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DENDRITIC MAGNETITE AND ILMENITE IN 590 Ma GRENVILLE DIKES NEAR OTTER LAKE, QUEBEC, CANADA

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Abstract

Northwest of Ottawa, near Otter Lake, Quebec, branching crystals of magnetite occur in gabbro dikes ranging in width from 60 m to 0.2 m, but highly complex dendrites (500 to 40 μm across) were found only in nine dikes, 2 to 0.2 m wide. Cooling rates in these small dikes are estimated at 0.6 to 60°C per hour. Complex dendrites are characterized by three intersecting primary plates (parallel to {100}), terminated by secondary arrowhead plates, bound by {111} planes. Many small projections have grown out from the primary plates, thereby isolating small cylindrical volumes of melt. Rare octahedra, ~ 20 μm across, and clusters of octahedra also are present. Ilmenite dendrites consist of two or more thin interconnected plates. Dendritic growth of magnetite and ilmenite is attributed to gradients of temperature, resulting from a large heat of crystallization, and of concentration in the melt about growing crystals, and to a tendency for the formation and persistence of {111} planes (magnetite) and {0001} planes (ilmenite).

Keywords: Grenville gabbro, magnetite, ilmenite, SEM, dendrite, crystal growth, heat of crystallization, diffusion, interface instability, Otter Lake, Quebec.

Sommaire

Au nord-ouest d'Ottawa, près du lac Otter, au Québec, des filons de gabbro allant de 60 m à 0.2 m en largeur contiennent des cristaux dendritiques de magnétite, mais les morphologies les plus complexes (cristaux de 500 à 40 μm de diamètre) ont été trouvées dans neuf filons seulement, entre 2 et 0.2 m en largeur. Le taux de refroidissement des ces filons plus étroits auraient été entre 0.6 et 60°C par heure. Les dendrites complexes contiennent trois plaques primaires dont l'intersection est parallèle à {100}; elles sont terminées par des plaques en flèche, à faces {111}. Plusieurs petites projections émanent des plaques primaires, isolant de petits volumes cylindriques de bain fondu. Sont aussi présents de rares octaèdres ~20 μm de diamètre et des groupes d'octaèdres. Les dendrites d'ilménite sont faites de deux (au moins) minces plaques interconnectées. La croissance de magnétite et d'ilménite dendritiques serait due aux gradients de température qui résultent de la chaleur dégagée lors de la cristallisation, et de concentration dans le bain fondu autour des cristaux en train de croître, et à la tendance qu'ils ont de former et de conserver les faces parallèles aux plans {111} (magnétite) et {0001} (ilménite).

(Traduit par la Rédaction)

Mots-clés: filons de gabbro, essaim de Grenville, magnétite, ilménite, microscopie électronique à balayage, dendrite, croissance cristalline, chaleur de cristallisation, diffusion, instabilité de l'interface, lac Otter, Québec.

Introduction

The term *dendrite* was introduced by J.D. Dana (1878) to describe branching crystals, and this term is now widely used (Shewmon 1969, Chan *et al.* 1976, Langer 1980, Galenko & Zhuravlev 1994). In Mineralogy, where the term *skeletal* has been used more frequently, branching crystals in mafic and ultramafic rock were described by Schneiderhöhn (1952, magnetite), Preston (1966, augite), Rice *et al.* (1971, pseudobrookite), Bryan (1972, olivine, pyroxene, magnetite), Greenbaum (1977, chromite), Ramdohr (1980, magnetite), Petersen (1985, feldspar), Shore (1996, olivine, chromian spinel), Roeder *et al.* (2001, chromian spinel), and Kontak *et al.* (2002, clinopyroxene, Fe–Ti oxides), and examples of dendritic magnetite and ilmenite were illustrated by Haggerty (1976). Also, dendritic crystals of some minerals were produced experimentally by Lofgren (1974, plagioclase), Donaldson (1976, olivine), Walker *et al.* (1976, olivine, pyroxene, chromian spinel),

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Nakamura (1984, diopside, anorthite), and Swanson & Fenn (1986, quartz). In the past few decades, the crystallization of dendrites, including snowflakes, has attracted attention in the field of Physics, where progress was summarized by Glicksman & Marsh (1993).

In a previous study of the Grenville swarm of gabbro dikes (Kretz *et al.* 1985), data were reported on the microstructure of the gabbro, especially on the shape, size, and spatial distribution of crystals of olivine, calcic pyroxene, pigeonite, and plagioclase. The focus at present is on the shape of Ti-bearing magnetite, especially on crystals found in a relatively narrow (2 m wide) dike. From many random sections through these crystals, it is possible to construct an idealized three-dimensional dendrite, and this model can be used to propose a history of growth, beginning with a nucleus, which is presumed to be an octahedron, to a fully grown crystal. Associated dendrite-like crystals of ilmenite are also examined and compared with magnetite. The formation of these crystals is then considered in terms of local gradients of temperature and concentration, and the attachment of atoms to crystal surfaces.

Dendrite Defined

Three kinds of dendrites, all crystallized from a melt, are illustrated in Figure 1. Obviously, the meaning of the word *dendrite* can differ, depending on the shape of the crystal or cluster of crystals being examined.

Figure 1A (type I) shows the shape of the terminal region of a crystal of the organic compound $NC–(CH_2)_2–CN$, referred to as SCN, which crystallized from a melt of the same composition at 0.1°C below the melting temperature. The upward-advancing tip (in the figure) is a paraboloid of revolution, and secondary branches formed during growth. The shape resembles that of the arms of some snowflakes. This is the kind of dendrite that has attracted the attention of several physicists, who, beginning with G.P. Ivantsov in 1947, have built a theory of dendrite growth that was reviewed by Müeller-Krumbhaar (1987) and Glicksman & Marsh (1993). In this theory, variables that were initially proposed or progressively brought into the picture are the production and flow of the latent heat of crystallization, diffusion of atoms in the melt (where crystal and melt do not have the same composition), attachment of atoms to the crystal surface, and interfacial energy. Some progress has been achieved in predicting experimentally determined growth-rates, but the formation of the secondary branches is not well understood.

The dendrite shown in Figure 1B (type II) is a digitized image of altered olivine in a gabbro sill from Munro Township, Ontario, in the Archean Abitibi Subprovince, studied by Fowler *et al.* (1989). Because different branches have very different orientations, it is possible that this was not a single crystal prior to alteration, but a cluster. Similarly shaped forms that occur on surfaces of limestone and are composed of Mn oxide have in the past been referred to as "mineral dendrites", and some of these were studied by Chopard *et al.* (1991). Both Fowler *et al.* and Chopard *et al.* have shown that the forms they examined have fractal or near-fractal properties, and in both studies, the forms could be satisfactorily simulated by diffusion-limited aggregation, *i.e.,* by a process in which the diffusion of atoms is the principal determinant. In these studies and in another by Vicsek (1984), some restrictions were introduced to the simulations to produce anisotropy and other effects.

Dendrites of the kind shown in Figure 1C (type III) are described in the present report. They are distinctly

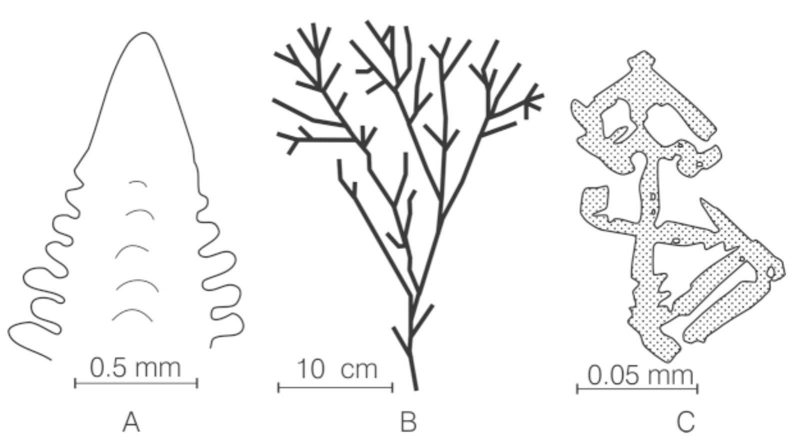


FIG. 1. Examples of dendrites. A. Organic compound, SCN (from Glicksman & Marsh 1993). B. Olivine (altered) in a gabbro sill (Fowler *et al.* 1989, Thériault & Fowler 1995). C. Magnetite in Grenville gabbro (dike E3), present study.

three-dimensional objects that are partially bound by low-index faces.

For crystals that are not polyhedral, a complex terminology exists, as compiled by Lofgren (1974) and Donaldson (1976). At present, any branching crystal or cluster of connected crystals is referred to as a dendrite.

The Grenville Gabbro

The Grenville swarm of gabbro dikes, dated at 590×10^6 years (Kamo *et al.* 1995), extends from north of Montreal to Georgian Bay, a distance of 700 km (Stockwell *et al.* 1970). Northwest of Ottawa, the swarm is comprised of more than 40 dikes, 1 to 100 m wide, and many smaller dikes (Kretz *et al.* 1985). The principal minerals are Ca pyroxene (~40%), plagioclase (~55%), magnetite (~5%) and ilmenite (~0.5%); other minerals locally present are olivine, pigeonite, hornblende, K-feldspar, and quartz. In two dikes, the composition of magnetite was found to be 62 mol.% ulvöspinel; the ilmenite is close to $FeTiO_3$.

Commonly, tablets of plagioclase are partially embedded in larger anhedral crystals of calcic pyroxene, whereas magnetite crystals range from equant to dendritic. In large dikes, magnetite crystals are mainly equidimensional, but dendritic crystals have formed locally (Fig. 2). Most of the dikes of the swarm are 30 to 40 m wide, and in one of these (I 2), magnetite crystals similar to that shown in Figure 2 occur from the center of the dike to points 0.3 m from the contacts, as crystal size decreases from 1 to 0.1 mm. The most complex dendrites were found in nine dikes, 0.2 to 2 m wide [E3, F2 (group of six), F3, F9, Appendix 1]. These consist of calcic pyroxene and plagioclase, 1 mm in largest dimension, and about 30% of groundmass, in which magnetite and ilmenite dendrites have crystallized. In dikes narrower than 0.2 m, and in the narrow (0.2 m) margins of larger dikes (in contact with country rock), magnetite occurs as very small compact crystals.

Regarding the depth of emplacement and cooling rates, Sabourin (1965) found members of the swarm 2 km horizontally from Lower Ordovician Beekmantown Group dolomite, which was deposited on Precambrian basement at approximately 490 Ma (Johnson *et al.* 1992). Assuming a mean rate of erosion of 2 mm/100 years, the gabbro as presently exposed crystallized at a depth of 2 km. A country-rock temperature of 100°C was therefore adopted for rate-of-cooling calculations for dikes of different width, as listed in Table 1.

Dike E3 (2 m wide), referred to above, was selected for detailed study, and all of the SEM results presented in Figure 3 are from a single thin-section, cut from a fragment that was centrally positioned in the dike. This dike is exposed alongside the Picanoc road, 10.7 km from Otter Lake Village. Another dike, 3 m wide, is located 60 m to the southwest. The two dikes cut amphibolite, granite, and minor skarn.

TABLE 1. TENDENCY TO DENDRITIC SHAPE OF MAGNETITE CRYSTALS IN CENTERS OF DIKES OF GRENVILLE GABBRO, AND ESTIMATES OF COOLING RATE*

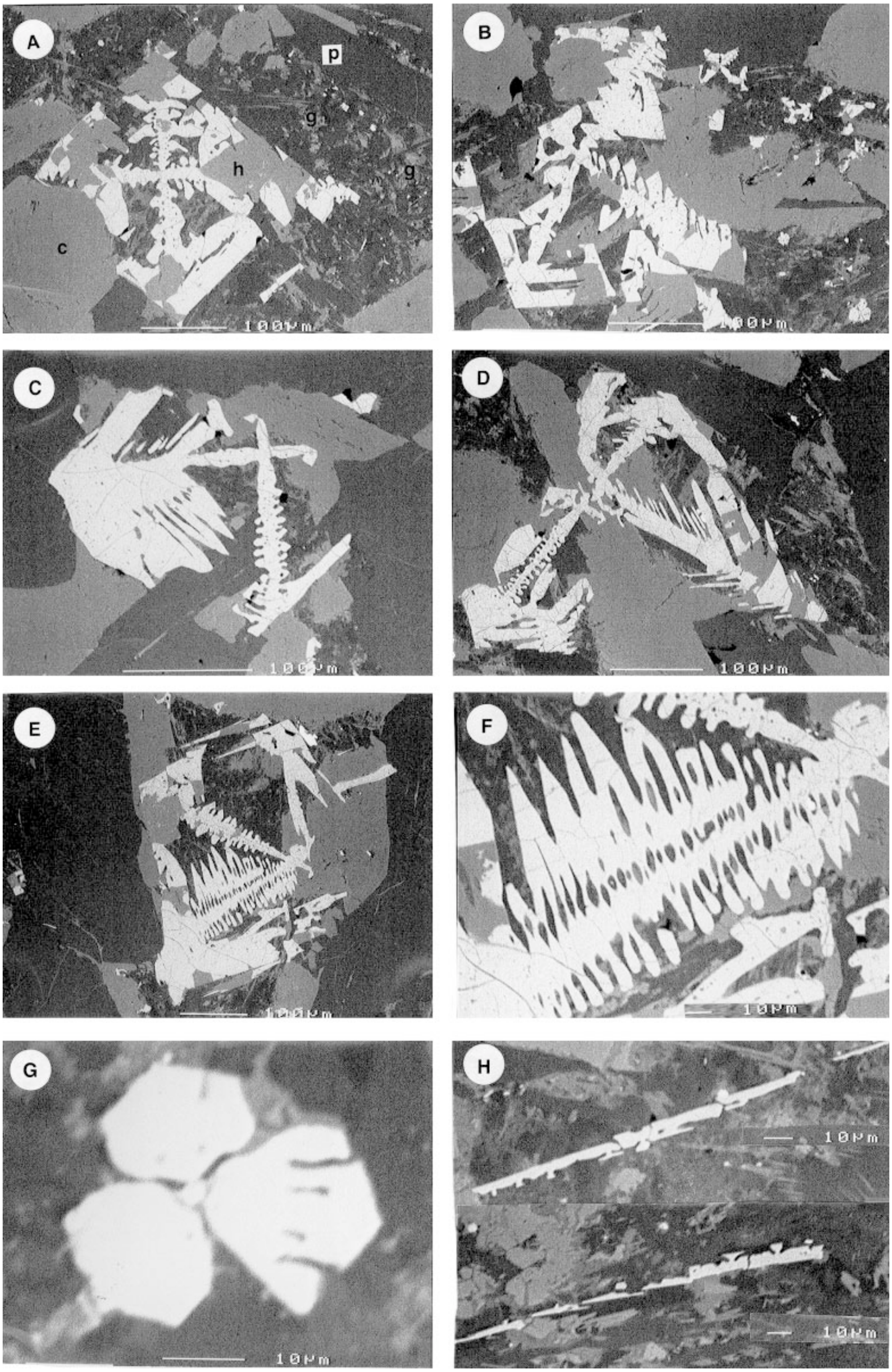
Dike width m	Mean cooling-rate °C /day	°C /hour	Tendency to dendrite development
>40	<0.037		weak to moderate (F1, Fig. 2)
30	0.065	0.003	mainly moderate (nine dikes)
2	15	0.63	moderate to strong (E3, Fig. 3)
0.5 to 0.2		10 to 61	moderate to strong (dikes F2)
<0.2		>61	mainly poor

* Cooling rates are based on equations of Jaeger (1957); see Kretz *et al.* (1985) for details.

Magnetite

The structure of magnetite can be viewed as alternating layers of oxygen atoms and of iron and titanium atoms, lying parallel to {111} (Lindsley 1976). In general, the most common form for magnetite is the octa-

FIG. 2. Dendritic crystal of magnetite and associated non-dendritic crystals of calcic pyroxene and plagioclase in gabbro dike F1, 62 m wide (from Kretz *et al.* 1985).


A
p
g
h
g
c
100µm
B
100µm
C
100µm
D
100µm
E
100µm
F
10µm
G
10µm
H
10µm
10µm

hedron, {111} (cubes are rare), and hence {111}–melt interfaces are expected to dominate over other orientations.

A few of the many magnetite dendrites that were found in dike E3 are illustrated in Figures 3A to E. The dominant pattern is a cross, which varies in diameter from 500 to 40 μm. They resemble some dendrites from basalt, illustrated by Haggerty (1976, p. Hg-107). Also present are rare clusters of crystals (Fig. 3B, bottom right) to be described below.

From random sections through many crystals, a three-dimensional dendrite of magnetite can be constructed, as follows. Beginning with an octahedron, suppose that continued growth occurred by the rapid advance of the *margins* of each of the eight triangular faces, as perceived by Vogel (1921) (see Buckley 1951, p. 491), resulting in the rapid advance into the melt of each of the twelve *edges*, to produce three intersecting plates, which in Figure 4A are shown as three incompletely drawn planes. These are the "arms" of the cross (Fig. 3) and are referred to as the *primary* plates. After the edges of each plate had advanced a certain distance into the melt, *secondary* plates formed, to produce the "arrowheads" (shown well in Figure 3B, bottom left) and smaller secondary projections. The result is a partially hollow crystal (Fig. 4B). A section through this model, normal to crystallographic a_3, and above the a_1a_2, plane, appears in Figure 4C, which can be compared with Figures 3A to 3D. In Figure 4C, the primary plates are vertical with respect to the page, and the {111} faces of the central octahedron and the secondary (arrowhead) plates are inclined at 54° to the page.

In Figure 4C, the primary plates are bound by planes parallel to {100}, but these could initially have been corrugated, with ridges and valleys parallel to the lines drawn on the {100} planes in Figure 4A. This possibility is shown in Figure 4D, which is a section through the model dendrite to include a_3 and the line [110], *i.e.*, a line bisecting a_1 and a_2. In this section, all planes are vertical to the page, and the primary plate is bound on both sides by alternating (111) and $(\bar{1}\bar{1}1)$ planes, intersecting at lines normal to the page. Steps of this kind on dendrites of KCl were described by Wilcox (1977b).

Much variation exists in the shape of the small secondary projections that have grown out at intervals from the primary plates, resulting in the entrapment of bodies of silicate melt (Figs. 3A–E). In Figure 5, for example, which is an enlargement of a part of Figure 3C, note that all of the projections on the right of the primary plate are, at least in part, bound by {111} interfaces, whereas the projections on the left are almost entirely bound by irrational, smoothly curved, planes. These and other secondary projections have possibly grown out from ridges of the kind postulated in Figure 4D, and most are presumably plate-like in shape (*e.g.*, Fig. 3D, center). Others (Fig. 3C, upper left) are, in section, not "connected" to the adjacent primary plate, as would be expected if, in three dimensions, they are elongate or lath-like projections.

Sections through magnetite dendrites in which the "arms" are at angles greater than or less than 90° (Fig. 3E) are obviously oblique sections. Other asymmetries result from impingement with neighboring crystals of calcic pyroxene or plagioclase. In large dikes (Fig. 2), the two silicates and magnetite locally crystallized simultaneously, until all melt was consumed, but in dike E3, the material which in Figure 3A is designated as groundmass (g) was evidently a residual quasi-glass, subsequently altered to a fine-grained aggregate of minerals. Here, evidently, some crystallization ceased, not because of impingement, but because of atom immobility.

A random section through an octahedron produces a four-sided or six-sided polygon, and several very small outlines of this kind (7 to 26 μm in diameter) accompany the dendrites described above (Fig. 6). These small crystals have evidently nucleated and grown late in the interval of magnetite crystallization. In addition, some curious three-lobed forms are present, one of which is visible in Figure 3B (bottom right corner) and another is shown magnified in Figure 3G. They are interpreted as sections through clusters of octahedra. Beginning with a central octahedron, imagine the growth of a new octahedron at each of the six apices, as in Figure 4E. The growth of a new crystal from the apex of a crystal of the same or similar kind has been reported for other minerals (Grigor'ev 1965, Roeder *et al.* 2001). A section through the model cluster of Figure 4E, parallel to and slightly below one of the {111} faces of the central octahedron, will intersect three of the satellite octahedra, as in Figure 3G. Each of these satellites has not grown from the center outward, but from one apex, as in Figure 4F, where embayments are present similar to those in Figure 3G, right lobe.

FIG. 3. SEM images of Ti-bearing magnetite and ilmenite in dike E3. A to E. Magnetite dendrites (white); the associated minerals are calcic pyroxene (gray, c) and plagioclase (black, p); magnetite is locally altered to titanite (light gray, h), and fine-grained (patchy) groundmass is labeled g. F. Enlarged view of center of Figure E. G. Cluster of magnetite crystals. H. Ilmenite (white) associated with above magnetite.

ILMENITE

Ilmenite commonly occurs as stout hexagonal plates bounded by {1010}, {1121}, and {0001} faces. The {0001}(basal) faces are parallel to repeated layers of Fe, O, and Ti atoms (Lindsley 1976), and these faces are expected to dominate.

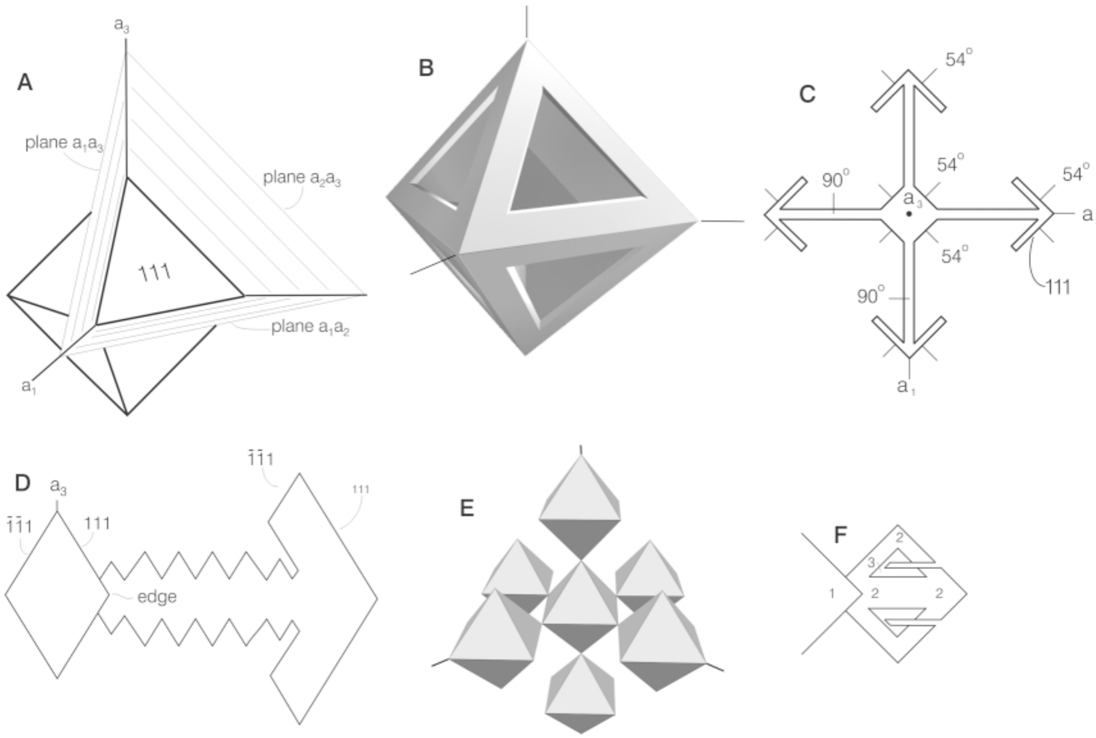


FIG. 4. A. Proposal for the formation of primary plates, shown as three incompletely drawn planes. B. Model magnetite dendrite. C. Horizontal section through model dendrite. D. Section through model dendrite in which all {111} planes are vertical. E. Idealized cluster of magnetite octahedra. F. Schematic growth of one satellite of a cluster, to produce groundmass embayments (*cf*. Fig. 3G).

In dike E3, ilmenite occurs as thin plates (Fig. 3H) that have evidently resulted from an advance of prismatic {1010} and pyramidal {1121} faces that was rapid relative to advance of {0001}. In addition, projections (presumably cylindrical in shape) have locally grown out from basal {0001} planes. Three such projections, spaced at 10 μm, are well shown in Figure 3H (upper half, left segment), and larger, more closely spaced projections are not uncommon (Fig. 7). After advancing some distance into the melt, a new plate crystallized on the peaks of some projections, as shown in Figure 3H. Continued growth of these satellite plates, leaving behind the parent crystal, explains why ilmenite, in section, commonly appears as a number of "disconnected" plates, slightly offset from each other (Fig. 3H). Ilmenite crystals of this kind were illustrated by Haggerty (1976, p. Hg-107) and have been found in Kilauea Iki lava lake (P.L. Roeder, pers. commun.). Gorodetsky & Saratovkin (1958) referred to clusters of interconnected and parallel thin plates as "foliated dendrites".

DISCUSSION

Consider a one-component crystal (c) – melt (m) system at constant pressure, for example,

$$Fe_3O_4 \text{ (melt)} \rightleftharpoons Fe_3O_4 \text{ (crystal)} \qquad (1).$$

At equilibrium, the molar Gibbs energy (G) of melt and crystal must be equal,

$$G^{Mgt(m)} = G^{Mgt(c)} \qquad (2)$$

and

$$\Delta G = \Delta H - T\Delta S = 0 \qquad (3).$$

ΔH is the heat released (negative) as one mole of melt crystallizes, and values of this "heat of crystallization" for some minerals are listed in Table 2. Crystallization is a change that results in a local *decrease* in entropy (ΔS), but this is overcompensated by the release of heat

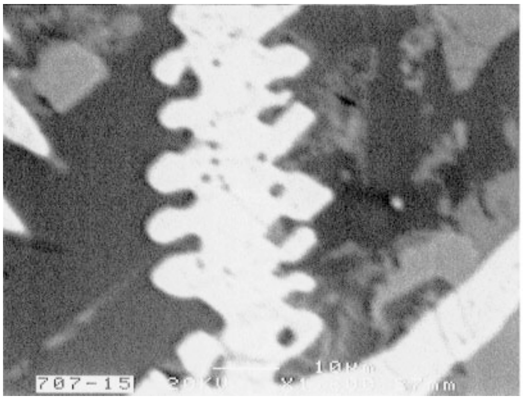


FIG. 5. Enlarged view of secondary projections shown in Figure 3C; note variation in shape of projections. Scale bar: 10 μm.

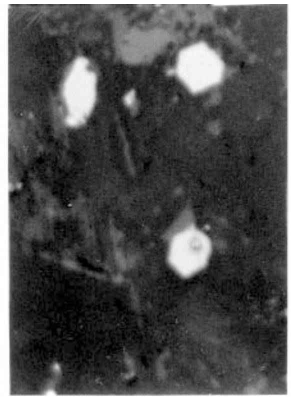


FIG. 6. Sections through small crystals of magnetite, associated with dendrites shown in Figure 3. Diameter of hexagons is 10 μm.

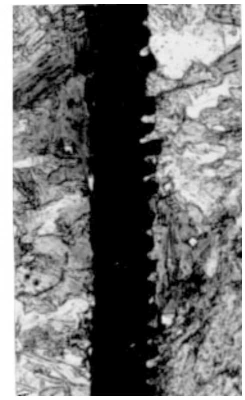


FIG. 7. Projections from a (0001) surface of ilmenite in dike E3, transmitted light; width of crystal is 60 μm.

to the surroundings, resulting in an overall *increase* in entropy, as required by the Second Law. In (3), T is the (absolute) temperature at which crystal and melt are at equilibrium, and with a decrease in temperature by an amount ΔT, departure from equilibrium can be discussed in terms of ΔT or ΔG.

Yoder & Tilley (1962) and others have shown experimentally that under certain conditions, the crystallization of magnetite, calcic pyroxene, and plagioclase from a melt of gabbro composition occurs simultaneously and continuously over a range of temperature (100 to 200°C), in agreement with microstructural data obtained from natural basalt and gabbro. For crystal–melt equilibrium in multicomponent systems, there are, in place of (2), equations of the kind

$$\mu^{m}{}_{mgt} = \mu^{Mgt}{}_{mgt} \quad (4)$$

$$\mu^{m}{}_{usp} = \mu^{Mgt}{}_{usp} \quad (5)$$

where μ denotes chemical potential, and mgt and usp stand for *components* Fe_3O_4 and Fe_2TiO_4. Other equations must be satisfied for other components and phases. Crystallization now requires that the chemical potential of a component in the crystal be less than that in the melt; departures from equilibrium can now be discussed in terms of ΔT and differences in chemical potential.

The first step in crystallization is the formation of a nucleus, which, according to the classical theory of nucleation, requires that an energy barrier, identified as interfacial energy, must be overcome, and that is why ΔT in many systems is a few degrees or more, and not infinitesimally small. The next step, crystal growth, is frequently observed to occur even where ΔT is very small, and in general the rate of advance of crystal faces increases with increasing ΔT or ΔG (Kirkpatrick 1975).

It is commonly assumed that dendritic crystals form only where ΔT is large, and terms *near-equilibrium crystallization* (producing compact, commonly polyhedral crystals at small ΔT) and *far-from-equilibrium crystallization* (producing dendrites and spherulites at larger ΔT) have been used. Support for this view is found, for example, in basalt pillows (Bryan 1972) and in experimental work, *e.g.,* by Lofgren (1974, plagioclase) and Donaldson (1976, olivine).

With regard to Grenville dikes, the conspicuous decrease in crystal size from center to margins in large dikes (Gray 1970, Kretz *et al.* 1985), including magnetite, referred to above, can certainly be related to an increase (center to margin) in the rate of cooling, resulting in an increase in the rate of nucleation. But given that mafic melts crystallize with ease, the amount of undercooling (ΔT) in margins of large dikes and in small

TABLE 2. HEAT OF CRYSTALLIZATION OF SOME MINERALS*

	T_m °C	−ΔH /J mol^{-1}	/J cm^{-3}
Plagioclase			
Albite ($NaAlSi_3O_8$)	1118	59 280	590
Anorthite ($CaAl_2Si_2O_8$)	1557	81 000	804
Calcic pyroxene ($CaMgSi_2O_6$)	1391	77 400	1170
Ilmenite ($Fe^{2+}TiO_3$)	1370	90 670	2860
Magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$)	1597	138 070	3100

* T_m : melting temperature; ΔH: heat of crystallization. Data taken from Robie *et al.* (1978).

dikes, as crystallization progressed, need not have been large. In addition, as no simple relation exists between deduced rate of cooling and tendency toward a dendritic geometry for magnetite (Table 1), other variables must have played a role. For example, it is unclear why moderately formed dendrites crystallized in the center of dike F2 (Fig. 1) that is 62 m wide and cooled at 6°C/year, but not in the centers of some dikes 30 m wide, where cooling rates are estimated at 24°C/year. Nevertheless, confinement of the most complex or "best" dendrites to some narrow dikes (0–2 to 2 m wide) does suggest that rate of cooling (or ΔT) was an important variable.

Regarding the mechanism of dendrite crystallization, consider first the possible role of the heat of crystallization (Table 2). As crystal growth occurred, and the crystal–melt interface advanced into the melt, heat was created at the interface to raise the temperature of the melt in the vicinity. The nature of the temperature field surrounding a polyhedral crystal was calculated by McLachlan & Carlson (1952) and is illustrated (in two dimensions) in Figure 8. Notice that margins of faces will encounter a lower temperature than the center of faces (larger ΔT and ΔG), and growth at these places is expected to be enhanced, to produce conditions favorable for dendrite formation (Vogel 1921). The large ΔH for magnetite and ilmenite, relative to that for associated silicates (Table 2), might explain why silicates in the dikes did not form dendrites. Where the composition of a growing crystal differs from that of the melt, atoms that are concentrated in the crystal must move by diffusion toward the crystal–melt interface, whereas

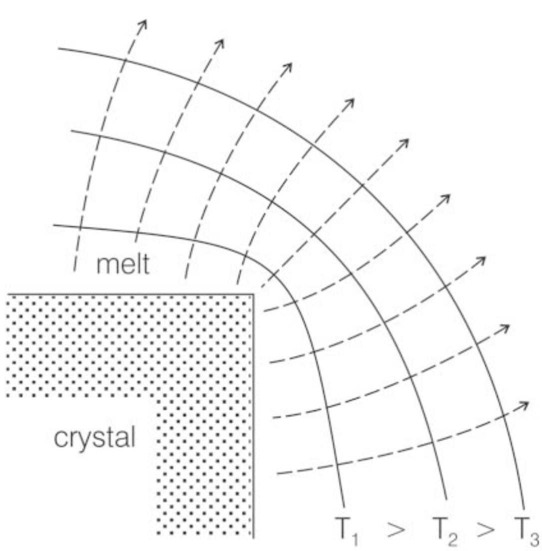


FIG. 8. Two-dimensional temperature field about a growing crystal, from McLachlan & Carlson (1952).

other atoms, not accommodated by the crystal, must be displaced in the opposite direction. Thus, approaching the magnetite–melt interface from the melt, negative concentration gradients of Fe and Ti, and positive gradients of Na, K, Ca, Al, Mg, and Si must have existed during growth, although the magnitude of these gradients need not have been large. The gradients would resemble the temperature gradients shown in Figure 8 (Berg 1938, Wilcox 1977a). Now the margins of faces encounter higher concentrations of magnetite and ulvöspinel components (larger contrasts in chemical potential compared with those at face centers, *i.e.*, larger ΔG) to again favor a more rapid advance of face margins.

The crystallization of magnetite dendrites can be discussed in added detail by referring to Figure 9, which is a two-dimensional analogue of a magnetite dendrite, in successive stages of growth. The advance of crystal faces by the spreading of growth layers from points of two-dimensional nucleation (Volmer method) or emerging screw dislocations (Frank method) is well established (Bunn & Emmett 1949, Christian 1975, De Yoreo *et al.* 2001); it is here proposed that the layer-growth mechanism, with centers of growth occurring at many points (Volmer method) enabled the margins of faces to advance more rapidly than face centers, to produce the primary arms (Fig. 9). Note that in three dimensions, the primary arms are plates, not spines as in Figure 1A, and the terminals of these plates, prior to the crystallization of the arrowhead plates, could have been parabolic, rather than sharp as in Figure 9.

A proposal for the formation of the small secondary arms also appears in Figure 9. In this figure, the rapid advance of the outer *margins* of faces numbered 1 to 4, determined by temperature or concentration gradients (as above), gives rise to secondary plates, whereas the abandonment of {111} planes in favor of irrational, smooth surfaces (far right) can lead to the entrapment of small cylindrical volumes of melt, which is a common feature of the magnetite dendrites (Figs. 3, 5). But in general, the mode of formation of the small secondary projections remains unclear. For example, in Figure 5, what determined the spacing of the projections, and why have {111} faces formed on some but not on others? Also puzzling is the creation of clusters of octahedra (Fig. 3G), in place of the more common dendrites.

The growth of ilmenite crystals (Fig. 3H), including the formation of thin plates from what was presumably a more equidimensional crystal, was possibly also determined by temperature or concentration gradients in the melt. The projections from {0001}, and the immediately adjacent depressions (Fig. 3H, bottom, far right), as well as the more closely spaced projections (Fig. 7), which resemble cellular interfaces in metals, both on the scale of 10 to 25 μm, are precisely the features that are explained in large part by the theory of interface instability, as outlined by Sekerka (1969) and Coriell &

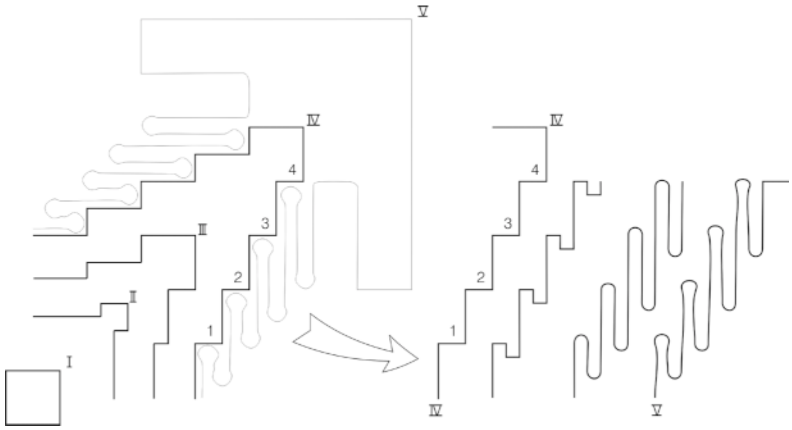


FIG. 9. Two-dimensional analogue of a magnetite dendrite, showing proposed stages of growth, I to V, and the formation of secondary projections, resulting in the isolation of pods of melt.

McFadden (1993). In this theory, slight protuberances, arising by chance on a crystal surface, become enlarged, and thereby compete with spreading growth-layers, which tend to maintain the surface planar (Sekerka 1969). Evidently (Fig. 3H), some projections advanced into the melt until a point was reached when the growth of a new plate at those sites became favorable.

Several authors, including Dowty (1980) and Kirkpatrick (1981), have pointed out that because the transfer of heat in a melt greatly exceeds that of atoms, the rate of crystal growth in multicomponent melts is determined by diffusion rather than the flow of the heat of crystallization. But Burke (1965) has argued that transformation rates can be controlled by two or more processes, acting in unison, and in the present study, all of heat flow, diffusion, and interface kinetics are referred to, and no one mechanism is identified as having "controlled" the formation of dendrites or their rate of growth.

Perhaps the most remarkable aspect of the crystallization of magnetite and ilmenite dendrites is a change of shape with time. This growth behavior is in sharp contrast with that of plagioclase, which commonly produces crystals of near-constant habit, as determined for example by Sempels (1978). Thus dendrites, including snowflakes, tell us that under certain conditions, crystal growth is extremely sensitive to the environment and is, in detail, a complex process.

CONCLUSIONS

This note concludes with a proposal for the growth history of a magnetite dendrite of the kind illustrated in Figure 3A, based on data presented above.

1) Following the emplacement of a volume of gabbroic melt (with 5% suspended crystals of calcic pyroxene and plagioclase) at 1200°C, cooling commenced, resulting from loss of heat to the cold country-rock. Clusters of Fe, Ti and O atoms now appeared in the melt, and disappeared, continuously (the embryo of the classical theory of nucleation) until by chance, some reached a size of 1 nm, and became nuclei. The shape of the nucleus was an octahedron, the shape of lowest interfacial energy for a given volume, *i.e.*, the equilibrium shape.

2) As temperature declined, atoms of Fe, Ti, and O were constantly added to and removed from the octahedron faces, with a net addition, resulting in crystal growth. Advance of the faces occurred by the formation (at dislocation sites) and spreading of growth layers (Frank method), until octahedra 10 μm in dimension were produced. Growth and the nucleation of new crystals occurred simultaneously, as did the continued growth of crystals of calcic pyroxene and plagioclase.

3) With further cooling, gradients of temperature and concentration about growing octahedra became more pronounced, causing the margins of faces to advance into the melt more rapidly than face centers. Growth now occurred by the nucleation of layers on face margins, *i.e.*, by the Volmer method. Consequently, the twelve edges advanced into the melt, to produce plates which were bound by planes nearly parallel to {100}, but in detail consisted of ridges and valleys, resulting in a tendency for low-energy {111} faces to form in place of {100}.

4) Once the principal plates had advanced into the melt a distance of 200 μm, secondary (arrowhead) plates began to grow out from the terminations of the primary

plates, and these were bound by {111} interfaces. Simultaneously, small secondary projections were growing out at intervals along the primary plates, these having various shapes from tabular, to lath-like, to irregular, whereas terminations varied from faceted to round.

5) Finally, as temperature reached 1000°C, further growth was terminated by immobility of diffusing species, and the remaining melt solidified.

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APPENDIX 1. LOCATION OF DIKES OF GRENVILLE GABBRO REFERRED TO, OTTER LAKE AREA, QUEBEC

Reference	Sample	Width in m	Location	
E3	707	2	45° 56.3'N	76° 28.7'W
F1	1351	62	59.2	03.4
F2	1394 – 2 to 7	0.5 to 0.2	59.7	02.8
F3	1349 B	0.2	59.3	01.3
F9	1393-2	1.2	52.4	03.9
I2	1387	38	43.3	12.3