SHORT COMMUNICATIONS

Diagenetic and supergene braunites in the Proterozoic Manganese Group, Western Australia

BRAUNITE of general composition $Mn^{2+} Mn_6^{3+} SiO_{12}$ (Fleischer, 1983) is most commonly considered a typical mineral of metamorphosed manganese deposits, such as the gondites of India (Roy 1981), where it occurs in association with spessartine, hausmannite, bixbyite, and secondary supergene manganese oxides. The mineral exists in two polysomes, normal braunite (or braunite I) which corresponds to chemical composition $3Mn_2O_3.MnSiO_3$ with about 10% SiO_2 and a rarer form, braunite II, which appears to contain certain essential calcium and iron, much less SiO_2 (about 4%) and has an ideal formula $Ca(Mn_{12}Fe_2)^{3+}SiO_{24}$ (de Villiers, 1980). The existance of other elements, such as magnesium, barium and boron, in the mineral has been reported by Frenzel (1980). Studies by Kleyenstuber (1984) on the Kalahari manganese ores of South Africa suggest that braunite I is a product of sedimentary–diagenetic to very low grade metamorphism, (Mamatwan-type ores) while braunite II is characteristic of hydrothermal alteration zones (Wessels-type ore). Braunite is thus currently considered to have a wide oxide stability field and a number of modes of origin, i.e. sedimentary–diagenetic, metamorphic and hydrothermal. However, supergene formation of braunite, postulated by Hewett (1972), is considered 'extremely doubtful' (Roy 1981).

Studies by the author, presented here, suggest that braunite in Proterozoic Age manganese sediments, Western Australia, has crystallised from supergene manganese oxides during Tertiary Age enrichment.

Braunite in the Pilbara Manganese Group

The Pilbara region of Western Australia contains a concentration of manganiferous sediments within an area roughly defined by lat. 21°–23° S, long. 120°–122°E. These occur within sediments of Protcrozoic Age, (2600–2400 Ma) consisting mainly of shales and limestones, less commonly of banded iron formations in which a poorly-defined, sedimentary-diagenetic and a supergene manganese paragenesis have been recognized. The term 'Manganese Group' was intitally applied to these deposits by de la Hunty (1963) in a general study of the mineralisation. The term was also used by Goode (1981), who classified the group as a member of the larger Hamersley Group. Muhling and Brakel (1985), however, classed the manganese occurrences as belonging to the younger Bangemall Basin sediments. With the exception of some studies on the unusual braunite mineralisation which appears to be the earliest sedimentary–diagenetic phase in the manganese sedimentation (de la Hunty, 1963; Ostwald and Bolton, 1990), practically nothing has been published on the manganese occurrences. De la Hunty (1963) considered pyrolusite and cryptomelane to be the main manganese mineral present, together with hausmannite, bixbyite and 'wad'. The identification of hausmannite and bixbyite by combined mineragraphic and X-ray diffraction methods is interesting as these lower valency manganese oxides are usually considered to be of metamorphic or hydrothermal origin (Roy, 1981).

The present study is based on an examination of a suite of manganese-oxide-enriched sediments, collected from major locations in the Pilbara Manganese Province. All samples were chemically analysed, and sub-samples of these were examined mineragraphically and selected areas microanalysed by quantitative X-ray energy dispersive spectroscopy (EDS). In particular, over 200 microanalyses of braunite were carried

out on polished sections, using an EDAX model PV9100 energy-dispersive microanalysis (EDS) system attached to a Philips model 505 scanning electronic microscope. Analyses were performed under the following instrumental conditions: accelerating voltage 14.0kV, beam current 2.00nA, tilt angle 0.0°, and take-off angle 25.5°. All the analtyical data were fully ZAF corrected using a version of FRAME (Myklebust *et al.*, 1977). As EDS cannot distinguish valency state, appropriate valencies have to be nominated for the elements in the braunite analyses.

On the basis of textures and microanalyses four types of (or parageneses) braunite were detected. Textures are shown in Fig. 1 (*a–d*).

(a) *Sedimentary–diagenetic braunite (de la Hunty 1963; Ostwald and Bolton 1990).* The earliest manganese mineralisation recognizable in the Manganese Group is represented by the presence of braunite in the form of flattened concretions

(Fig. 1*a*) which post-date the sedimentation of the enclosing shale and pre-date its lithification. Ostwald and Bolton (1990) presented evidence to show that the braunite concretions grew in the moist sediment by reaction between Mn^{2+}, liberated from an earlier form of manganese by anoxia, produced by decay of organic matter, and silica.

(b) *Recrystallised braunite.* The author identified zones of polycrystalline braunite, with well-defined 120° triple junctions, sometimes in the form of stellate aggregates (Fig. 1*b*), which he interprets as recrystallised braunite (Ostwald and Bolton, 1990). Such recrystallised braunite appears to be typical of manganese occurring as cavity-infilling in breccias and dolomite rather than as replacements in shales. There is no evidence of metamorphism in the area and the recrystallisation appears to have been influenced by migrating groundwater.
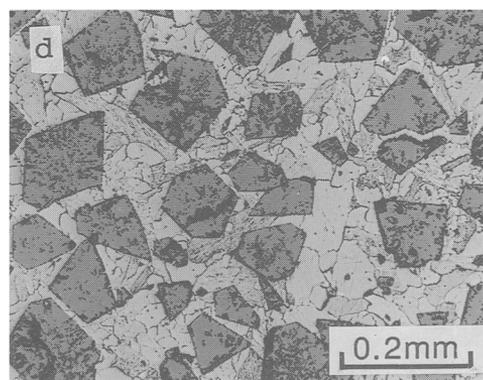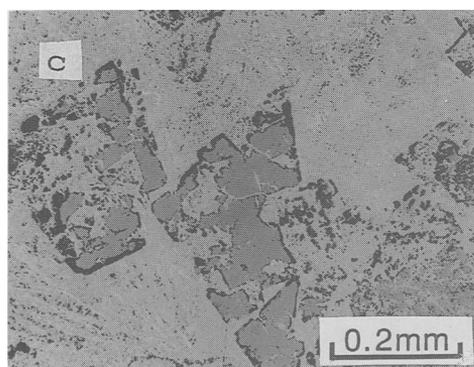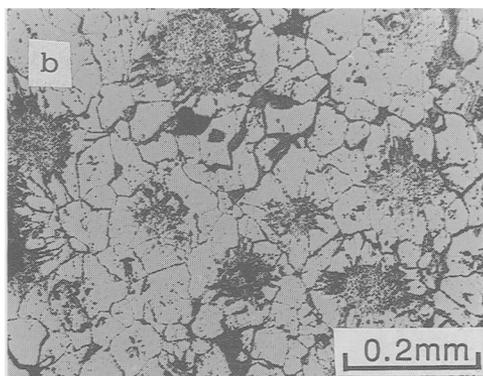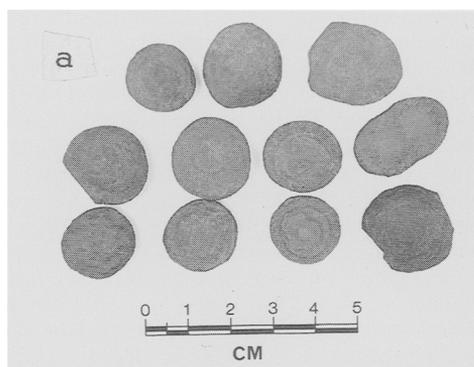
FIG. 1. (*a*) Photograph showing discoid concretions of braunite, weathered out of shale. (*b*) Reflected light micrograph showing recrystallised braunite with minor intergranular quartz (dark). (*c*) Reflected light micrograph showing two grains of weathered braunite (dark) in cryptomelane (light). (*d*) Reflected light micrograph showing euhedral crystals of braunite (dark) in cryptomelane (light).

(c) *Weathered braunite.* The Manganese Group sediments are locally enriched by supergene weathering producing cavity-filling and cappings of variable Mn/Fe ratio. In some localities supergene oxides are cryptomelane or romanechite, in others, layered cryptomelane and goethite occur. This variation in mineralogy is the result of varying degrees of separation of Mn from Fe during weathering. This supergene ore commonly contains crystals of braunite (Fig. 1c), and irregular polycrystalline areas. These braunite grains may show corrosion and alteration to manganese oxides such as chalcophanite or birnessite. The textural evidence indicates that this braunite is a relict of occurrences of types (*a*) and (*b*).

(d) *Euhedral braunite in supergene manganese oxides.* Braunite of euhedral to subhedral morphology (Fig. 1d) also occurs in the same occurrences of that type *c*, i.e. in supergene zones. Microanalysis of this braunite indicates that it is high in calcium than the braunite of types *a*, *b* and *c*. The well developed crystal shape and lack of alteration are interpreted here as textual evidence for the supergene origin of this type of braunite.

Discussion

While practically all of the braunite belonging to these four classes contains about 10% SiO_2, and thus is braunite I, the contents of Ca vary with respect to the mode of occurrence, as indicated by Table 1. This well-defined pattern, based on over 200 microanalyses, indicates the existence of three braunite parageneses. The original sedimentary–diagenetic braunite formed in a siliceous environment, with only minor amounts of biogenic calcium being present. Recrystallised braunite, including the weathered polycrystalline and anhedral monocrystals in supergene matrix, shows an increase in calcium. The euhedral crystals in supergene manganese samples (Fig.

Table 2. Calcium contents of Manganese Group Braunite

Lithology	CaO Content (WT%)*	Samples
Sedimentary - Diagenetic	0.1 - 0.8	125
Recrystallised and Corroded	0.8 - 1.4	32
Euhedral in supergene manganese oxides	1.3 - 2.2	44

* Based on fully ZAF corrected X-ray energy dispersive microanalyses.

Table 1. Microanalyses an Manganese Group Braunite

Sample	Mn_2O_3	Fe_2O_3	SiO_2	CaO	MgO	Na_2O	K_2O	Total
1	90.2	0.6	9.9	0.3	0.1	ND	ND	101.1
2	88.1	0.4	10.1	0.8	0.3	ND	ND	100.0
3	89.1	0.11	10.2	0.4	ND	0.1	0.1	99.6
4	88.3	ND	10.2	0.4	ND	0.1	ND	99.0
5	87.8	0.3	10.4	0.3	0.1	ND	ND	98.9
6	88.2	0.1	10.3	0.6	ND	ND	ND	99.2
7	88.3	ND	10.2	0.7	ND	0.2	ND	99.4
8	89.2	ND	10.3	0.4	ND	ND	ND	99.9
9	87.2	ND	10.2	0.8	ND	ND	ND	98.2
10	89.2	ND	10.2	0.5	ND	ND	ND	99.9
11	87.7	0.1	10.3	1.2	ND	ND	ND	99.3
12	88.5	0.1	10.2	0.7	ND	ND	0.2	99.7
13	89.3	ND	10.3	0.7	ND	ND	ND	100.3
14	87.3	ND	10.4	1.4	0.3	0.1	0.1	99.6
15	87.5	ND	10.3	0.8	0.4	0.2	ND	99.2
16	87.5	0.3	10.2	1.1	ND	ND	ND	99.1
17	88.8	ND	10.2	1.2	ND	ND	ND	100.2
18	87.8	0.5	10.3	0.9	0.1	ND	ND	99.6
19	87.7	ND	10.3	1.0	0.2	ND	0.1	99.3
20	88.3	ND	10.2	1.1	ND	0.1	ND	99.7
21	87.7	ND	10.2	1.4	ND	ND	0.1	99.4
22	88.2	0.6	9.9	1.3	ND	ND	0.3	100.3
23	87.5	ND	10.0	2.2	0.3	0.1	ND	100.1
24	87.3	ND	10.1	1.8	0.4	ND	ND	99.6
25	87.4	0.4	10.3	1.6	ND	ND	ND	99.7
26	87.3	ND	10.4	2.1	ND	ND	ND	99.8
27	87.0	0.8	10.2	1.9	ND	0.2	0.2	100.2
28	87.7	ND	10.3	1.6	0.6	0.3	ND	100.5
29	85.6	1.2	10.3	1.8	ND	ND	ND	98.9
30	87.1	ND	10.4	1.9	ND	ND	ND	99.4

Analyses 1-10, sedimentary - diagenetic; 11-20, recrystallised (including weathered grains); 21-30 euhedral grains in supergene oxides.
ND = Not Detected

Table 3. Braunite compositions from the Manganese Group and the
Hotazel Formation (Wt. %)

	Braunite (P)*	Braunite (R)*	Braunite (S)*	Braunite I**	Braunite II**	Braunite (new)**
Mn_2O_3	88.6	88.0	87.3	80.54	75.53	77.70
Fe_2O_3	0.2	0.1	0.3	5.82	13.73	15.91
Al_2O_3	ND	ND	ND	0.18	0.07	0.30
SiO_2	10.2	10.3	10.2	10.36	5.48	3.02
CaO	0.5	1.0	1.8	1.83	5.09	3.04
MgO	<0.1	0.1	0.1	0.77	0.04	0.04
BaO	ND	ND	ND	0.03	0.10	0.05
Na_2O	<0.1	<0.1	<0.1	0.02	ND	ND
K_2O	<0.1	<0.1	<0.1	0.01	ND	ND
Total	99.4	99.6	99.8	99.56	100.04	99.97

*   Average of 10 microanalyses. P = sedimentary-diagenetic, R = recrystallised and
        weathered, S = supergene, Manganese Group, Western Australia.
**   Averages of an unknown number of microanalyses, from Kleyenstuber (1984).

1d) show the highest Ca values. The fact that the three calcium contents hardly overlap, (Table 2) and relate to textually distinct types, shows that Pilbara braunite occurs in at least three distinct parageneses, and also demonstrates the existence of braunite supergene origin.

The braunite compositions listed in Table 1 suggest a stoichiometry 3Mn$_2$O$_3$ Mn SiO$_3$ (Hewett and Fleischer, 1960), as this formula implies 10% SiO$_2$. A limited number of microanalyses on Manganese Group braunite crystals, however, have lower SiO$_2$ values though not as low as that of braunite II of de Villiers and Herbstein (1967), which contains 4.4% SiO$_2$. For example, a good microanalysis on a recrystallised monocrystal (as indicated by an analytical total of 100%) indicated Mn$_2$O$_3$ = 90.2%, SiO$_2$ = 8.5%, CaO = 1.2% and nil Fe$_2$O$_3$. Recent studies by de Villiers and Buseck (1989) suggest an explantion of this chemistry. These investigators have determined that the braunite minerals (braunite I, braunite II and calcium-braunite, neltnerite) and bixbyite have a common general formula M$_8$O$_{12}$ and form a polysomatic series (Thompson, 1978), with individual minerals consisting of a stacking of chemically distinct but crystallographically related modules. In particular, they defined three modules A, A' and B i.e. A consisting of Mn-O octahedral layers, A' consisting of distorted Mn-O octahedra, and B composed of Mn^{2+} of Ca in distorted cubic coordination, Si in tetrahedral coordination and Mn^{3+} in octahedral coordination. The stacking sequences in the ordered polysomes is braunite I [B]$_4$, braunite II [A'B]$_4$, bixbyite [A']$_2$.

Computer simulation of the chemistry, especially SiO$_2$% content, of ordered and theoretical mixed-layer polysomes (hybrid crystals), indicated possible SiO$_2$ values of 10%, 8.6% 6.7%, 5%, 4% and 2.8%.

Stoichiometric braunite containing 10% SiO$_2$ is widely known (Roy, 1981) and natural braunite II, with 4.4% SiO$_2$, has been described by de Villiers and Herbstein (1967). Braunites with other values, such as the braunite with 8.5% SiO$_2$ from the Manganese Group noted above, could well be mixed-layer polysomes. For example de Villiers and Buseck (1989) considered the theoretical 8.6% SiO$_2$ braunite is a seven module polysome of stacking sequence BBBBBBA'. The braunite from the Hotazel Formation of South Africa belongs to at least three types (Kleyenstuber, 1984), as shown in the comparative table (Table 3). These differ in both SiO$_2$ and Fe$_2$O$_3$ from the Manganese Group braunite. It is not impossible that the phase labelled braunite (new), with 3.02% SiO$_2$, by Kleyenstuber (1984), might be equivalent to either the 2.8% SiO$_2$ or the 2.9% SiO$_2$ polysomes of de Villiers and Buseck (1989).

Thus, the mineralogy of braunite is conceptually far removed from the 'naturally-occuring homogeneous solid . . . with a definite chemical composition and an ordered atomic management' (Berry and Mason, 1959) mineral definition of current texts.

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Micro-scale trimethylsilylation for the characterisation of some silicate ions

During the study in 1983 of the new mineral mattheddleite, $Pb_{20}(SiO_4)_7(SO_4)_4Cl_2$, from Leadhills, Scotland (Livingstone *et al.*, 1987), we wanted to confirm that only monomeric silicate anions were present, but the available material was limited to microgram quantities. It is possible to distinguish between SiO_4^{-4}, $Si_2O_7^{-6}$, and other low molecular weight silicate ions in minerals by treatment with acids in the presence of trimethylsilylation reagents. The various silicic acid species released from the solid samples are converted into neutral, volatile trimethylsilyl (TMS) derivatives, $Si[OSi(CH_3)_3]_4$ ('Si_1'), $Si_2O[OSi(CH_3)_3]_6$ ('Si_2'), etc., which can be isolated and quantified by gas chromatography (GC). The major TMS product in each case corresponds to the anion originally present, although hydrolysis and condensation of the silicic acids before they are trapped as TMS derivatives may give rise to small amounts of TMS derivatives not characteristic of the parent silicate. The trimethylsilylation technique, in various modifications, has been used extensively to speciate silicate ions (see review by Currell and Parsonage, 1981) but the published methods require relatively large samples, from a few to 500 mg. However, it was found that the method of Kalmychkov (1982), which employs trimethylchlorosilane, a base (pyridine) and an optional co-solvent such as dimethylformamide, can be adapted to a micro-scale if, as is common practice for the trimethylsilylation of organic compounds, the reaction mixture is injected into a gas chromatograph without further treatment.

A few crystal fragments of mattheddleite (<10 μg) were treated at 20°C with trimethylchlorosilane (2 μl), dry pyridine (1.5 μl) and dry dimethylformamide (1.5 μl), typically for 1 hour, then 0.5 μl of the mixture was analysed by GC (for GC conditions see Table 1). The chromatogram showed a large peak due to Si_1, and a small peak due to Si_2 formed as a byproduct. No peak due to the TMS derivative of SO_4^{-2} was present in the chromatograms of mattheddleite and ellestadite, nor was one seen when ammonium sulphate, which is readily trimethylsilylated, was treated in the same way. This, the sulphate TMS derivative appears to be unstable under the analytical conditions employed (cf. Mawhinney, 1983).

The results for mattheddleite and some refer-