample CA/SS-81-24)
3. hornblende gabbro, Orb Hill area, Fisher Lake (McKinney, 1985, table 3.1, sample CA/SS-79-22)
4. andesitic basalt, Aleutians (Marsh, 1982)
5. high-aluminum basalt, Medicine Lake Highlands, California (Yoder & Tilley, 1962, p363, no.16)
6. high-aluminum basalt, ocean rift floor, Sargasso Sea, N. Atlantic Ocean (Nicholls 1965, table 2, analysis 2)

* total Fe reported as Fe₂O₃

** use of average CL host rocks reflects similarity of samples - see table 3.2 for individual analyses

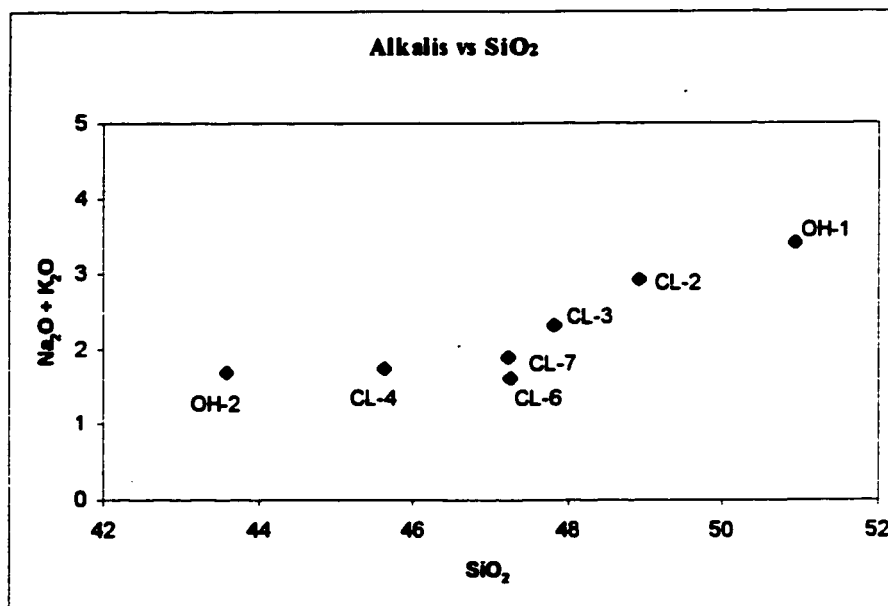
Table 3.2 XRF Analyses and norms for host rocks from Orb Hill (OH) and Comb Ledge (CL).

	96-OH-2	96-CL-4	96-CL-7	96-CL-6	96-CL-3	96-CL-2	96-OH-1	1	2	3	4
SiO ₂	43.58	45.62	47.26	47.28	47.81	48.92	50.93	48.61	49.86	48.27	47.94
TiO ₂	1.48	1.31	0.97	0.82	1.05	1.05	0.96	1.02	1.11	0.89	0.75
Al ₂ O ₃	20.26	20.39	20.30	19.08	20.90	20.12	20.65	20.99	20.63	18.28	17.45
Fe ₂ O ₃	4.51	4.69	3.22	3.37	3.56	3.60	2.72	9.87 *	9.83 *	1.04	1.21
FeO	6.73	6.39	6.89	6.88	6.31	5.86	6.27			8.31	8.47
MnO	0.15	0.14	0.16	0.16	0.17	0.16	0.18	0.17	0.16	0.17	0.13
MgO	7.42	6.70	7.32	7.89	5.75	5.44	4.73	4.89	4.24	8.96	10.19
CaO	12.45	12.06	10.52	12.10	10.65	9.72	9.59	9.98	9.79	11.32	11.26
Na ₂ O	1.36	1.52	1.74	1.46	2.08	2.70	3.17	3.38	3.48	2.80	2.37
K ₂ O	0.34	0.23	0.16	0.15	0.25	0.23	0.24	0.19	0.31	0.14	0.09
P ₂ O ₅	0.10	0.08	0.26	0.05	0.33	0.31	0.27	0.16	0.19	0.07	0.08
LOI	1.40	0.50	0.90	0.70	0.40	1.50	0.10			0.22	0.38
TOTAL	99.78	99.63	99.71	99.94	99.25	99.60	99.80	99.26	99.60	100.47	100.32
Q	-	-	-	-	-	0.45	2.05	-	0.72	-	-
Or	2.00	1.35	0.96	0.90	1.45	1.33	1.39	1.11	1.67	0.56	0.6
Ab	11.51	12.86	14.72	12.35	17.60	22.84	26.82	28.82	29.34	23.58	20
An	48.18	48.14	47.11	45.06	46.97	42.12	41.43	41.42	39.75	36.97	36.7
Di	10.37	9.13	2.75	11.96	3.07	3.36	3.59	4.1	4.32	15.23	15.2
Hy	8.43	13.78	25.38	19.01	23.98	22.25	18.04	10.23	13.22	-	4.5
Ol	8.30	7.83	2.61	5.69	0.06	-	-	3.78	-	20.55	19.7
Mt	6.54	4.07	3.58	3.36	3.69	3.69	3.94	5.8	5.8	1.39	1.8
Il	2.80	2.48	1.84	1.55	1.98	1.99	1.82	1.98	2.13	1.67	1.4
Ap	0.24	0.20	0.62	0.12	0.77	0.72	0.64	0.34	0.34	0.17	0.2
Hed								1.74	2.23		
Total	98.38	99.84	99.58	100.00	99.58	98.76	99.71	97.58	97.29	100.12	100.10

1. diorite host phase, Orb Hill area, Fisher Lake (McKinney, 1985, table 3.5, no.1, sample CA/SS-80-140)
2. diorite host phase, Comb Ledge area, Fisher Lake (McKinney, 1985, table 3.5, no.2, sample CA/SS-81-24)
3. high-aluminum basalt, Medicine Lake Highlands, California (Yoder & Tilley, 1962, p363, no.16)
4. high-aluminum basalt, ocean rift floor, Sargasso Sea, N. Atlantic Ocean (Nicholls, 1965 table 2, analysis 2)

* FeT reported as Fe₂O₃

Figure 3.1 Graph showing linearity of host rocks when plotted as alkali wt% versus SiO_2 wt%.



- (96-OH-2) melanocratic gabbro
- (96-CL-4) 2 m from comb layering, adjacent to mafic enclave
- (96-CL-7) 2.5-3 m from comb layering in leucogabbro
- (96-CL-6) 1 m from comb layering in homogeneous leucogabbro
- (96-CL-3) 2.5 from comb layering in homogeneous leucogabbro
- (96-CL-2) 1 m from comb layering in homogeneous leucogabbro
- (96-OH-1) leucocratic gabbro

results (table 3.2) show very high amounts of anorthite that reflect the high wt % of Al_2O_3 and CaO and the very low amount of Na_2O .

The host rocks plot nearly linearly on an alkalis vs. SiO_2 graph (fig. 3.1). A linear regression line through the data (excluding point CL-6) produces a r^2 value of 0.84. Error bars were calculated for the analyses according to Kretz and Hartree (1998) at $\text{SiO}_2 \pm 0.06$ wt% and $\text{Na}_2\text{O} + \text{K}_2\text{O} \pm 0.016$ wt%. These values are so small that they are within the size of the dot representing the data on the graph. With the exception of 96-CL-6, this linearity in the data suggests that differentiation may have taken place between the most mafic Orb Hill magma (96-OH-2) and the most felsic Orb Hill magma (96-OH-1) with all the samples from Comb Ledge

Table 3.3 XRF Analyses for Host Rocks from Orb Hill (OH) and Comb Ledge (CL)

	96-OH-2	96-CL-4	96-CL-7	96-CL-6	96-CL-3	96-CL-2	96-OH-1	average CL	average OH
SiO ₂	43.58	45.62	47.26	47.28	47.81	48.92	50.93	47.38	47.26
TiO ₂	1.48	1.31	0.97	0.82	1.05	1.05	0.96	1.0362	1.2165
Al ₂ O ₃	20.26	20.39	20.30	19.08	20.90	20.12	20.65	20.16	20.46
Fe ₂ O ₃	4.51	4.69	3.22	3.37	3.56	3.60	2.72	3.69	3.62
FeO	6.73	6.39	6.89	6.88	6.31	5.86	6.27	6.47	6.50
MnO	0.15	0.14	0.16	0.16	0.17	0.16	0.18	0.16	0.16
MgO	7.42	6.70	7.32	7.89	5.75	5.44	4.73	6.62	6.08
CaO	12.45	12.06	10.52	12.10	10.65	9.72	9.59	11.01	11.02
Na ₂ O	1.36	1.52	1.74	1.46	2.08	2.70	3.17	1.90	2.27
K ₂ O	0.34	0.23	0.16	0.15	0.25	0.23	0.24	0.20	0.29
P ₂ O ₅	0.10	0.08	0.26	0.05	0.33	0.31	0.27	0.21	0.19
LOI	1.40	0.50	0.90	0.70	0.40	1.50	0.10	0.80	0.75
TOTAL	99.78	99.63	99.71	99.94	99.25	99.60	99.80	99.62	99.79
V	402	388	230	295	252	265	221	286	311.5
Cr	40	69	70	200	35	33	16	81	28
Co	34	42	34	38	27	31	22	34	28
Ni	24	36	23	50	18	17	11	29	17.5
Zn	90	110	114	105	118	115	121	112	105.5
Rb	10	6	4	5	6	4	5	5	7.5
Sr	565	635	734	597	815	773	690	711	627.5
Y	18	17	9	10	11	11	10	12	14
Zr	26	37	19	21	14	11	12	20	19
Nb	1	2	<0.0	1	<0.0	<0.0	1	1	1
Ba	124	191	164	127	193	209	237	177	180.5
La	2	20	2	1	26	19	<0.0	14	1
Ce	40	<0.0	26	<0.0	38	17	20	16	30
Nd	18	12	18	9	10	9	12	12	15
Pb	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
Th	6	6	4	3	6	6	5	5	5.5
U	<0.0	1	<0.0	<0.0	1	3	<0.0	1	<0.0
A	10.72	11.79	11.80	9.85	16.17	20.56	23.64		
F	42.46	43.06	42.76	41.99	43.86	41.20	43.53		
M	46.82	45.15	45.43	48.16	39.97	38.24	32.84		

trace elements in ppm

AFM calculations shown below from Philpotts (1990)

 $A = 100 * (Na_2O + K_2O) / (FeO + MgO + Na_2O + K_2O)$ $F = 100 * FeO / (FeO + MgO + Na_2O + K_2O)$ $M = 100 * (MgO) / (FeO + MgO + Na_2O + K_2O)$

falling between. The implication of a differentiation trend has some support when comparing the average of the two Orb Hill analyses to the average of the five Comb Ledge analyses since the two averages are remarkably similar for both the major oxides and the trace elements (table 3.3).

Trace element concentrations determined by XRF were quite low for half of the elements analyzed. In the semi-quantitative range are Rb, Y, Nb, La, Ce, Nd, Th, U at < 10 ppm. This left few trace elements with which to search for trends. None of the trace elements could be directly correlated with increasing SiO_2 via linear trends in order to investigate the evidence for magma mixing. Trace elements were plotted against each other, e.g. Zn vs. Ba, Rb vs. Sr, but no trends were found.

The V vs Ti graph (fig. 3.2) shows that the host rocks fall into two groups with the most

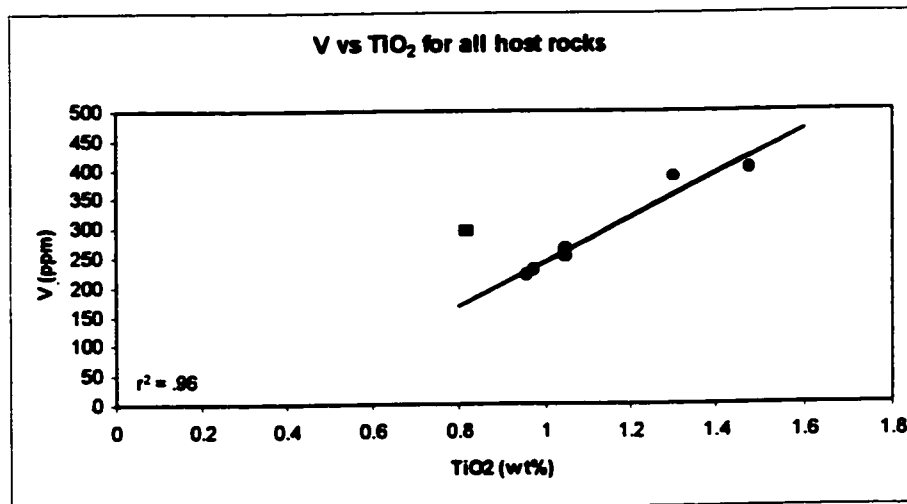


Fig. 3.2 Regression line through V vs TiO_2 through all the host rocks except for 96-CL-6 (square marker) which is more weathered than the other samples produces $r^2 = 0.96$. Inclusion of 96-CL-6 produces a regression value of $r^2 = 0.67$. The linear trend indicates that both V and Ti have been partitioned into Fe-Ti oxides (Green, 1980). The upper two points on the line are the two most mafic samples 96-OH-2 and 96-CL-4 while the lower four points are the more felsic host rocks.

mafic host rocks in the upper group and the less mafic ones in the lower group. These two groupings suggest the presence of two distinct magmas and the possibility of magma mixing. Error bars for the points on the graph as calculated from Kretz and Hartree (1998) are smaller than the points on the graph, i.e. $\text{TiO}_2 \pm .005 \text{ wt\%}$ and $\text{V} \pm 3 \text{ ppm}$ for 1 standard deviation.

An attempt was made to test the chemical data for differentiation versus magma mixing mechanisms. Differentiation would be the process connecting the host rocks if three elements could be found that, when plotted as ratios of each other, produced a single cluster and thereby demonstrating that they were incompatible or conserved elements. One of these elements would then be used as the denominator for Pearce element ratio plots which produce linear trends of specific slope depending on the mineral chemical formula used in the numerator. A magma mixing mechanism would be apparent if no elements could be found that produce a single cluster except in the unlikely event that the two magmas have identical concentrations of the conserved elements.

Plots of trace elements and major oxide components did not produce a single cluster of points but often did produce two clusters (fig. 3.3). Pearce plots for plagioclase and/or orthopyroxene did not produce the expected slopes for differentiation and have zero intercepts (see appendix B for these graphs). However these plots may have been affected by the inability to devise a complex numerator that could also take into account amphibole which has been shown to crystallize nearly simultaneously with the orthopyroxene and plagioclase. Thus the Pearce element ratio plots were inconclusive in helping to identify the differentiation mechanism of the host rocks.

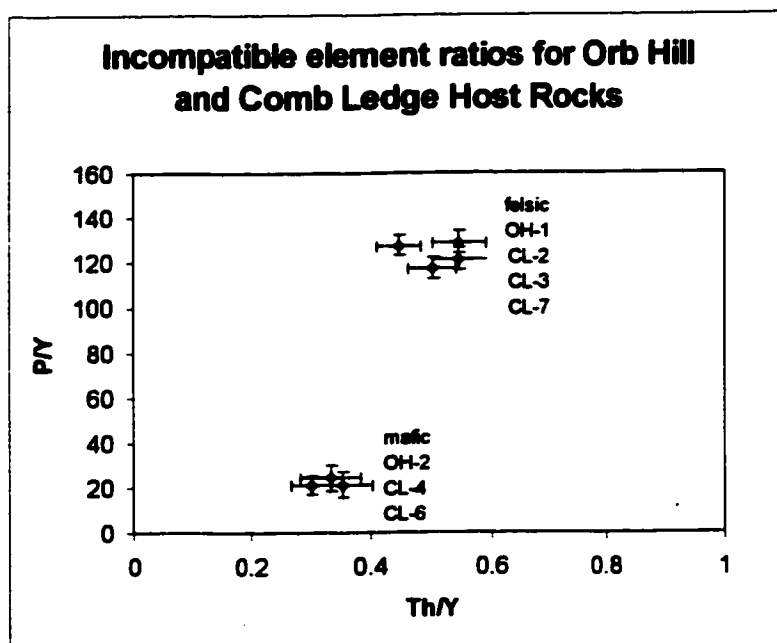


Fig. 3.3 Graph of incompatible trace element ratios showing two groupings of conserved elements that separate the more mafic host rocks from the more felsic.

Analyses of the REE contents of the host rock samples (table 3.4) were found by NAA. A chondrite-normalized REE plot of samples normalized to the chondrite values of Wakita and Zellmar (unpublished, from Wakita *et al.*, 1971) shows two trends. The two most mafic samples are slightly depleted in HREE and have small Dy and Nd positive spikes. The felsic samples have small Eu and Dy positive spikes and are depleted in HREE (fig. 3.4). Both trends have similar LREE and diverge towards the HREE. The positive Eu spike attests to the high amount of plagioclase while the Dy and Nd spike could be due to the presence of amphibole (Henderson 1984). The depletion of HREE in the felsic trend could be due to removal of orthopyroxene from the magma (Wilson 1989, p 18).

Summary

The chemical evidence implies the presence of two distinct magmas. There is some evidence that suggests that there was one magma which underwent fractionation of alkali

Table 3.4 REE data collected by NAA for the Orb Hill (OH) and Comb Ledge (CL) host rocks.

	96-CL-2	96-CL-3	96-CL-4	96-CL-6	96-CL-7	96-OH-1	96-OH-2
La	8.7	9.8	8	5.9	6.1	8.8	5.7
Ce	18.3	22.4	20.2	13.5	13.1	16.8	16.5
Nd	10.6	12.4	14.3	9.2	9.1	11.1	13
Sm	2.43	2.49	3.67	2.16	2.06	2.3	3.6
Eu	1.05	0.98	1.09	0.87	0.78	1.18	1.15
Tb	0.32	0.31	0.57	0.32	0.29	0.32	0.61
Dy	2.2	2.2	3.9	2.2	1.9	2	4.3
Ho	0.38	0.41	0.77	0.38	0.33	0.3	0.7
Yb	0.88	0.84	1.72	1.08	0.77	0.84	1.71
Lu	0.13	0.14	0.27	0.17	0.13	0.15	0.28
Ta	0.15	0.16	0.18	0.07	0.13	0.17	0.18
Th	0.41	0.62	0.48	0.21	0.36	0.45	0.21
U	0.13	0.19	0.17	0.06	0.12	0.15	0.06

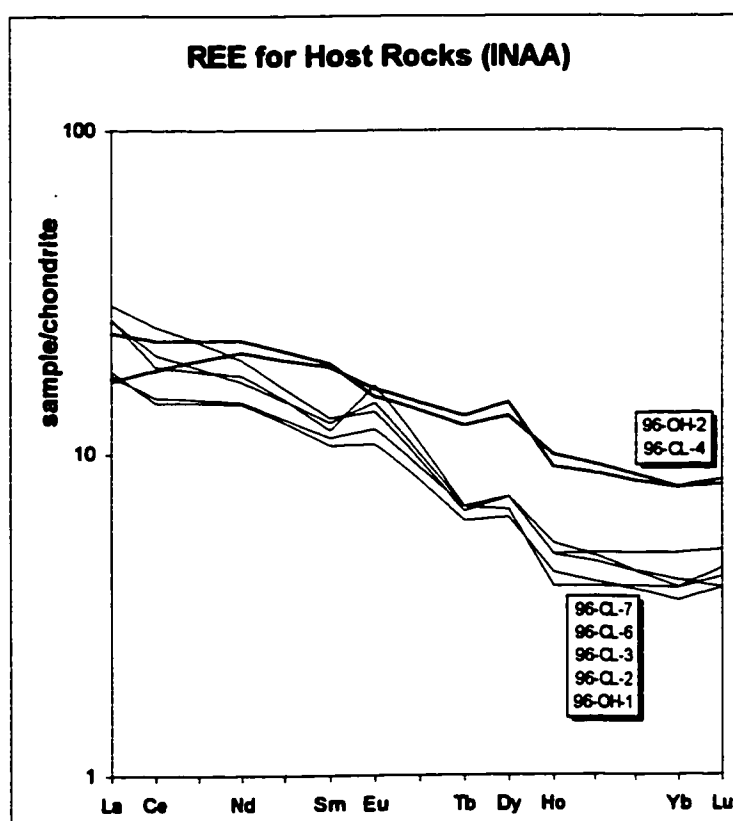


Fig. 3.4 REE plot of host rock samples normalized to chondrite (Wakita & Zellmar, 1971) showing two different trends. The upper trend contains the two most mafic samples while the lower trend is of the more felsic samples.

components as demonstrated by the linear trend of the alkalis vs SiO_2 (fig. 3.1) but this cannot be confirmed by the Pearce plots due to the lack of a conserved, incompatible element with which to use these plots.

There is evidence for magma mixing in the photos in figures 1.19 and 1.22. Also there is petrological evidence of more than one magma as documented in chapter 2 where two nearly identical felsic host rocks at both Orb Hill and Comb Ledge as well as two nearly identical mafic host rocks again at both Orb Hill and Comb Ledge have been found. The chemical evidence in chapter 3 substantiates magma mixing as seen by the two clusters of points on the V vs TiO_2 plot (fig. 3.2), the two clusters of incompatible elements found in figure 3.3, the similarity of the averages of the compositions of the Orb Hill rocks versus the Comb Ledge rocks (table 3.1) and the two groupings on the REE-chondrite normalized plot (fig. 3.4).

3.3 Orb Shells and Core Analyses

Since the heterogeneity and exquisite detail found within an orbicule would be lost in a simple whole rock analysis, XRF was done on portions of a “typical” multishelled orbicule, specifically, the core (c), the innermost radial, felsic shell (r1), the outer anhedral, mafic shell package (containing many more than one anhedral shell but no thick radial shells) (m3), and then three ‘supershells’ which are a combination of at least one radial, felsic shell plus a package of anhedral, mafic shells (ss1, ss2, and ss3) (fig. 3.5). The supershell concept was devised as an option to the inability to isolate each of the very thin shells within the orbicule individually.

The rationale for this sampling is that the compositions of the supershells and the core should reflect the magma, or magmas, that they formed from while the radial, felsic shell and the

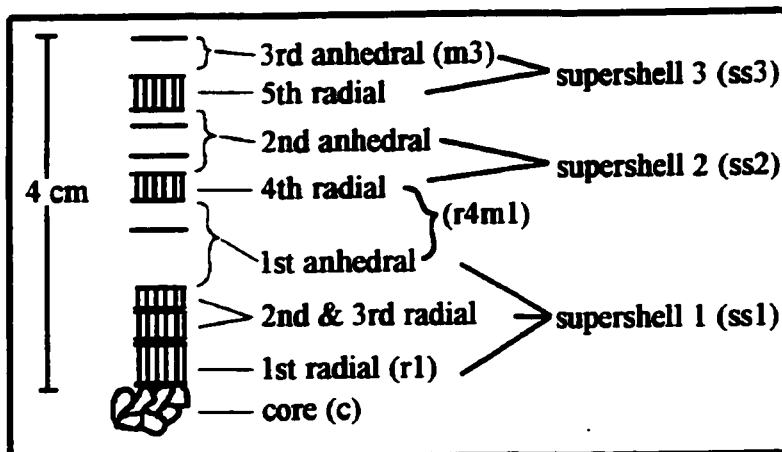


Fig.3.5 Schematic diagram of the shell morphology (radial vs. anhedral) of orbicule 95-OH-9. The sample names used for the XRF analyses are in brackets.

mafic, anhedral shell analyses should reflect the mineral mode differences between these two types of shells.

The major oxide data (table 3.5) show that the first, or innermost, radial shell (r1) is the most felsic, reflecting its high plagioclase content. A comparison of this shell, as well as the other shells, to the host rock analyses shows significant differences. The orbicule is much lower in TiO_2 , Na_2O and P_2O_5 than the host rocks and much higher in MgO . These chemical differences are reflected in the mineral modes, i.e. the host rocks have higher amounts of Na-rich plagioclase and lower amounts of Mg-rich orthopyroxene.

The core has an SiO_2 composition closest to the felsic Comb Ledge host rocks (e.g. 96-CL-2) but is somewhat lower in FeO_T and higher in MgO and CaO . These differences in composition from the host rocks chemistry may be due to (1) formation of the core from another magma, (2) same magma but slightly different growth conditions that are reflected in the higher amount of plagioclase and amphibole and lower amount of orthopyroxene than in the host rocks or (3) mobility of some components upon partial melting of a partially solidified portion of the

Table 3.5 XRF analyses of parts of the multi-shelled orbicule from figure 3.5 (upper portion of table) compared to Orb Hill (OH) and Comb Ledge (CL) host rock analyses (lower portion).

	c	r1	m3	r4m1	ss1	ss2	ss3	ast
SiO ₂	48.33	49.84	43.61	47.53	48.21	44.61	44.97	46.63
TiO ₂	0.84	0.23	0.09	0.13	0.16	0.08	0.12	0.14
Al ₂ O ₃	19.77	19.30	15.47	18.92	18.93	16.39	17.09	19.24
Fe ₂ O ₃	7.73	9.26	14.31	9.50	9.74	12.88	12.23	10.23
MnO	0.10	0.16	0.19	0.16	0.16	0.18	0.17	0.15
MgO	7.18	9.54	18.08	12.94	11.53	17.11	15.53	12.66
CaO	10.90	9.09	7.73	9.76	9.24	8.35	8.66	9.66
Na ₂ O	2.86	1.73	0.53	0.54	1.19	0.46	0.58	0.81
K ₂ O	0.32	0.21	0.06	0.06	0.16	0.04	0.12	0.09
P ₂ O ₅	0.10	0.03	0.03	0.02	0.03	0.02	0.03	0.03
LOI	1.30	0.40	0.20	0.00	0.70	0.00	0.60	1.10
Total	99.42	99.78	100.29	99.56	100.04	100.11	100.09	100.73

	96-OH-2	96-CL-4	96-CL-7	96-CL-6	96-CL-3	96-CL-2	96-OH-1	average CL	average OH
SiO ₂	43.58	45.62	47.26	47.28	47.81	48.92	50.93	47.38	47.26
TiO ₂	1.48	1.31	0.97	0.82	1.05	1.05	0.96	1.04	1.22
Al ₂ O ₃	20.26	20.39	20.30	19.08	20.90	20.12	20.65	20.16	20.46
Fe ₂ O ₃	11.99	11.79	10.87	11.01	10.58	10.11	9.69	10.87	10.84
MnO	0.15	0.14	0.16	0.16	0.17	0.16	0.18	0.16	0.16
MgO	7.42	6.70	7.32	7.89	5.75	5.44	4.73	6.62	6.08
CaO	12.45	12.06	10.52	12.10	10.65	9.72	9.59	11.01	11.02
Na ₂ O	1.36	1.52	1.74	1.46	2.08	2.70	3.17	1.90	2.27
K ₂ O	0.34	0.23	0.16	0.15	0.25	0.23	0.24	0.20	0.29
P ₂ O ₅	0.10	0.08	0.26	0.05	0.33	0.31	0.27	0.21	0.19
LOI	1.40	0.50	0.90	0.70	0.40	1.50	0.10	0.80	0.75
Total	100.53	100.34	100.47	100.70	99.96	100.25	100.50	100.34	100.51

ast - all shells together

m3 - 3rd mafic shell

ss3 - supershell 3 is the 5th radial + 3rd mafic shells

ss2 - supershell 2 is the 4th radial + 2nd mafic shells

ss1 - supershell 1 is the 1st, 2nd, 3rd felsic + 1st mafic shells

r4m1 - 1st mafic + 4th radial shells

r1 - 1st radial shell

c - core

*all Fe reported as Fe₂O₃

Comb Ledge magma that gets incorporated into the Orb Hill magma as a xenolith and becomes surrounded by precipitating shells. The similarity between the chemistry of the first shell and the core suggests that the core may have influenced the mineralogy of the first shell either by partial melting of the core and contribution of some melt to the host magma, i.e. small scale mixing or that the core changed the conditions in the host magma in such a way as to affect which minerals precipitated.

Supershell 2 and supershell 3 are similar in composition to each other with only small differences in MgO, FeO_T and Al₂O₃. Supershell 1 has twice as much plagioclase as the other two supershells and this is reflected in the higher amounts of SiO₂, Al₂O₃, CaO, and Na₂O and lower

	core	ast	96-OH-2	96-OH-1
SiO ₂	48.33	46.63	43.58	50.93
TiO ₂	0.84	0.14	1.48	0.96
Al ₂ O ₃	19.77	19.24	20.26	20.65
Fe ₂ O ₃	7.73	10.23	11.99	9.69
MnO	0.10	0.15	0.15	0.18
MgO	7.18	12.66	7.42	4.73
CaO	10.90	9.66	12.45	9.59
Na ₂ O	2.86	0.81	1.36	3.17
K ₂ O	0.32	0.09	0.34	0.24
P ₂ O ₅	0.10	0.03	0.10	0.27
LOI	1.30	1.10	1.40	0.10
Total	99.43	100.73	100.53	100.50

Table 3.6 Chemistry of the two Orb Hill (OH) host rocks compared to the core and all the shells together (ast) of orbicule 95-OH-9.

MgO and FeO_T. Comparison of the total shell package (ast) to the two Orb Hill host rocks and the core shows significant differences in the amounts of TiO₂, MgO, Na₂O and K₂O (table 3.6). These differences must reflect changes in growth conditions between the early precipitation of the shells of the orbicule, which are rich in orthopyroxene and low in plagioclase, and that of the later precipitation of the rest of the host magma with its higher modal plagioclase and lower orthopyroxene.

Trace element analyses show that the core and shells are low in many trace elements as are the host rocks (table 3.7). The shells have less V, Cr, Y, Zr, and more Co, Ni than the core and the host rocks. Both the core and shells have less Sr than the host rocks and this is reflected in the lower modal percentage of plagioclase in the orbicule than in the host rocks. Ba is also lower in all three supershells than in the host rocks again reflecting the lower plagioclase content of the shells. Ba only increases in the core and in the first radial shell (r1) where plagioclase is most abundant in the orbicule. It is unknown as to why the shells have less V and Cr than the core and host rocks since V and Cr preferentially go into Fe-Ti oxides (Cameron & Papike, 1980) which are higher in abundance in the shells than elsewhere. Ni can be found in orthopyroxene which explains the increase in Ni in the shells since orthopyroxene is most abundant there.

Summary

The differences in the chemical compositions between the shells in an orbicule from Orb Hill and the Orb Hill host rocks mainly reflect the mineralogical differences between them. Higher MgO in the shells mirrors the higher orthopyroxene content while lower Sr, Ba, Na, K, Al, Ca, all correspond to lower amounts of plagioclase in the shells than in the host rocks. The

core is most similar to the felsic Comb Ledge samples though differences in chemistry may be due to mobilization of some elements during partial melting of the core as the orbicule formed, as well as due to differences in mineralogy.

Table 3.7 Trace elements (ppm) for sections of the multi-shelled orbicule 95-OH-9 (fig. 3.5) as determined by XRF.

	core	r1	r4m1	ss1	ss2	ss3	m3	ast	average CL host	average OH host
V	308	112	60	78	33	42	36	65	286	312
Cr	23	18	20	18	16	16	12	22	81	28
Co	31	35	54	47	87	90	101	56	34	28
Ni	17	10	40	29	77	67	89	38	29	18
Zn	54	88	68	84	99	97	108	87	112	106
Rb	5	6	<0	3	<0	2	<0	<1	5	8
Sr	544	569	558	552	467	477	423	542	711	628
Y	12	3	2	2	<1	3	<1	2	12	14
Zr	46	12	9	10	8	13	8	11	20	19
Nb	4	2	<1	2	<1	1	2	<1	1	1
Ba	203	205	110	117	102	91	100	171	177	181
La	23	17	30	<0	43	<0	36	<0	14	1
Ce	46	<10	<0	12	<0	<10	<0	<0	16	30
Nd	19	<10	<0	<10	<0	<10	<10	<10	12	15
Pb	4	<0	<0	<0	<0	<0	<0	<0	0	0
Th	1.16	1.13	<0	<1	1.59	<1	1.35	<0	5	6
U	<0	<0	<0	<0	<0	<0	<0	<0	1	0
Ga	19.6	17.3	14.7	15.6	12.4	13.3	12.7	16		

ast - all shells together

m3 - 3rd mafic shell

ss3 - supershell 3 is the 5th radial + 3rd mafic shells

ss2 - supershell 2 is the 4th radial + 2nd mafic shells

ss1 - supershell 1 is the 1st, 2nd, 3rd felsic + 1st mafic shells

r4m1 - 1st mafic + 4th radial shells

r1 - 1st radial shell

c - core

3.4 Orbicular Mineral Chemistry

The chemistry of the minerals in the orbicules, comb layering and host rocks was determined by scanning electron microprobe during seven sessions at McGill University from May 1996 to June 1998 on a JEOL Superprobe 8900-L (see Appendix A for methodology). The error in these chemical analyses is less than about 0.03 wt % and is always smaller than the symbol on the graphs (see appendix A for calculation of error in standards measurements).

3.4.1 Orthopyroxene

As described in chapter 2, some of the orthopyroxene in the unaltered orbicules from Orb Hill have a branching/budding morphology. The branching orthopyroxene is best developed in the innermost radial shell of orbicule 95-OH-3. These crystals were analyzed by electron microprobe along their long axes at roughly 50 to 200 nm intervals along with several transects across the short axis near the beginning, the middle and the end of a crystal. Figure 3.6 shows that branching crystal Opx1 began growth at Mg#68 and gradually increased to Mg#74 along the crystal length. Mg# has been calculated as $100 * \text{Mg} / (\text{Mg} + \text{Fe})$. Ca has been excluded from all the Mg# calculations for all orthopyroxene crystals since the amount of Ca never exceeds 1 wt% and is usually less than 0.5 wt%. The increase in MgO and corresponding decrease in FeO_T are not an artifact of the microprobe, i.e. machine drift, since SiO_2 is constant over the same interval.

Branching crystal Opx 4 (fig. 3.7) shows the same patterns as Opx1 (fig. 3.6) with growth starting at Mg#68 and gradually increasing to Mg#75 along the crystal length. Transects normal to the long axis have variable Mg# but most have the highest Mg# in the middle decreasing

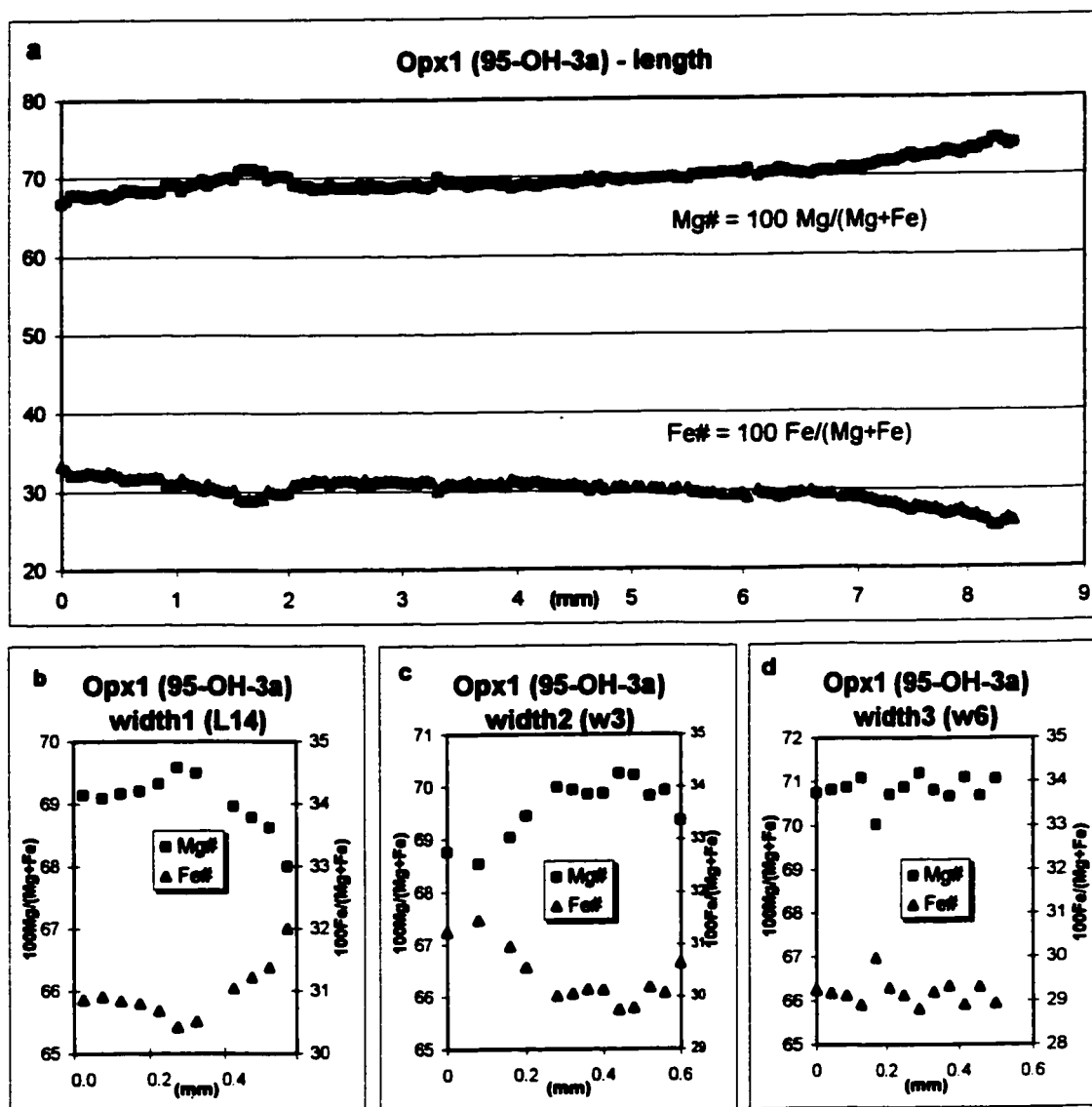


Fig. 3.6 Graphs showing the Mg# and Fe# for Mg and Fe in an elongated budding orthopyroxene (Opx1) from orbicule (95-OH-3). SiO_2 is not shown since it remains essentially constant at about 53 wt % even as the MgO and FeO become gradually reversed zoned along the length of the crystal as it grows from left to right (graph "a"). Graphs "b-d" shows analyses across the crystal with graph "b" closest to the origin of the crystal and graph "d" farthest.

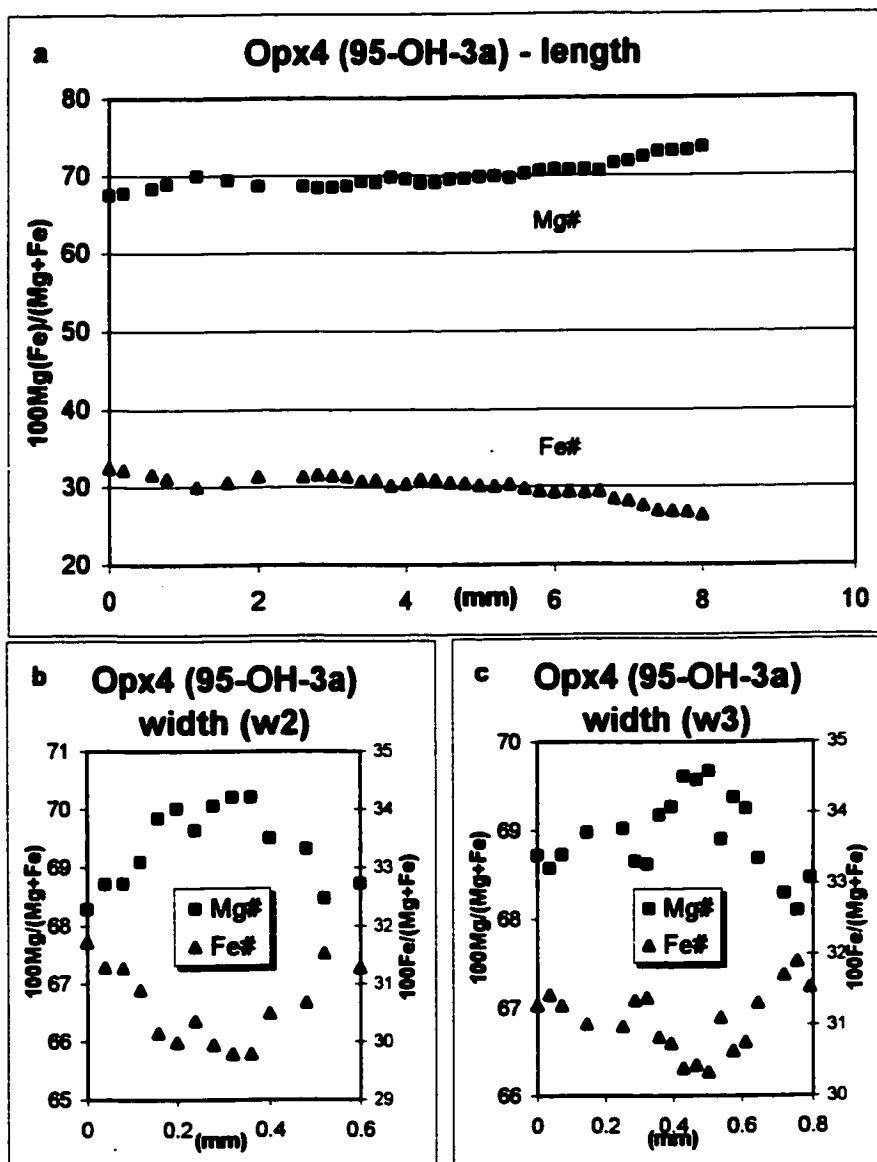


Fig. 3.7 Graphs showing Mg# and Fe# for Mg and Fe along the the length of a branching, elongated orthopyroxene (Opx4) from orbicule 95-OH-3. SiO_2 is not shown since it remains essentially constant at about 53 wt % even as the MgO and FeO become gradually reversed zoned along the length of the crystal as it grew from left to right (graph "a"). Graphs "b-c" show analyses across the crystal with "b" closest to the origin of the crystal and "c" farthest.

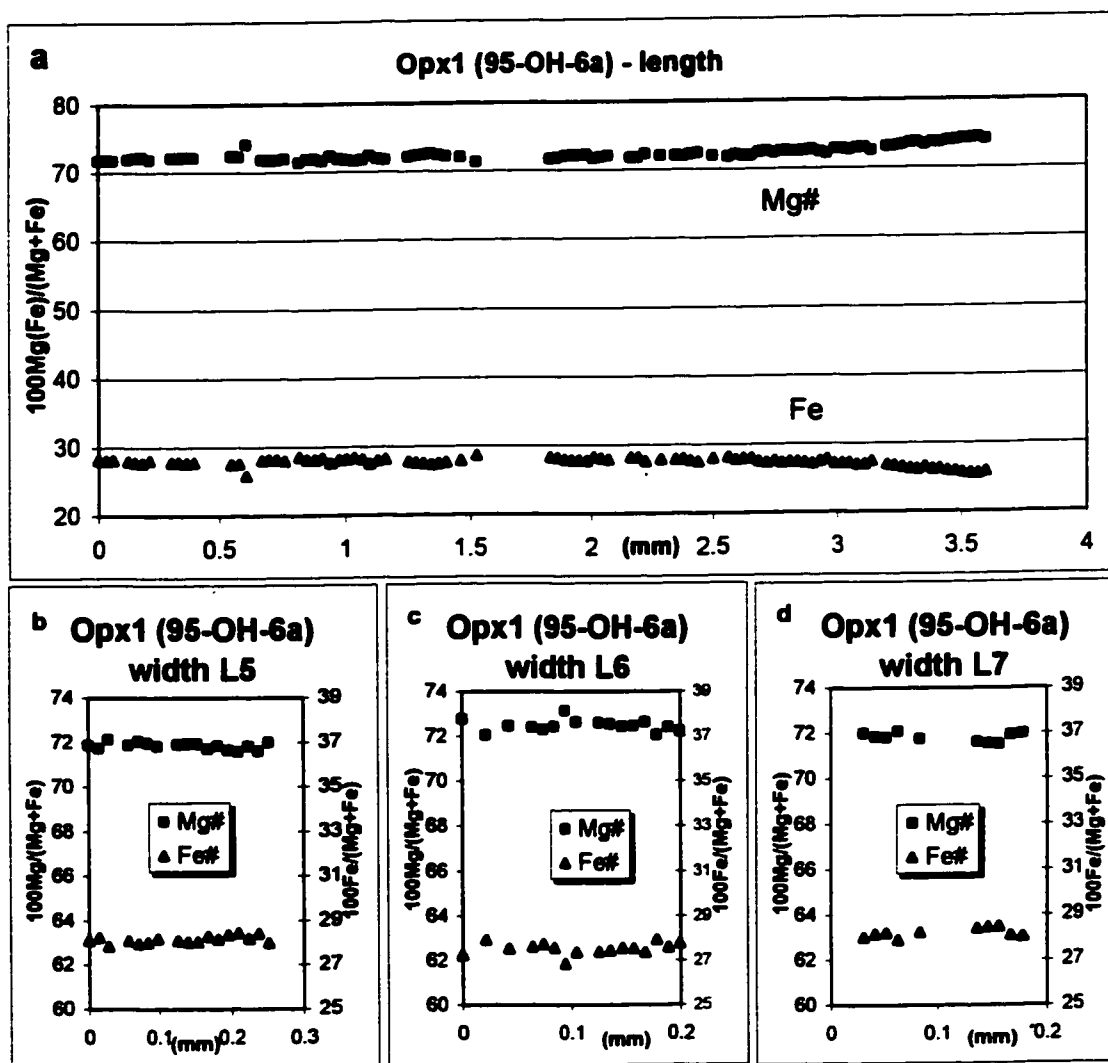


Fig. 3.8 Graphs showing Mg# and Fe# for Mg and Fe in an elongated, budding orthopyroxene (Opx1) from orbicule 95-OH-6. SiO_2 is not shown since it remains essentially constant at 53 wt %, the same value as the previous two crystals (fig. 3.6 & 3.7, graph "a"). MgO and FeO become gradually reversed zoned along the length of the crystal as it grew from left to right. Note the difference in Mg and Fe#'s between crystals from different orbicules. Both orthopyroxenes from orbicule 95-OH-3 have $\sim\text{Mg}68-74$ (fig. 3.6 & 3.7 graph "a") while graph "a" above shows $\sim\text{Mg}72-75$. Graphs "b-d" show analyses across the crystal with "b" closest to the origin of the crystal and "d" farthest.

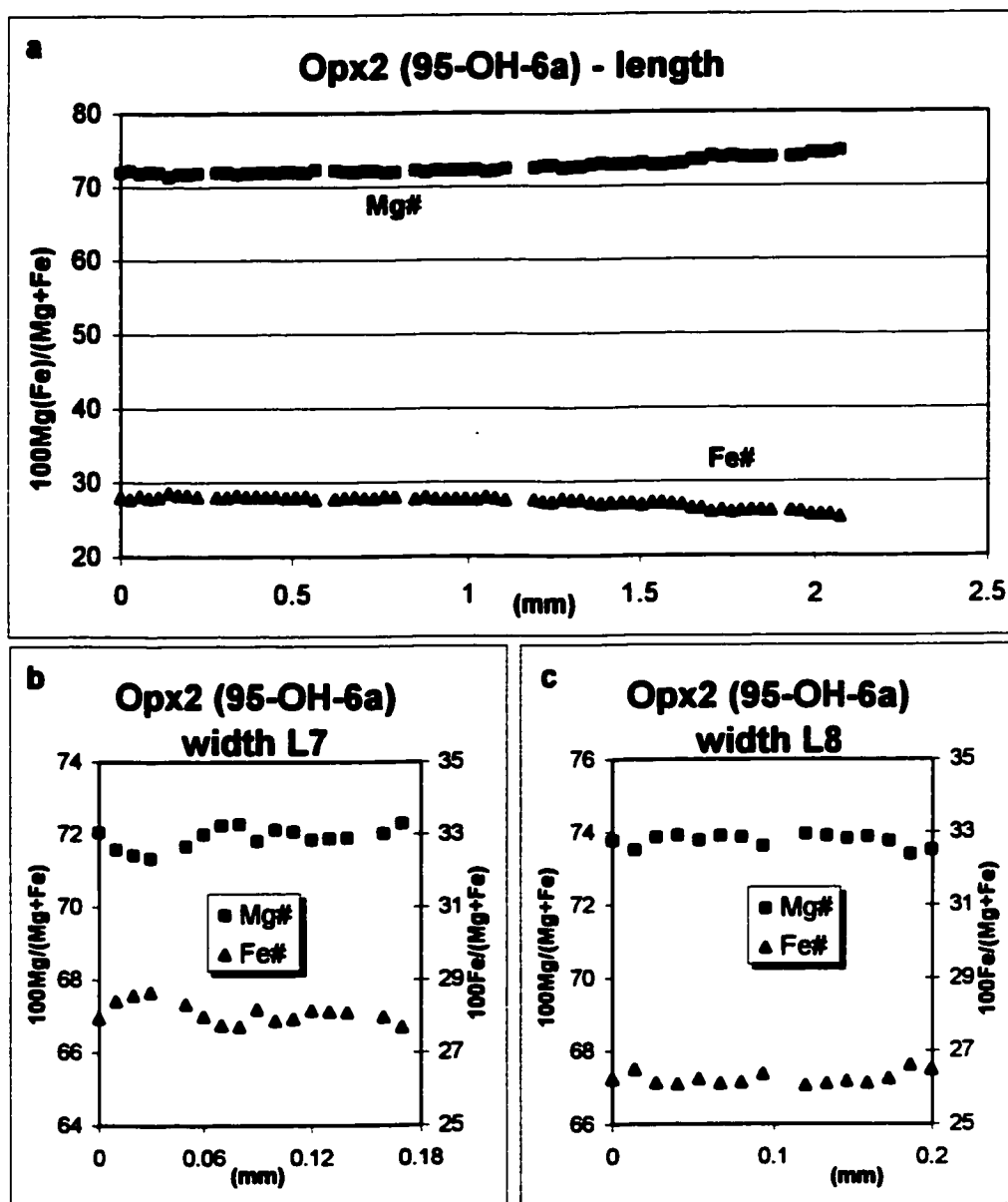


Fig. 3.9 Graphs of an elongated, budding orthopyroxene (Opx2) from orbicule 95-OH-6 showing Mg# and Fe#. Note that these values have the same range as Opx1 from the same orbicule (fig. 3.8) and that they are different from the other orbicule (95-OH-3). Graphs "b-c" show analyses across the crystal with "b" closest to the origin and "c" farthest. SiO_2 is again constant at about 53 wt % and growth direction is from left to right in graph "a".

towards the outer edges of the crystals, i.e. normal zoning. SiO_2 is nearly constant at ~53 wt % and, along with MgO and FeO_T , make up ~98 wt % of the chemical analyses in both the Opx1 and Opx4 crystals. Percentages of En, Fs, and Wo along with the mineral formula have been calculated for many of the orthopyroxene crystals mentioned in section 3.4. These values as well as the calculation methodology can be found in Appendix E.

Two budding orthopyroxene crystals from another orbicule (95-OH-6) show the same pattern of increasing MgO from start to end but the actual Mg#'s are slightly different with growth beginning at Mg#72 and gradually increasing to Mg#75 along the long axes of the crystals (fig. 3.8 and 3.9). The crystals in this orbicule are much narrower than in the previous orbicule (95-OH-3) and the short axis transects show less variation in composition.

Thus both orbicules contain branching/budding, gradually reversed-zoned, orthopyroxene where the Mg# range is the same for orthopyroxene within one orbicule but slightly different from the other orbicule. This indicates that either the magma was chemically heterogeneous on a scale equivalent to that of the orbicules, and/or, growth conditions were slightly different on local scales perhaps due to small differences in chemical potentials or kinetic processes.

3.4.2 Plagioclase

Five feather-shaped plagioclase were analyzed by electron microprobe in orbicule 95-OH-3 to determine if they were zoned. Four of the crystals were not, having instead compositions that were fairly constant. One plagioclase crystal showed gradual reverse zoning (fig. 3.10a) with $\text{SiO}_2 + \text{Na}_2\text{O}$ decreasing and $\text{CaO} + \text{Al}_2\text{O}_3$ increasing (i.e. An_{47} increasing to An_{93}) towards the end of the crystal. One transect across the short axis also showed reverse zoning with low CaO

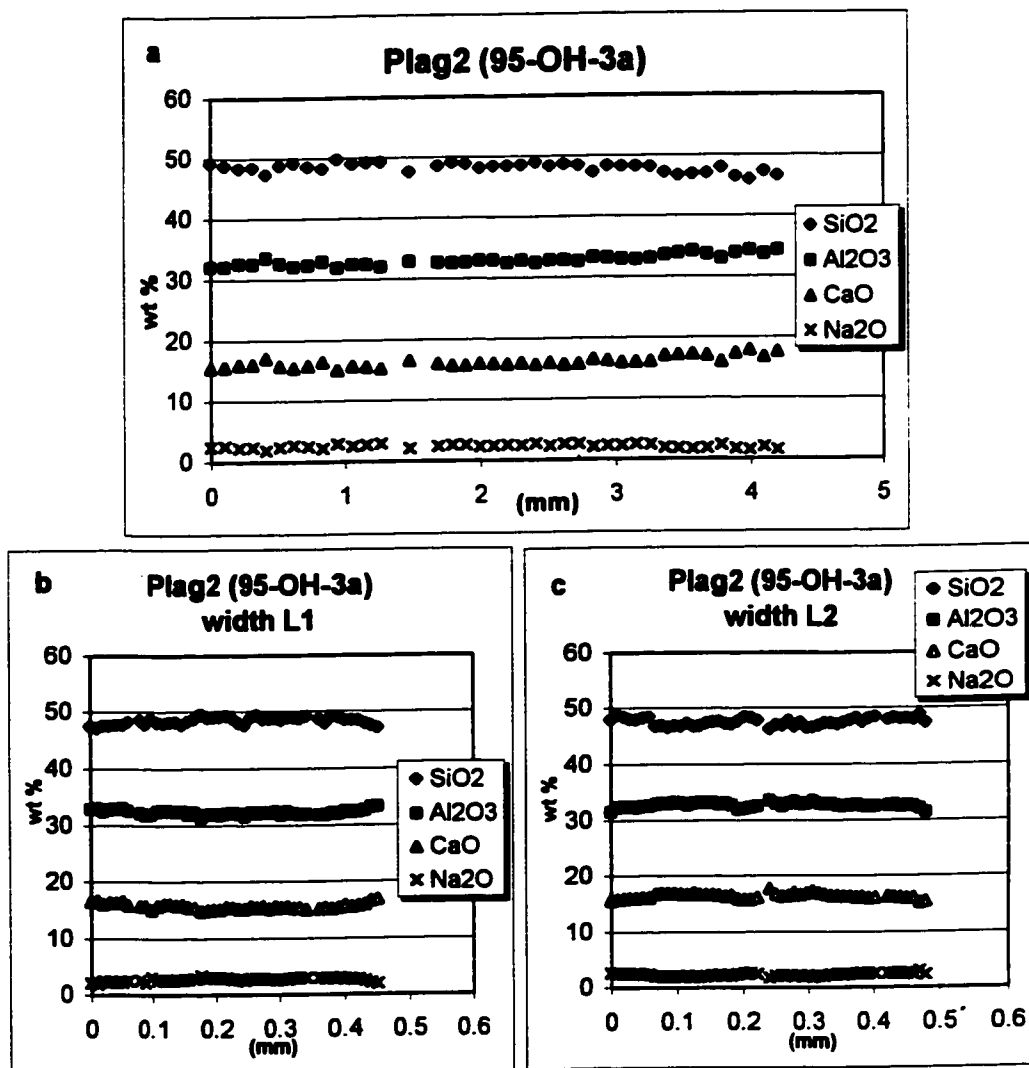


Fig. 3.10 Graphs showing the weight percentages of the four main chemical components of a plagioclase (Plag2) from orbicule 95-OH-6. Graph "a" shows gradual reverse zoning towards the end of the long axis of the crystal. Graphs "b" and "c" show analyses across the short axis with "b" closer to the origin of the crystal and "c" closer to the end of the crystal. Growth direction is from left to right in graph "a" and from the middle outwards in graphs "b" and "c".

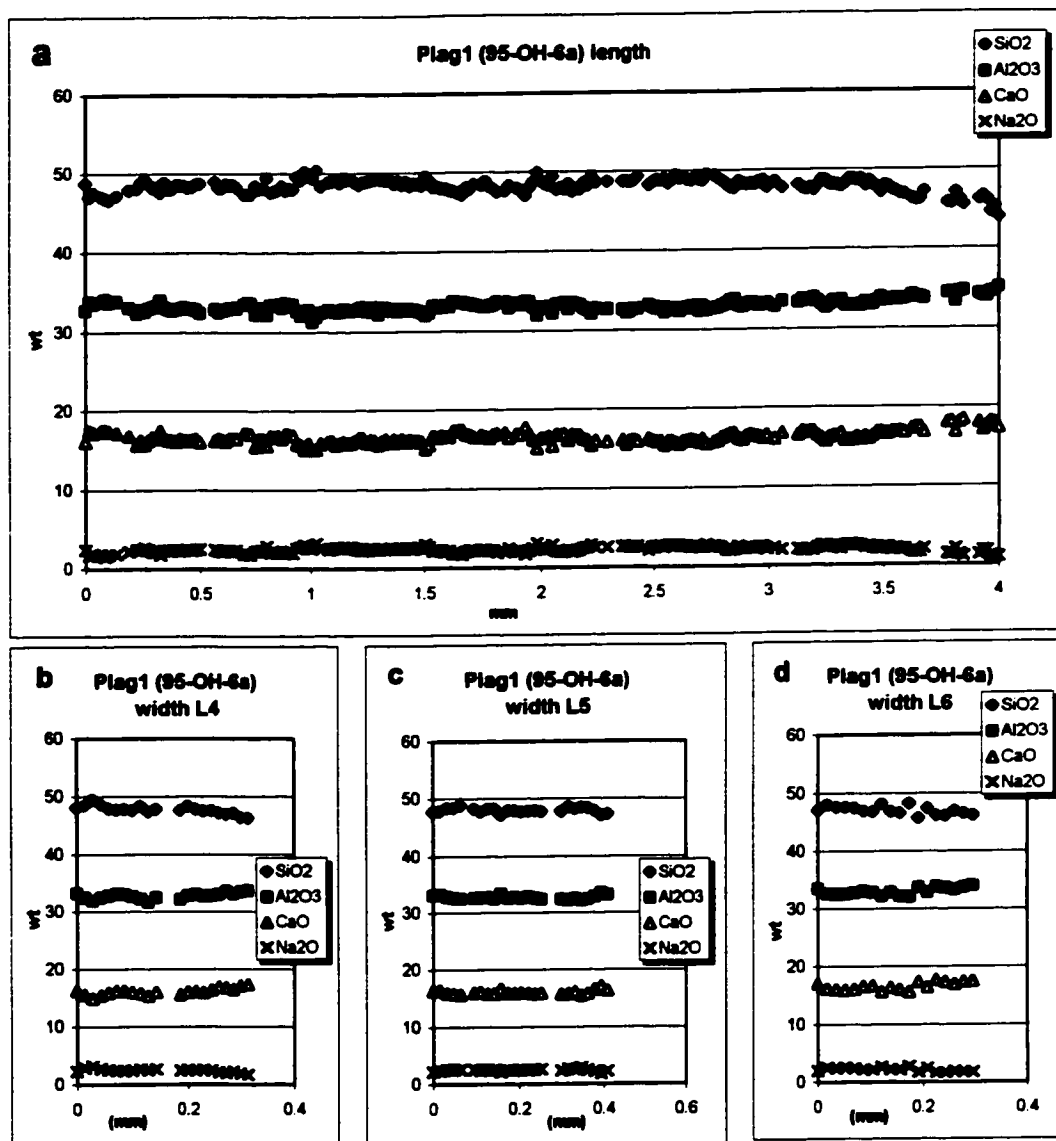


Fig. 3.11 Graphs showing the weight percentages of the four main chemical components of a plagioclase (Plag1) from orbicule 95-OH-6. Graph "a" shows gradual reverse zoning towards the end of the long axis of the crystal. Graphs "b-d" show analyses across the short axis with "b" closer to the origin of the crystal and "d" closer to the end of the crystal. Growth direction is from left to right in graph "a" and from the middle outwards in graphs "b", "c", and "d".

in the centre increasing towards the edges of the crystal (fig. 3.10b) but the other transect shows normal zoning with CaO decreasing from An_{88} to An_{23} towards the outer edges (fig. 3.10c). This difference between the beginning and end of the crystal indicates that growth conditions were not exactly the same everywhere, even over the length of a 4 mm crystal.

One of two feather plagioclase crystals analyzed in orbicule 95-OH-6 also produced gradual reverse zoning along the long axis with An_{91} at the beginning of the crystal increasing to An_{96} to the end (fig. 3.11a). The transects across the short axis again show the dichotomy in the growth environment along the length of the crystal with two showing reverse zoning where CaO is low in the centre and increases towards the outer edges (fig. 3.11c,d) and one showing high CaO at one edge and decreasing to the other edge (fig. 3.11b).

3.4.3 Amphibole

Microprobe analyses of amphiboles showed that they tend to vary in composition, even across a single crystal, but they mainly fall into the calcic amphibole range of composition. The hornblende in the core of orbicule 95-OH-3 was the most homogeneous with nearly equal amounts of MgO, FeO_T , Al_2O_3 and CaO at 10 - 15 wt % each along with 45 wt % SiO_2 . Mineral formula calculations produce a formula of $(K_{0.1}Na_{0.5}Ca_{1.8})(Mg_3Fe^{+2}_{1.5}Ti_{0.2}Al_{0.3})(Si_{6.5}Al_{1.5})O_{22}(OH)_2$ which is an edenite. Some of the crystals analyzed in the inner shell had similar compositions but with slightly less CaO, Na_2O , Al_2O_3 and FeO and more MgO and SiO_2 producing a formula of $(K_{0.1}Na_{0.3}Ca_{1.7})(Mg_{3.6}Fe^{+2}_{1.3}Ti_{0.1}Al_{0.3})(Si_{6.9}Al_{1.1})O_{22}(OH)_2$ which is a magnesiohornblende. The calculations were done following the techniques of Klein and Hurlbut (1985) and Leake *et al.* (1997) and can be found in Appendix E.

3.4.4 Fe-Ti Oxides

The oxides in the orbicules are small and anhedral but not randomly distributed as seen in chapter 2. In orbicule 95-OH-3, the oxides appear to increase in concentration towards the ends of the branching/budding orthopyroxene in the innermost shell. Fifteen Fe-Ti oxide crystals were probed to see if the composition of the oxides changed along the length of these orthopyroxene crystals. Analyses showed that the oxide crystals were either magnetite (about two thirds) or ilmenite (about one third). The compositions of each of the minerals are fairly constant and do not change with respect to position along the length of the branching orthopyroxene. Since the microprobe cannot distinguish between Fe^{+2} and Fe^{+3} , it is unknown if the proportions of these two components within the magnetite change with respect to the position of the magnetite along the length of the branching orthopyroxene crystals. A quick scan of both orbicules under back-scatter conditions showed that (1) magnetite crystals tended to be slightly larger than ilmenite, (2) the two oxides were found side by side as often as found alone and, (3) they appear to be randomly mixed together in the shells where Fe-Ti oxides are present, i.e. there was no segregation of a particular oxide mineral into any particular shell.

Summary

The branching/budding orthopyroxene crystals within two orbicules show distinct, reverse chemical zoning along the long axes of the crystals and normal zoning perpendicular to the long axes. The reverse zoning is gradual and continuous along the crystal length. Plagioclase compositions are generally constant over the length of the crystal but can also show gradual reverse zoning near the end of the long axis of the crystal.

3.5 Comb Layering Mineral Chemistry

As shown in figure 2.9, this sample of comb layering consists of spectacular, elongated, budding hornblende crystals almost 1 cm long. Given the gradual reverse zoning found in the elongated minerals in the orbicules, it was suspected that these hornblende would also show gradual reverse zoning. Electron microprobe analyses along the lengths of three elongated hornblende crystals did not show gradual reverse zoning but did show oscillatory zoning. Figure 3.12 shows the SiO₂ wt % content for crystal 'Amphibole1'. There are seven cycles with peaks at 0, 0.8, 1.6, 2.7, 3.8, 5 and 6.4 mm. These same peaks can be seen in the MgO content which varies in tandem with the SiO₂. FeO_T and Al₂O₃ vary opposite to MgO and SiO₂ with lows at nearly the same positions as the SiO₂ peaks. CaO (not shown) stays nearly constant at about 11.5 wt%. These five components account for roughly 90 wt % of the chemical composition of the hornblende. Na₂O and TiO₂ which make up about 5 wt %, vary approximately with the FeO_T and Al₂O₃. Remaining components such as K₂O, F, Cl, MnO, Cr₂O₃ and NiO are too low in concentration and too variable for comparison. Calculation of the mineral formula produces (K_{0.1}Na_{0.6}Ca_{1.8})(Mg_{3.2}Fe_{1.4}Ti_{0.3}Al_{0.3})(Si_{6.3}Al_{1.7})O₂₂(OH)₂ which is a pargasite.

The oscillations raises the question, at what scale are these oscillations taking place, i.e. are they extremely local to the one crystal or wider scale over several crystals or common to the whole comb textured layer?

Two more elongated amphibole were analyzed in detail by electron microprobe. Figure 3.13 shows that one hornblende, Amphibole6, appears to have the same oscillations in SiO₂ content as Amphibole1. Unfortunately, the other crystal, Amphibole3 appears to have no regular oscillations. Amphibole6 is located in the subsequent comb textured layer about 7 mm directly

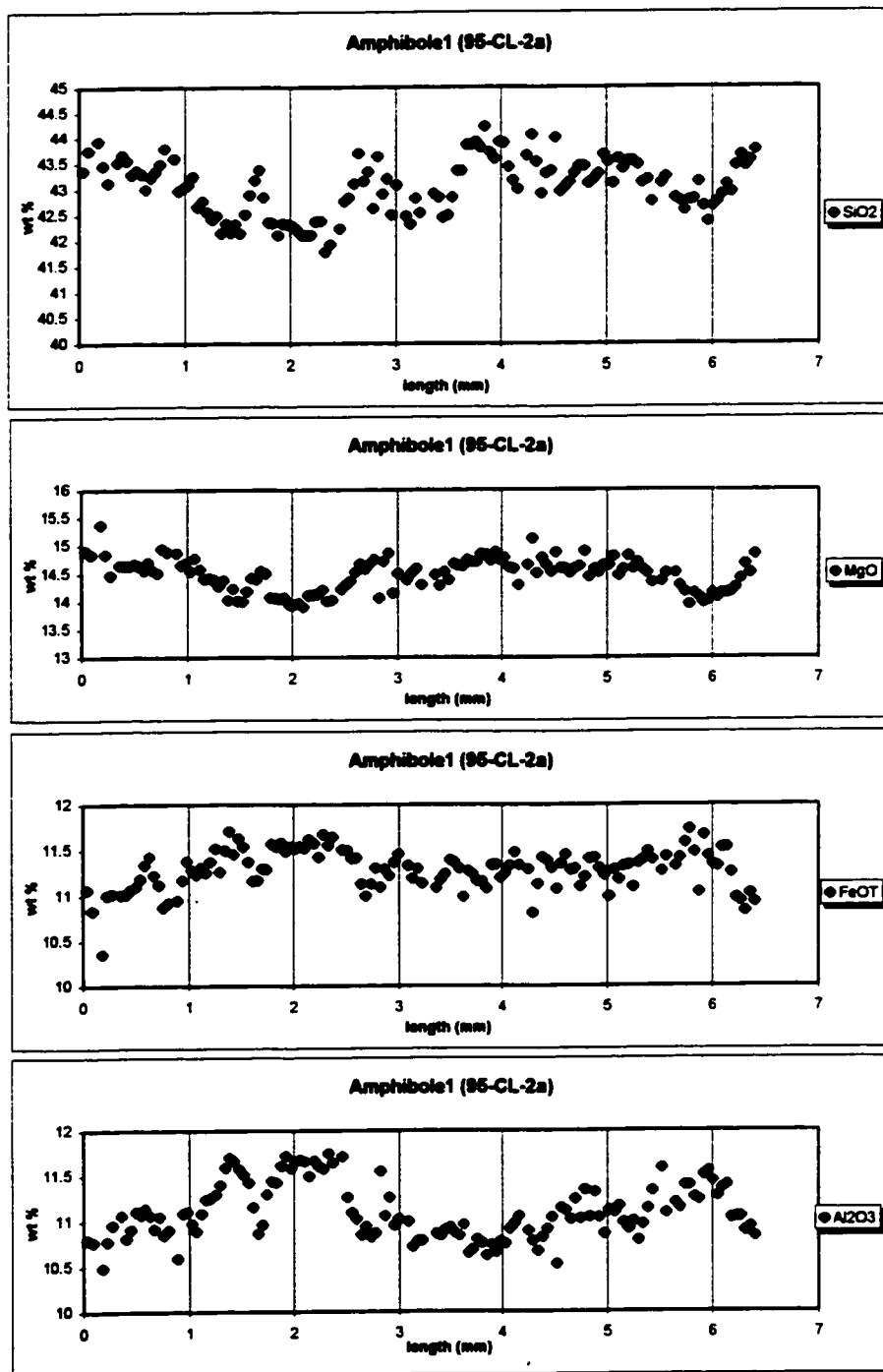


Fig. 3.12 Plots of some major oxides for an elongated, budding amphibole (Amphibole1) in comb layering sample 95-CL-2. There is no gradual reverse zoning like that seen in the elongated orthopyroxenes from the orbicules but there are oscillations along the length of the crystal. SiO₂ and MgO vary together and opposite that of FeO_T and Al₂O₃.

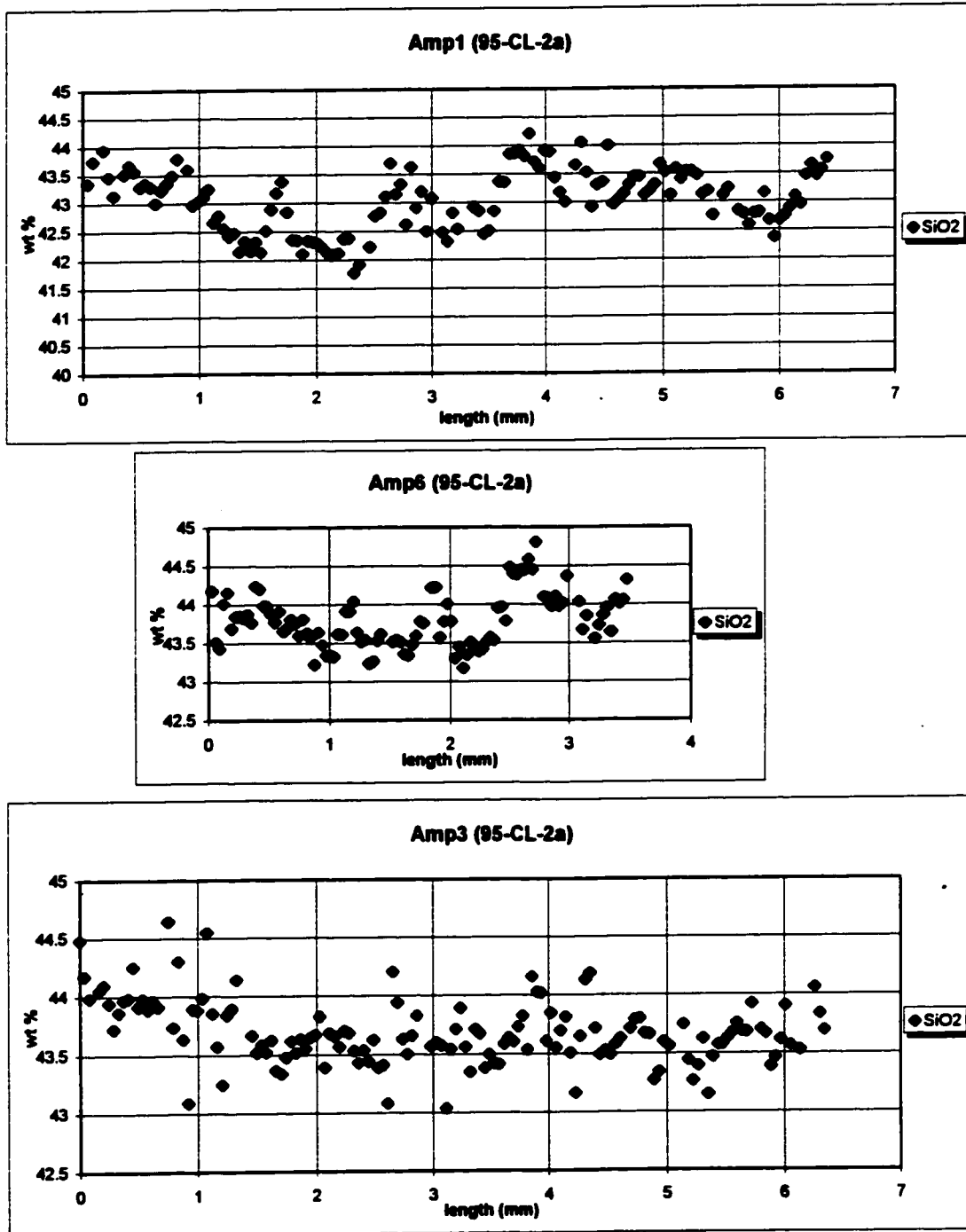


Fig. 3.13 Plots of SiO₂ for three elongated, budding amphibole crystals from the same comb layer in sample 95-OH-2. Amp1 and Amp6 show a similar set of oscillations but Amp3 does not even though these three crystals are within 2 cm of each other.

“downriver” from Amphibole1. Amphibole3 is located in the same layer as Amphibole1 about 7 mm away. These trends suggest that the oscillations seen in these hornblende crystals are local changes in concentrations, on the scale of a single crystal, and not large, magma chamber wide, variations. Analyses across the short axes of these crystals showed no systematic variation.

Other crystals analyzed were two clinopyroxene crystals that showed no zoning under the light microscope. The electron microprobe found nearly constant compositions with CaO at 23 wt %, $\text{FeO}_T \sim 8$ wt %, MgO ~ 15 wt % and, $\text{SiO}_2 \sim 53$ wt %. Mineral formula calculations indicate a composition of En_{43} , Fs_{12} , Wo_{45} .

Five small orthopyroxene crystals located within an elongated hornblende (Amphibole1) at various positions along its length were analyzed for any compositional variations. All five crystals showed constant compositions with $\text{SiO}_2 \sim 53.5$ wt %, MgO ~ 26 wt % and $\text{FeO}_T \sim 18.5$ wt % with Mg# of 58. CaO makes up less than 0.5 wt % and Al_2O_3 reaches 1 wt % producing a mineral formula of En_{70} , Fs_{29} , Wo_1 .

One elongated feather plagioclase 4 mm long was analyzed and found to have constant composition along the length of the crystal at An_{89} . Na_2O is very low at only ~ 2 wt % and CaO is high with ~ 16.5 wt %. Transects across the crystal were also found to be constant at the same An content.

Summary

The elongated budding hornblende crystals found in the comb layering showed oscillatory chemical zoning along their lengths that reflect extremely local changes in the magma since the variations in three crystals situated within a centimetre of each other could not be correlated.

Elongated feather plagioclase have constant compositions and are Ca-rich. The pyroxenes also do not show any zoning. The composition of the orthopyroxene is very similar to that seen in the orbicules, i.e. very low in CaO and classified as an enstatite just like the orbicular orthopyroxenes.

3.6 Mineral Chemistry in the Host Rocks

Three host rock samples were analyzed by electron microprobe, the two from Orb Hill and one from Comb Ledge. Extensive analyses were not done since the focus of this research is on the comb texture and the orbicules and how they formed.

3.6.1 Orb Hill Felsic Host Rock 96-OH-1

Two subhedral orthopyroxene crystals were analyzed along their lengths and widths. Both crystals have nearly constant compositions in both directions at En_{60} , Fs_{38} , Wo_2 .

One subhedral plagioclase was analyzed and found to have a rim at An_{70} and a core of An_{45} with no other systematic variations.

The one anhedral primary amphibole crystal analyzed was found to be quite homogenous both in a lack of chemical variation and in that the major components, MgO, FeO, CaO, Al_2O_3 all have nearly the same wt % between 10 and 15 ($\text{SiO}_2 \sim 45$ wt %). This composition is the same as the primary amphibole analyzed from the core of orbicule 95-OH-3 (section 3.4.3) and has been determined to be edenite with $(\text{K}_{0.1}\text{Na}_{0.4}\text{Ca}_{1.8})(\text{Mg}_{3.1}\text{Fe}_{1.8}\text{Ti}_{0.2}\text{Al}_{0.3})(\text{Si}_{6.5}\text{Al}_{1.5})\text{O}_{22}(\text{OH})_2$.

Two types of Fe-Ti oxides were found; magnetite and ilmenite.

3.6.2 Orb Hill Mafic Host Rock 96-OH-2

Two anhedral plagioclase were found to have nearly constant compositions at An_{85} . Two anhedral amphibole crystals had the same chemical composition and character as the amphibole in 96-OH-1 (section 3.6.1); that of edenite $(K_{0.1}Na_{0.4}Ca_{1.8})(Mg_{3.1}Fe_{1.6}Ti_{0.2}Al_{0.3})(Si_{6.5}Al_{1.5})O_{22}(OH)_2$. Fe-Ti oxides again included crystals of both magnetite and ilmenite.

3.6.3. Comb Ledge Host Rock 96-CL-4

Only one Comb Ledge host rock sample was looked at since the mineralogy of all the Comb Ledge host rock samples is so similar. Two anhedral clinopyroxene crystals have nearly constant composition with only small non-systematic variations. Calculation of the mineral formula produces En_{42} , Fs_{13} , Wo_{45} ; same as the clinopyroxene in the comb layering (sec. 3.5).

One subhedral plagioclase crystal showed only small non-systematic variations along its length and had $\sim An_{95}$.

Fe-Ti oxides again included crystals of both magnetite and ilmenite. Anhedral amphibole crystals had similar chemistry and character as in the previous two host rock samples discussed in sections 3.6.1 and 3.6.2, that of edenite $(K_{0.1}Na_{0.4}Ca_{1.8})(Mg_{3.1}Fe_{1.6}Ti_{0.2}Al_{0.3})(Si_{6.5}Al_{1.5})O_{22}(OH)_2$.

Summary

All of the host rocks are quite similar in their mineral chemical compositions. None of the minerals demonstrated reverse zoning, gradual or otherwise suggesting that these rocks cooled in a more "traditional" manner in comparison to the comb textured phenomena within them.

3.7 Summary

The crystal morphologies seen in chapter 2 (e.g. fig. 2.6) suggest that crystal growth in the orbicules did not take place under near-to-equilibrium conditions. The elongated, branching/budding, feather, and wedge shapes of the crystals suggests higher growth rates than those found under the more common, slow, plutonic, cooling conditions. The microprobe analyses of these minerals supports the hypothesis of far-from-equilibrium formation. The gradual reverse chemical zoning found in both the orthopyroxene and the plagioclase does not form in more typical crystallizing environments.

4. Reverse Zoning

The presence of gradual reverse chemical trends in large crystals of branching/budding orthopyroxene and feather plagioclase in the Fisher Lake orbicules is clearly substantiated by nearly 1000 electron microprobe analyses (chapter 3.4). In orthopyroxene, the reverse zoning is defined by an initial growth of Mg68 (orbicule 95-OH-3) followed by a gradual increase along the c-axis to Mg74 (fig 4.1a). Normal zoning is found across the short axis of the crystal with Mg70 at the centre decreasing to Mg68 at the edges. In plagioclase, the zoning is defined by an initial growth of $\sim \text{An}_{17}$ that gradually increases along the 4 mm crystal length to $\sim \text{An}_{93}$ (fig 4.2). Normal zoning is found across the crystal with $\sim \text{An}_{48}$ at the centre decreasing to $\sim \text{An}_{33}$ at the edges.

4.1 Historical Review

Detailed studies of gradual reverse zoning are rare. The most common form of reverse zoning is that of a single abrupt change in composition between the core and the rim of a crystal (e.g. Mathews, 1957) which is usually attributed to an equally abrupt change in the magmatic environment, i.e. change in temperature, increasing f_{O_2} due to change in pressure (e.g. van Kooten & Buseck, 1978), or magma mixing (e.g. Mathews, 1957; Eichelberger, 1975; Gerlach & Grove, 1982). Dallwitz *et al.* (1966) recorded reverse-zoned orthopyroxene, giving three data points from core to rim and then attributing them to increasing f_{O_2} or temperature. Simonetti and Bell (1995) also give 3-point data sets but they also include a graph showing gradual reverse zoning over a 300 micron transect in diopside phenocrysts which they called oscillatory zoning and ascribed to a “complex crystallization history” and magma mixing. Eichelberger *et al.* (1973)

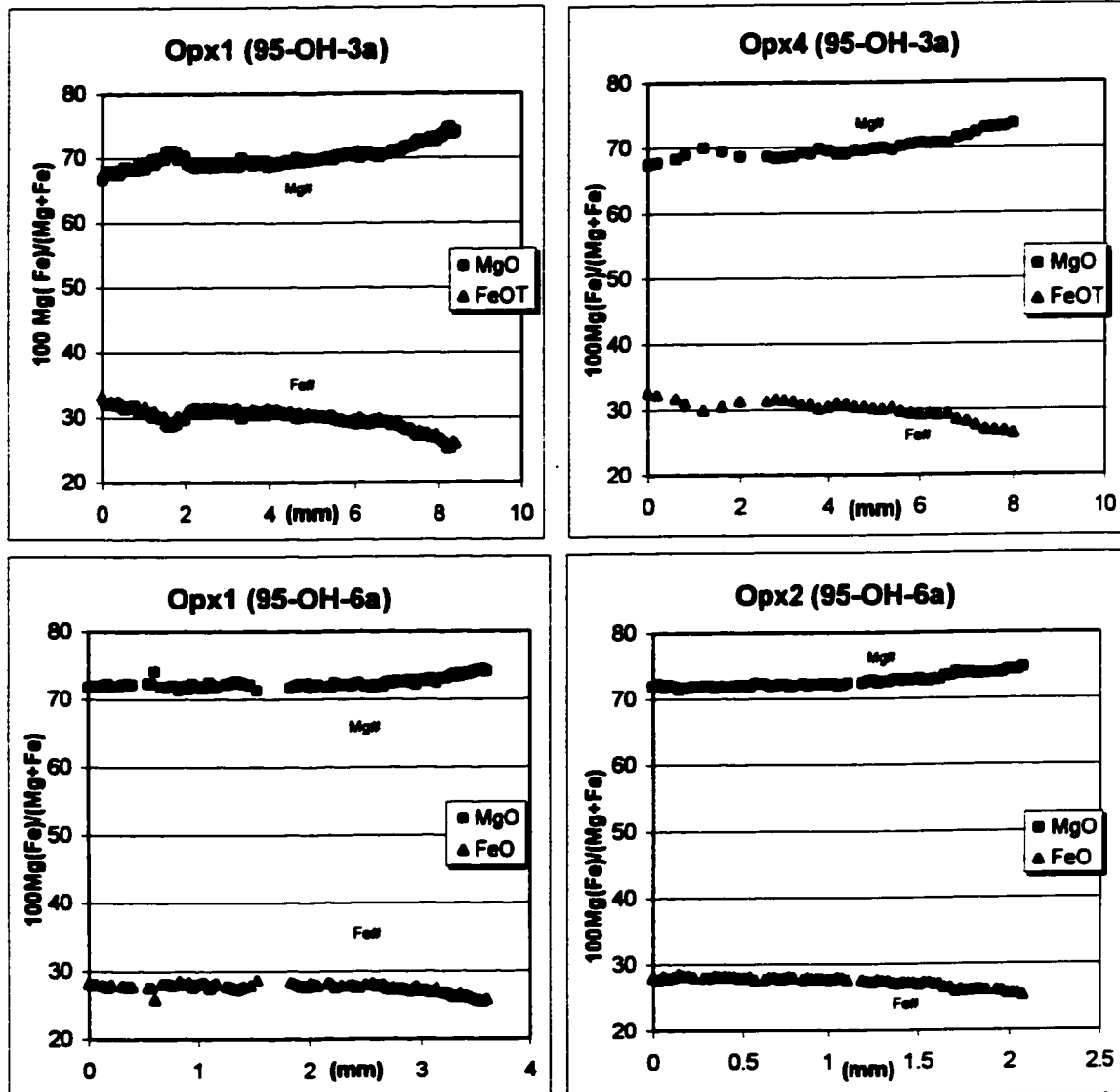


Fig. 4.1 Profiles of MgO and FeO_T (represented as Mg# and Fe#) measured along the length (c-axis) of several branching/budding orthopyroxenes from two orbicules. The crystals show gradual reverse chemical zoning as the crystals grew from left to right. SiO₂ content is nearly constant at ~ 53 wt%.

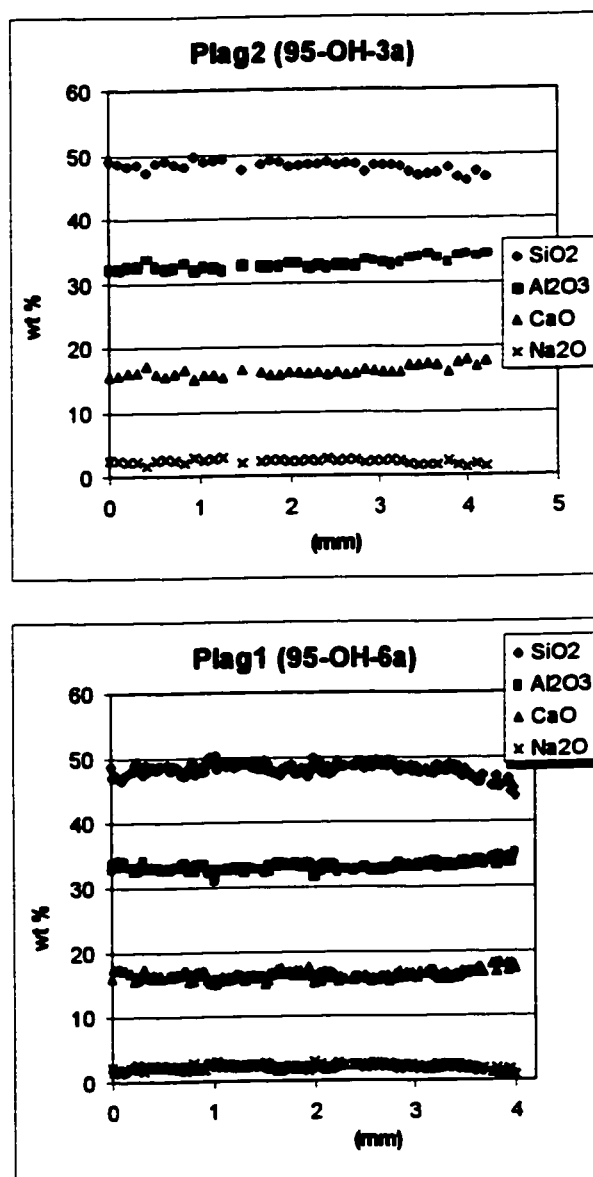


Fig. 4.2 Profiles along the c-axis of SiO₂, Na₂O, Al₂O₃ and CaO for two feather plagioclase crystals from two orbicules showing gradual reverse chemical zoning as the crystals grew from left to right.

observed gradual reverse zoned plagioclase in rhyolite flows at Glass Mountain, CA which he attributed to gradually increasing contamination of the magma.

Reverse zoning has been experimentally reproduced in plagioclase by Lofgren (1973, 1974) in zoned crystals that have an overall normal trend (i.e. Na increases from core to outer edge) but whose individual shells have gradual reverse zoning in up to five, 25 to 50 micron thick, shells. He attributed the reverse zoning to a two stage process of initial rapid undercooling of more than 50 - 75 °C followed by isothermal crystal growth. This mechanism is a function of the effective distribution coefficient, growth rate, amount of supercooling, melt composition, and P_{H_2O} (Lofgren, 1973) and will be discussed in more detail in section 4.2.3.

In a theoretical treatment of solute redistribution at a crystal growth front during crystallization, Hopper and Uhlmann (1974) concentrate on using Gibbs free energy changes as the controlling force for the distribution coefficient at constant temperature and growth velocity. They attribute solute levels at the growth front to minimum free energy changes for which they obtain apparent reverse zoning (see their fig. 5, p.206). Unfortunately, they do not discuss this model in the context of reverse zoning and they go on to use an approximation that removes this zoning from their model. Tsuchiyama (1985) has experimentally grown, micrometre sized, gradual reverse-zoned, clinopyroxene for which he proposes a combination of Lofgren's model (1973, 1974) along with Hopper and Uhlmann's ideas of minimum ΔG to show that the reverse-zoned solid composition is due to interface attachment kinetics.

A mechanism for reverse zoning in orthopyroxene has been outlined by Czamanske and Wones (1973) and van Kooten and Buseck (1978) wherein rising f_{O_2} causes Fe^{+2} to oxidize to Fe^{+3} which becomes partitioned into Fe oxides. Since the orthopyroxene structure cannot

incorporate Fe^{+3} , it must accept Mg in order to grow. This mechanism results in an increase in Fe oxides along with increasingly Mg-rich orthopyroxene and will be discussed in more detail in section 4.2.1.

4.2 Reverse Zoning Formation Theories as Applied to the Fisher Lake Orbicules

A significant problem in understanding the origin of the reverse zoning is finding a single mechanism for both the orthopyroxene and the plagioclase. It is possible that two different mechanisms operated at the same time, even in nearly the same location, but a common mechanism is more sensible and desirable.

4.2.1 Fugacity Mechanism

The fugacity mechanism detailed by Czamanske and Wones (1973) and later by Lalonde and Martin (1983) has possibilities in that some of the branching orthopyroxene crystals are accompanied by an apparent increase in Fe-Ti oxides near the ends of some of the branches. However, there are several discrepancies when applied to the reverse-zoned orthopyroxenes in the Fisher Lake orbicules. First, not all of the reverse-zoned orthopyroxene crystals have increasing amounts of Fe-Ti oxides along their lengths, e.g. those found in the outer radial shells. Second, if increasing f_{O_2} causes more Fe^{+3} to be formed and to be incorporated into Fe-Ti oxides then there would also be an increased uptake of TiO_2 by the Fe-Ti oxides. This would result in a corresponding decrease in TiO_2 along the length of the orthopyroxene crystals that should correlate with the decreasing FeO (Czamanske & Wones, 1973). Microprobe data clearly show that TiO_2 does not decrease along the lengths of any of the orthopyroxene crystals (fig. 4.3).

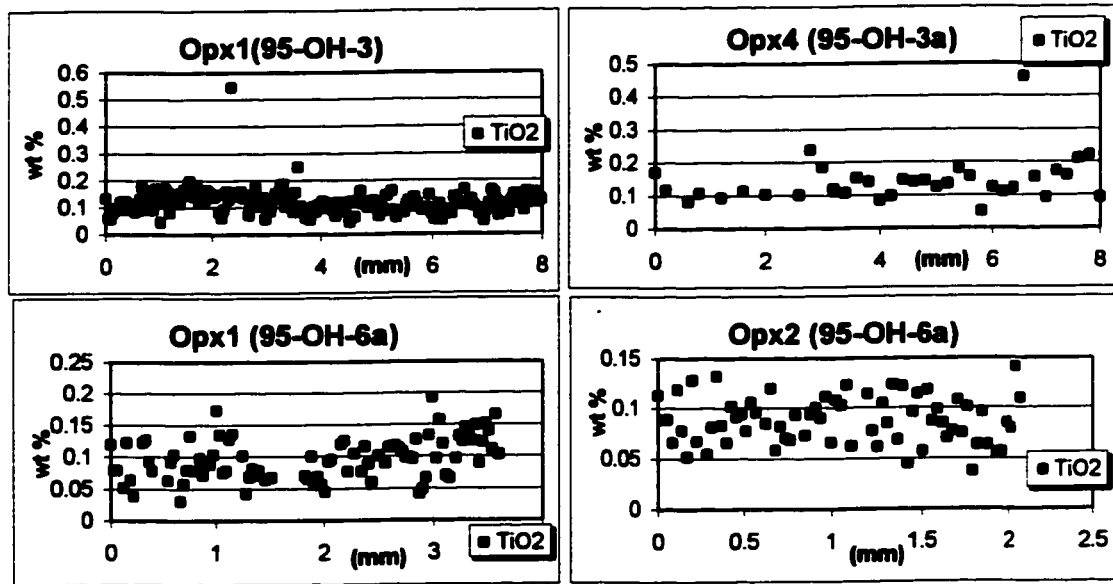


Fig. 4.3 Profiles of TiO_2 for the branching/budding orthopyroxenes shown in figure 4.1 show that TiO_2 does not decrease as FeO_T decreases thereby ruling out loss of FeO_T (and TiO_2) to increasing amounts of Fe-Ti oxides produced by increasing oxygen fugacity.

Finally, increasing f_{O_2} can not explain the reverse zoning of the plagioclase.

4.2.2 Magma Mixing

Abrupt reverse changes in crystal composition, such as that of a Na-rich core surrounded by a Ca-rich rim in plagioclase are often attributed to magma mixing (e.g. Mathews, 1957; Eichelberger, 1975; Gerlach & Grove, 1982). The introduction of a second magma into a pre-existing crystallizing magma alters crystal growth conditions. The subsequent change in magma

composition and temperature results in different chemical components being incorporated into the growing crystals, i.e. a change in composition. The reverse-zoned crystals at Fisher Lake are not abruptly zoned but are gradually zoned suggesting that the cause of the zoning is not due to a sudden event. Also, the composition of the orthopyroxenes differs from orbicule to orbicule as seen in figure 3.6 and 3.7 where Mg# increase from 68 to 74 for orbicule 95-OH-3a but in orbicule 95-OH-6a increases from Mg72 to Mg75 (fig. 3.8). Thus it is unlikely that magma mixing, during crystallization, is the direct cause of the gradual reverse chemical zoning.

4.2.3 Coupled Diffusion - Growth Mechanism

A simple, coupled, diffusion-growth model should be considered. Upon initiation of orthopyroxene growth at high temperature, more Mg is incorporated into the crystal than Fe which causes a Mg-depleted and Fe-enriched boundary layer, with respect to the bulk liquid, to form. Since Mg ions are smaller, they should diffuse faster through the melt than larger Fe ions, and, since there is a strong down-gradient towards the growth front, Mg will get to the crystal front faster than Fe. As long as the temperature is high and there is replenishment of Mg from the melt into the boundary layer, the crystal should continue to incorporate Mg over Fe. Crystal growth stops before Fe becomes so enriched in the rejected boundary layer that the crystal must switch to incorporating Fe instead of the preferred Mg. To show that Mg does diffuse faster than Fe, diffusion coefficients were calculated from Hofmann (1980) for basalt at 1300°C.

$$\log_{10} D_{1300} = -1.47 \log (Z^2 r) - 5.56 \quad (4.1)$$

where D is the diffusion coefficient, Z is ionic charge and r is ionic radius. Using ionic radii from Whittaker and Muntus (1970) for Mg and Fe⁺² with coordination number of VI for hypersthene

(table 4.1), eq.(4.1) produces $D_{\text{Mg}} = 4.98 \times 10^{-7} \text{ cm}^2/\text{s}$ and $D_{\text{Fe}} = 4.48 \times 10^{-7} \text{ cm}^2/\text{s}$. Therefore, assuming isothermal conditions, the Mg has the higher diffusion coefficient and should be able to move into the growth front faster than Fe enabling the crystal to incorporate more Mg than Fe as is seen in the reverse zoned orthopyroxene crystals.

In applying this model to plagioclase, Ca needs to diffuse faster than Na through a Na-enriched, rejected boundary layer in order to produce reverse zoning. The calculations show that the smaller Ca ion actually has a lower diffusion coefficient, almost ten times less than the larger Na, mainly because Na has an oxidation number of only +1 as compared to +2 for Ca. These diffusivities should produce increasingly Na-rich, Ca-poor crystals; the opposite of that seen.

Regardless of whether Hoffmann's equation can be strictly applied to major elements and to magmas other than basalts, the diffusion coefficients indicate that a simple coupled diffusion-growth model is insufficient for creating the gradual reverse chemical zoning seen in the orthopyroxene and the plagioclase.

element	co-ord #	ionic radius ($\text{\AA}$) ^c	diffusion rate (cm^2/s) ^d
Mg	VI ^a	0.80	4.98×10^{-7}
Fe ⁺²	VI ^a H ^e	0.86	4.48×10^{-7}
Ca	IX ^b	1.26	2.56×10^{-7}
Na	IX ^b	1.40	1.68×10^{-6}

a Cameron & Papika (1980)
b Smith & Brown (1988, p.69)
c Whittaker & Muntus (1970)

d calculated from Hofmann (1980)
e High spin form of Fe
(Denis Rancourt, pers.comm.)

Table 4.1 Data and sources used to calculate diffusion rates for the four main components that take part in the reverse zoning in the orthopyroxene and the plagioclase.

4.2.4 Plagioclase Reverse Zoning - Lofgren Model

As mentioned in section 4.1, reverse zoning has been experimentally reproduced in plagioclase by Lofgren (1973, 1974). He produced multi-zoned crystals during a stepwise decrease in crystallization temperature where the crystals had an overall, normally zoned trend (i.e. Na increases from core to outer edge) but whose individual shells had gradual reverse zoning in up to five, 25-50 micron thick, shells. He also produced single-zoned plagioclase crystals, when crystallization took place at a single temperature, with centres of constant composition that became gradually reversed-zoned near the edges of the crystals. Chemical analyses of glass adjacent to the crystal boundary showed enrichment of Na+Si and depletion of Ca+Al with respect to the parent melt.

Lofgren postulated a rapidly undercooled melt (ΔT_1 , fig. 4.4) where crystallization begins at liquid, L_1 , to produce a solid, S_1 . If the temperature is held constant then the growing crystal will move in composition towards the equilibrium solid (S) as the liquid also moves towards equilibrium (L), i.e. precipitation takes place along the phase diagram tie-line. As the liquid moves towards equilibrium, ΔT decreases (from ΔT_1 to ΔT_2), resulting in decreasing growth rates and more homogeneous precipitation at composition S. This explains the flattening out of an content that he found in the multi-zoned crystals towards the crystal edges.

Lofgren then goes on to say that the reverse zoning “is a complex function of the effective distribution coefficient, the growth rate, the amount of supercooling, the composition of the melt, and the amount of water present” (Lofgren, 1973, p.374). However he gives no further explanation or detail as to how the reverse zoning forms. He also does not explain how this mechanism could produce the single reverse-zoned crystals that start off nearly homogeneous

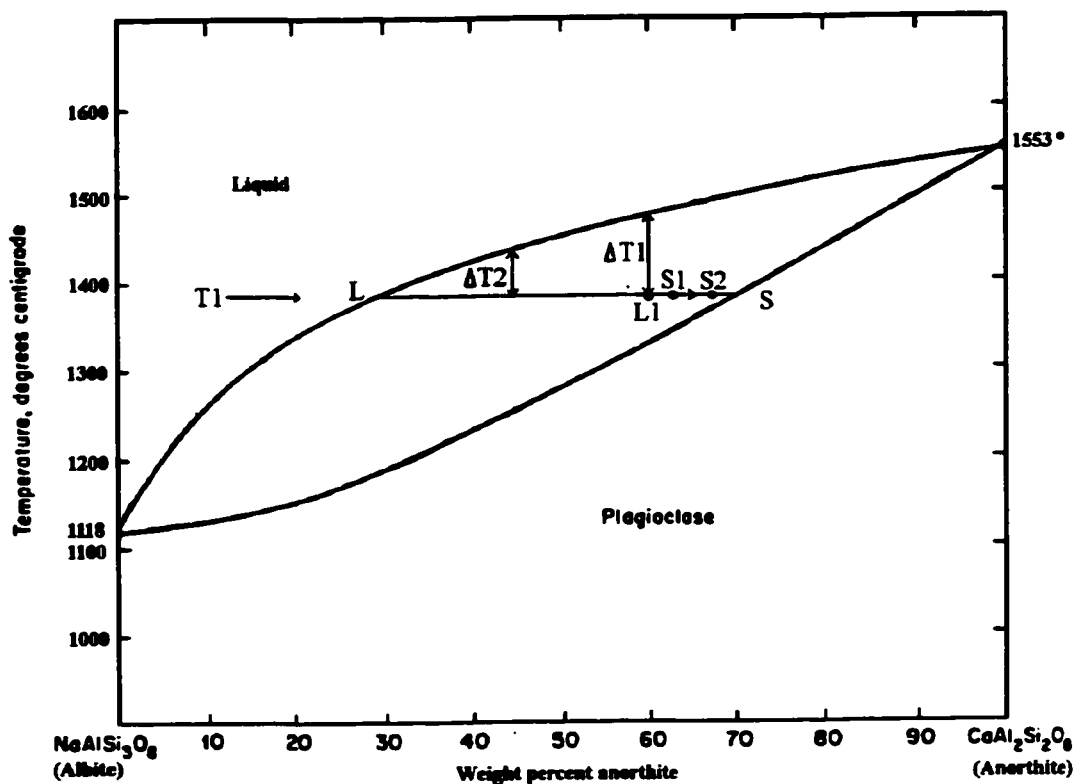


Fig. 4.4 Under relatively large undercoolings (ΔT_1) and isothermal (T_1) conditions, crystallization could take place along a tie line from S_1 to S_2 thereby increasing the Ca uptake over Na as compared to near-to-equilibrium crystallization. As crystallization proceeds, the amount of undercooling decreases (e.g. ΔT_2) as the liquid composition gradually moves towards L on the liquidus and the corresponding solid S crystallizes (after Lofgren, 1973).

in composition and then become reverse-zoned towards the crystal edge. Also the reverse zones that he produced were on the order of 25-50 microns and he does not speculate on the application of this mechanism to larger crystals. The branching orthopyroxene crystals in the Fisher Lake orbicules are nearly 1 cm long and the gradual reverse zoning takes place over the entire length of the crystal not just at the outer edge.

4.3 Proposed Theory for Gradual Reverse Zoning in Minerals

Any theory that will explain the formation of the crystals in the orbicules and the comb layering found in this study must be based on far-from-equilibrium (FFE) melt conditions. The presumption of FFE conditions is based on the branching/budding morphology of the orthopyroxene, the feather-shaped morphology of the plagioclase, the gradually, reverse chemically zoned orthopyroxene and plagioclase, the radial crystal growth about a core in the orbicules and the unidirectional growth along planar interfaces in the comb layering. This type of FFE growth is in contrast to near-to-equilibrium (NTE) growth where crystals typically are unzoned, have equant, euhedral habits, and occur as part of a random, homogeneous mosaic of crystals.

Initial conditions are assumed to be high temperature and isothermal for a supersaturated magma. The basis of these assumptions will be discussed in chapter 5. The anhydrous En-Fs equilibrium phase diagram will be used to demonstrate the formation of reverse zoning in the orthopyroxene. The use of the phase diagram assumes that it holds the same basic shape for the system in FFE conditions as it does in near equilibrium conditions. There is evidence, but alas no data, to suggest how the stability fields of a given phase alter at FFE.

The proposed model presumes a small but rapid initial undercooling of the magma which either causes, or increases, supersaturation. The resulting temperature places the magma in a thermal regime where nucleation is low and crystal growth is high (fig. 4.5). A paucity of nuclei, coupled with a low nucleation rate means that initial precipitation mainly takes place on xenolithic bits of a partly crystallized neighbouring magma (incorporated during emplacement). This first

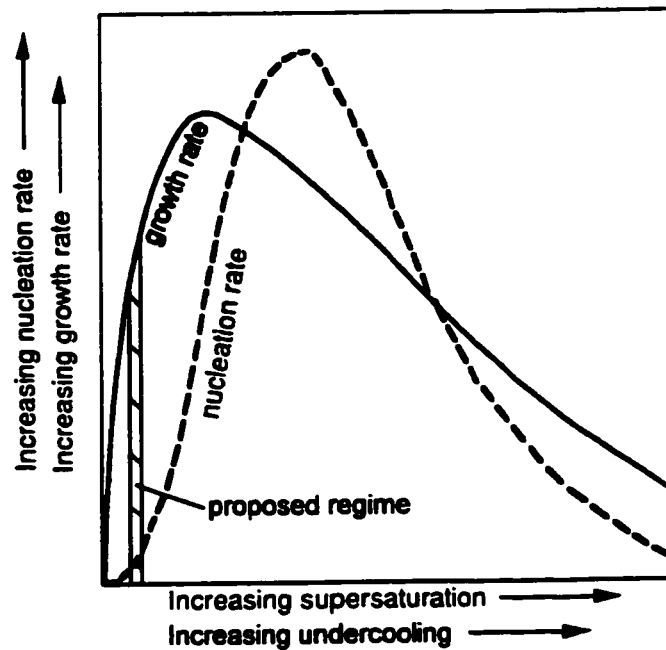


Fig. 4.5 Schematic diagram showing a proposed thermal regime where nucleation rate is low and crystal growth rate is high as a result of a small amount of undercooling in the magma (modified from Naslund & McBirney, 1996)

growth, “a”, which takes place under supersaturation, has a chemical composition close to the liquid, “x”, but not in equilibrium with the chemistry of the bulk magma (fig. 4.6a). This results in similar conditions to that shown in figure 4.4.

The microprobe data show that the first precipitate, “a”, is a solid of composition Mg68 (fig. 4.6a). The first liquid, “x”, around the crystal has now been altered to a boundary layer of components rejected by the first precipitate and is thus Mg-depleted/Fe-enriched with respect to a bulk magma, “m”, which was chosen as a composition between the known first precipitate and its probable first liquid (fig 4.6a). Since crystal growth is at a tip rather than a planar face (in the branching crystals) and that growth is fast compared to the diffusion of the required components through the melt, two things happen. First, there is not enough time for diffusion to completely level out the concentration gradients between the depleted liquid and the bulk liquid and, second, the growing tip pushes some of the remaining depleted boundary layer to the side, out of the way (fig 4.7b). Because of the pushing outwards by the tip, the rejected boundary layer thins at the tip and thickens at the sides of the growing crystal. Thus the crystal grows over the remaining depleted liquid boundary layer, or up the concentration gradient, towards the bulk liquid (fig 4.7c). The driving force for this reverse zoning is the need to relieve the supersaturation of the magma and drive the precipitation back to a chemical composition nearer to the equilibrium composition. This results in a gradually reverse-zoned crystal that begins growth at Mg68 and ends at Mg74 (point “b”, fig 4.6a) which reflects the decrease in supersaturation but which is also normally zoned across the crystal from Mg70 at the centre decreasing to Mg68 at the edge. The normal zoning reflects growth in melt along the sides of the crystals that has been relieved of the supersaturation under nearer-to-equilibrium conditions.

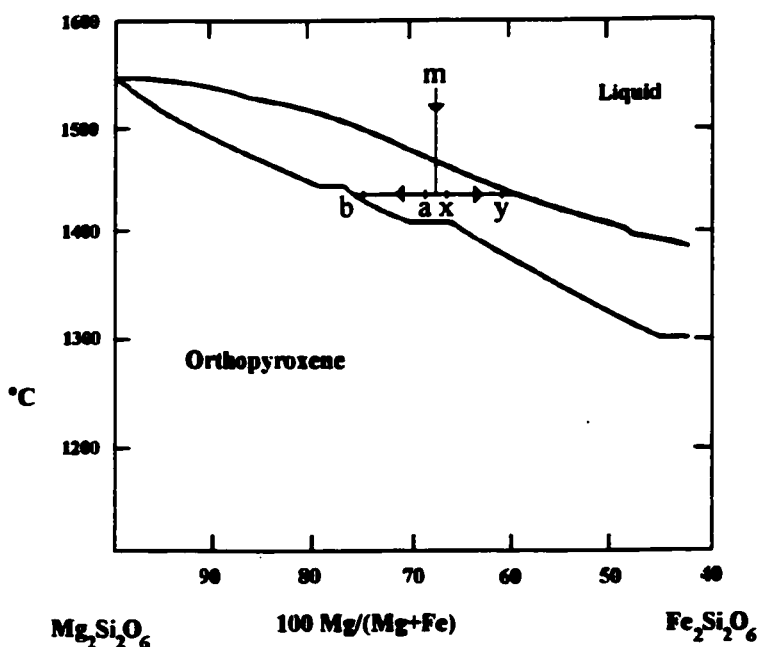


Fig. 4.6a Phase diagram of orthopyroxene. Postulated melt of composition "m" is undercooled such that a solid of composition "a" (Mg68) precipitates first with a corresponding melt composition of "x". As the melt moves to the liquidus composition "y", the solid composition gradually moves to "b" (Mg74), i.e. reverse chemical zoning, under constant T.

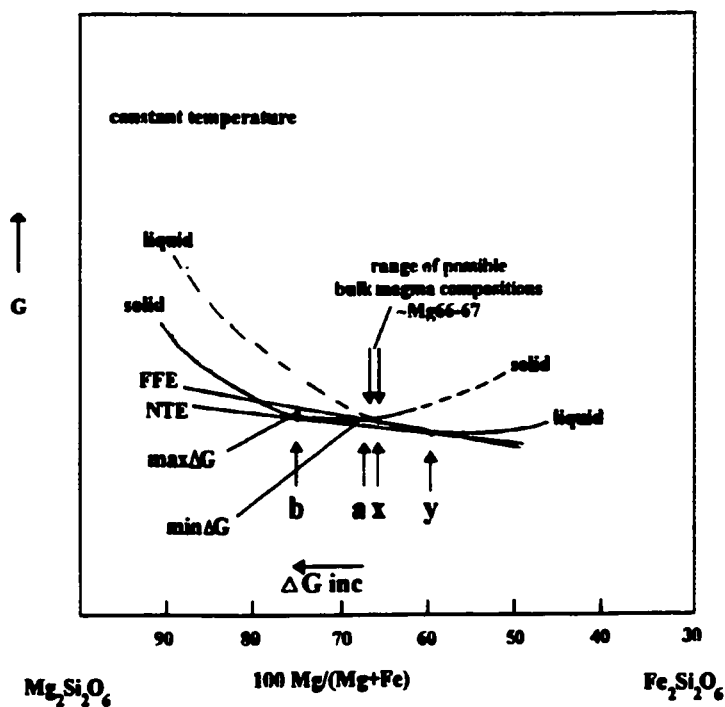


Fig. 4.6b Postulated Gibbs free energy diagram at constant temperature showing the same solid "a" as in fig. 4.6a at minimum ΔG with respect to the FFE (far-from-equilibrium) tangent. Precipitation moves towards maximum ΔG compositions on the NNE (near-to-equilibrium) tangent as supersaturation is relieved.

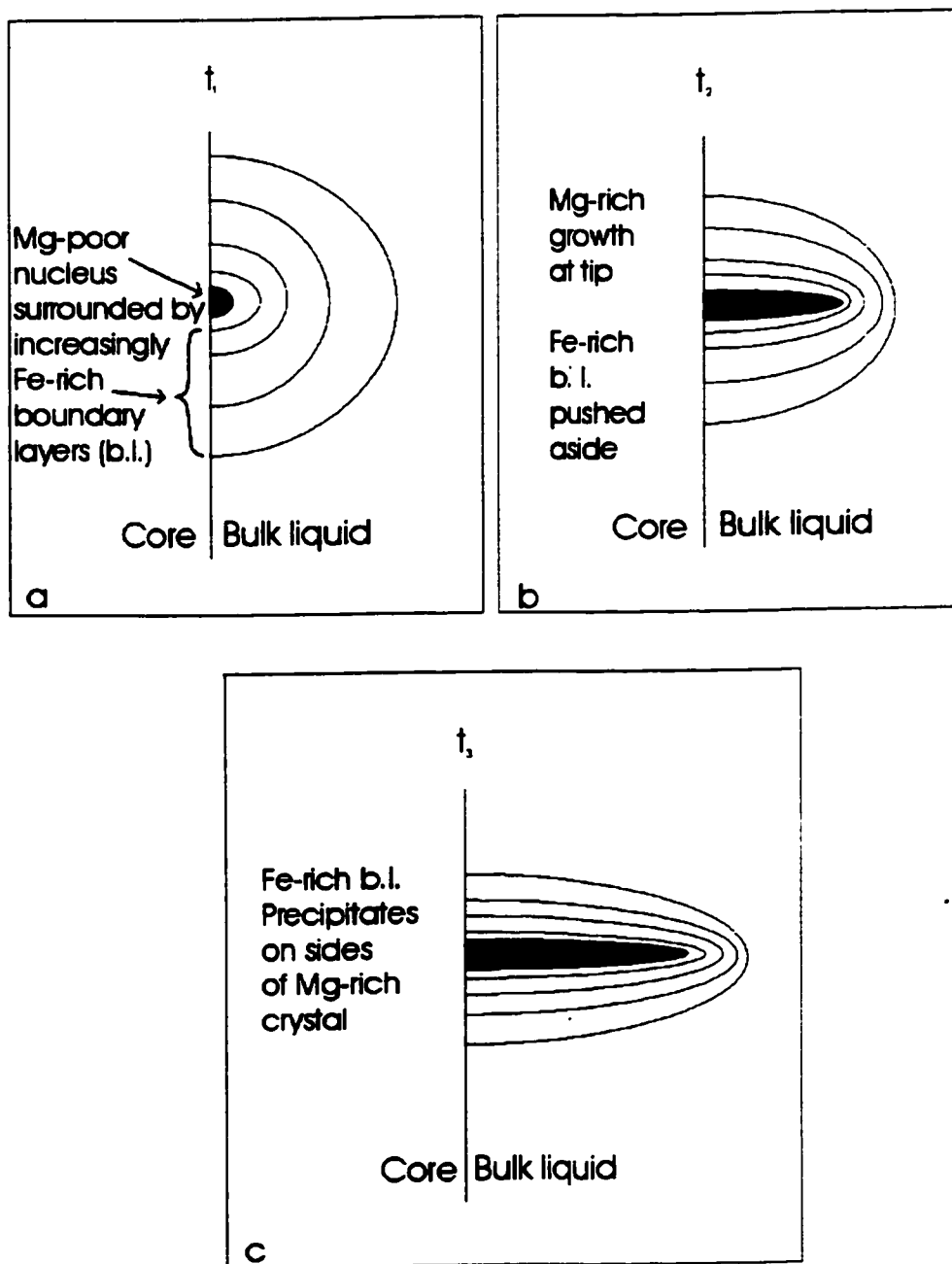


Fig. 4.7 Schematic diagram showing growth of an initially Mg-poor orthopyroxene nucleus situated on the orbicule core surrounded by a Fe-rich boundary layer (b.l.). Through time (t_1 to t_3) and isothermal conditions, the crystal tip grows through the b.l. into the Mg-rich, bulk magma, pushing the Fe-rich b.l. to the side of the crystal where it later precipitates creating normal zoning across the crystal.

Thus we have a magma that would normally crystallize the equilibrium solid and liquid but, due to the rapid undercooling and the resulting supersaturation, is forced to precipitate a solid that is closer to the liquid composition than to the equilibrium solid. Supersaturation overrides the tendency for a magma to precipitate the solid with the maximum ΔG value (i.e. near- to-equilibrium) causing precipitation of a solid with a minimum ΔG (far-from-equilibrium). As supersaturation is relieved, the magma precipitates solids with gradually larger ΔG 's until reaching equilibrium. Thus, under isothermal conditions, supersaturation controls the precipitate composition.

This can be shown on the Gibbs free energy-composition diagram. Even though absolute values of G are not known, the shapes of the liquid and solid G - X curves can be inferred from the thermodynamics of the system. Anderson (1996) details the procedure for drawing G - X curves for binary systems. In drawing the Gibbs free energy curves, the following rules apply: (1) $G_{Ab_{solid}} > G_{An_{solid}}$ and $G_{Fs_{solid}} > G_{En_{solid}}$, (2) G - X curves are asymptotic at the pure end members, (3) the lowest G - X curve is the stable phase, and (4) the equilibrium solution at a given temperature is found by drawing the tangent to the two curves. Based on the liquid and solid curves for the solid solution En-Fs, having the topology at T_1 as shown in figure 4.6b, then the tangent (line "NTE") to the curves shows the equilibrium assemblage of the initial solid composition Mg74 (point "b", fig 4.6b) and liquid composition Mg60 (point "y"). The intersection of the curves separates the stable phases (solid lines) from the metastable (dashed lines) and is located at Mg67 ("m", fig 4.6a). We can draw a line "FFE" through the initial fluid (x) and initial solid (a) such that the equilibrium final solid (b) has the maximum ΔG between the two tangents and the initial solid has the minimum ΔG . Any composition on the solid curve under tangent FFE could

precipitate with the bulk liquid composition “m” (Dowty, 1980; Hopper & Uhlmann, 1973). The crosshatched area between the two tangent lines, the solid G curve, composition “a”, and composition “b” show that ΔG increases gradually from composition “a” to “b” demonstrating how the system moves from far-from-equilibrium to near-to-equilibrium through relief of supersaturation.

The growth of gradual reverse-zoned plagioclase follows essentially the same path except that the plagioclase is growing in magma that is found between the branching orthopyroxene, i.e. in magma that is depleted in the high temperature orthopyroxene component, MgO. This pocket of altered fluid would have different kinetics than the undepleted bulk magma, e.g. lower T_L for plagioclase, and thus the amount of magmatic undercooling would be less than that in which the orthopyroxene grew. Smaller undercooling means less supersaturation which would decrease the reverse-zoned gradient, i.e. plagioclase crystals would grow more nearly homogenous in composition than the orthopyroxene, until the crystal grows into some undepleted bulk magma whereupon it will become reverse zoned and approach equilibrium with the bulk magma.

The phase diagram and the G-X diagram can again be used to demonstrate how reverse zoned plagioclase can form using the An-Ab, 1 atm, equilibrium phase diagram from Bowen (1913) and again assuming that the far-from-equilibrium phase diagram is similar to the near-to-equilibrium diagram. The microprobe data show that after the initial undercooling a solid of An_{87} precipitates (point “c”, fig. 4.8a) in far-from-equilibrium conditions. There is a corresponding initial fluid composition (point “v”) found on the isothermal tie line on the other side of the bulk fluid composition (point “n”, fig. 4.8a). Since the amount of supersaturation has decreased (due to the lower T_L), the difference between the minimum ΔG and the maximum is smaller and the

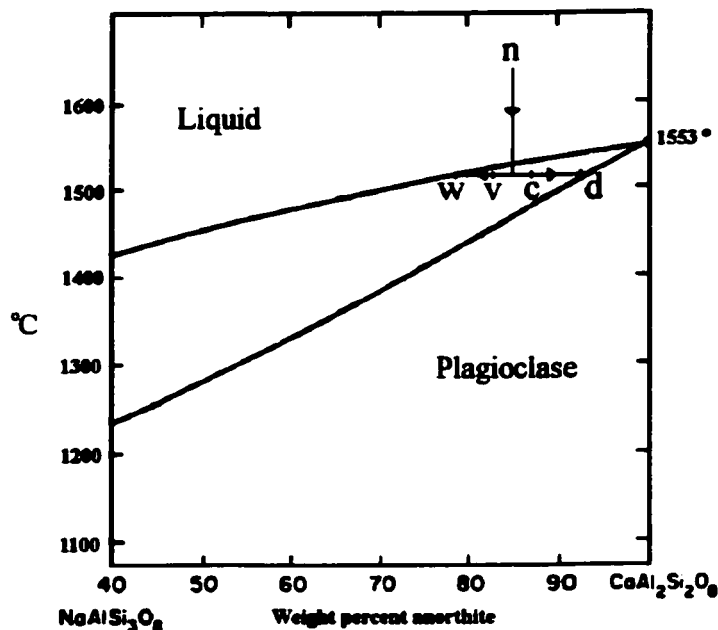


Fig. 4.8a An expanded portion of the phase diagram for plagioclase. As seen in fig. 4.6a, a melt of composition "n" is undercooled such that a solid of composition "c" (An87) precipitates first with a corresponding liquid composition of "v". As the melt moves towards the liquidus composition "w", the solid composition gradually moves towards the solidus "d" (An93) producing chemically, reversed zoned, Ca-rich plagioclase, under constant T.

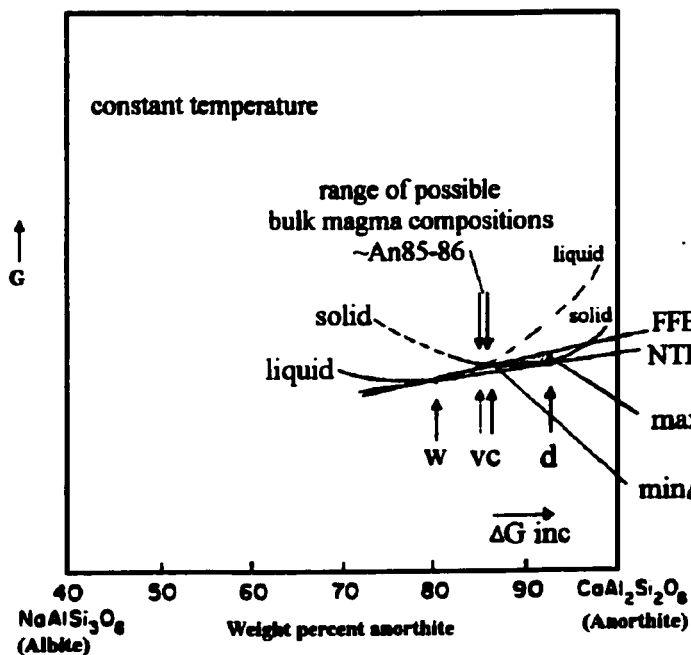


Fig. 4.8b Postulated Gibbs free energy diagram at constant temperature showing the same solid "c" as in fig. 4.8a at minimum ΔG with respect to the FFE (far-from-equilibrium) tangent. Precipitation moves towards maximum ΔG compositions on the NTE (near-to-equilibrium) tangent as supersaturation is relieved. Dashed liquid and solid curves are metastable phases.

system takes a longer time to respond to this driving force because it is much smaller. The composition of the lengthening crystal stays nearly constant while growing, in the shadow of the orthopyroxene, in altered melt. The depletion of SiO_2 in the altered melt due to orthopyroxene crystallization ensures that the precipitating plagioclase is a Ca-rich plagioclase since anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) requires less SiO_2 to grow than albite ($\text{NaAlSi}_3\text{O}_8$). As the plagioclase increases in length, it approaches the undepleted bulk magma and then grows with the reverse-zoned composition nearer to the end of its growth ending at An_{93} (point “d”), a nearer-to-equilibrium value than the initial growth (An_{47}).

As was just done for the G-X diagram for the orthopyroxene, the same can be done for the plagioclase. Assuming that the liquid and solid curves for An-Ab at T_1 have the topology as shown in fig. 4.8b, then the tangent, NTE, to the curves shows the equilibrium assemblage of the final solid composition An_{93} (point “d”, fig. 4.8b) and liquid composition An_{40} (point “w”). We can draw a tangent FFE through the initial fluid (“v”) and initial solid (“c”) such that the equilibrium solid (“d”) has the maximum ΔG and the initial solid has the minimum ΔG . Any composition on the solid curve under the tangent FFE could precipitate from the bulk liquid composition “n” (Dowty, 1980; Hopper & Uhlmann, 1973). The crosshatched area between the two tangents and the solid G curve show that ΔG increases gradually from composition “c” to “d” demonstrating how the system moves from far-from-equilibrium to near-to-equilibrium through relief of supersaturation.

4.4 Conclusion

A magma at far-from-equilibrium can move to near-to-equilibrium growth conditions by relieving supersaturation of the magma through the precipitation of maximum ΔG products. However, when the temperature of the system is held constant, the supersaturation is not relieved by precipitation of maximum ΔG , near-to-equilibrium, compositions but by precipitation of minimum ΔG , far-from-equilibrium, compositions which are close in composition to the liquid. As supersaturation is relieved, magmatic conditions become nearer-to-equilibrium and higher ΔG compositions are precipitated.

5. Orbicule and Comb Layering Formation Theory

Orbicular and comb layering occurrences are rare world-wide but they are found in almost all magma compositions (Leveson, 1966) suggesting that environment may be more important than composition in considering a mechanism to form the comb texture.

5.1 Orbicules: Formation Theories

The formation of orbicules has been speculated on since the late 1800's (Hatch, 1888) and numerous theories have been devised. Many of these theories (listed in chapter 1.3) can be categorized by an essential component as outlined below.

5.1.1 Water

Formation mechanisms based on water as an essential ingredient in the magma have been very popular due to the frequent presence of hydrous minerals within the orbicules. Water has been incorporated in many ways such as; buoyant bubbles (van Diver, 1970) or water vapour rich pockets of magma (Iddings, 1888) produced by H_2O flash inputs (Owen, 1991); rhythmic metasomatic crystallization (Leveson, 1963, 1966, 1973; van Diver, 1968) from reaction with fluids trapped in a crystallizing granitic magma (Sinclair & Richardson, 1992; Samson & Sinclair, 1992; Thompson & Gilles, 1974); streams of a water-rich fluid (Moore & Lockwood, 1973; Rodda, 1976; Walawender, 1976); oscillatory secondary hydrous mineralization formed when the orbicules are occasionally carried up into water-rich magma (Maggetti *et al.*, 1978); and finally fluctuating, p_{H_2O} caused by oscillating release and containment of volatiles (van Diver &

Maggetti, 1975) that resulted in changes in mineral stability fields between mainly mafic versus mainly felsic minerals (Yoder, 1954; Emerson, 1962; Enz *et al.*, 1979; Symes *et al.*, 1987).

Most of these mechanisms lack an experimental or theoretical basis and some contradict observations, e.g. the lack of experimentally reproduced macroscopic immiscible water globules, or, the lack of evidence for highly convecting water-rich fluids at the outcrops. Some theories rely on water fluctuations on a magma chamber scale which can happen (e.g. eruptions) but this neither explains how nearly a thousand layers could be precipitated as seen in the 10 m section at Fisher Lake, i.e. one eruption/fluctuation per layer would require a thousand eruptions, nor why only such a small portion of the magma crystallizes into orbicules or comb layering.

5.1.2 Reaction Rims

The theory that the orbicular shells are a result of chemical reactions between a xenolith, either liquid or solid, and the surrounding magma has been suggested by many, e.g., Leveson (1963, 1966), Moore (1984), Bryhni and Dons (1975), and Barrière (1972). While the first shell precipitated around a core may indeed be a reaction rim around a xenolith, it is hard to imagine how the many subsequent shells (up to 40 as seen in one orbicule from Fisher Lake) could develop when the shell package covers a volume several times larger than the xenolithic cores and the chemistry of the minerals does not change from the first shell (the “most contaminated” by the core) to the last (the “least contaminated” by the core). McKinney (1985) measured orbicular shell thicknesses versus xenolithic core sizes to show that there was no relation between the total shell thickness and the core size. He also showed that the overall composition of minerals in the inner shells and outer shells were the same and was substantiated by the work done for this thesis.

5.1.3 Viscosity

High viscosity in a magma has been suggested by Sederholm (1928) as causing low diffusion rates that would, in turn, allow magma crystallizing around the orbicules to become enriched in components of minerals that would then precipitate. Hildebrand (1950) also proposed a high viscosity magma to explain flow lines in the matrix and orbicules that are elongated in the direction of flow. Low viscosity is advocated by Moore and Lockwood (1973) in order to create the elongated, delicate, curved, branching crystals found in the comb layering next to the orbicules.

Viscosity is a rheological property of a magma that is mainly dependent on chemical composition, percent crystallinity and temperature. Since orbicules are found in all magma compositions, viscosity would vary accordingly. Orbicules must form when the overall crystallinity in the magma is low and there is room for the large crystals found in the orbicules to grow outward from the core into the host magma without interference. Generally, viscosity of the bulk magma is not considered an over-riding control of crystallization.

5.1.4 Superheating and Supercooling

Some recent studies have shown consensus on at least two steps in orbicule formation; that the magma was superheated, thereby destroying nuclei, and then supercooled in order to limit crystal nucleation and growth to the cores (Barrière, 1972; McKinney, 1985; Symes *et al*, 1987; Yazgan and Mason, 1988; Owen, 1991; Ort, 1992; Shackleton, 1994). Supercooling, the term used in much of the literature, implies that large amounts of undercooling are needed to produce the large, branching or budding crystals in the orbicules and the comb layering, but this is

inconsistent with that required to produce the coarse grained subhedral crystals of the matrix. The theory suggested by this dissertation will also include these two steps but will show that the amount of superheating and supercooling are minimal.

5.2 Historical Orbicule and Comb Layering Combination Formation Theories

Comb layering is a relatively new phenomenon in the geology literature, recognized (Poldervaart & Taubeneck, 1959) and named (Moore & Lockwood, 1973) only in the last forty years. The combination of orbicules and comb layering together appears to be a very rare one with less than a dozen locales found in the literature (table 5.1). Most authors agree that the

Dehesa, CA	Lawson, 1904
Pine Valley, CA	Merriam, 1958
Willow Lake, OR (gabbro - Bald Mountain Batholith)	Taubeneck & Poldervaart 1960
Eagle Lake, CA	Loomis, 1963
Fisher Lake, CA (diorite - Sierra Nevada Batholith)	Moore & Lockwood, 1973
Pyrénées, France (gabbro-Néouvielle granodiorite massif)	Barrière, 1972
Vestby, Norway (lamprophyre dike)	Bryhni & Dons, 1975
Reichenbach, Germany (synorogenic gabbro)	van Diver & Maggetti, 1975
Deshai, Pakistan (diorite - Transhimalayan plutonic belt)	Symes, Bevan & Jan, 1987
Sandia Mtns, New Mexico (Sandia granite)	Enz <i>et al.</i> , 1979

Table 5.1 List of localities and sources where both orbicules and comb layering are found.

orbicules form the same way as the comb layering with the comb texture forming on xenoliths to make orbicules and on lateral surfaces in comb layering (e.g. van Diver & Maggetti, 1975; Moore & Lockwood, 1973; McKinney, 1985).

The several localities found in California (table 5.1) have led to three distinct theories as to the formation of comb layering.

5.2.1 Aqueous Fluid Streaming

The theory from Moore and Lockwood (1973) describes a supercritical, aqueous fluid that has high velocity, low density, low viscosity, is free of suspended crystals, and supersaturated in Ca plagioclase, hornblende and clinopyroxene. This fluid originates from various parts of the pluton and streams up the contact between magma and wall rock along furrows, precipitating curved, branching, unbroken crystals while transporting broken chunks of comb layering. The alternating mineralogy is due to changes in the chemistry of the aqueous fluid.

There are several unanswered questions regarding this theory. Moore and Lockwood do not explain how a fluid torrent powerful enough to break off chunks of comb layering, and then transport those chunks away from the location of origin could simultaneously be gentle enough in its motion to allow the formation of the delicate, branching, unbroken crystals of the comb texture itself (both in the comb layering and the orbicules). Another problem is the large amount of aqueous fluid required to make comb layering packages up to 10 m thick at Fisher Lake and 19 m thick at Los Pinos California; a locale described by Walawender (1976) who supports the Moore and Lockwood theory. There is no evidence of large amounts of hydrothermal alteration in the surrounding rocks. A third, and very critical, problem is the very low solubility of silicates

in aqueous fluids. An unrealistic amount of fluid would be needed in order to deposit such thick comb layering sequences of silicate minerals. No intense alteration halo was found in the area to attest to the passage of this large an amount of fluid. Also, typical pegmatite-type minerals, such as tourmaline, are not found.

5.2.2 Supersaturated, Vigorously Stirred Magma

The original theory for the formation of comb layering was suggested by Poldervaart and Taubeneck (1959) and Taubeneck and Poldervaart (1960) who postulated that comb layers form from undercooling and crystallization in an oversaturated magma that was subjected to vigorous disturbances that brought fresh magma into the oversaturated region. Undercooling along the walls resulted in rapid crystallization and elongated crystals that grew perpendicular to the cooler wall (kept cool by water streaming through the surrounding rock). Influxes of fresh magma produced plagioclase and pyroxene while older magma, with its higher water content (after anhydrous crystallization), crystallized plagioclase and amphibole. This repeated change between crystallization of one mafic mineral to another meant that the chemical composition of the parent magma must have been near the eutectic on the pyroxene-amphibole temperature-phase diagram.

The idea that crystals grow near walls due to undercooling of an oversaturated magma is good, however, the unanswered question in this theory is the number of fresh influxes of magma needed to produce the alternating layers of pyroxene and amphibole. The comb layers themselves are usually on the order of only 1 cm and thus a huge number of influxes would be required to produce the more than 10 m thick sequences of comb layers seen at Fisher Lake. Also, influxes of vigorously stirred magma flowing past the delicate elongated branching crystals

in the layering would surely break these crystals as well as jostling the orbicules together and breaking those elongated crystals along with spreading the orbicules throughout the magma chamber.

This theory has the same problem as that of the previous theory of aqueous fluid streaming; the large amount of water that is postulated to be flowing through the surrounding rock, that in this case, keeps the wall cold enough to undercool the adjacent magma. There is no evidence of hydrothermal alteration in the country rock. These authors also did not consider how the orbicules could have formed.

5.2.3 Supercooled, Mobile Interface

McKinney (1985) postulated superheating of the host magma, to destroy nuclei, followed by injection of that magma into a high temperature, partially crystallized, magma mush. Supercooling of the host magma occurred along this slightly cool boundary (the mush being only slightly cooler than the newly injected magma) where, like a chill margin, rapid crystal growth took place on the boundary and on xenoliths within this supercooled, magmatic, boundary layer.

McKinney used the curving (fig 1.21), and sometimes splayed (fig 1.13) comb layering as evidence that the comb layers were gently moved as if on a mobile interface showing that cold, rigid, country rock could not be at the boundary. If the host diorite had injected into another magma, then there would be evidence of extensive mixing which is not seen. Therefore the host diorite must have injected into a partly crystallized, partly molten magma or mush.

The essentials of McKinney's thesis are the basis for the theory that will be proposed in this dissertation as outlined in the next section.

5.3 Proposed Theory

This section proposes a mechanism consistent with the chemical data and the field observations along with some components of the theory formulated by McKinney (1985).

The Fisher Lake orbicules and comb layering are located in a zoned, composite granodiorite-diorite-gabbro pluton having no metamorphic aureoles between zones implying that subsequent magmas intruded into very warm surroundings.

Field evidence shows that there was limited magma mixing near the margins and that inclusions have no, or very small, reaction rims (figs. 1.22 and 1.23). It is proposed that the orbicule/comb layering host magma (hereafter referred to as the host magma) was injected into a very warm, pre-existing crystal mush (as also proposed by McKinney, 1985).

The boundary between the host magma and the crystal mush would have only a small difference in temperature producing only a small undercooling in the host magma adjacent to the slightly cooler crystal mush. A small undercooling coincides with a regime of low nucleation rates and high crystal growth rates (fig. 5.1). The resulting supersaturation (from the undercooling) in this nuclei-poor portion (from the low nucleation rate) of the host magma allowed heterogeneous nucleation (i.e. growth) on xenoliths and at the interface with the adjacent crystal mush. These limited number of heterogeneous nuclei would have been subjected to a high crystal growth rate. Orthopyroxene and plagioclase were the two minerals that grew first in the orbicules and, under these conditions of high growth and low nucleation, they formed elongated branching/budding orthopyroxene crystals and feather plagioclase.

Orthopyroxene and plagioclase are both anhydrous minerals that, as they grew, rejected components such as H_2O and Fe_2O_3 into a surrounding boundary layer. The concentration of

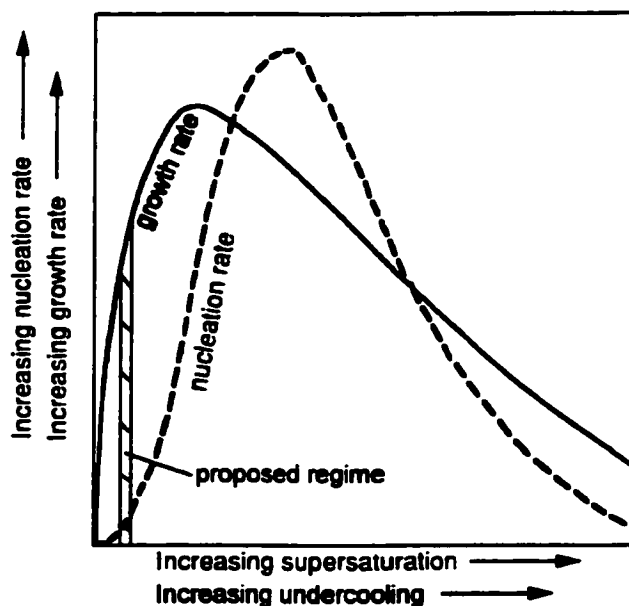


Fig. 5.1 Schematic diagram showing the relationship between increasing nucleation and crystal growth rates to increasing supersaturation or undercooling. At both very small and very large amounts of undercooling, nucleation rate is very low but only at small undercooling is there a very high growth rate. The proposed regime for comb texture formation is outlined by the hatched area. (modified from Naslund & McBirney, 1996).

these components increased in this boundary magma until precipitation of Fe-Ti oxides, amphibole and biotite occurred. Depletion of the rejected components by growth of these Fe³⁺ rich and hydrous minerals allowed new growth of elongated orthopyroxene and plagioclase. Comb texture growth ended when undercooling decreased as the warmth of the host magma warmed up the crystal mush close to the interface. This would cause a decrease in the crystal growth rate along with decreased nucleation rates in the magma, creating conditions that are more typical of plutonic crystallization, i.e. slow nucleation and growth that result in coarse grained plutonic textures, a regime that would be located to the left of the hatched area on figure 5.1.

5.4 Nucleation and Crystal Growth in a Radial Shell

Crystal growth in the host magma begins with only a few elongated, large crystals

developing on xenolithic cores or near the magma/mush boundary. This suggests that there were either few nuclei for growth to take place on or that the growth conditions were such that growth in one direction was highly favoured. If it were just the latter then large crystals would be able to grow anywhere in the magma as opposed to being restricted to a pre-existing growth horizon. If it were just the former then we would not expect to see so many shells/layers within the comb texture that consist of only small anhedral crystals. It is likely that a combination of the two is at work. Homogeneous nucleation is restricted by the initial undercooling thus making crystal growth easiest on preexisting surfaces where crystals that are oriented with the fastest growing faces in the correct direction grow preferentially into the least depleted magma, i.e. growth is away from other growing crystals and away from the substrate (fig. 5.2).

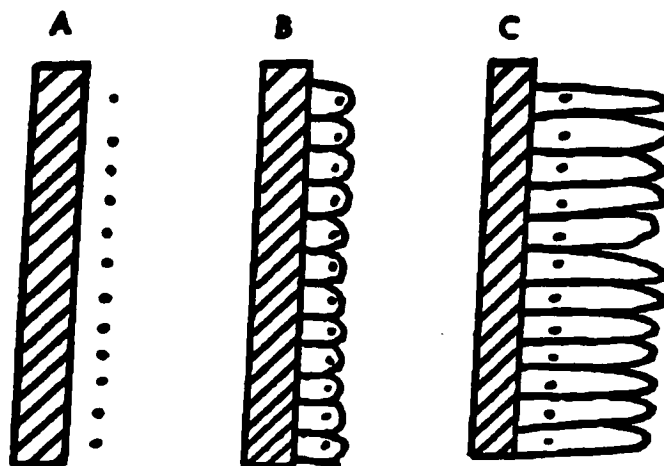


Fig.5.2 Schematic showing that nuclei near, or on, a boundary will grow into crystals that are oriented perpendicular to the boundary. Crystals of all orientations may nucleate at a boundary but those that are oriented towards undepleted magma will be able to grow fastest since they can obtain the correct components easiest, i.e. those crystals that are oriented perpendicular to the boundary will grow fastest and largest while at the same time blocking the growth of the other crystals ensuring that otherwise oriented crystals stay very small (modified from Schragar, 1961).

There are other ways to limit nucleation besides having a small ΔT ; superheating causing dissolution of nuclei, and/or, delayed nucleation. Lofgren (1974) showed in experiments that plagioclase grew easier on pre-existing crystals (heterogeneous nucleation) rather than nucleating new ones.

While superheating has been invoked by many authors, there is no obvious evidence of superheating, e.g. corroded crystals. McKinney (1985) used the chemical similarity of the comb layered host diorite to high aluminum basalts, and their similarity to andesites as evidence of superheating. Andesites have been shown by Marsh (1978) to be superheated as they rise through the conduit to the surface. The Aleutian andesites are generated at a depth of 100-150 km and, as they rise, may generate 60°C/100km of reversible cooling due to adiabatic expansion (Marsh, 1978). Whereas the depth of origin of the Fisher Lake magmas is unknown, the roots of the Sierra Nevada Batholith only extend downwards to a depth of about 50 km (Carmichael, Turner & Verhoogen, p.578, 1974). Since the Fisher Lake magma is plutonic and probably rose to a height of about 10 km below the surface (McKinney, 1985; Cowan & Bruhn, 1992), comparison to a volcanic lava is less than ideal.

The growth of branching/budding orthopyroxene is very closely, if near simultaneously, followed by the growth of feather plagioclase between the orthopyroxene crystals. Lofgren (1974) has shown that two simultaneously growing minerals can have differing morphologies. One of his experimental runs (#3) on natural oceanic ridge basalt produced simultaneous growth of elongated pyroxene with tabular plagioclase at undercoolings of less than 30°C.

Ending the growth of the elongated branching/budding orthopyroxenes and the elongated, feather plagioclase of the innermost shell of an orbicule is most likely caused by the high crystal

growth rates. As seen in chapter 4, crystallization at constant T causes the liquid composition to move down the T_L curve resulting in decreased ΔT and decreased crystal growth rates. Also, high growth rates would cause large amounts of lower temperature rejected components such as H_2O and Fe^{+3} to accumulate in the surrounding boundary layer. This results in a lowering of the T_L and a decreased ΔT which slows crystal growth.

It has been shown that the host magma has undergone a small amount of undercooling of some ΔT . It has also been shown that the reverse zoning in the elongated crystals indicates crystallization took place at constant temperature. The lateral spread of the branches in the branching orthopyroxene (fig 1.24) suggests that crystal growth was becoming more difficult, i.e. the necessary components for growth were becoming scarce in the same fashion as diffusion-limited aggregation (e.g. Fowler & Roach, 1996). The initial fast growth of the orthopyroxene and plagioclase that constitute the innermost shell of the orbicule would result in an increase of rejected components such as H_2O , Fe_2O_3 , Al_2O_3 and CaO ahead of the growing crystal front (see appendix C for mass balance calculations). Increasing amounts of rejected components in the crystal boundary layer cause a decreased T_L in the altered magma resulting in a decreased ΔT and eventually, saturation of the rejected components. This causes crystal growth to slow down and/or increased nucleation rate of other minerals such as magnetite, ilmenite, amphibole and biotite that nucleate and grow on the ends of the elongated crystals (Gibb, 1974) using up the rejected components from the plagioclase and the orthopyroxene. This change in mineralogy (and habit) defines the end of one shell and the beginning of the next. These new minerals consume the rejected components clearing the way for renewed growth of elongated orthopyroxene and plagioclase.

These two different types of shells of mainly elongated orthopyroxene and plagioclase and that of anhedral Fe-Ti oxides and hydrous minerals can combine to create four different boundaries as described in the next section.

5.5 Shell Formation - Morphological Interfaces

Crystal habit in the Fisher Lake orbicules is of essentially two types; anhedral or elongated/radial, leading to four possible morphological interfaces; radial to anhedral, radial to radial, anhedral to radial, and anhedral to anhedral. Morphological interfaces are not to be confused with changes in mineralogy since some morphological interfaces represent changes in mineralogy and some do not.

5.5.1 Type I (Radial to Anhedral) and Type II (Anhedral to Radial)

The branching orthopyroxene crystal seen in figure 1.24 spreads out very near to the edge of the shell, becoming almost as wide as it is long with nearly sixteen small branches very close to the outer shell edge. This widening into many more small branches just before the next shell consisting of large numbers of small anhedral crystals suggests that the crystal was growing either by diffusion limited aggregation (DLA) or into a barrier, i.e. something interfering with the diffusion of growth-required components. Since the shells grow sequentially away from the central core, there should only be fresh magma in front of the growing, branching crystal. DLA experiments generally take place at high undercoolings and have not been shown to be a factor in crystal growth at low undercooling.

Thus the widening of the crystal is likely the result of growth into a barrier caused by a

boundary layer enriched in rejected components. As described above, the fast growth of orthopyroxene would deplete the boundary melt layer in Mg and Fe^{+2} and components such as OH^- and Fe^{+3} would be pushed ahead of the ever widening, growing pyroxene. Eventually, Mg and Fe^{+2} from the undepleted melt can not diffuse between the rejected components resulting in cessation of the growth of the branching orthopyroxene while anhedral Fe-Ti oxides, amphiboles and biotite precipitate. Anhedral shells with these minerals (Fe-Ti oxides, amphibole and biotite) are usually very thin quickly changing back to elongate/radial habits suggesting that the actual amount of rejected component buildup is very small.

Given the thinness of the anhedral shell (shell 2 in orbicule 95-OH-3 is ~ 0.5 mm, figure 2.5) compared to the radial shell (shell 1 is 8 mm, figure 2.5), the question of whether the buildup of these rejected components (H_2O and Fe^{+3}) is actually enough to stop the growth of these much larger crystals should be asked. In subsequent shells of the same morphological interface type but further away from the core, plagioclase occasionally grows through a thin anhedral shell and in orbicule 95-OH-6, the subsequent anhedral shell is as thick as the preceding radial shell (fig. 2.7). This suggests that it may not simply be a buildup of the obvious rejected components that stops the elongated crystal growth, but something else as well, some particular component that may be inhibiting pyroxene and plagioclase growth.

The presence of growth inhibitors is well documented in the 'aqueous chemistry' literature where studies have shown that Mn^{+2} inhibits calcite growth (Wang & Merino 1990), CaCl_2 inhibits illite (Eberl *et al.*, 1986), and Sr and Mg affect apatite (Zawacki *et al.*, 1986). The 'metallurgy' literature documents how impurities affect the growth of metal crystals, e.g. Cockayne *et al.* (1969) showed that the addition of yttrium alters the shape of $\text{Dy}_3\text{Al}_5\text{O}_{12}$ crystals

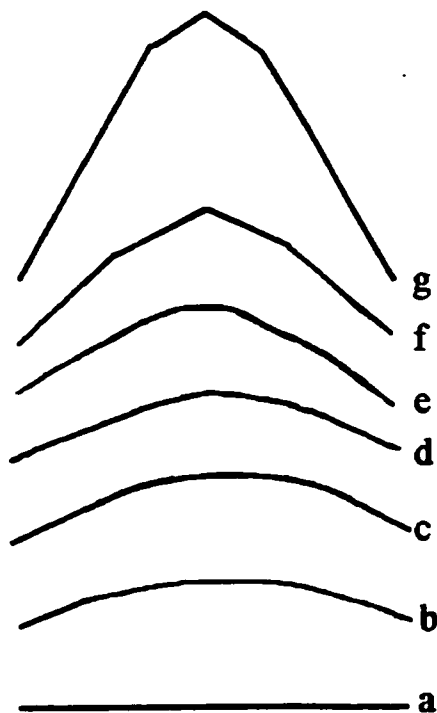


Fig.5.3 Diagram showing how the shape of the crystal interface changes as an impurity (Y) is added to $\text{Dy}_3\text{Al}_5\text{O}_{12}$ (interface 'a'). The other interfaces are as follows (modified from Cockayne *et al.*, 1969):

- g - $\text{Y}_3\text{Al}_5\text{O}_{12}$
- f - $\text{Dy}_{.15}\text{Y}_{2.85}\text{Al}_5\text{O}_{12}$
- e - $\text{Dy}_{2.45}\text{Y}_{2.55}\text{Al}_5\text{O}_{12}$
- d - $\text{Dy}_{.75}\text{Y}_{2.25}\text{Al}_5\text{O}_{12}$
- c - $\text{Dy}_{1.5}\text{Y}_{1.5}\text{Al}_5\text{O}_{12}$
- b - $\text{Dy}_{2.25}\text{Y}_{.75}\text{Al}_5\text{O}_{12}$
- a - $\text{Dy}_3\text{Al}_5\text{O}_{12}$

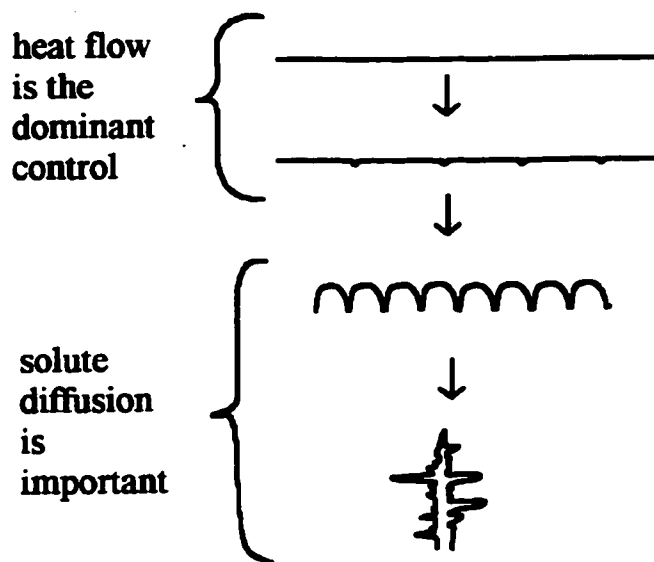


Fig. 5.4 Changes in the solid/liquid interface as impurities are added to a pure metal melt. The interface is initially flat, then begins to develop very small instabilities. This type of interface is usually controlled by heat flow. As the instabilities grow, heat becomes less important than solute diffusion. The instabilities are portions of the interface that reach into undepleted melt and are thus able to grow. Eventually one instability dominates taking the shape of a dendritic crystal (after Jackson, 1969).

(fig. 5.3) while Jackson (1969) shows how impurities changes a crystal's shape along an initially linear isotherm to dendritic structures (fig. 5.4). He explains that too many impurities block faces from growing and that only a high growth rate allows the crystal to break through the impurity blockage into undepleted melt. Even just crystal growth into a wall will thicken a crystal (Tiller 1971). The 'aqueous geochemistry' literature also discuss this phenomenon, e.g. Al^{+3} causes twisting of silica fibres (Wang & Merino, 1992), Mg causes curving of gypsum crystals while Na does not (Franchini-Angela & Rinaudo, 1989). In the 'geology' literature, Speidel (1970) has shown that exsolution of ilmenite from magnetite increases as MgO in the melt increases. All of these examples suggest the possibility of the presence of one, or more, growth inhibitor components in ceasing branching crystal growth within an orbicule. Unfortunately minor elements as well as Fe^{+3} analyses can not be resolved by electron microprobe and not all major elements are determined for all the minerals, i.e. plagioclase is only analyzed for SiO_2 , Na_2O , MgO , Al_2O_3 , K_2O , CaO and FeO while orthopyroxene is analysed for these components plus TiO_2 , MnO , Cr_2O_3 , and NiO . Comparisons of the common components were inconclusive in suggesting possible growth inhibitors and thus this mechanism remains unproven.

5.5.2. Type III - Radial to Radial

In this type of morphological interface, the mineralogy does not change. An example of this interface is seen in shell 5 in orbicule 95-OH-3 (fig. 2.5). Plagioclase grows in a radial direction throughout the shell with crystals starting and ending at no particular horizons. Elongated pyroxenes also start growing at the inner edge of shell 5 but the majority of them end about one third of the way across the shell and then new crystals start to grow from this horizon.

This is repeated two more times, i.e there are three horizons of orthopyroxene within shell 5. There is no precipitation of amphibole or Fe-Ti oxides at these horizons. In fact, there is very little of any of these minerals throughout the shell. The absence of these minerals indicates that pyroxene growth did not stop because of increased amounts of rejected components such as H_2O or Fe^{+3} which may be responsible for the radial to anhedral morphological interface (type I). The repeated precipitation of the budding orthopyroxene is suggestive of enrichment and depletion of some other component (perhaps a trace element) that appears to only affect the orthopyroxene. Major oxide chemical analyses of these crystals show that only the Mg and Fe change systematically over the length of these reverse-zoned crystals. Trace element analyses along the crystals was not done. These elongated, budding crystals are much smaller than the branching ones of the innermost shell suggesting that decreasing growth rates may also be playing a role, along with rejected/impurity components in controlling pyroxene crystal shape.

5.5.3 Type IV - Anhedral to Anhedral

Orbicle 95-OH-6 (fig. 2.7) has a thick package of almost a dozen shells that alternate between mostly anhedral amphibole and mainly anhedral Fe-Ti oxides. This mineralogical alteration is possibly due to oscillating P_{H_2O} and Fe^{+3} on a local scale due to enrichment and depletion of chemical components in the boundary layer as Fe-Ti oxides precipitate (depleting Fe^{+3} and increasing OH^-) followed by amphibole precipitation (decreasing OH^- and increasing Fe^{+3}). Preceding the precipitation of this package of anhedral shells is a radial shell consisting of orthopyroxene and plagioclase, minerals that reject both H_2O and Fe^{+3} . Why a thick package like this should form in one orbicle and not in another is unknown. Also, why the Fe-Ti oxides and

amphiboles should precipitate into separate shells at the expense of new growth of orthopyroxene and plagioclase is also not known.

5.6 The End of Comb Texture Growth

To end the growth of the far-from-equilibrium textures of comb layering and orbicules, a change in the environment must have occurred.

The orbicules seem to form in protected pockets near the tops of magma chambers (McKinney, 1985) where large pods of magma can cool quietly. The growth of fragile, branching crystals all around the orbicular cores strongly suggests that they formed while supported by buoyancy forces (Brigham, 1983) in a quiet, non-convecting environment. The slight flattening of many of the orbicules into ellipsoids from spheres provides evidence that some of the orbicules have been at least, slightly strained after formation. The close proximity of the orbicules to the comb layering in the outcrop necessitates that any movement could not have been far.

While it is possible that some external (to the magma chamber) event, such as magma injection or ejection, could change the ideal growth regime for comb textures, there are other, less catastrophic ways, to end comb texture growth.

Dissipation of high chemical potential gradients could change the crystallization pattern. As seen in chapter 4, crystallization of the chemically reverse-zoned orthopyroxenes and plagioclase occurs under far-from-equilibrium conditions. Crystallization of these minerals would relieve these conditions gradually leading to near-to-equilibrium crystallization. Evidence of this dissipation can be seen in the orbicules in that the largest branching crystals with the most branches are found in the innermost shell. Subsequent shells contain smaller crystals with buds

but no branches. This change in habit suggests that the driving force behind the growth of the branching crystals decreases as subsequent shells form.

Comb textures, which form as a result of a low temperature difference at the interface between two warm bodies (one magma and one crystal mush), stop forming when the magmatic conditions become more plutonic-like during which the rest of the magma crystallizes as a “normal”, near-to-equilibrium, coarse grained, plutonic rock. It is known that plutonic rocks cool very slowly in a regime of low nucleation and low crystal growth rates. It is proposed that the interface, which was initially cooled by the surrounding crystal mush, is subsequently warmed by the large bulk of magma that has not yet begun widespread crystallization. Warming of the comb texture forming magma would change the conditions of low nucleation rate and high crystal growth rate to lower nucleation rates and low crystal growth rates (fig. 5.5).

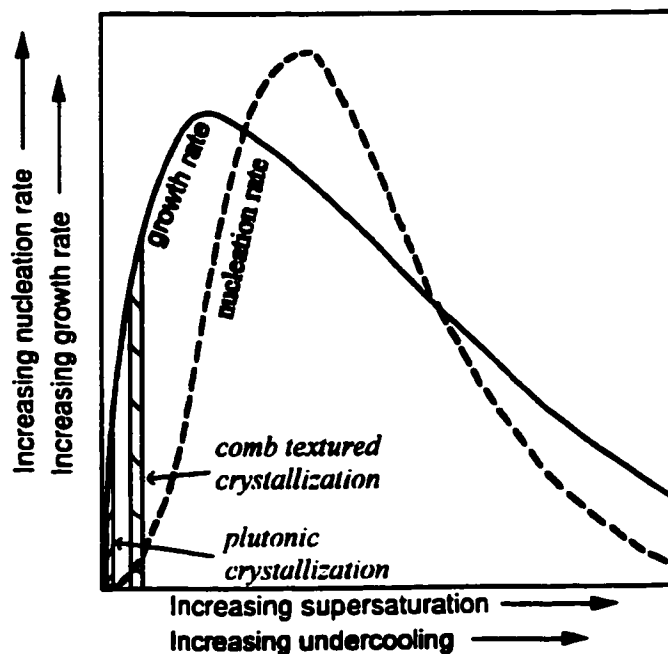


Fig. 5.5 The comb textured crystallization occurs where nucleation rate is low and crystal growth rate is high. The large bulk magma warms up the growth interface, decreasing undercooling, resulting in lower nucleation rates and lower crystal growth rates - conditions of near-to-equilibrium plutonic crystallization (modified from Naslund & McBirney, 1996).

This brings to an end the initial stage of formation of orbicules and comb layering. The normal chemical zoning seen across the orthopyroxene is evidence of subsequent crystallization under near-to-equilibrium conditions. Also the large anhedral amphiboles seen in the innermost shell between the large orthopyroxenes probably crystallized slowly from pods of melt trapped between the fast growing, branching crystals. The fact that the orbicules were slightly flattened after formation without any sign of fracturing is evidence that these pockets of future amphibole had not yet crystallized, i.e. the orbicule must not have been completely solid upon flattening.

5.7 Summary

A summary of the proposed formation mechanism is as follows: (1) injection of a magma into a warm surrounding “mush” leading to only a small drop in magmatic temperature at the magma/mush interface, (2) at small undercoolings, low nucleation and high growth rates produce comb textured crystallization resulting in orbicules (growth on xenoliths) and comb layering (growth at the interface), (3) the increasing number of branches in orthopyroxene towards the crystal tip implies a chemical barrier: precipitation of amphibole and Fe-Ti oxides suggest increased rejected components at the barrier but the thinness of the shell may also suggest an increase in an unknown growth inhibiting element, (4) comb texture crystallization ends when the interface undercooling decreases to the low crystal growth rates and nucleation rates associated with coarse grained plutonic texture, and (5) subsequent crystallization of normal zoning along the sides of the branching/budding orthopyroxenes, trapped pockets of melt that become amphibole in the orbicular shells, large euhedral interstitial hornblende and plagioclase found between the orbicules, and coarse grained mosaic texture of the bulk diorite.

It has been shown that the comb textures can be formed without the need to invoke any oscillating intensive parameters at a large scale in the magma chamber. This suggests that the comb textures are a self-organizing phenomenon that grow in response to far-from-equilibrium conditions in the magma. The term self-organizing is used because the comb textures form an oscillating pattern that does not reflect any large scale oscillating parameter. Self-organization has been used by McBirney *et al.* (1990) to explain spheroidal layering around dendritic cores in a dike. He describes their formation as a self-organization reaction in a hydrous, warm, late-stage crystallizing magma. The comb textures of Fisher Lake also form in a late injected magma in the warmth of the Sierra Nevada batholith environment without the need for any other external constraints.

6.0 Mathematical Modelling

6.1 Introduction

Modelling of oscillatory behaviour can be traced back to Liesegang and his experiments in the late 1800's. He discovered that a drop of silver nitrate on photographic film gel containing potassium dichromate produced concentric rings of silver dichromate that increased in width, but decreased in frequency away from the central silver nitrate drop (Liesegang, 1896). This type of patterning was ascribed to supersaturation by Ostwald (1897).

Since then, many authors have duplicated and enhanced Liesegang's experiments of two soluble salts in a gel: more than 600 papers had been written by 1954 (Stern). The newer experiments have produced more complex patterns such as reverse Liesegang rings (e.g. Flicker and Ross, 1974), helices (e.g. Chernavski *et al.*, 1991), and finer banding using denser gels (Mueller, 1984). All this work demonstrates that the patterns form as a result of a moving reaction front between salts where nucleation causes depletion, or enrichment, of particular ions just ahead of the front. Nucleation causes local depletion of ions incorporated in the nuclei and relative enrichment of those that are not. The increased build-up of the rejected components and depletion of the incorporated components eventually results in insufficient material for nucleation and then the system nucleates a new phase consisting of the formerly rejected components. A cycle of enrichment and depletion develops as the system alternates between nucleation and precipitation of one salt followed by the other (Sultan *et al.*, 1990).

There are mathematical models in the literature that model the growth of Liesegang rings (e.g. Sultan *et al.*, 1990; Smith, 1984; Stern, 1954), crystal growth (e.g. Lasaga, 1982), and oscillatory precipitation within a crystal (e.g. L'Heureux and Fowler, 1996a, 1996b; Higman and

Pearce, 1993).

Modelling of oscillatory mineral layering in intrusions has been done (e.g. Boudreau, 1995), but it is based on layering that consists of minerals either unoriented, or oriented parallel to the layering and, in the case of Ostwald ripening, is post-nucleation. There are also models for metamorphic orbicules (e.g. Ortoleva, 1994) based on pressure-driven concentration gradients.

Models based on post-nucleation or metamorphism will not be discussed any further since the Fisher Lake orbicules are neither. There is no evidence of metamorphic minerals, textures or structures at either a micro- or macro-scale. Comb texture growth can not be post-nucleation since it is unlikely that the elongated, branching crystals could grow if there was serious competition from many surrounding, growing, nuclei for necessary chemical components. The crystallization history developed in the previous chapter also makes the case for formation of comb textures before most of the surrounding magma nucleates and crystallizes.

With the advent of the mathematics of fractals, nonlinear dynamics, and catastrophe theory, modelling of igneous phenomena has taken a new direction. Simulations based on fractal mathematics produce extremely complex forms with intricate patterns that often repeat themselves on smaller and smaller scales (Mandelbrot, 1982). Fractal dimensions have allowed geologists to quantify many phenomena that occur within a range of sizes or magnitudes such as earthquakes, fractures, coastlines, and ore deposits. It has also allowed mathematical simulation of the underlying growth processes of many natural phenomena that are poorly described by the usual Euclidean geometry, e.g. branching crystals (Fowler *et al.*, 1989a; Fowler *et al.*, 1989b; Fowler and Roach, 1996). Nonlinear dynamics dictates that a pattern resulting from “chaotic

dynamics" is predictable in the short range, but not in the long, because small uncertainties become amplified such that the nonlinear system evolves in a manner that can not be accurately forecasted (Lorenz, 1963). This realization has made geologists look closer at phenomena that are intricately textured and consider the mathematics behind the patterning, e.g. sand ripples (Rubin, 1992), and mineral zoning (Higman and Pearce, 1993).

Geochemical self-organization is the concept that patterns are generated spontaneously due to the coupling between reaction and transport in systems subjected to non-equilibrium conditions. When the boundary conditions of a system keep the system near-to-equilibrium, then the system is stable, i.e. any fluctuations within the system decrease and eventually die off. But if the system is pushed into a far-from-equilibrium state, then positive feedback between reaction and transport creates amplification of any fluctuations in the system and patterning can spontaneously occur (Ortoleva, 1994). The patterning is a construct of the system that allows that system to dissipate those energies that pushed it into the far-from-equilibrium state and thus, the patterning is not a template forced onto the system by the boundary conditions. Self-organized structures can be found in all types of rocks, e.g oscillatory zoning in igneous crystals, and metamorphic and diagenetic reaction fronts (Ortoleva, 1994).

Newer theories continue to arise, e.g. catastrophe theory which is the study of discrete structures such as singularities and bifurcations that arise from smooth changes in external conditions (Arnold, 1986) and self-organized criticality where the complexity of a system is a response to the internal dynamic interactions among individual components within the system (Bak, 1996).

Catastrophe theory and geochemical self-organization offer us the tools with which to

describe how textures form from a cooling magma. A magma that cools near-to-equilibrium (NTE) in deep, plutonic, slow cooling conditions, is typically characterized by a homogeneous mix of nearly euhedral crystals that have no reaction rims or zoning. Far-from-equilibrium (FFE) crystallization conditions may produce spherulites, glass, or crystals with rims or zoning (reverse or oscillatory) that may have dendritic or radiating shapes arrayed in a heterogeneous or patterned arrangement. The Fisher Lake orbicules and comb layering show all the characteristics of FFE cooling; radiating crystals with reverse zoning organized in a highly complex pattern. The orbicules and comb layering are in turn surrounded by a homogeneous mosaic of crystals which are characteristic of NTE cooling. Thus it seems logical that the magma cooled first through FFE conditions and then under NTE conditions.

The realization that crystallization started at far-from-equilibrium and changed to near-to-equilibrium or steady-state conditions allows us to consider catastrophe theory. The essence of this theory can be seen in figure 6.1 which shows a system starting from a stable state, i.e. all points in the system move to one stable focus in the centre (A). The system is perturbed (B) to a conditionally stable state where any point in the system moves to a limit cycle (C), i.e. points near the centre move outward while points outside move inward with all points meeting at the limit cycle which represents a regularly oscillatory solution. Further perturbation (D) of the conditionally stable state results in instability, i.e. oscillations are aperiodic (E) and the system may then jump to another, completely different, stable state (F).

An example of a system that behaves in a catastrophic way is the forced pendulum. The simplest pendulum system is one that is subject only to gravity. Initially, the pendulum hangs straight down, not moving, i.e. it sits in one position at the centre or the focus of the system

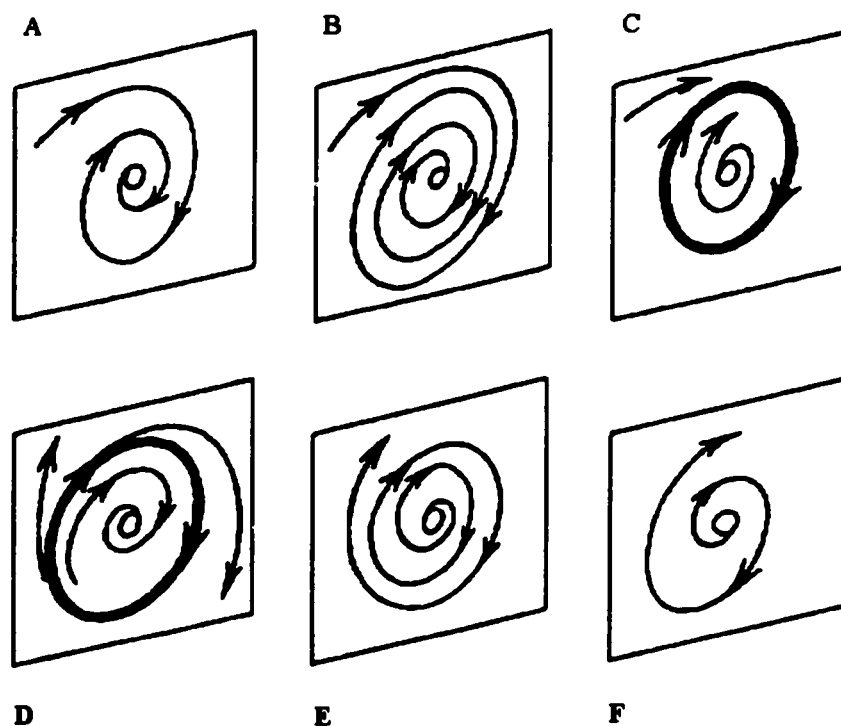


Fig. 6.1 Diagrams showing the movement of system from a stable focus to a stable limit cycle to a new stable state. In A, all points in the system move quickly to one stable focus located at the centre. The system is perturbed such that it now takes much longer for the points in the system to reach the equilibrium point or central focus (B). Further stress produces a limit cycle (C), a quasi-stable condition where points near the centre move outward while points outside move inward with all points meeting at the limit cycle which represents a regularly oscillatory solution. Further perturbation (D) of the conditionally stable state results in instability, i.e. oscillations are aperiodic (E) and the system may then jump to another, completely different, stable state (F). (from Arnold, 1986)

(fig.6.1a). If the pendulum is pushed, it will move from side to side, losing momentum with each swing. After only a few swings, the pendulum stops at the focus (fig.6.1b). The addition of three magnets set in a circle forces the pendulum to move to a limit cycle (fig.6.1c). Perturbing the pendulum from a central position will send it into a circular movement around the centre while pulling the pendulum to the outside of the magnet ring and letting it go will also send the pendulum into a circular movement around the centre following the arrows in figure 6.1c into the limit cycle.

In comparing the Fisher Lake magma cooling sequence to catastrophe theory, it seems likely that the magma which moved from a FFE state to a NTE one is not a catastrophic system even though the style of precipitation, which appears to be so different between the orbicules and the surrounding homogeneous matrix, looks as if there has been a change in state. As has been shown in chapters 2 and 3, the whole rock chemistry and petrology of the orbicules are very similar to the surrounding rock. This suggests that the formation of the orbicules did not form in response to a large change, or fluctuation, in intensive variables in the cooling magma, e.g. sudden changes in p_{H_2O} as proposed by several authors (equivalent to pushing the pendulum between the magnets). Given the similarities in mineralogy and chemistry of the layered rocks and the host rocks, it is more likely that the formation of the orbicules and comb layering is the result of smooth changes in system parameters after emplacement of the magma.

6.2 The Volterra-Lotka Equations and Anhedra Shell Precipitation

The presence of orbicules and comb layering in so many different types of igneous rocks makes it desirable to limit as much as possible any step in the formation mechanism that could be

dependent on a particular magma chemistry. Since relative trace element (TE) and rare earth element (REE) abundances are very particular to most types of igneous rocks and, since TE and REE are present in such small amounts, it seems more likely that the major oxides rather than the TE and REE would be a factor in magma crystallization.

The interactions that take place between the chemical components within a magma can be compared to the relationship between prey and predators in the animal kingdom. The Volterra-Lotka equations were developed (Volterra 1926, Lotka 1920) as a model for animal population dynamics. The typical species considered are rabbits and foxes. In the model, the rabbits have an infinite source of food and the only thing that kills them are foxes. The foxes only eat rabbits and die out when there are not enough rabbits. The interaction between these two species can be described by two coupled, first order, differential equations:

$$\begin{aligned}\frac{dx}{dt} &= ux - vxy \\ \frac{dy}{dt} &= -wy + zxy\end{aligned}\tag{6.1}$$

where u , v , w , z are constants usually set to one, x is the number of rabbits, y , foxes and t , time. The nonlinear terms, $-vxy$ and $+zxy$, describe the meeting of the two species whereupon the number of rabbits decrease and foxes increase. The linear terms reflect food dependence of each species with rabbits increasing due to their infinite food supply and foxes decreasing due to their limited food supply. The interaction between the two species produces a closed, continuous feedback loop.

The biological analogy of prey and predator can be replaced by two chemical components competing for precipitation. Higman and Pearce (1993) showed that the precipitation of Na_2O

versus CaO in oscillatory zoned plagioclase could be simulated by the Volterra-Lotka equations because these two chemical components are part of a solid solution and in a certain sense exhibit feedback behaviour just as the rabbits and foxes. As CaO (coupled with Al_2O_3) is incorporated into An-rich plagioclase, the amount of CaO decreases in the surrounding residual melt while Na_2O (coupled with SiO_2) increases, providing that the growth rate of the crystal into the residual fluid is faster than diffusion of CaO from the parent magma. Eventually saturation of Na_2O occurs and begins to precipitate thereby decreasing its presence in the residual melt while CaO diffusion through the parent magma allows CaO to increase in the residual melt. Consequently, saturation of CaO will occur and then CaO- Al_2O_3 will precipitate in the plagioclase. This process is autocatalytic since no other chemical components are necessary to keep the reaction going. Higman and Pearce numerically iterated the predator-prey equations and then plotted every 12th-18th iteration (randomly chosen), producing a graph that simulates the behaviour of CaO and Na_2O . Their justification for choosing the points in this manner was to remove the constant time aspect of the predator-prey solutions since it is unknown if the growth rate of each zone in the plagioclase is the same as the others.

Comb texture consists of a complex interaction between crystal habit and crystal mineralogy. As detailed in chapter 2, there are radial shells with elongated crystals of mainly orthopyroxene and plagioclase as well as two types of anhedral shells defined by the presence, or absence, of Fe-Ti oxides. These three types of shells can be found in orbicule sample 95-OH-6. As seen in figure 2.7, this orbicule has two radial shells that alternate with two packages of anhedral shells. Each anhedral package consists of about a dozen anhedral shells rich in hornblende and biotite, as well as plagioclase and orthopyroxene, and alternate in the presence

or absence of Fe-Ti oxides.

The oscillation of this mineralogy within the anhedral shell packages is reminiscent of the oscillatory zoning in a plagioclase crystal. The shells are quite uniform in thickness and have sharp boundaries even though they are quite narrow, on the order of a millimetre or less in thickness. The shells within the anhedral shell package are delimited by the presence or absence of Fe-Ti oxides. Shells with no Fe-Ti oxides have increased amounts of plagioclase. These minerals incorporate different major oxide components and thus do not compete for any necessary elements. In previous chapters the case has been made for high crystal growth rates that are faster than the diffusion of growth components through the magma. If plagioclase crystals grow fast, then they would create a residual melt zone that is depleted in plagioclase components such as Ca, Al, Si, and Na and rich in rejected components such as Fe^{+3} , Fe^{+2} , Ti, Mn, and Cr. These are components incorporated by Fe-Ti oxides. Thus we have a feedback loop in saturation and depletion in components used by plagioclase and Fe-Ti oxides. Modelling this particular change in mineralogy but not morphology does not address the problem of changing from radial to anhedral crystal shapes or *vice versa* where an unknown growth rate inhibitor/enhancer may be involved (described in section 5.5.1).

There are many chemical components involved in the formation of plagioclase and Fe-Ti oxides, but we can represent these two anhedral minerals by the components most distinctive to each; Ca in plagioclase and Fe^{+3} in Fe-Ti oxides. Thus we can model the interaction through time of just these two components using the Volterra-Lotka equations.

In this context, equations 6.1

$$\begin{aligned}\frac{dx}{dt} &= ux - vxy \\ \frac{dy}{dt} &= -wy + zxy\end{aligned}\tag{6.1}$$

become

$$\begin{aligned}\frac{dx}{dt} &= x - xy \\ \frac{dy}{dt} &= -y + xy\end{aligned}\tag{6.2}$$

where x is Fe^{+3} and y is Ca. The nonlinear terms, xy , describe the interaction between the two chemical species in that while one species is increasing in the residual melt, the other must be decreasing due to precipitation and *vice versa*.

To run the computer model, an overall time scale of 16000 seconds for formation of 0.75 cm of layering in one anhedral shell package compares well with the postulated growth rate of 4 cm/day or 5×10^{-5} cm/s for 10 cm long tourmaline in a Himalayan line-rock (oscillatory precipitation) dike (Webber *et al.*, 1999). This value is one of the few cited in the literature for an intrusive body with crystals that grew perpendicular to the sides of the dike. Initial values of x and y (Fe^{+3} and Ca) were chosen such that Fe^{+3} would be higher in order to reflect the presence of Fe-Ti oxides in the first shell of the anhedral shell package and such that the value was approximately the same as subsequent peak values i.e. $(x_o, y_o) = (4, 2)$. Setting $(x_o, y_o) = (1, 1)$ always produced a trivial solution; a horizontal line equal to 1. The constants u , v , w , and z were set to equal one.

Student Matlab version 5 was used to run the simulations of these equations. The differential equations were numerically iterated using the Matlab ODE45 solver which is based

on “an implementation of the explicit Runge-Kutta (4,5) pair of Dormand and Prince” (Shampine & Reichelt, 1997). The program code can be found in Appendix D.

The result is plotted as $x(\text{Fe}^{+3})$ versus time (fig. 6.2). There is an initial transience of closely spaced, uneven oscillations in the first 3000 seconds that changes into wide spaced, oscillations of similar heights. The shells within the anhedral shell package also show an initial irregularity in thicknesses with the first two shells (#2 and #3) being the same (table 2.7). Then the shell thicknesses seem to gradually settle down to thin Fe-Ti oxide shells approximately 0.5 mm thick that alternate with non Fe-Ti oxide shells approximately 1 mm thick.

The similarity between the model, using only two chemical components, and the anhedral shell package indicates that a periodically, oscillating force, external to the precipitating orbicule, is not necessary in forming the oscillating Fe-Ti oxide shells. The Volterra-Lotka equations are smooth functions with no singularities and indicate that when the growth conditions are correct, that of smoothly changing growth conditions, then the internal dynamics of the magma self-organize into oscillatory precipitating shells.

6.3 The Modified Volterra-Lotka Equations and Orbicular Formation

All crystallization within a magma is an attempt by the chemical components within that magma to reach an equilibrium consistent with the intensive variables imposed on the magma. As has been shown throughout this thesis, comb textures reflect FFE conditions that occurred in only a small portion of the magma within a much larger magma chamber where much of the crystallization took place at near-to-equilibrium conditions. The comb texture itself can be interpreted as the response of this pod of FFE magma toward achieving

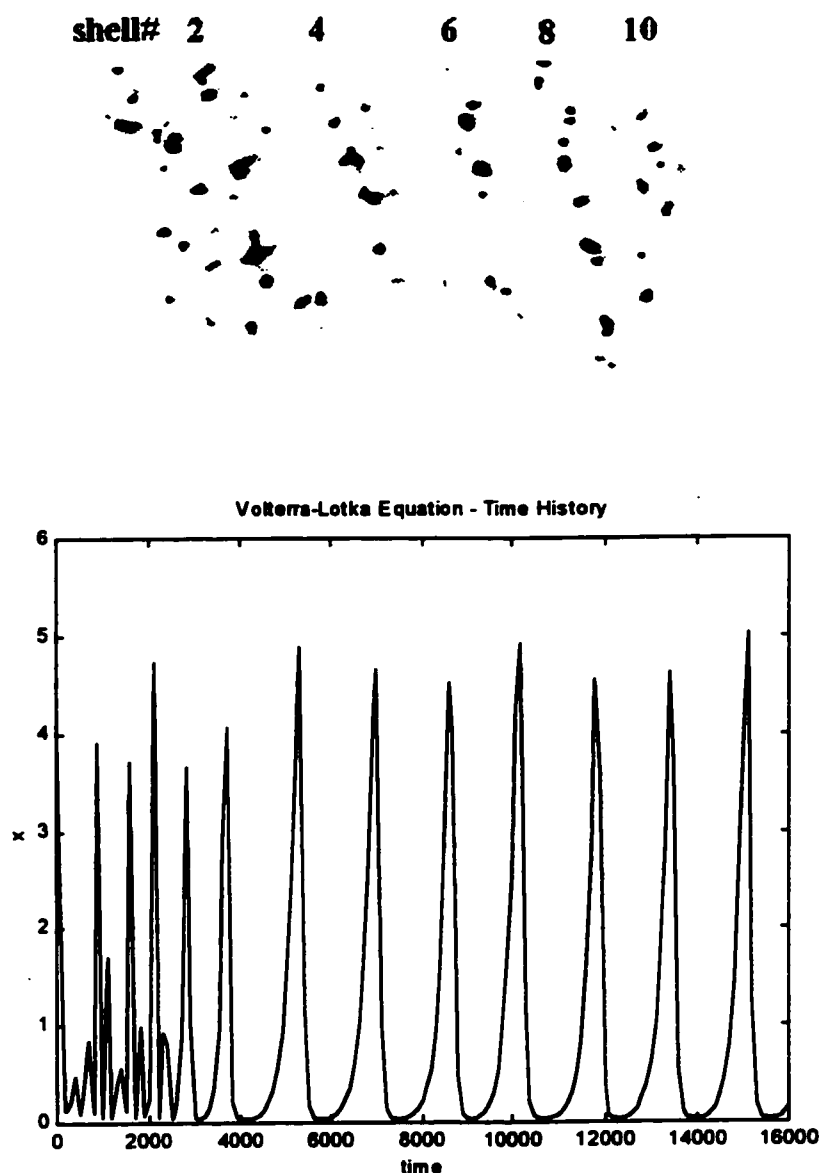


Fig. 6.2 Lower graph of the Volterra-Lotka equations (6.2) shows the oscillation in the amount of Fe^{+3} over time. After an initial intransigent, the pattern becomes regular. This pattern is an approximation to the package of anhedral shells in orbicule 95-OH-6 where high amounts of Fe^{+3} in the form of Fe-Ti oxides alternate with low amounts of Fe^{+3} or higher amounts of plagioclase. Top figure shows the Fe-Ti oxide rich shells within the anhedral shell package (photograph is in fig. 2.7 and mineralogy is in table 2.7). Initial shells (2 and 3) are thicker than in the model curve but subsequent shells (4 through 10) are fairly regular as is the model curve.

equilibrium, i.e. the first shell which contains the largest and most spectacular reverse zoned branching orthopyroxenes represents the largest step towards NTE (near-to-equilibrium). Rapid precipitation of minerals from the melt would decrease the free energy of the system (or chemical potential) and may even cause an overshooting of equilibrium conditions. The system dynamics would resemble a non-forced pendulum, pulled away from the rest position, swinging back and forth with less momentum with each swing until it is once again at rest or equilibrium.

Potential evidence for a mechanism such as this can be seen in figure 6.3 which shows

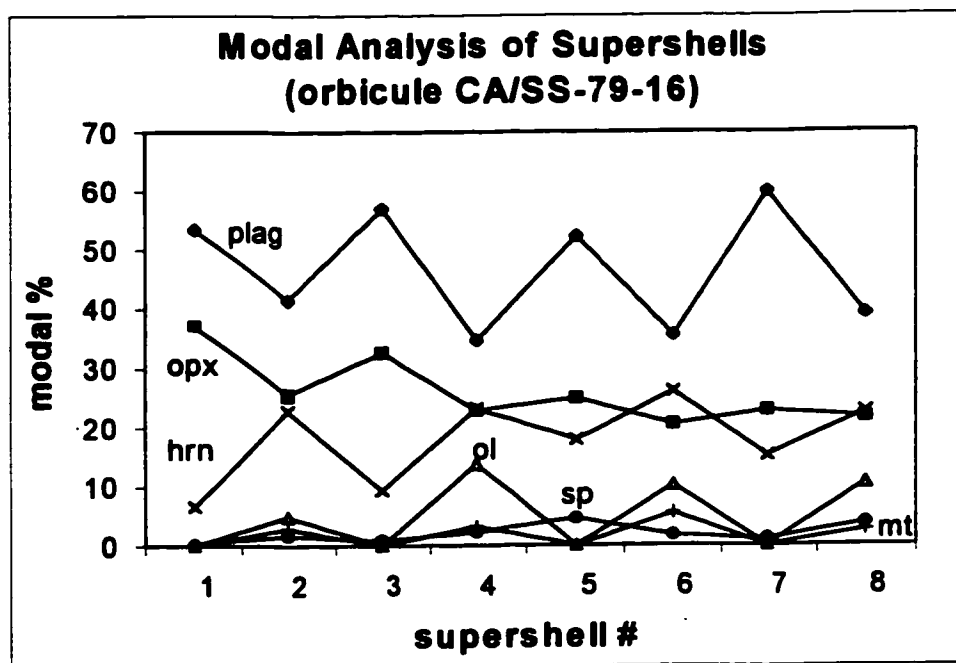


Fig. 6.3 A graph showing the modal oscillations of six minerals in an orbicule (sample CA/SS-79-16). Each supershell consists of a radial shell rich in plagioclase (plag) and a package of anhedral, mafic shells. The plagioclase has a fairly constant oscillation while the orthopyroxene (opx) and the hornblende (hrn) have initially high oscillations that gradually flatten out to a more constant value, much like a damped pendulum. The other minerals are olivine (ol), spinel (sp), and magnetite (mt). Data is from McKinney, 1985.

a plot of mineral modes from eight supershells (one radial felsic shell + mafic anhedral shells) from a single orbicule. The data, from McKinney (1985), show a decrease in the oscillatory nature of the orthopyroxene and the amphibole, both gradually flattening out to a baseline concentration.

As we saw in section 6.2, regular oscillatory precipitation in the orbicule within an anhedral shell package can be produced without external forcing by the self-organization of the chemical components within the system under the correct growth conditions. This same type of mechanism can be used to form an entire orbicule if the Volterra-Lotka equations are modified by the addition of a squared term to account for other ways of decreasing the abundance of a chemical species, e.g. slow diffusion of the components through the melt. Another modification is made by adding a time delay to the decreasing amount of Ca (due to precipitation) since Ca precipitation does not begin as soon as the Fe begins to decrease when it precipitates, i.e. the amount of Ca in the residual will decrease by a substantial amount and the Fe will increase by a substantial amount over a given length of time before the Fe will begin to precipitate. The modified Volterra-Lotka equations (from Cook, 1994) are

$$\begin{aligned}\frac{dx}{dt} &= ux - vxy - ax^2 \\ \frac{dy}{dt} &= -wy + zxy - w\tau y \frac{dx}{dt}\end{aligned}\tag{6.3}$$

where a is a constant set to one and τ is the time delay.

Computer simulations were again run in Student Matlab version 5 using their ODE45 routine for solving first-order differential equations. The results (fig. 6.4) show a curve with

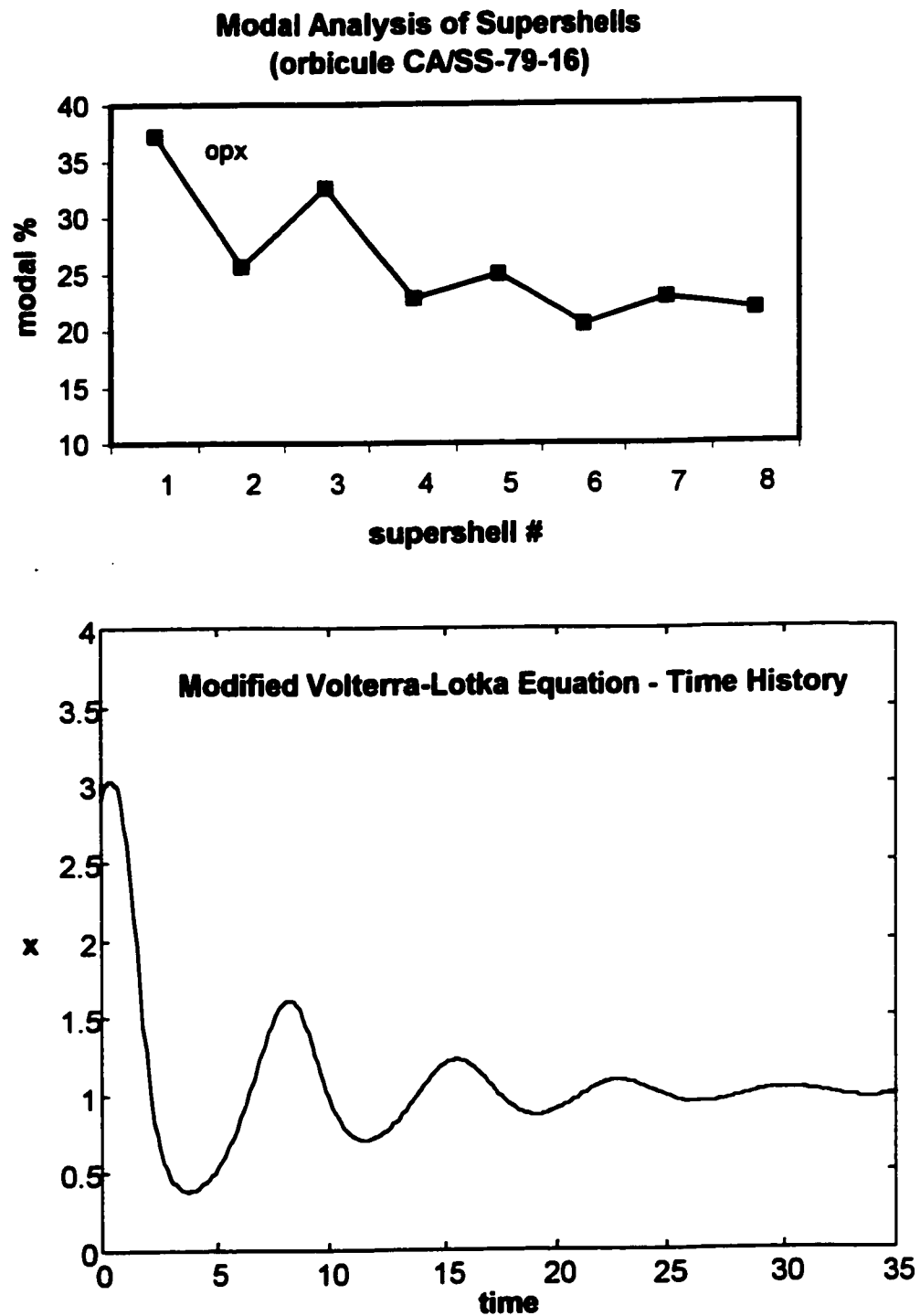


Fig. 6.4 Lower graph shows the results of running the modified Volterra-Lotka equations (6.3) as compared to the upper graph showing modal orthopyroxene from an orbicule (fig.6.3) The model curve starts at a high value reflecting the high amount of orthopyroxene in the innermost supershell. The oscillations gradually decrease to a constant value.

increasingly damped oscillations that eventually flatten out to a baseline or stable state. This curve is very similar to the orthopyroxene modal abundance curve in figure 6.3. Thus it appears that the orbicule can form without an external forcing mechanism and that under the correct, smoothly changing, growth conditions, the mineral components of a magma can self-organize into the oscillatory precipitation of an orbicule. The two minerals take part in a feedback loop or autocatalytic reaction, i.e. when plagioclase is precipitating, Fe-Ti oxide components increase in the residual while plagioclase components decrease. When the Fe-Ti oxide components saturate the residual boundary layer, Fe-Ti oxides precipitate. This causes the Fe-Ti oxide components to decrease in the residual melt while rejected components, such as those found in plagioclase, increase.

The change in the free energy of the magma, by precipitation, from far-from-equilibrium towards near-to-equilibrium conditions can be seen in the phase plane plot of the two mineral components (fig. 6.5). Under FFE conditions, orthopyroxene abundance is high and hornblende is low. In order to decrease the free energy of the system, orthopyroxene decreases while hornblende increases (point A to B). Just like a pendulum, the system does not immediately attain a stable state but oscillates, at decreasing amplitudes, between larger and smaller amounts of orthopyroxene and hornblende (e.g. point C). The system gradually spirals into a stable focus on the graph (point D) or to an equilibrium state in chemical potential. The graph shows that no matter how far-from-equilibrium the free energy of a magma may be, that under smoothly changing external conditions, the magma will gradually attain equilibrium (or NTE) by crystallization of its components and that in order to do this, the components may self-organize to achieve the lowest free energy, or equilibrium, state.

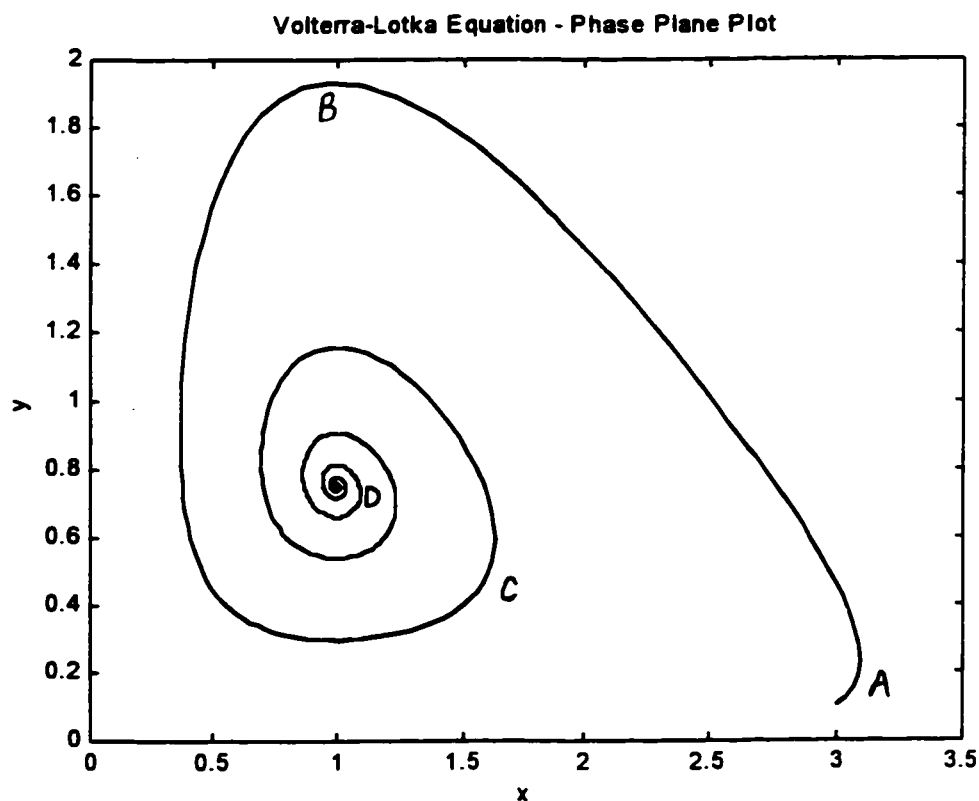


Fig. 6.5 Graph of the modified Volterra-Lotka equations in phase plane space. X and y represent two minerals. The curve starts at the bottom right corner (A) under far-from-equilibrium conditions with a high amount of x and a low amount of y . As x decreases and y increases (B), the system moves towards the center. The changes in x and y decrease as the system matures (C), moving towards a center, stable point or equilibrium (D).

6.4 Proposed Mathematical Modelling

The Volterra-Lotka equations roughly simulate the appearance of the anhedral shell packages seen in one orbicule. The simplicity of these equations makes it unrealistic to expect them to simulate any further complexities of comb textures such as the oscillatory crystal habit from elongated to anhedral. More complex equations are necessary if simulation of the various crystal habits as well as other mineralogies are to be accomplished.

Higher complexity mathematical modelling of the orbicular oscillatory precipitation using models such as that of L'Heureux (1993) and L'Heureux and Fowler (1994, 1996a, 1996b) is beyond the scope of this thesis but I would like to suggest possible modifications. Their model describes the oscillatory precipitation of anorthite within plagioclase crystals but it could possibly be expanded to show the oscillatory precipitation of plagioclase across an orbicule.

They begin with the general mass balance equation or the concentration-diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + V \frac{\partial c}{\partial x} - \Gamma(c - \hat{c}) \quad (6.4)$$

where D is the constant diffusion coefficient (independent of temperature and concentration), $c(x,t)$, concentration at the surface of the growing crystal, $\hat{c}$, concentration of the bulk magma far from the growing crystal, t , time, and Γ is the input flow rate per unit volume or inversely proportional to the average residence time of the component in the magma. $V(t)$, velocity of the moving front, is a function of growth rate and equals $G_T(c(0,t))$ where G_T is a series of

equations based on several parameters including the change in Gibbs free energy, ΔG . The derivation uses

$$\Delta G = \Delta H \Delta T / T_L \quad (\text{change in enthalpy} * \text{change in temperature} / \text{liquidus temperature})$$

where

$$\Delta H = \Delta H_f + \Delta H_m \quad (\text{heat of fusion} + \text{heat of melting})$$

and

$$\Delta T = T_L - T \quad (\text{liquidus temperature} - \text{actual temperature})$$

This formulation for molar ΔG is suitable for pure phases with only one component. For the Fisher Lake orbicules where plagioclase and orthopyroxene are the major mineral phases, a one component system is unsuitable; at least two components if not three are necessary for the mathematical modelling. While the plagioclase in the orbicules is well represented by one component, An, (the plagioclase generally contains greater than An₄₀) the pyroxene contains approximately 60:40 MgO:FeO and thus may need to be represented by two components. Since a three component system is undesirable because of the complexity of solving these equations and the fact that the relevant thermodynamic parameters are unknown, working with two components would be ideal. The component that best represents orthopyroxene in the orbicules is MgO since none of the other minerals in the orbicules contain any significant amount of MgO (except amphibole which forms later). FeO would be less acceptable as the representative component since it is found in magnetite, ilmenite, and plagioclase as well as the orthopyroxene and the later forming amphibole.

Solving ΔG for a system of more than one pure component can become very complex. The solution of one pure component (signified by the 'o' superscript) under mineral-fluid

equilibrium (i.e. $\Delta G = 0$) is (equation 6.5)

$$(\Delta \bar{G}_j^o)^{P,T} = (\Delta \bar{H}^o)^{1,298} + \int_{298}^T \Delta C_p^o dT - T \left[(\Delta \bar{S}^o)^{1,298} + \int_{298}^T \frac{\Delta C_p^o}{T} dT \right] + \int_1^P \Delta \bar{V}_s^o dP + \gamma_k RT \ln(f_k^o)^{P,T} = 0$$

where the subscript j is the phase, k is fluid, γ , stoichiometry of the component in the fluid, and f, fugacity. The first four terms include both fluid and solid states of the component in the phase while the fifth term is for solids only and the sixth for liquid. This equation can be solved for CaO in anorthite and it can be solved for MgO in enstatite.

Solving equation 6.5 using the Gibbs free energy formulation for just CaO should be attempted first. If this formulation does not produce the concentration profile as seen in the orbicule, then a two system set of partial differential equations should be done; one set for CaO representing plagioclase and the other set for MgO representing pyroxene providing that enough of the relevant parameters can be found in the literature.

6.5 Summary

The Volterra-Lotka equations, both modified and unmodified, demonstrate the type of oscillatory precipitation mechanism envisaged and that pattern formation can occur without a periodic external forcing of the intensive variables of the magmatic system as the magma cools and solidifies. Smooth changes in these variables from far-from-equilibrium conditions to near-to-equilibrium conditions will induce self-organization of chemical and mineral components in the magma in order to produce the oscillatory precipitation phenomena of orbicules and comb layering.

7.0 Summary

The multiphase, composite, hypersthene diorite pluton at Fisher Lake is one of less than a dozen in the world that contain comb textures found as both orbicules and comb layering.

Petrologic analyses revealed branching/budding orthopyroxene crystals, 0.8 cm long, in the innermost shell of a multi-shelled orbicule. Smaller, budding orthopyroxene crystals were found in subsequent shells and feather plagioclase were found throughout. Shells containing minerals with these non-equilibrium habits oscillate with shells having anhedral crystals of the same minerals. The net result is multi-layered orbicules having elongated, radially oriented, plagioclase and orthopyroxene shells that alternate with shells of anhedral hornblende, Fe-Ti oxides, plagioclase and orthopyroxene. The centre of the orbicules consists of cm-scale cores containing coarse-grained, subhedral, unoriented plagioclase, orthopyroxene and hornblende.

Many hundreds of electron microprobe analyses demonstrated that the elongated crystals of orthopyroxene and plagioclase are characterized by their gradual, chemical reverse zoning. The orthopyroxene gradually increase in Mg (and decrease in Fe) in the growth direction (away from the core) whereas plagioclase increase in Ca + Al (and decrease in Na + Si) close to the ends of the crystals. Gradual, chemical reverse zoning over the length of an entire branching crystal (cm scale) has not been previously reported.

In this thesis I propose a theory of autonomous growth that does not require fluctuation of intensive parameters to produce the orbicule shells. Intrusion of a diorite magma into a pre-existing crystal mush produces a boundary zone with a small temperature gradient between crystals (incipient cores) and the diorite magma. Crystal growth at this boundary is similar to that of a chill margin but at low ΔT , where precipitation takes place under conditions of low

nucleation and high growth rates. Hence the first few crystals that precipitate do so only on the interface or on xenoliths, producing comb layering or orbicules respectively. These first crystals grow quickly in branching, budding or feather crystal habits. Crystal morphology and mineralogy changes when rejected components such as H_2O and Fe^{+3} (and perhaps, an element that inhibits elongated crystal habits) are unable to diffuse away from the fast moving growth front. These build up in the boundary layer until precipitation changes to incorporate them, usually as anhedral hornblende and Fe-Ti oxides. Once these rejected elements have decreased, then elongated crystals begin growing again resulting in a change from anhedral back to radial shells. The branching/budding crystal habits, along with the reverse zoning, indicate that the comb textures formed under far-from-equilibrium conditions that occurred before widespread crystallization of the magma. Near-to-equilibrium crystallization conditions result in unzoned, euhedral, unoriented crystals.

Another of my contributions is to use this information to detail how Gibbs free energy can form gradual, chemical reverse zoning. After a small, but sudden drop in the temperature of a supersaturated magma, below the liquidus temperature, the first precipitate will be close to the liquid composition. Under conditions of constant temperature and high growth, crystal composition moves away from the liquid composition towards the equilibrium solid composition. This produces gradual reverse zoning. Gibbs free energy diagrams show that the highest ΔG 's occur when crystallization from the liquid takes place under near-to-equilibrium conditions. Thus, Gibbs free energy provides a driving force that pushes the composition of the crystal towards a near-to-equilibrium composition, away from the liquid composition that represented far-from-equilibrium conditions (a result of the sudden undercooling).

I present a mathematical formulation that is based on the Volterra-Lotka equations that produces the oscillatory precipitation of anhedral, hornblende-rich shells alternating with anhedral, Fe-Ti oxide-rich shells. Modification of the Volterra-Lotka equations, in adding two additional non-linear terms, generates a curve similar to that of the modal percentage of orthopyroxene across an entire orbicule, i.e. an oscillating line that gradually decreases in amplitude (comparable to a damped pendulum).

Orbicules and comb layering, while very uncommon, are found in most types of igneous rocks. This suggests that the formation of comb texture is not dependent on magma composition. I have undertaken to devise a formation mechanism that is independent of magma composition and of any condition particular to a magma such as viscosity and I believe that this has been achieved.

There are many theories in the literature as to how comb textures are formed, nearly one per paper published. I believe that the work done in this thesis will help to broaden the scope of many of these site specific formation theories and aid in figuring out how comb texture, in all magma compositions, forms.

Appendix A - Analytical Methods

I) Microprobe

The scanning electron microprobe at McGill University is a JXA 8900L WD/ED combined microanalyzer made by JEOL and was used over a period of two years in approximately eight different sessions. Polished thin sections were prepared by George Mrazek. The measurements were made using an accelerating voltage of 15.0 kV, 20 nA probe current and probe diameter of 10 - 20 μm for the silicates. Various silicate and oxide standards were provided by Glenn Poirier of McGill University for comparison to the minerals of Fisher Lake, i.e. plagioclase, orthopyroxene, clinopyroxene, amphibole, magnetite and ilmenite. Run times using wds mode (wavelength-dispersive X-ray spectrometry) varied from 2 min for a plagioclase analysis to 3 min for pyroxenes, olivine and oxides to 5 min for an amphibole. The samples were not run unless multiple runs of the standards were within a certain range of each other. This range was calculated from dividing the coefficient of variation by the standard deviation. This value must be less than 3 during the calibration runs on the standards if the samples were to be run. This value roughly corresponds to 0.03 wt % in the analyses.

Given the elongated morphology and the reverse chemical zoning in the minerals, many of the minerals were analysed by the "line analysis" where a start point and an end point were chosen along with a spacing (often on the order of 50 μm). Numerous analyses could be done along each line, the number depending on the distance between the two points. This procedure could be done because the minerals were elongated and indeed needed to be done in light of the gradual nature of the reverse zoning. The only problem with this procedure was that occasionally points were selected by the computer that the individual selection of points by eye would not have chosen, e.g. inclusions. This resulted in the exclusion of some analyses and the appearance of holes in the graphs.

II) Fe Titration Methodology

Fe titration experiments to determine the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratios were carried out on the seven host rock samples as well as the eight samples from the multi-shelled orbicule 95-OH-9. The analyses were carried out over the two day period of 14-15 April 1999. The set of samples contained one blank or one standard inserted after every five rock samples with each rock sample being done twice for a total of 36 samples consisting of three blanks, 3 standards of syenite rock sy-3, and two times 15 rock samples. The methodology was obtained from John Loop at the University of Ottawa, Geochemistry Lab who developed it from Whipple (1974) and Wilson (1955).

Methodology - Day 1

(1) Weigh approximately 0.2 g of each powdered sample and place into a numbered reaction flask. Record weight accurately along with the sample name and the flask number.

(2) Make up ammonium metavanadate solution (approx. 0.1 N) containing 5 g of ammonium metavanadate (record exact amount) in 55 ml of 50% sulphuric acid and 250 ml of deionized water.

(3) To each of the numbered flasks add 5 ml of the ammonium metavanadate solution and 10 ml of 37% hydrofluoric acid. Cap the flasks and place on a shaker table for the next 24 hours.

(4) Make two solutions to be used the next day; (a) ferrous ammonium sulphate solution (0.05 N) containing 9.8 g of ferrous ammonium sulphate (record exact amount), 20 ml of 50% sulphuric acid and 250 ml of deionized water, and (b) potassium dichromate solution (0.0125 N) containing 0.6130 g of potassium dichromate (record exact amount) in 500 ml of deionized water.

Methodology - Day 2

(5) Make up two more solutions; (a) phosphoric/sulphuric acid containing 100 ml of phosphoric acid in 400 ml of 50% sulphuric acid, and (b) saturated boric acid containing 100 g of boric acid dissolved

in 2 litres of deionized water.

(6) On 4 samples at a time and using 4 numbered 600 ml pyrex beakers, do the following:

- i) examine flasks for black or white residue and record
- ii) add 25 ml of boric acid to beaker
- iii) add ~20 ml of boric acid to flask
- iv) transfer contents of flask into beaker
- v) rinse flask with ~20 ml of boric acid and transfer to beaker
- vi) add 10 ml of phosphoric/sulphuric acid to beaker
- vii) accurately add 10 ml of ferrous ammonium sulphate solution to beaker
- viii) add 3 drops of the indicator barium diphenylamine p-sulphonic acid
- ix) add magnetic stirring rod.

(7) Place the beaker on the magnetic plate and titrate in the potassium dichromate solution until the contents of the beaker turn purple. Accurately record the amount of solution added.

Sources of Errors (Lalonde *et al.* 1998)

- (1) Iron oxidation during sample pulverization during sample preparation can increase Fe^{+3}/Fe by up to 2.5 times.
- (2) Sample contamination can occur by oxidizing (e.g. magnetite or hematite) or reducing (e.g. pyrite or pyrrhotite) phases present before sample preparation or added during (e.g. reduced metallic iron from the crushing apparatus), the preparation procedure.
- (3) Iron oxidation during the acid-attack decomposition when the flasks are not sealed.
- (4) There is a lack of reference standards for result comparisons and a lack of inter-laboratory standardization.

III) XRF

X-ray fluorescence was done in 1996 by Ron Hartree at University of Ottawa on a PW2400 sequential X-ray spectrometer, fully automated with Philips X-40 software and Hybred inter-element alpha coefficients calculated using Rousseau Software's 'CiLT' version 4.1 program.. The samples were powdered by the author while Mr. Hartree made the pucks needed to do the analyses.

IV) Neutron Activation (NAA)

Neutron activation analyses were done by Jean St-Pierre (aided by Greg Kennedy) at l'École Polytechnique, l'Université de Montréal in 1996 using their SLOWPOKE reactor. The powdered samples, weighing 1.5 g each, were irradiated for 2 hours and then placed in a gamma ray spectrometer to count the number and strength of the gamma rays. The standards used were BCR-1, AGV-1, GSP-1 and BE-N. Precision for the analyses is $\pm 5 \%$.

Appendix B - Pearce Element Ratio Plots

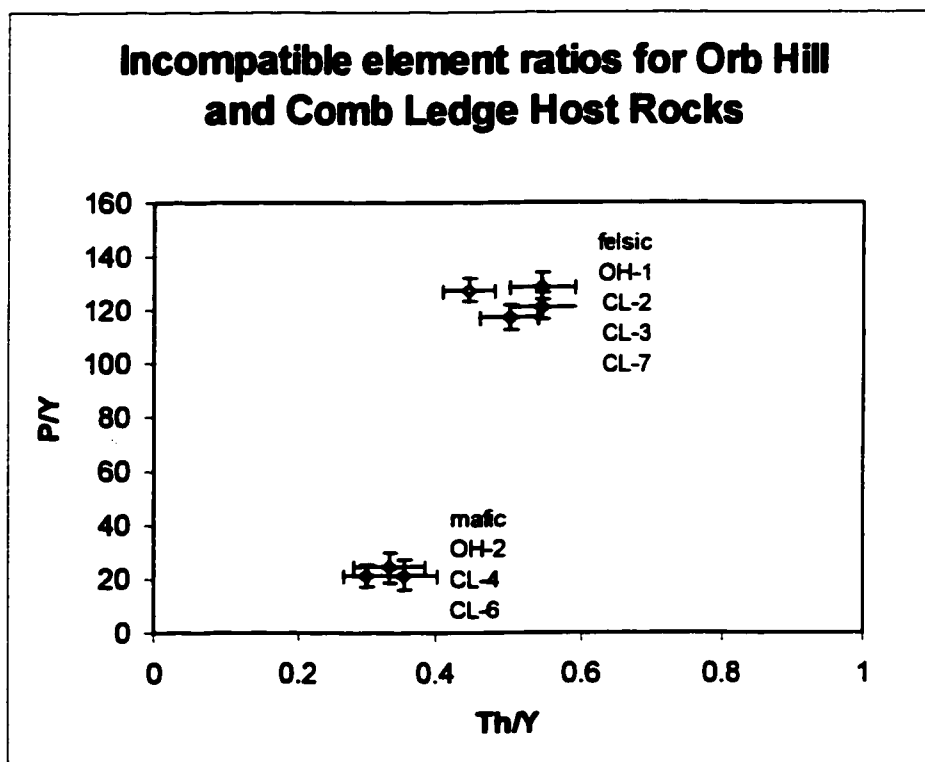
The search for three incompatible, conserved elements to be the basis of Pearce element plots was a long one. Graphs of the usual incompatible oxides, MnO, K₂O and P₂O₅, did not show the clustering that is indicative of incompatibility and nor did the three major oxides that remain fairly constant, Al₂O₃, K₂O and MnO. Various combinations of trace elements such as Y/Zr vs. Th/Zr, Y/Zr vs. P/Zr, Zr/Y vs. Th/Y, Th/Zr vs. P/Zr, Zr/Y vs. P/Y, Nd/Y vs. Zr/Y, Nd/Zr vs. Y/Zr, P/Nd vs. Y/Nd, Y/Zn vs. Ba/Zn, etc., also had scatter well beyond analytical error. One combination, Th/Y vs. P/Y, did produce two clusters of points; one of them interpreted to be the more mafic host rock and the other the felsic host rocks (fig B.1). The error bars on this graph were calculated for the ratios of $x/y = z$ using (Kretz, 1985).

$$\sigma_z^2 = \frac{1}{\mu_y^2} \sigma_x^2 + \frac{\mu_x^2}{\mu_y^4} \sigma_y^2$$

Since the trace elements could not produce a single group of points, some of the REE data obtained by INAA were used to try to find a conserved element. Only three REE's were felt to be present in high enough amounts to produce reliable results, i.e. Ce, La and Nd (table 3.4). The ratios Ce/Y vs P/Y, P/Y vs La/Y, P/Ce vs La/Ce and La/Nd vs P/Nd all produced two groupings with the same samples as seen in figure B.1 though the points were not as tightly clustered as that of P/Y vs Th/Y.

The presence of two clusters of points on various different diagrams of the trace and REE ratios suggests the possibility of two magmas, one felsic and the other mafic.

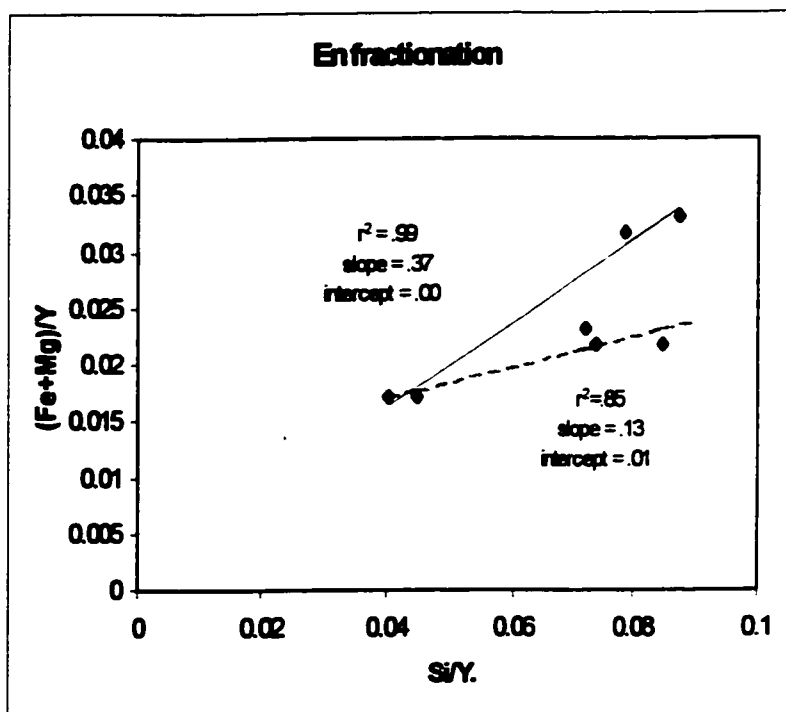
Fig. B.1 Graph of incompatible trace element ratios showing two groupings separating the more mafic host rocks from the more felsic.



Pearce element ratio plots (Pearce, 1970) were done using Y as the conserved element to see if these plots would produce trends that might support magma mixing or fractionation. A Pearce element ratio plot for enstatite fractionation shows two linear trends (fig B.2) however, the trends do not have a slope of one and the intercept is nearly zero. A Pearce plot for plagioclase fractionation shows a single linear trend but not at the expected slope equal to one for plagioclase fractionation and the intercept is at zero (fig B.3).

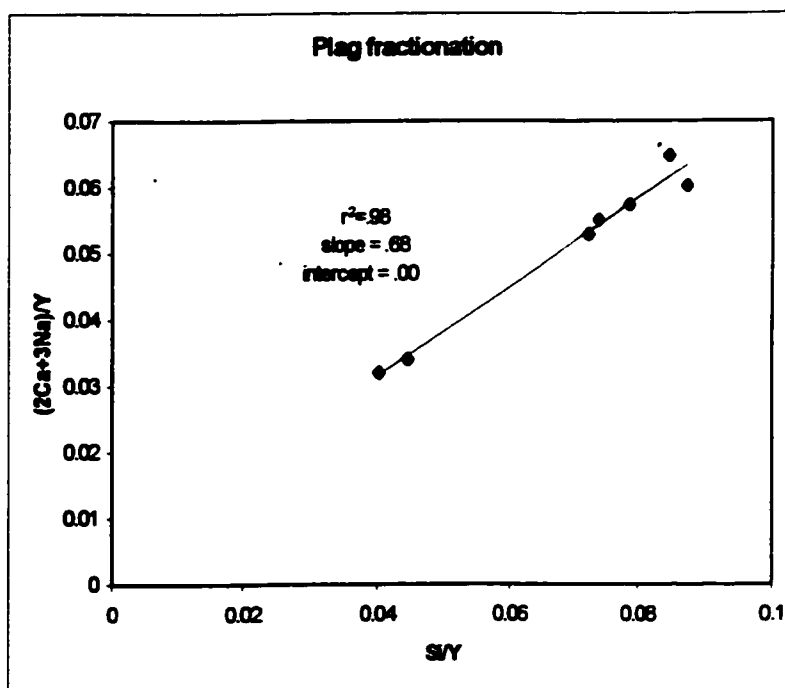
	Si/Y	(Fe+Mg)/Y
96-OH-2	0.040	0.017
96-CL-4	0.045	0.017
96-CL-7	0.087	0.033
96-CL-6	0.079	0.032
96-CL-3	0.072	0.023
96-CL-2	0.074	0.022
96-OH-1	0.085	0.022

Fig. B.2 Pearce plot for enstatite fractionation showing two lines with slopes not equal to one and intercepts very close to zero. The two most mafic samples occur at the intersection of the two lines while the three most felsic samples are on the dashed lower line.



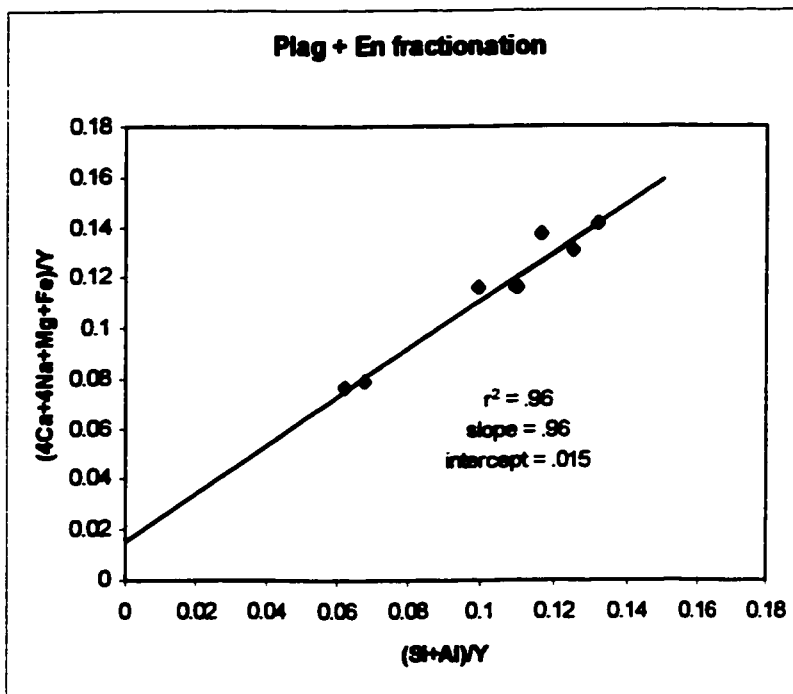
	Si/Y	(2Ca+3Na)/Y
96-OH-2	0.040	0.032
96-CL-4	0.045	0.034
96-CL-7	0.087	0.060
96-CL-6	0.079	0.057
96-CL-3	0.072	0.053
96-CL-2	0.074	0.055
96-OH-1	0.085	0.065

Fig. B.3 Pearce plot for plagioclase fractionation produces a high r^2 value but the slope is not equal to one and the intercept is within the error range of zero.



	(Si+Al)/Y	Mg+Fe/Y
96-OH-2	0.062	0.076
96-CL-4	0.068	0.079
96-CL-7	0.132	0.141
96-CL-6	0.116	0.137
96-CL-3	0.110	0.117
96-CL-2	0.110	0.117
96-OH-1	0.125	0.131

Fig. B.4 Pearce plot for plagioclase plus enstatite fractionation produces a significant line with slope equal to one and with a high r^2 value but the intercept is within error of a zero intercept.



A slope not equal to one for the enstatite or the plagioclase could mean that two minerals have been fractionated together. This is born out in figure B.4 where a slope of nearly one is attained from plagioclase plus enstatite fractionation. Unfortunately, this line has an intercept of zero. Pearce (1987) has demonstrated that intercepts of zero on these plots means that the trends are spurious and may indicate that the element used as the divisor is not constant. It is also possible that the components of hornblende may need to be accounted for in the y-axis ratio. The plots do still show the segregation of the data into two groupings with the more mafic samples at the lower part of the lines and the more felsic ones near the tops. This could be a reflection of the two groupings produced by the divisor in the conserved element plot except that sample 96-CL-6, the altered sample, which is present in the conserved element plot with the other mafic samples is grouped with the more felsic samples on the Pearce plots. Alteration may have

mobilized some of the trace and REE in the conserved plot or the major elements used in the Pearce plots and thus its precise location on any of these plots is suspect.

The lack of a valid trend on the Pearce plots suggests that fractionation may not account for the chemical compositions of the two groups of host rocks found in figure B.1

Appendix C - Mass Balance Calculations

While at The Johns Hopkins University in April 1992, the chemical composition of the orbicular host diorite from McKinney(1985) was entered into the SILMAN computer program (version 1) written by Mark Ghiorso in 1983. This program was designed to calculate the temperature a mineral would begin to precipitate along with its modal percentage under equilibrium conditions. Initial conditions entered into the program included $P = 1$ Kb and oxygen fugacity = FMQ or -7.25. Table C.1 shows the results.

Orb Diorite composition	T °C	log fO2	modal %	phase	wt% chemical components
SiO ₂	49.29	1300	-7.25	99.99	liquid
TiO ₂	1.03	1280	-7.45	99.99	liquid
Al ₂ O ₃	21.28	1280	-7.65	98.18	liquid
FeO	4.68		1.81	plag K.07Na2.37Ca16.03Al33.12Si48.41	
Fe ₂ O ₃	4.68	1240	-7.86	86.88	liquid
MnO	0.17		13.11	plag K.08Na2.70Ca15.46Al32.64Si49.12	
MgO	4.96	1220	-8.08	77.13	liquid
CaO	10.12		22.86	plag K.09Na3.02Ca14.90Al32.15Si49.84	
Na ₂ O	3.43	1200	-8.3	68.67	liquid
K ₂ O	0.19		31.32	plag K.10Na3.33Ca14.36Al31.70Si50.51	
P ₂ O ₅	0.16	1180	-8.53	53.25	liquid
LOI	0		43.64	plag K.11Na3.84Ca13.47Al30.94Si51.64	
			3.1	olivine Mg39.05Fe22.46Si38.49	
TOTAL	99.99	1160	-8.76	40.93	liquid
			53.08	plag K.13Na4.21Ca12.83Al30.38Si52.45	
			5.98	olivine Mg37.00Fe24.99Si38.02	
	1140	-9.01	32.88	liquid	
			58.94	plag K.15Na4.41Ca12.47Al30.08Si52.90	
			8.17	olivine Mg35.11Fe27.31Si37.58	
	1120	-9.25	0	liquid	
			71	plag K.25Na4.76Ca11.74Al29.45Si53.80	
			7.03	olivine Mg33.53Fe29.25Si37.22	
			4.6	opx Mg25.87Fe19.36Si54.76	
			6.93	cpx Ca20.82Mg13.71Fe12.37Si53.09	
			4.53	spinel Fe ⁺²	

Table C.1 Results of SILMAN. Explanations are in text.

The first two columns are the chemical composition of the orbicular host diorite. The third and fourth columns indicate the temperature entered in 20 ° increments and oxygen fugacity as calculated by SILMAN. The fifth, sixth and seventh columns show the resulting modes, phase and wt% chemical composition of the components in the mineral. At 1260 °C, the first precipitate appears; a Ca-rich (16.03 wt%) plagioclase with minor Na (2.37 wt%) and K (0.07 wt%). As temperature decreases, more plagioclase crystallizes until, at 1180 °C and about 44 modal %, olivine begins to precipitate. The amount of both plagioclase and olivine increases until 1120 °C when small amounts of orthopyroxene, clinopyroxene and spinel precipitate and no melt remains.

Ultimately, the diorite, under equilibrium conditions, crystallizes approximately 71 % plagioclase, 7 % olivine, 4.6 % orthopyroxene, 7 % clinopyroxene and 4.5 % spinel. These values are much different from that seen in the orbicules. Table 2.6 shows the modal analyses for an orbicule. Plagioclase averages only about 40 % while orthopyroxene can make up to 54 % of a shell (shell 3 - radial type). Olivine and clinopyroxene are absent from the orbicular shells while Fe-Ti oxides range from 2 - 21 %. Petrologic analysis of this orbicule also tells us that plagioclase and orthopyroxene precipitated simultaneously not one after the other as in the equilibrium cooled diorite. Thus the mineral modes and the order of appearance of the minerals during crystallization provides evidence for formation of the orbicules under far-from equilibrium conditions.

In order to provide further evidence that the orbicule host magma did not crystallize under equilibrium conditions, mass balance calculations was done on the innermost shell of an orbicule in order to determine if all the chemical components found in the magma were used in making the minerals found in that shell. XRF analyses on the complete shell package for orbicule 95-OH-3

were used as the most likely chemical composition of the magma from shell 1 precipitated, along with the mineral modes from shell 1. The explanation for table C.2 is as follows:

Section A)

- ast = the XRF chemical composition of the total shell package of orbicule 95-OH-3,
- plag2, opx1, amp3, bio, 3mt, 3 il = the average microprobe composition of particular crystals of plagioclase, orthopyroxene and amphibole with three crystals being used for magnetite and ilmenite

Section B)

- mol wt = molecular weight of the chemical components
- mol prop = molecular proportion of the component in the sample and is found as the weight % of the component in the sample divided by the molecular weight of the component

Section C)

- mineral modes for shell 1, the innermost shell of orbicule 95-OH-3 in weight percentage and decimal format

Section D)

- ast = bulk is the bulk composition of the melt from section B
- b-p = bulk - plagioclase
- b-p-o = bulk - plagioclase - orthopyroxene
- b-p-o-m = bulk - plagioclase - orthopyroxene - magnetite
- b-p-o-m-i = bulk - plagioclase - orthopyroxene - magnetite - ilmenite
- b-p-o-m-i-a = bulk - plagioclase - orthopyroxene - magnetite - ilmenite - amphibole
- b-p-o-m-i-a-bio = bulk - plagioclase - orthopyroxene - magnetite - ilmenite - amphibole - biotite

Table C.2**A)**

	ast	plag2	opx1	3 mt	3 il	amp3	bio
SiO ₂	46.63	48.09	53.48	0.22	0.01	45.21	38.21
TiO ₂	0.141	—	0.12	0.19	48.21	1.94	2.38
Al ₂ O ₃	19.24	32.94	1.17	0.58	0.03	9.33	15.53
Fe ₂ O ₃	1.641	0.17	—	57.31	—	—	—
FeO	8.586	—	19.63	28.65	48.03	13.23	9.67
MnO	0.1532	—	0.42	0.02	0.70	0.18	0.03
MgO	12.657	0.01	25.40	0.14	1.61	15.24	19.19
CaO	9.657	16.24	0.38	0.04	0.02	9.92	0.17
Na ₂ O	0.81	2.22	0.05	—	—	1.40	0.43
K ₂ O	0.093	0.04	0.04	—	—	0.48	8.45

B)

		ast	plag2	opx1	3 mt	3 il	amp3	bio
	mol wt	mol prop	mol prop	mol prop	mol prop	mol prop	mol prop	mol prop wt%/mwt
SiO ₂	60.0843	0.7761	0.8005	0.8901	0.0036	0.0002	0.7525	0.635907
TiO ₂	79.8988	0.0018	—	0.0015	0.0024	0.6034	0.0243	0.02979
Al ₂ O ₃	101.9613	0.1887	0.3231	0.0114	0.0057	0.0003	0.0915	0.152313
Fe ₂ O ₃	159.6922	0.0103	0.0011	—	0.3589	—	—	—
FeO	72.8464	0.1179	—	0.2695	0.3933	0.6594	0.1817	0.132759
MnO	70.9374	0.0022	—	0.0060	0.0003	0.0098	0.0025	0.001
MgO	40.3044	0.3140	0.0002	0.6302	0.0035	0.0400	0.3782	0.476127
CaO	56.0794	0.1722	0.2896	0.0068	0.0007	0.0004	0.1769	0.0031
Na ₂ O	61.9789	0.0131	0.0359	0.0009	—	—	0.0225	0.007
K ₂ O	94.1960	0.0010	0.0004	0.0004	—	—	0.0051	0.08971

C)

	modes	
plag	39.5	0.395
opx	46.1	0.461
amp	7.2	0.072
mt	2.5	0.025
il	2.5	0.025
bio	2.2	0.022
total	100	1

D)

	ast= bulk	b-p	b-p-o	b-p-o-m	b-p-o-m-i	b-p-o-m	b-p-o-m	wt %
						-i-a	-i-a-bio	left over
SiO ₂	0.7761	0.4599	0.0496	0.4599	0.0495	-0.0047	-0.0187	
TiO ₂	0.0018	—	0.0011	0.0010	-0.0141	-0.0158	-0.0165	
Al ₂ O ₃	0.1887	0.0611	0.0558	0.0557	0.0557	0.0491	0.0457	4.66
Fe ₂ O ₃	0.0103	0.0099	—	0.0009	—	—	—	0.14
FeO	0.1179	—	-0.0064	-0.0162	-0.0327	-0.0458	-0.0487	
MnO	0.0022	—	-0.0006	-0.0006	-0.0009	-0.0010	-0.0010	
MgO	0.3140	0.3139	0.0234	0.0233	0.0223	-0.0049	-0.0154	
CaO	0.1722	0.0578	0.0547	0.0546	0.0546	0.0419	0.0418	2.35
Na ₂ O	0.0131	-0.0011	-0.0015	—	—	-0.0031	-0.0033	
K ₂ O	0.0010	0.0008	0.0006	—	—	0.0003	-0.0017	

The calculations show that after precipitation of shell 1, there is Al_2O_3 (4.66 wt%), Fe_2O_3 (0.14 wt%) and CaO (2.35 wt %). These are components found in plagioclase. The negative values in these calculations represent deficits of the components suggesting that diffusion of components from surrounding magma was necessary for growth. The extra unprecipitated plagioclase components corresponds to the extra plagioclase found in the SILMAN run. SILMAN showed that this magma should crystallize 70 % plagioclase but in reality only crystallizes 40 %. Even when the mineral modes are varied by up to 10 %, extra Al_2O_3 and CaO remains.

The extra plagioclase components found in the mass balance calculations shows that while the necessary plagioclase components are present, something is preventing them from precipitating as plagioclase. Therefore, both the SILMAN and the mass balance calculations suggest that the orbicular host magma crystallized under far-from-equilibrium conditions.

Appendix D - Program Code for Computer Modelling

D.1 The Volterra-Lotka Equations

The Volterra-Lotka equations (eq. 6.2) are outlined in section 6.2. The code below was entered into Matlab Student Version 5. Percent signs indicate comments that the program ignores. The program, “dlotka” calls a subroutine or function called “dlot” that encodes the two first-order ordinary differential equations as finite difference equations in matrix format. The “dlot” function is included as comments within the “dlotka” code but is run as a separate program. This code produces the graph seen in figure 6.2. Explanation of the variables are found in sec. 6.2.

```
% dlotka - a program to solve the Lotka-Volterra equations
% using Matlab function ODE45 to solve the 1st order ODE's
clear; help dlotka;
pause
clc
t0=0;
tfinal=16000;
y0=[4 2]';
tfinal=tfinal*(1+eps);
tstep=100;
[T,Y]=ode45('dlot',[t0:tstep:tfinal],y0);
z=[T,Y];
plot(T,Y(:,1)),title('Volterra-Lotka Equation - Time History')
    xlabel('time'), ylabel('x');
    ymin = 0; ymax = 6; xmin = 0; xmax = 16000;
    pscale = [xmin xmax ymin ymax];
    axis(pscale);
pause
%plot(Y(:,1),Y(:,2)), title('Volterra-Lotka Equation - Phase Plane Plot');
%xlabel('x'), ylabel('y');
%pause
```

```

clc
disp('end')
%
%function yp = dlot(t,y)
%LOTKA Lotka-Volterra predator-prey model.
%
% Copyright (c) 1984-96 by The MathWorks, Inc.
% $Revision: 5.1 $ $Date: 1996/01/01 22:07:57 $
%
%yp = diag([1 - y(2), -1 + y(1)])*y;

```

D. 2 The Modified Volterra-Lotka Equations

The modified Volterra-Lotka equations (eq. 6.3) are outlined in section 6.3. The code below was again entered into Matlab Student Version 5. This program, “dmodlotka” calls function called “dmodlot” that encodes the two first-order ordinary differential equations as finite difference equations in matrix format. The “dmodlot” function is included as comments within the “dmodlotka” code but is run as a separate program. The “dmodlotka” code below produced the lower graph seen in figure 6.4. Explanation of the variables are found in sec.6.3. The code for the curve seen in figure 6.5 (Phase Plane plot) is included as comments below the code that produced the Time History plot (fig. 6.4).

```

% dmodlotka - a program to solve the modified Lotka-Volterra equations
% from Cook (1994) using Matlab function ODE45 to solve the 1st order ODE's
clear; help dmodlotka;
pause
clc
t0=0;
tfinal=70;
y0=[2.9 .1]';
tfinal=tfinal*(1+eps);
tstep=.1;

```

```

[T,Y]=ode45('dmodlot',[t0:tstep:tfinal],y0);
z=[T,Y];
plot(T,Y(:,1)),title('Modified Volterra-Lotka Equation - Time History')
    xlabel('time'), ylabel('x');
    ymin = 0; ymax = 4; xmin = 0; xmax = 35;
    pscale = [xmin xmax ymin ymax];
    axis(pscale);
%plot(Y(:,1),Y(:,2)), title('Modified Volterra-Lotka Equation - Phase Plane Plot');
%xlabel('x'), ylabel('y');
%pause
clc
disp('end')
%
% function yp = dmodlot(t,y)
% LOTKA Lotka-Volterra predator-prey model.
%
% yp = diag([1 - y(2)-.25*y(1), -1 + y(1)-.01*(1-y(2)-.25*y(1))])*y;

```

Appendix E - Mineral Formulae and Calculations

Mineral formulae were calculated for crystals discussed in sections 3.4, 3.5 and 3.6 and those found in figures 3.6, 3.7, 3.8, 3.9 and 3.12. The nomenclature of the pyroxenes is based on Morimoto (1989) and that of the amphiboles is from Leake *et al.* (1997).

Opx1 - orbicule (95-OH-3) enstatite					Opx4 - orbicule (95-OH-3) enstatite				
	location in xtal	%En	%Fs	%Wo zoning		location in xtal	%En	%Fs	%Wo zoning
fig 3.6a	initial growth	66.1	33.3	0.6	fig 3.7a	initial growth	66.8	32.5	0.7
	final growth	73.6	26	0.4 reverse		final growth	73	26.5	0.5 reverse
fig 3.6b	centre	68.9	30.1	0.7	fig 3.7b	centre	69.6	29.8	0.6
	edge	67.2	32	0.8 normal		edge	67.6	31.7	0.7 normal
fig 3.6c	centre	68	29	3	fig 3.7c	centre	69.2	30.4	0.4
	edge	67.7	31.4	1 normal		edge	67.4	31.9	0.7 normal
fig 3.6d	centre	70.5	28.8	0.7					
	edge	70.2	29.3	0.5 normal					
Opx1 - orbicule (95-OH-6) enstatite					Opx2 - orbicule (95-OH-6) enstatite				
	location in xtal	%En	%Fs	%Wo zoning		location in xtal	%En	%Fs	%Wo zoning
fig 3.8a	initial growth	71.2	28.2	0.6	fig 3.9a	initial growth	71.5	28.1	0.4
	final growth	73.5	25.9	0.7 reverse		final growth	74.1	25.3	0.6 reverse
fig 3.8b	average	71.3	28.2	0.5 none	fig 3.9b	centre	71.8	27.8	0.4
fig 3.8c	centre	72.6	26.9	0.5		edge	70.8	28.7	0.4 oscillatory
	edge	71.5	28	0.5 none	fig 3.9c	centre	73.5	26.2	0.4
fig 3.8d	centre	71.1	28.3	0.6		edge	72.9	26.7	0.4 none
	edge	71.5	28.1	0.5 reverse					
Cpx1&2 - comb host (96-CL-4) augite					Cpx1,2,3 - comb layering (95-CL-2) augite				
%En	42.3				%En	42.8			
%Fs	13.1				%Fs	12.0			
%Wo	44.6				%Wo	45.3			
Opx1 - felsic host rock (96-OH-1) enstatite					Opx1,2,3,4,5 - comb layering (95-CL-2) enstatite				
%En	59.8				%En	70.3			
%Fs	38.8				%Fs	28.6			
%Wo	1.4				%Wo	1.1			
Opx2 - felsic host rock (96-OH-1) enstatite									
%En	59.8				%En	59.9			
%Fs	38.8				%Fs	38.4			
%Wo	1.4				%Wo	1.7			

Amp3 - core (95-OH-3) edenite		Amp4 - inner shell (95-OH-3) magnesianhornblende		Hm1 - comb layering (95-CL-2) pargasite	
Si	6.5	Si	6.9	Si	6.4
Al	1.5	Al	1.1	Al	1.6
Al	0.3	Al	0.3	Al	0.3
Ti+1	0.2	Ti+1	0.1	Ti+1	0.3
Cr+3	0.0	Cr+3	0.0	Cr+3	0.0
Fe+3	0.0	Fe+3	0.1	Fe+3	0.0
Fe+2	1.5	Fe+2	1.3	Fe+2	1.4
Mg+2	3.1	Mg+2	3.6	Mg+2	3.2
Ni+2	0.0	Ni+2	0.0	Ni+2	0.0
Mn+2	0.0	Mn+2	0.0	Mn+2	0.0
Ca+2	1.8	Ca+2	1.7	Ca+2	1.8
Na+1	0.4	Na+1	0.3	Na+1	0.6
K+1	0.1	K+1	0.1	K+1	0.1
Amp2 - felsic host (96-OH-1) edenite		Amp2,3,4 - comb host rock (96-CL-4) edenite		Amp1,2 - mafic host (96-OH-2) edenite	
Si	6.5	Si	6.5	Si	6.5
Al	1.5	Al	1.5	Al	1.5
Al	0.3	Al	0.3	Al	0.3
Ti+1	0.2	Ti+1	0.2	Ti+1	0.2
Cr+3	0.0	Cr+3	0.0	Cr+3	0.0
Fe+3	0.2	Fe+3	0.2	Fe+3	0.1
Fe+2	1.6	Fe+2	1.4	Fe+2	1.5
Mg+2	3.1	Mg+2	3.1	Mg+2	3.1
Ni+2	0.0	Ni+2	0.0	Ni+2	0.0
Mn+2	0.0	Mn+2	0.0	Mn+2	0.0
Ca+2	1.8	Ca+2	1.8	Ca+2	1.8
Na+1	0.4	Na+1	0.4	Na+1	0.4
K+1	0.1	K+1	0.1	K+1	0.1

The calculations for the pyroxene formulae are based on Klein & Hurlbot (1985).
 Explanations for each column are found below the table.

1	2	3	4	5	6	7	8	9	10	11	12
analysis #	wt %	mol wt	mol prop	# cations	# oxygens	cations on 6 O basis	cation	assignment			
SiO ₂	51.974	60.084	0.865	0.865	1.730	1.926	Si	1.926			
Al ₂ O ₃	1.919	101.961	0.019	0.038	0.056	0.084	Al	0.074	2		
							Al	0.010		MgO	0.61
TiO ₂	0.133	79.879	0.002	0.002	0.003	0.004	Ti	0.004		FeO	0.28
FeO	20.228	71.846	0.282	0.282	0.282	0.627	Fe	0.627		CaO	0.01
MnO	0.473	70.937	0.007	0.007	0.007	0.015	Mn	0.015		total	0.90
MgO	24.483	40.304	0.607	0.607	0.607	1.353	Mg	1.353		%En	67.69
CaO	0.473	56.077	0.008	0.008	0.008	0.019	Ca	0.019		%Fs	31.37
Na ₂ O	0.013	61.979	0.000	0.000	0.000	0.001	Na	0.001		%Wo	0.94
K ₂ O	0.019	94.196	0.000	0.000	0.000	0.001	K	0.001	2.029		
Total	99.715				2.694						

column explanation of example calculation done in Excel

- 1 chemical components
- 2 chemical analysis in wt%
- 3 molar weight
- 4 wt%/mol wt = molar proportion
- 5 # of cations from column 1 * mol prop
- 6 # of oxygens from column 1 * mol prop
- 7 since pyroxene formula has 6 oxygens -> 6/total # of oxygens from bottom of column 6
- 8 cation from column 1
- 9 Si and enough Al to equal 2 - the ideal # of Si atoms
left over Al is assigned to M1 and M2 sites
- 10 total # of cations in T site (=2) and in M1 and M2 (~2)
- 11 chemical components for calculating En, Fs, Wo
- 12 chemical analysis in mole proportion (column 4) are totaled and recalculated to 100

The calculations for amphibole formulae are based on Klein & Hurlbot (1985) and Leake et al (1997). Explanations of the columns are found on the following page.

Hornblende general formula $(Ca,Na)_{2-3}(Mg,Fe,Al)_5Si_6(Si,Al)_2O_{22}(OH)_2 \rightarrow 15-16$ cations

1	2	3	4	5	6	7	8	9	10	11
	wt%	mol wt	mol prop	# cations	# oxygens	cations on 23 O basis	cation	assignment	sums	
SiO ₂	44.202	60.084	0.736	0.736	1.471	6.552	Si	6.552		
Al ₂ O ₃	10.369	101.961	0.102	0.203	0.305	1.811	Al	1.448	8	
							Al	0.363		8.363
TiO ₂	2.173	79.879	0.027	0.027	0.054	0.242	Ti+1	0.242		
Cr ₂ O ₃	0.011	151.990	0.000	0.000	0.000	0.001	Cr+3	0.001		
Fe ₂ O ₃		159.692					Fe+3			
FeO	12.367	71.846	0.172	0.172	0.172	1.533	Fe+2	1.533		
MgO	14.051	40.304	0.349	0.349	0.349	3.105	Mg+2	3.105		
NiO	0.009	74.689	0.000	0.000	0.000	0.001	Ni+2	0.001		
MnO	0.146	70.937	0.002	0.002	0.002	0.018	Mn+2	0.018	5.264	13.264
CaO	11.089	56.077	0.198	0.198	0.198	1.761	Ca+2	1.761		15.025
Na ₂ O	1.563	61.979	0.025	0.050	0.025	0.449	Na+1	0.449		15.474
K ₂ O	0.532	94.196	0.006	0.011	0.006	0.101	K+1	0.101	2.311	
Total	96.511				2.583	15.575		15.575		15.575

8	12	13	14	15	16	17	18	19	20
cation	renormalized	calculating Fe				check new stoichiometry			
Si	6.541	sum R4+ *2	13.082 Si			Si	6.541		
Al	1.808	sum R3+ *1.5	2.714 Al, Cr			Al	1.459	8	
Al		sum R2+	6.408 Fe,Mg,Ni,Mn,Ca			Al	0.349		8.349
Ti+1	0.242	sum R+1 *5	0.791 Ti,Na,K			Ti+1	0.242		
Cr+3	0.001					Cr+3	0.001		
Fe+3		sum Ox	22.994			Fe+3	0.011		
Fe+2	1.530	(23-sumOx)*2	0.011			Fe+2	1.519		
Mg+2	3.100	Fe+3 =	0.011			Mg+2	3.100		
Ni+2	0.001	FeT-Fe+3=	1.519			Ni+2	0.001		
Mn+2	0.018	Fe+2 =	1.519			Mn+2	0.018		13.242
Ca+2	1.758	15				Ca+2	1.758		15
Na+1	0.448					Na+1	0.448		15.448
K+1	0.100					K+1	0.100	15.549	

Requirement summations for calcic amphiboles (Leake *et al.* 1997)

$$\Sigma \text{Si} < 8$$

$$\Sigma \text{Si} + \text{Al} > 8$$

$$\Sigma \text{Si} + \text{Al} + \text{Ti} + \text{Cr} + \text{Fe} + \text{Mg} + \text{Ni} + \text{Mn} > 13$$

$$\Sigma \text{Si} + \text{Al} + \text{Ti} + \text{Cr} + \text{Fe} + \text{Mg} + \text{Ni} + \text{Mn} + \text{Ca} < 15$$

$$\Sigma \text{Si} + \text{Al} + \text{Ti} + \text{Cr} + \text{Fe} + \text{Mg} + \text{Ni} + \text{Mn} + \text{Ca} + \text{Na} > 15$$

$$\Sigma \text{Si} + \text{Al} + \text{Ti} + \text{Cr} + \text{Fe} + \text{Mg} + \text{Ni} + \text{Mn} + \text{Ca} + \text{Na} + \text{K} < 16$$

column	explanation of example calculation done in Excel
1	chemical components
2	chemical analyses in wt%
3	molar weight
4	molar proportion = wt% / mol wt
5	# of cations from column 1 * mol prop
6	# of oxygens from column 1 * mol prop
7	since amphiboles analysed by electron microprobe (no H ₂ O data) - calculation is based on 23 oxygens -> 23 / total # of oxygens from bottom of column 6
8	cations with charges from column 1
9	Si and enough Al to equal 8 - the ideal value left over Al is assigned to the other sites
10	total # of cations in three sites
11	various summations to check requirements for calcic amphiboles as explained at the top of this page
12	since the ΣCa is over 15 (the only requirement broken), then assignment values must be renormalized such that the $\Sigma \text{Ca} = 15$
13	$\Sigma \text{Ca} = 15$
14	since electron microprobe does not measure Fe ⁺³ , it can be calculated e.g. $\Sigma \text{R}^4 * 2$ is the sum of cations with valence = + 4. Sum Ox = sum of all the values from the four Σ 's (in this example ≈ 22.99). The amount needed to make 23 is assigned to Fe ⁺³ . This amount is subtracted from the Fe _T to find Fe ⁺² .
15	values from the calculations described in column 14
16	the cations that are included in each summation
17	cations - same as in column 8
18	check the new stoichiometries to ensure that the requirements are still filled
19	check of two sums
20	check of summation requirements for calcic amphibole

Appendix F - Index for CD Containing Photos and Data

To list all of the microprobe data used in this thesis would definitely have made this thesis a valuable doorstop. So to alleviate this condition, the data has been put onto a CD. The CD is formatted for PC's.

On this CD can be found three directories

- 1) ch1and2 - contains the text, with colour photos *in situ* for chapters 1 and 2 in WordPerfect 9
- 2) photos - contains just the photos in either .jpg format or .cpt (Corel Photo Paint)
- 3) microprobe - contains the microprobe data for crystals whose mineral formula was calculated and listed in the text. The data are in Microsoft Excel 2000 format. The file names include the mineral (e.g. amp, opx, cpx) and the rock that the mineral came from (e.g. sample 95-OH-3).

The data files are listed below.

amp_95CL2 (Comb Ledge comb layering)
amp_96CL4 (Comb Ledge host rock)
amp_96OH1 (Orb Hill felsic host rock)
amp_96OH2 (Orb Hill mafic host rock)
cpx_95CL2
cpx_96CL4
opx_95CL2
opx_95OH6 (Orb Hill orbicule)
opx_96OH1
opx1_95OH3 (Orb Hill orbicule)
opx4_95OH3

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