Al-rich warwickite from Inglefield Land, North-West Greenland

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Abstract

Warwickite constitutes about 5% of an outcrop of metamorphosed ultramafic rocks of Precambrian age in North-West Greenland. It occurs as slender grains, several millimetres long, and in anhedral grains up to 5 mm in size, together with forsterite, pleonaste, phlogopite, magnetite ± tourmaline. Post-metamorphic alteration of warwickite produced a network of boron-rich minerals and magnetite. The warwickite, containing up to 9.72% Al_2O_3, displays a significantly different chemical composition from warwickite elsewhere, such as that in recrystallized limestones from the type locality Warwick, New York, and in lamproitic and carbonatite-like rocks at Jumilla, Spain.

KEYWORDS: warwickite, oxyborate, Inglefield Land, Greenland, aluminium.

Introduction

THE type locality for the rare orthorhombic oxyborate warwickite is near Warwick, Orange County, New York (Bradley, 1909), where it occurs in nodules hosted in coarsely crystallized marbles as rough black prisms together with forsterite, spinel and chondrodite with accessory minerals including pyrrhotite, dravite, titanite, magnetite and flecks of graphite.

Warwickite has been found in Korea (Watanabe, 1954), in Ontario (Sabina, 1977) and in the Tayezhnoye ore deposit, southern Yakutia, Siberia (Malinko *et al.*, 1986). In Korea warwickite occurs together with forsterite, spinel, ludwigite, clinohumite, pyrrhotite and calcite in a marble supposedly altered by boron metasomatism. In Ontario, warwickite is found in a crystalline limestone, as disseminated masses 2 to 5 mm in diameter and as slender prisms 2 mm long. It is black with a reddish black streak and occurs together with mica, dolomite, tremolite, szaibelyite, serpentine, apatite, dark green spinel, sinhalite, anatase, fluorite, chondrodite, scapolite, ilmenite, marcasite, pyrrhotite, pyrite, graphite and goethite. The warwickite-bearing lamproitic rocks of Spain are partly porphyritic lavas and partly porphyritic coarse-grained subvolcanic rocks. They consist of phlogopite, olivine, apatite and occasional clinopyroxene as phenocrysts in a groundmass of the same phases together with sanidine or analcime, K-rich richterite, subordinate carbonates and accessory pseudobrookite, ilmenite, magnetite and warwickite. The warwickite constitutes up to 10% of the rock (Bigi *et al.*, 1991). Warwickite is also found in carbonatite-like veins associated with the lamproitic rocks.

Geologic setting

Inglefield Land is situated around 79° North and 69° West in North-West Greenland. Only limited geological work has been carried out in the area which consists of early Proterozoic gneisses and supracrustal rocks overlain by late Proterozoic and Cambrian platform strata (Dawes, 1988). The crystalline basement comprising pelitic schists, marbles, calc-silicate rocks and amphibolites were intruded by a meta-igneous complex of mainly granites and syenites. The area was repeatedly deformed and metamorphosed under amphibolite facies conditions in early Proterozoic time.

A geophysical survey and photogeological interpretation was carried out in 1994 (Bengaard, 1995; Stemp and Thorning, 1995). The following year the Geological Survey of Denmark and Greenland (GEUS) carried out field work and a strong magnetic anomaly was investigated and shown to be caused by an extensive magnetite mineralization (Appel *et al.*, 1995). This magnetic anomaly can be traced for tens of kilometres across poorly exposed ground, but is

Mineralogical Magazine, October 1997, Vol. 61, pp. 693–698

locally betrayed by magnetite float. In the eastern part of the magnetic anomaly exposures of magnetite bands in an ultramafic rock were found by P.R. Dawes and B. Thomassen (GEUS) (private communication), who undertook a brief investigation and sampling which showed that the ultramafic rocks were intruded by syenites, and that the emplacement predates at least one phase of deformation and an amphibolite facies metamorphic event.

Warwickite-bearing rocks

Warwickite occurs in an ultramafic rock in central Inglefield Land. The exposure is several tens of metres wide and consists of a light-coloured medium-grained rock with abundant cm-sized black patches. Magnetite-rich bands up to tens of centimetres thick locally occur. The rock has been deformed and metamorphosed under amphibolite facies conditions.

The ultramafic rock consists of olivine, spinel, warwickite, phlogopite and magnetite listed in order of decreasing abundance. The olivine, which is forsterite with 51% MgO, occurs in a metamorphic fabric in up to cm-sized grains locally enclosing, and being enclosed by, tourmaline. The spinel is a pleonaste with a minor hercynite component, and exhibits abundant small exsolutions of magnetite and magnesioferrite. Minor minerals are apatite. Tourmaline makes up about 5% in one sample, but is absent in others. After metamorphism forsterite has been partly altered to a network of serpentine and magnetite, whereas warwickite has been partly altered to a network of boron-rich alteration minerals and magnetite.

Warwickite which constitutes about 5% of the two samples investigated occurs in large black anhedral grains, up to 5 mm, which are somewhat altered. Warwickite also occurs in slender unaltered crystals a few millimetres long, locally enclosed in grains of forsterite. In thin section warwickite is mostly opaque but along grain boundaries and in extreme thin section it is translucent. The colour varies slightly: in one sample it is dark brown with pleochroism from brown to very dark brown in another sample it shows pleochroism from brown to deep brownish red. In reflected light warwickite is grey with a slight bluish brown tinge and a reflectivity higher than spinel (7 R%) and lower than magnetite (21 R%). No internal reflections were observed in reflected light. Alteration of warwickite resulted in a network of alteration minerals (Fig. 1) resembling the network of serpentine and magnetite after forsterite. The alteration minerals from warwickite are fine-grained and consist of magnetite and a colourless mineral with low birefringence which in reflected light is dark grey with very low reflectivity. The grain-size does not allow determination by transmitted light microscopy. Back scatter photos by scanning electron microscopy (SEM) reveal that the colourless alteration mineral consists of several phases (Fig. 2). The black phase (Fig. 2) appears fairly homogeneous, whereas there are several lighter grey phases many of which are less than 1 μm wide. Some of the small bright spots (Fig. 2) are probably magnetite, whereas the thin wisp-shaped light grey grains and the homogeneous dark grey grain appear to have different compositions.

FIG. 1. Photomicrograph showing warwickite (W) and its alteration products: boron-rich minerals (A) and magnetite (M). Forsterite (F) is partly altered to serpentine (S) and magnetite (M). Sample GGU 425360.

Experimental techniques

X-ray determination by Gandolfi camera was made on a small fragment of warwickite from a polished thin section (GGU 425360). The crystallographic calculations carried out with a modified Refbase III programme were based on the assumption that the warwickite lattice was of the space group *Pnma*. The observed and calculated $d_{(hkl)}$ values and the relative intensities are shown in Table 1. The present cell parameter results are listed in Table 2 together with

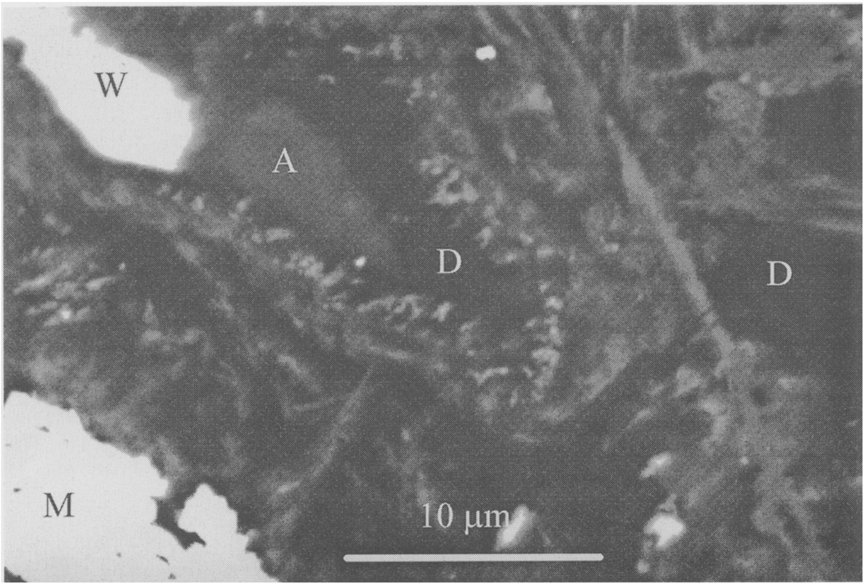

FIG. 2. Back scatter image (SEM) showing a relict grain of warwickite (W) and alteration minerals from warwickite: magnetite (M), a dark (D) phase and several lighter grey phases of which the larger and more homogeneous (A) was analysed by microprobe. Sample GGU 425359.

cell parameters from other occurrences, and the Greenland warwickite compares well with warwickite from elsewhere, apart from the *a* axis which is a good deal shorter than that of other warwickites.

Twenty-five analyses of warwickite have been carried out on a GEOL 733 Super microprobe at 15 kV and 15 nA with the following standards: olivine, hematite, corundum, rutile and Cr_2O_3. The chemical composition from one grain to another within one sample is fairly constant, whereas there is some variation from one sample to another, especially the Fe_2O_3, Al_2O_3 and Cr_2O_3 differ, whereas MgO and TiO_2 contents are quite similar (Table 3). The deep reddish brown warwickite in sample GGU 425359 has higher iron contents and lower aluminium contents compared with the brown warwickite in sample GGU 425360.

TABLE 1. Observed and calculated $d_{(hkl)}$ values and relative intensities

h k l	*d* Observed	*d* Calculated	Relative intensity
1 1 0	6.6000	6.5307	20
1 2 0	4.1800	4.1871	50
1 3 0	2.9690	2.9745	80
2 3 0	2.5760	2.5839	100
1 5 0	1.8510	1.8500	10
3 3 1	1.7870	1.7846	10
3 4 1	1.5950	1.5964	10
6 0 0	1.5050	1.5059	10

TABLE 2. Cell parameters of warwickite from Inglefield Land compared with warwickite from elsewhere

Locality	This study	Amity, Warwick[1]	Jumilla, Spain[2]	Japan[3]
a (Å)	9.037	9.197	9.246	9.20
b (Å)	9.450	9.358	9.384	9.45
c (Å)	3.116	3.085	3.0927	3.01

[1] Moore and Araki (1974). [2] Sample S1 in Bigi *et al.*, (1991). [3] Takéuchi *et al.* (1950).

Two grains of warwickite from sample GGU 425360 have been analysed with the CRPG-CNRS Cameca ims3f ion microprobe with the following instrumental parameters: primary beam O^- at 10 kV accelerating voltage and 16 nA intensity, secondary beam: positive ions 11B+, 24Mg+ and 27Al+, secondary accelerating voltage 4.5 kV, mass resolution: M/DM = 1400, energy filtering:- 60 ± 10 V. The emissivity of B, Mg and Al were determined on CRPG glasses (Chaussidon and Libourel, 1993). Silicate glass standards were used because no warwickite standard was available. This induced a large uncertainty in the determination of the B content because of likely differences in the emissivity of B between silicate glass and warwickite. This is estimated to be 30% relative from the comparison between ion probe analyses of Al and Mg with the electron probe analyses. The results are 25.00% and 28.30% B_2O_3 respectively (Table 3).

The alteration minerals from warwickite have been analysed by microprobe with the same working conditions and standards as for warwickite. Two microprobe analyses were made in the magnetite, which showed small amounts of Ti and Mg (Table 4). Nine microprobe analyses were made in the boron-bearing alteration products (Fig. 2) and the results are listed in Table 4. They show a wide range in composition depicting that the boron-bearing alteration product consists of at least two phases. The light coloured phase (Fig. 2) has more than 9% TiO_2, whereas the dark coloured phase has down to less than 1% TiO_2. One boron analyses of the boron-bearing alteration minerals has been carried out on the ionprobe under the same conditions as the analyses of warwickite. It is not known which of the alteration phases shown in Fig. 2 were analysed. The analyses yielded 13% B_2O_3 (Table 4). No further elements have been detected in the boron-bearing alteration minerals, and it is assumed that they contain approximately 25 percent H_2O.

Comparison with warwickite from other areas

The cell parameters of the Inglefield Land warwickite correspond well with cell dimensions of warwickite from elsewhere.

Its chemical composition is significantly different from warwickite found at the type locality near Warwick, but shows similarities with warwickite found in lamproitic and carbonatite-like rocks at

TABLE 3. Average composition of two sets of warwickite compared with warwickites from elsewhere

	425359 (6 anal.)	425360 (19 anal.)	Warwick[1]	Jumilla, Spain[2]
Fe_2O_3%	39.94	35.84	14.87	26.21–44.48
MgO%	25.99	26.30	35.64	28.26–32.58
TiO_2%	4.04	4.28	24.85	2.02–9.16
Al_2O_3%	7.88	9.72	2.83	0.21–1.19
Cr_2O_3%	0.91	0.30		0.80–11.88
CaO%				0.04–0.06
MnO%				0.03–0.14
SiO_2%				0.30–0.86
B_2O_3%		25.00–28.30	21.27	22.45–23.37

[1] Moore and Araki (1974). [2] Range in chemical composition of 7 warwickite crystals (Bigi *et al.*, 1991). Samples analysed are from Geological Survey of Greenland (GGU) collection.

TABLE 4. Range of composition of the alteration minerals from warwickite (GGU 425360)

	Dark coloured phase	Light coloured phase	Magnetite
Fe_2O_3%	1.46–2.60	1.95–5.64	86.50–94.50
MgO%	39.34–41.92	35.79–38.75	1.08–3.05
TiO_2%	0.70–2.28	3.77–9.39	3.40–3.73
Al_2O_3%	17.59–19.95	9.70–17.06	1.40–1.75
Cr_2O_3%	0.12–0.45	0.33–0.62	0.28–0.46
B_2O_3%	13		

Jumilla, Spain. The iron, magnesium and titanium contents of warwickites from Greenland and Spain are quite similar, whereas the contents of aluminium and chromium differ. The high aluminium content of the Greenland warwickite appears to be unique.

Summary and conclusions

Warwickite from Inglefield Land constitutes about 5% in the rock samples collected from a Precambrian ultramafic complex consisting of an amphibolite facies assemblage of forsterite, pleonaste, warwickite, phlogopite, magnetite ± tourmaline and small amounts of apatite. The composition of the Greenland warwickite resembles warwickite in lamproitic rocks in Spain apart from its high aluminium contents.

The warwickite-bearing ultrabasic rocks were intruded by a syenite complex and subsequently deformed and metamorphosed under amphibolite facies conditions. After this metamorphism, forsterite was partly altered to a network of serpentine and magnetite, and the warwickite was altered to a network of boron-rich minerals and magnetite. At the present time too few data are known of the boron-rich alteration minerals to determine their identity.

The field information available so far are not sufficient for a discussion of the origin of the Greenland warwickite. As for the source of the boron the following can be suggested. Boron could have been derived either from sediments digested by an ultrabasic magma, or alternatively fluids derived from the supracrustal rocks could have altered an ultrabasic intrusive complex prior to metamorphism. Finally the boron could be indigenous to the magma which gave rise to the ultramafic complex.

Acknowledgements

The author is grateful to Erik Leonardsen and Peter Toft for unit-cell determination, to Jørn Rønsbo for microprobe analyses at the Geological Institute, University of Copenhagen, Denmark, to Marc Chaussidon, CRPG, Nancy, France for ion-probe analyses for boron and to Henning Sørensen, GEUS for SEM analyses and back scatter image photos. The article is published with permission from the Geological Survey of Denmark and Greenland (GEUS).

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[*Manuscript received 1 October 1996: revised 11 February 1997*]