

STRATABOUND AXINITE IN THE WEELI WOLLI FORMATION AND ITS OCCURRENCE IN RELATED DOLERITES

by R. Davy and M. Pryce*

ABSTRACT

A member of the axinite group (a boron-bearing aluminosilicate series) has been identified in strata-bound layers in iron-formation of the Weeli Wolli Formation and is also present in intercalated dolerite sills.

The axinite member in both iron-formation and dolerite is strictly the mineral ferroaxinite, though that in the dolerite contains a slightly greater proportion of manganese. The habits are also different: axinite in the iron-formation is idiomorphic and contains abundant inclusions whereas that in the dolerite is porphyroblastic-irregular, with no inclusions. In both cases it is incorporated into the body of the rock rather than occurring as discrete veins.

It is inferred that axinite formed during burial metamorphism at temperatures of about 250°C and a pressure of 200-500 MPa. The origin of the boron is less certain; it has probably been integral to the dolerite magma, being carried to the sediments by fumarolic activity, or, less likely, it may have been derived from pre-existing detrital tourmaline within the sediment.

INTRODUCTION

During logging of a diamond-drill core through the Weeli Wolli Formation and its associated dolerite sills, grey-white 'rhombic' grains were noted in specific bands. The character and position of these grains initially suggested pseudomorphs of former evaporite minerals (Fig. 1). However, microscope and X-ray diffraction studies showed that the mineral was in the axinite group, a boron-bearing Ca-Fe-Mg-Mn aluminosilicate of general formula $\text{HCa}_2(\text{Mn,Fe})\text{BA}_2\text{Si}_4\text{O}_{15}\text{OH}$.

Though axinite had been recognized previously in the dolerite sills of this core (de Laeter and others, 1974) this is the first time that it has been seen as an apparently integral part of an iron-formation. A literature search has shown that, though axinite is well known in metamorphic contact deposits or in hydrothermal veins, it has been described rarely as a rock-forming mineral in a strata-bound environment. Opportunity has been taken, therefore, to document this occurrence and to compare the axinites in the dolerite with those in the iron-formation.

LOCATION OF THE CORE

The Weeli Wolli Formation is one of eight constituent formations of the (Precambrian) Hamersley Group in the northwest of Western Australia. The formation's regional characteristics have been described by Trendall and Blockley (1970). The Weeli



GSWA 21018

10mm

Figure 1. Photograph of core at 175.6 m showing randomly oriented axinite grains concentrated in specific bands.

*Government Chemical Laboratories.

Wolli Formation is considered to have an age of 2.3 Ga (minimum) based on a Rb-Sr model age on a sill within the formation (Trendail, 1983). The Weeli Wolli Formation is less well exposed than other Hamersley Group formations, and DDH WW1 was drilled for stratigraphic purposes at 22°17'30"S and 118°24'00"E, about 44 km south of Wittenoom. The hole, angled at 60° to the horizontal, was collared in surficial material and passed through weathered 'dolerite and clay'. Recognizable iron-formation was reached at 27.1 m, and fresh iron-formation at 38.7 m, (down-hole distances from the collar to the position in the core). The hole terminated at a core length of 272.3 m, remaining in Weeli Wolli Formation throughout. A simplified log of the core, showing the location of the samples, is given in Figure 2. Axinite is reported from the two lower sills (in the cored hole) and from the metamorphosed sedimentary rocks between them. These sills are subsequently referred to as 'upper' and 'lower' respectively.

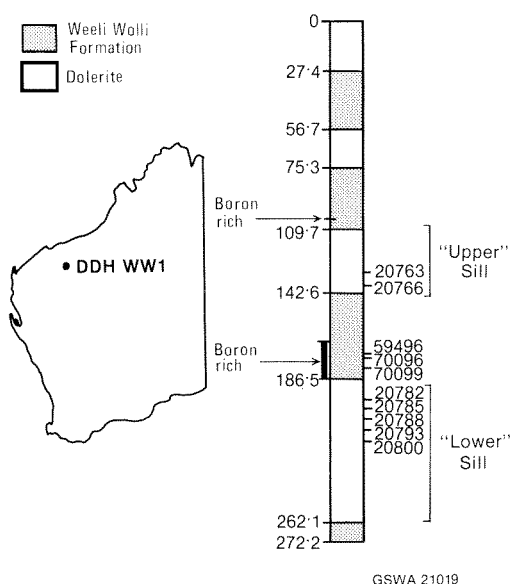


Figure 2. Log of Weeli Wolli core showing position of samples with analyzed axinite.

The sedimentary rocks hosting the axinite are commonly referred to as black and green shales with cherty bands. However they contain on average in excess of 15% Fe and could be called iron-formation following recent definitions of Kimberley (1978).

METHODS OF STUDY

Thin and polished sections of various parts of the core were prepared and studied. Some core samples which had been described by de Laeter and others (1974) were also included.

Identification of axinite was made optically and confirmed by X-ray diffraction analysis. The compositions of both axinite and epidote were determined by

electron-probe microanalysis at the CSIRO Division of Mineralogy, Floreat, W. A. Boron and H₂O were not determined except in bulk samples of core. The small amount of each sample available and the nature of the axinite precluded separation of the latter by heavy liquids.

DISTRIBUTION IN THE CORE

Traces of axinite were found in the upper dolerite. It is present in stratigraphically contained bands at specific positions within the iron-formation, especially at 175.6 m and 178.0 m, and is present as a common accessory mineral within the lower dolerite. The mode of occurrence of axinite is virtually the same in both dolerites but it has a quite different habit in the iron-formation.

Axinite in the iron-formation

The greatest concentration of the axinite-bearing bands occurs between 175.6 and 175.8 m, approximately 11 m above the 'lower' sill. However axinite-bearing bands have been found down to 180 m. Other boron-rich zones contain no detectable axinite (see later discussion).

The axinite occurs as euhedral to subhedral, wedge-shaped porphyroblasts of random orientation set in ferrostilpnomelane and minor chortite, in stratigraphically controlled layers up to 2.5 cm thick (Fig. 3). The maximum size of the axinite is about 1.2 mm long but most grains range between 0.5 and 0.8 mm long. Adjacent to some of the axinite-rich layers, in which axinite comprises 10-15% of the layer, are zones with lesser axinite (<5%). In those layers with small amounts of axinite, the axinite is consistently less well formed (subhedral to irregular) and is smaller (averaging 0.3 mm in length). Axinite is crowded with fine inclusions mainly of sphene or epidote, and also some stilpnomelane and quartz. A thin rim on the axinite crystals, some 5-10 µm thick, has enabled accurate probe analyses to be made.

The wedge-shaped axinite grains of the iron-formation contrast sharply with those in the dolerite, by virtue of their well-formed shape and the large proportions of contained inclusions.

The phyllosilicates in which the axinite has developed are very fine-grained (<5-10 µm) with random orientation. In a few places, local recrystallization has produced small rosettes (up to 25 µm in diameter) of radiating ferrostilpnomelane.

Axinite in the dolerite

The petrography of the dolerite has been described by de Laeter and others (1974). Both dolerite sills are now largely composed of secondary minerals. Thus, most primary pyroxene has been converted to actinolitic amphibole, and calcic plagioclase is altered to albitic feldspar. Exsolved calcium is now



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1 mm

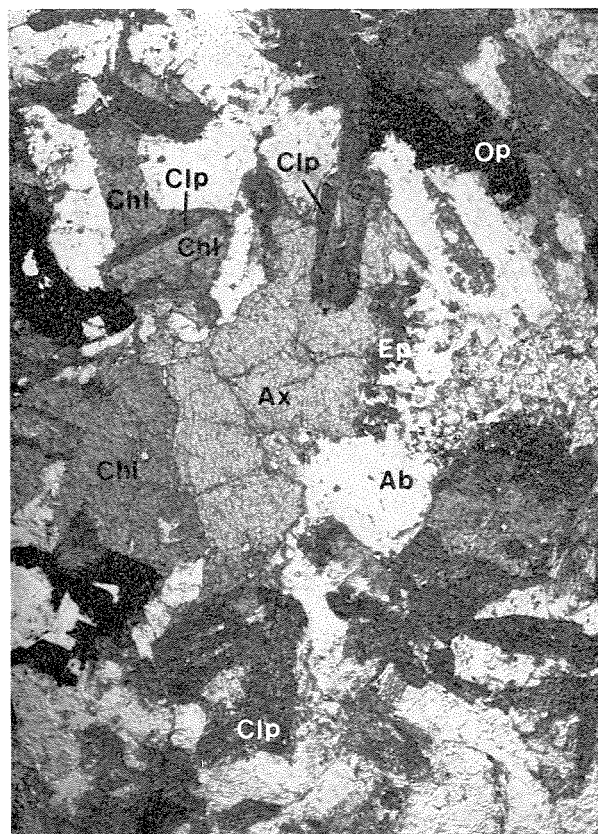
Figure 3. Photomicrograph of axinite porphyroblasts within iron-rich phyllosilicate of the Weeli Wolli Formation. The photomicrograph shows the euhedral shapes, clear rims, and inclusions of the axinite. Sample 59496.

represented by epidote, carbonate and axinite. Alteration of ferromagnesian minerals has progressed as far as chlorite and ferrostilpnomelane in places. Relict primary ophitic texture is, however, still recognisable. Interstitial pockets between former large grains of pyroxene and plagioclase are infilled with various assemblages of quartz, K-feldspar, apatite, zoisite, chlorite, carbonate and axinite. Within this interstitial material, axinite occurs as irregular grains 0.5-2 mm in diameter, commonly in association with granular quartz or epidote (Fig. 4); it does not occur where calcite is present. Though these interstitial minerals appear to have developed at a late stage, axinite does not occur in the last vein-phase which contains quartz, carbonate and epidote. Some of these veins cut pre-existing axinite grains. Axinite in the dolerite is free of inclusions and is not zoned.

Axinite is much more abundant in the lower sill than in the upper sill.

CHEMICAL COMPOSITION OF THE AXINITE

The mineral is a low-manganese ferroaxinite, with a variable composition. The ferroaxinite from the dolerite is consistently more manganiferous than that of the iron-formation, and the upper-sill axinite contains more manganese than that of the lower sill (Table 1).



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1 mm

Figure 4. An axinite grain within the lower dolerite at 202.7 m. Adjacent minerals include albite (Ab-white), chlorite (Chl-dark grey), opaques (Op-leucoxene after ilmenite), pyroxene (Cln-very dark grey) and epidote (Ep-small dark grains). Plane-polarized light. Sample 20785.

Axinite in iron-formation contains an extremely small content of manganese but is inherently more variable in composition (Table 1). This may be due, in part, to the micro-inclusions in the axinite.

In the lower sill, axinite composition changes with depth (Table 1), and probably reflects systematic changes of the composition of the dolerite as a whole (*cf.* de Laeter and others, 1974). A few axinite grains in the iron-formation contain traces of TiO_2 , K_2O and Na_2O , whilst traces of Cl , SO_3 and Na_2O have been detected in some grains from the dolerite.

DISCUSSION

Metamorphic Grade of the Core

The overall metamorphic grade of the rocks in the region suggested by Smith and others (1982) to be in the prehnite-pumpellyite-epidote facies of regional (burial) metamorphism. However, neither prehnite nor pumpellyite are known from the core. Comparison of analyses of epidote in dolerite (Table 2) with those cited by Smith and others (1982, Table 4, p. 94)

TABLE 1. COMPOSITION OF REPRESENTATIVE AXINITES FROM CORE WW1 ELECTRON-PROBE ANALYSIS

	Upper dolerite					Lower dolerite			
	Weeli Wolli Formation								
Sample	20766	59496	70096A	70096B	70099	20782	20788	20793	20800A
Depth (m)	137.2	175.6	175.7	175.72	180.0	198.1	206.2	213.4	224.0
Points counted	5	1	2	2	2	3	2	2	2
%									
SiO ₂	42.36	41.91	42.44	42.47	44.04	42.55	42.55	41.67	42.69
Al ₂ O ₃	17.28	15.64	17.55	17.73	18.02	17.24	17.26	17.30	17.66
FeO (a)	7.88	10.20	11.51	10.68	11.42	9.92	9.11	8.15	7.69
MnO	3.39	0.91	1.27	1.60	1.45	2.71	2.50	2.89	2.93
MgO	1.30	0.71	1.02	1.38	0.74	0.70	0.98	1.09	1.42
CaO	19.71	21.83	19.93	19.34	20.58	19.52	19.61	19.22	19.52
TiO ₂		5.23							
Cation proportions (cations = 18)									
Si	8.01	7.72	7.90	7.93	8.00	8.04	8.06	8.02	8.06
Al	3.84	3.38	3.86	3.89	3.85	3.83	3.84	3.92	3.92
Fe	1.25	1.57	1.79	1.67	1.73	1.56	1.44	1.31	1.21
Mn	0.54	0.14	0.20	0.25	0.24	0.43	0.40	0.47	0.46
Mg	0.36	0.19	0.28	0.39	0.22	0.19	0.27	0.31	0.40
Ca	3.99	4.30	3.97	3.87	3.95	3.94	3.98	3.96	3.94
Ti		0.70							

NOTES:

- (1) The total number of axinite grains analyzed (and used in figure 5) are; upper dolerite—1, iron-formation—22, lower dolerite—12.
- (2) Cation percentages have been calculated assuming that Ca + Fe + Mn + Mg + Al + Si = 18. It is clear that a small proportion of the iron is present as Fe₂O₃, though this cannot be determined from the electron probe analysis.
- (3) Sequential analyses along traverses across grains did not reveal clearly recognisable zoning although slight compositional variations were apparent.

(a) Total Iron as FeO

TABLE 2. COMPOSITION OF REPRESENTATIVE EPIDOTE GRAINS FROM DOLERITE IN CORE WW1, AND COMPARISON WITH EPIDOTE DATA FROM SMITH AND OTHERS (1982)

	This Study					Smith and Others, 1982, p. 94			
	Upper dolerite		Lower dolerite			Zone II		Zone III	
Sample	20763	20766	20785	20786	20793	10077	10064	10935A	10920
Points counted	2	2	3	2	3				
%									
SiO ₂	37.82	37.65	37.26	37.48	37.12	37.35	38.08	38.02	38.41
Al ₂ O ₃	23.10	22.23	21.29	21.22	22.09	22.41	22.96	24.01	26.17
FeO (a)	13.10	13.84	14.23	14.40	13.52	(b)13.38	12.76	10.41	8.25
CaO	23.61	23.52	23.15	23.00	23.03	21.45	22.58	23.65	24.04
V ₂ O ₅	0.24		0.39	0.33					
MgO						1.22	0.95		
Cation proportions (assuming Si + Al + Fe + Ca = 8)									
Si	3.00	3.00	3.00	3.00	3.01	3.00	3.01	3.03	3.01
Al	2.14	2.10	2.03	2.03	2.08	2.12	2.14	2.25	2.42
Fe	0.86	0.90	0.97	0.97	0.92	0.89	0.84	0.69	0.54
Ca	2.00	2.00	1.98	1.98	1.99	1.85	1.91	2.02	2.02
V	0.01		0.02	0.02					
Mg						0.14	0.11		

(a) Total Iron as FeO

(b) Fe₂O₃ converted to FeO for comparison

suggests that the metamorphic grade lies between their prehnite-pumpellyite-epidote zone (ZII) and their prehnite-pumpellyite-epidote-actinolite zone (ZIII). Amphibole in the dolerite suggests that the rocks should properly be in zone ZIII.

Constraints on the temperature of formation of the axinite-bearing rocks have been suggested by a number of workers. Liou (1971) determined the upper

stability limit of prehnite as 403°C at 300 MPa pressure. Similarly, Seki (1972) determined a lower limit for the stability of epidote as 220 ± 50°C for pressure of 100-500 MPa. Ayres (1972) postulated metamorphic temperatures in the range 205°-325°C for the Brockman Iron Formation, based on the depth of burial and an estimation of thermal gradients. Becker and Clayton (1976) concluded, from oxygen isotope studies, that the Dales Gorge Member of the

Brockman Iron Formation (some 500 m below the Weeli Wolli Formation) had experienced a maximum temperature in the range 270-310°C.

There is no indication in the core of drill hole WW1, of any metamorphic changes other than those caused by burial to a depth of about 5 to 6 km (cf. Smith and others, 1982), except, in the immediate vicinity of the dolerite sills, where contact metamorphism has produced reddening of the core over approximately 0.5 m.

The iron-formation of WW1 contains, at other intervals, both minnesotaite and greenalite. Greenalite is considered by some workers (e.g. French 1973) as an early diagenetic mineral, and minnesotaite as a slightly higher temperature mineral. Grubb (1971) experimentally converted greenalite to minnesotaite at about 150°C, but found that greenalite and minnesotaite could still coexist at 250°C and 100 MPa pressure. Melnik and Siroshtan (1973), however, calculate that minnesotaite decomposes to grunerite at temperatures of 250-280°C at 200-500 MPa pressures.

The implication from these observations is that the axinite in the Weeli Wolli core was formed at temperatures close to 250°C, and at pressures in the range 100-200 MPa.

Axinites from other regionally metamorphosed terrains

Axinite schists have been reported from Sambagawa (Kojima, 1944) and Sangun (Nureki, 1967), both in Japan. These occurrences of axinite schists are associated with mafic schists, and the axinite is part of an assemblage which includes stilpnomelane, (chlorite) and epidote. Axinite has also been noted in metasediments at four New Zealand localities. Near Dansey Pass, axinite occurs within 'stilpnomelane-chlorite-epidote laminae in a fine-grained hematitic chert' (Pringle and Kawachi, 1980, p 1121). Other axinites were found by these workers within pumpellyite-bearing metacherts.

In all the above occurrences, the axinite crystals are porphyroblastic, subhedral to euhedral grains, and contain masses of minute inclusions of quartz, hematite and, possibly sphene. Nureki (1967) notes the random orientation and the clean rims of the Sangun axinite.

It is clear that axinite forms readily in low-grade, regional-metamorphic environments where temperature and pressure conditions are appropriate, and there is a source of boron. Axinite may therefore prove to be much more common in this type of environment than is currently recorded.

Axinite has been reported from other regionally metamorphosed, mainly mafic, igneous rocks, but in the majority of cases it is present in veins rather than as an integral component of the rock (e.g. Ozaki 1969, 1972).

Composition compared with other axinites

A ternary diagram showing the position of the Weeli Wolli axinites in relation to some other published data is included as Figure 5.

The axinite is highly ferroan, as is axinite in monzonitic rock reported by Hietanen and Erd (1978). However the axinite from the regionally metamorphosed rocks in Japan are manganese rich, as are some of those from New Zealand. Most documented ferroaxinites are found as vein minerals (Ozaki, 1970; Hietanen and Erd, 1978; Benjamin, 1968; Simonen and Wiik, 1952; and Deer, Howie and Zussman, 1962).

A relationship between the composition of axinite and that of the surrounding host rocks does not appear to have been established by previous workers. However, the high iron and low manganese content most likely reflect the original composition of the rock. The Weeli Wolli Formation at least contains high concentrations of iron (21.9% Fe or 28.1% FeO in the main axinite-rich zone) and relatively low MnO (an average of 0.11% in the entire formation, 0.23% in the vicinity of the main axinite-rich bands).

Origin of boron in the iron-formation

The Weeli Wolli occurrences of axinite suggest that the iron-formation must have contained high primary boron concentrations in particular layers. This is an unusual feature since the normal trace-element level in iron-formations is very low (Davy, 1983). It seems likely that boron was precipitated from solution on clay minerals of the illite or hydromica group, possibly through the agency of magnesium-hydroxy clusters (brucite-type). Boron could also have been coprecipitated with hydroxy-iron or hydroxy-aluminium minerals (Sims and Bingham, 1967, 1968a, 1968b; Rhoades and others, 1970). Boron retention by micas and ferro-aluminous compounds lessens with aging (Sims and Bingham, 1968a), and it seems probable that the boron, now found in axinite porphyroblasts in the iron-formation, was expelled from its primary position either during compaction and dewatering, or during the metamorphism which changed the original phyllosilicates to ferro-stilpnomelane.

The formation of axinite is considered to post-date the dewatering process, since no compaction features are evident. Growth has been a two-stage process. An initial, fast developing period, in which the axinite surrounded its present inclusions, has been followed by a later period of slower growth in which extraneous material was displaced.

Origin of axinite in the dolerite

Boron may have been inherent within the dolerite even though axinite is a relatively late-formed mineral. Boron did not take part in the final metasomatic

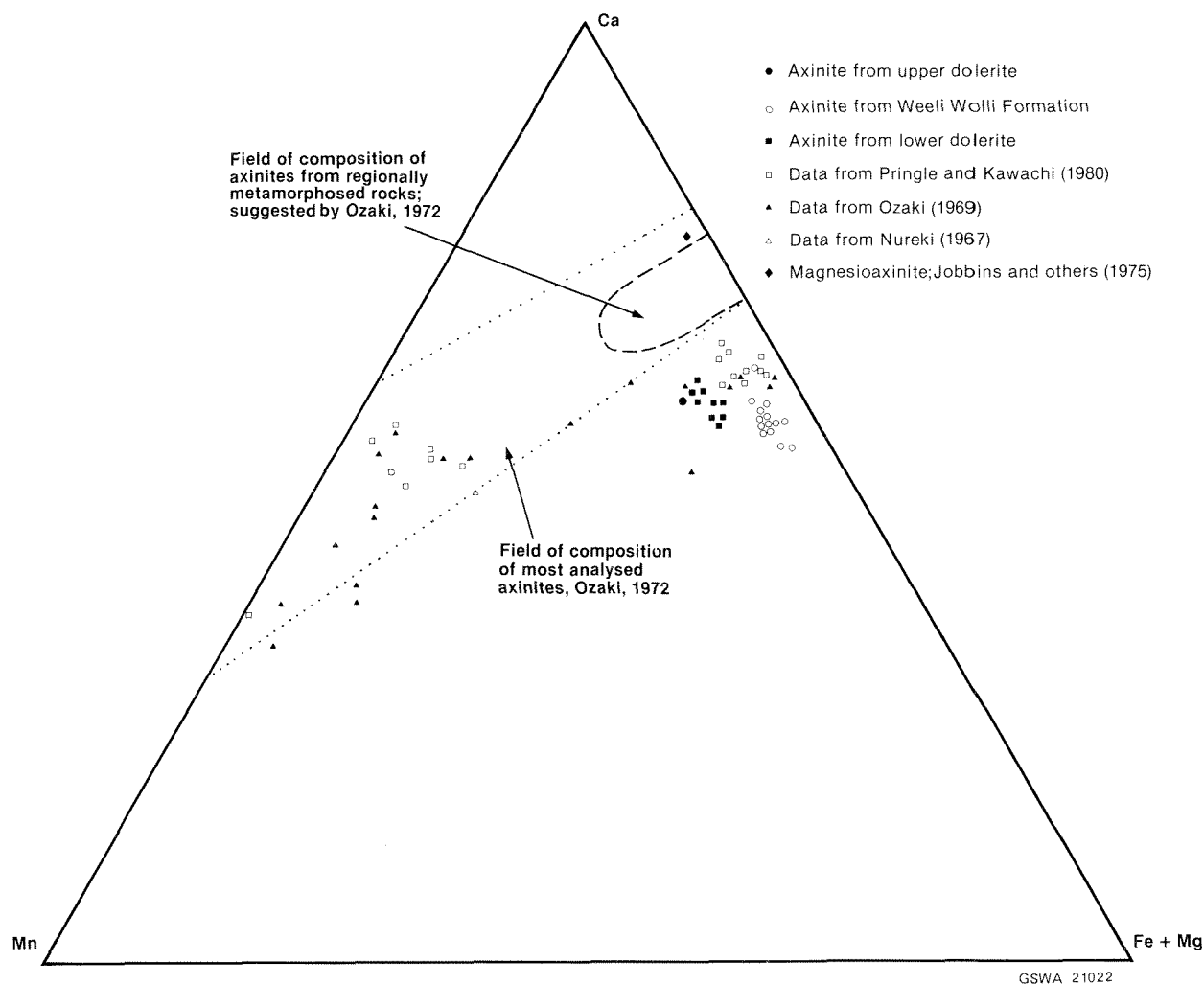


Figure 5. Comparison of axinites from core WW1 with other published values. Diagram of atomic ratios, based on Ozaki, 1969.

activity which produced the quartz-carbonate (-epidote) veins. However, axinite was formed during a retrogressive metamorphic phase (with Ca coming from plagioclase, and with Mn, Fe and Mg from pyroxene) along with epidote and calcite. Its habit is porphyroblastic but not idioblastic; it shows no evidence of strain, and has no inclusions.

There is no evidence to suggest that boron has been introduced to the dolerite.

Origin and petrogenetic significance of boron

Boron is not universal in the Weeli Wolli Formation. The average boron content, calculated as a geometric mean over the whole length of the fresh iron-formation, is 10 ppm. Within this length there are two main boron-rich zones, namely between 167.4 m and 186.5 m and between 103.6 and 104.6 m. The average boron concentration for these zones is in the range 70-75 ppm, but in axinite-rich layers boron values are much greater, viz. 975 ppm over 20 cm at 175.7 ± .1 m, and 189 ppm over 10 cm at 171.6 m. The 19.1 m thick boron-rich zone immediately overlies the lower dolerite, but the upper zone, though it overlies the upper sill is separated from it by 5 m of iron-formation with background values of <10 ppm boron.

The close spatial association of the boron-rich part of the iron-formation with the dolerite sills suggests a common origin for the boron. The boron may ultimately have been derived from sea water, the dolerite magma or some hydrothermal source unrelated to the magma but part of a larger metamorphic event.

The stratabound mode of occurrence of the axinite in the iron-formation suggests that, if the boron were derived from sea water, a pulsed inflow of boron-rich water is necessary. Alternations of pulses of boron-enriched water with ordinary, essentially boron-free sea water would account for the layered distribution of the axinite, assuming that other constraints were kept relatively constant. The close proximity of the boron-rich sediments to the dolerite suggests that the dolerite was the ultimate source of the boron. It is postulated that after intrusion, late hydrothermal or fumarolic activity, related to the magma, added fluids containing boron to the sediments overlying the sills. The observed distribution of that element is best accounted for by periodic outbursts of solfataric or fumarolic activity alternating with quiescent periods. If this hypothesis is correct, it implies that the magma emplacement was barely intrusive. The dolerite may well have been emplaced into wet, unconsolidated

sediments. It also implies that the dolerite and iron-formation are essentially contemporaneous. Some boron was retained in the dolerite, the remainder trapped in the phyllosilicates in the iron-formation.

Much of the fumarolic activity would be caused by the contact of magma at 1200°C with wet sediments, producing local boiling (the critical point for ordinary sea water is 408°C at 30.4 MPa pressure). Magmatic fluids supplied boron, but steam from pore waters was probably the main carrier to the sediments. Some of the steam generated may have circulated back through the dolerite and caused further leaching of boron. Movement of steam through the dolerite could have occurred along contraction cracks, and may account for Trendall's recent observation of a patchy distribution of fresh and altered dolerite and the presence of two chlorite species (Trendall and de Laeter, in prep.).

A more modern illustration of the effects of intrusion into wet sediments has been provided by Einsele and others (1980) in the Gulf of California.

This hypothesis of the origin of the boron is at variance with that of de Laeter and others (1974) who suggested that the dolerite magma assimilated some iron-formation and shale during intrusion and then acquired much of its present mineral composition by duteic activity. Assimilation of sediments could account for the high K₂O content (2.7%) of the dolerite, and de Laeter and others (1974) suggested that the boron was introduced into the dolerite from the incorporated sediment, possibly as detrital tourmaline (tourmaline had been reported earlier by Trendall and Blockley, 1970, in shales of the Brockman Iron Formation). This mechanism is considered unlikely because there is no sign of other detrital material, and, more particularly, because tourmaline once formed is resistant to later modification.

Whatever the origin of the boron the axinite seems to be of late origin, and related to the later metamorphic events.

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