SHORT COMMUNICATIONS

MINERALOGICAL MAGAZINE, SEPTEMBER 1992, VOL 56, PP. 417–419

Shigaite from Iron Monarch, South Australia

IRON MONARCH is one of a number of Precambrian sedimentary iron ore deposits, being worked by Broken Hill Proprietary Limited, in the Middleback Ranges of South Australia, some 500 km northwest of Adelaide (Miles, 1954). The deposit is mineralogically notable because the orebody contains pods of high-grade manganese ore. In combination with a deep weathering profile, the presence of iron and manganese, with minor amounts of copper, zinc, phosphorus and other elements, has resulted in an unusually diverse mineralogy. To date, over 90 mineral species, including a considerable number of phosphates and sulphates (Pilkington *et al.*, 1979; Pring *et al.*, 1989, 1990, 1992; Francis and Segnit, 1981; and Segnit and Francis, 1983) have been identified from the Iron Monarch deposit. Shigaite, a hydrated manganese aluminium sulphate, is one of the rare minerals from the deposit which have recently been identified (Pring *et al.* 1992). Shigaite was originally described from the Ioi mine, Shiga Prefecture, Japan, by Peacor *et al.* (1985). Insomuch as the Iron Monarch occurrence of shigaite is only the second to be recorded we felt that a more complete description was warranted.

At Iron Monarch, the occurrence of shigaite is limited to a small baryte-rich zone at the 130 metre level on the eastern side of the open-cut. The mineral occurs as hexagonal platy crystals and groups of crystals within cavities in a hematite–hausmannite–baryte–carbonate-rich matrix. It also occurs as thin films and fracture coatings. To date, only about 20 specimens have been recovered. The crystals range in colour from bright to golden yellow through to burnt orange; the surfaces of some individuals however, are covered with a fine film of black manganese oxide. The crystals of shigaite are up to 2 mm in diameter and are frequently twinned on (0001) (Fig. 1). In every respect the appearance of the shigaite at Iron Monarch appears to conform with that of the physical description given by Peacor *et al.* (1985) of the type material. Associated minerals include gypsum, arsenoclasite and an unidentified manganese phosphate.

Analyses of the Iron Monarch material were performed using a Jeol electron microprobe, operating at 15 kV and with a specimen current of 0.02 μA. The following standards were employed for the analyses: corundum, Al; sphalerite, S; synthetic periclase, Mg; manganese metal, Mn; hematite, Fe. The average of two electron microprobe analyses is given in Table 1. When calculated to a basis of two sulphate groups, these data gave the formula $Mn_7(Al_{2.91}Mn_{0.45}Fe_{0.41}Mg_{0.08})_{\Sigma 3.85}(SO_4)_2(OH)_{21.46}\cdot 10.3H_2O$, which is similar to general formula, $Mn_7Al_4(SO_4)_2(OH)_{22}.8H_2O$, proposed by Peacor *et al.* (1985). Unfortunately there was insufficient material available to allow an analysis for water to be made so the water figures in the analyses were calculated by difference.

An X-ray powder-type diffraction pattern of a cluster of small crystals of the Iron Monarch shigaite was recorded with a 57.5 mm diameter

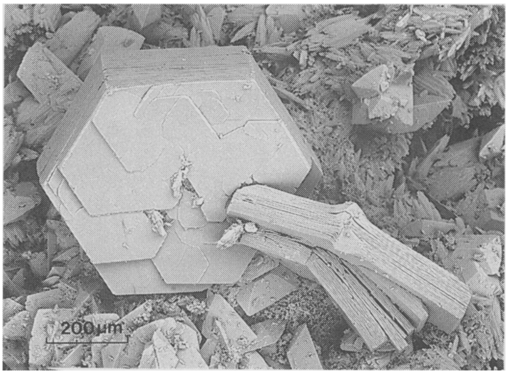

FIG. 1. Scanning electron micrograph showing a group of hexagonal shigaite crystals. Note the layer parting caused by partial dehydration in the scanning electron microscope vacuum.

TABLE 1. Electron microprobe analysis of shigaite.

Wt% Oxide	1.	2.	3.
Al_2O_3	11.8 (11.6 - 12.0)	15.3	16.9
Fe_2O_3	2.6 (2.4 - 2.8)	0.9	-
MnO	42.1 (41.7 - 42.5)	41.7	41.3
MgO	0.25 (0.2 - 0.3)	-	-
SO_3	12.75 (12.3 - 13.2)	13.6	13.3
H_2O	30.5	28.0	28.5
Total	100.00	99.5	100.00

1. Iron Monarch, South Australia; H_2O by difference. Formula of $Mn_7(Al_{2.91}Mn_{0.45}Fe_{0.41}Mg_{0.08})_{\Sigma 3.85}(SO_4)_2(OH)_{21.46}\cdot 10.3H_2O$ calculated on the basis of 2 sulphate groups.
2. Ioi Mine, Shiga, Japan (Peacor et al., 1985)
3. $Mn_7Al_4(SO_4)_2(OH)_{22}.8H_2O$.

TABLE 2. Powder X-ray diffraction data for shigaite from Iron Monarch, South Australia.

I	d_{obs}	d_{cal}	hkl
s	10.89	10.95	003
s	5.457	5.447	006
w	4.720	4.761	110
w	4.389	4.366	113
vw	3.949	3.999	202
		3.685	024
s	3.665	3.651	009
		3.677	018
w	3.085	3.062	122
vw	2.728	2.749	300
m	2.658	2.666	303
s	2.456	2.456	306
w	2.305	2.326	223
ms	2.199	2.203	134
		2.196	039
s	1.940	1.940	3.0.12
s	1.720	1.718	328
ms	1.580	1.581	3.0.17
ms	1.573	1.575	2.1.18
s	1.533	1.537	1.0.21

Cell parameters: $a = 9.52(1)$ $c = 32.89(6)$ Å

Gandolfi camera, using Mn-filtered Fe-$K\alpha$ radiation. The spacings and visually estimated intensities are given in Table 2. The unit cell parameters were refined by least squares methods using these data and the parameters for a trial hexagonal cell obtained from precession and oscillation photographs given by a very small single crystal. The final cell parameters are $a = 9.52(1)$, $c = 32.89(6)$ Å. These results are within experimental error of those reported by Peacor *et al.* (1985). A diffraction pattern was also recorded with the Gandolfi camera evacuated. Due to the partial dehydration of the sample under vacuum, its diffraction pattern is significantly different to that recorded at atmospheric pressure (see Table 3). Peacor *et al.* (1985) reported that partial dehydration (13.5% by weight) occurs under a strong vacuum (1×10^{-7} torr) at room temperature. This weight loss corresponds to the loss of 42 water moelcules per cell, there being three formula units per cell. The *en vacu* pattern given by the Iron Monarch shigaite, if indexed and refined on a hexagonal cell similar to the shigaite cell above, gives $a = 9.44(1)$, $c = 34.40(1)$ Å. The cell therefore expands nearly 3%, by volume, during dehydration; the expansion occurs chiefly along the c repeat, while the a repeat contracts slightly. Single-crystal photographs were not obtained for the dehydrated material and hence its true symmetry is uncertain. The pronounced parting along the prismatic axes of the hexagonal crystals, seen in Fig. 1, was probably caused by their partial dehydration and associated expansion in the evacuated scanning electron microscope chamber.

In structural terms, Peacor *et al.* (1985) sugested that shigaite is related to mooreite, $Mg_{9.1}Mn_{1.89}Zn_{4.04}(SO_4)_2(OH)_{26}.8H_2O$ (Hill, 1980) and lawonbauerite $(Mn,Mg)_9Zn_4(SO_4)_2$-$(OH)_{22}.8H_2O$ (Treiman and Pecor, 1982). The structures of both these minerals are based on the stacking of brucite-like units which are linked by $Mn(OH)_2(H_2O)_4{}^{2-1}$ octahedra with hydrogen bonding between hydroxide and water molecules. In both mooreite and lawsonbauerite, the brucite layers contain vacant octahedral sites. This feature probably causes the difference in stoichiometry between shigaite, mooreite and lawsonbauerite. The exact details of the shigaite structure and its relationship to mooreite and

TABLE 3. Powder X-ray diffraction data for shigaite en vacu from Iron Monarch, South Australia.

I	d_{obs}	d_{cal}	hkl
w	11.39	11.47	003
vs	8.66	8.60	004
w	4.70	4.72	110
s	4.40	4.37	113
w	4.30	4.30	008
vw	3.323	3.330	206
m	2.715	2.727	300
ms	2.605	2.607	1.1.11
		2.600	304
s	2.318	2.313	223
		2.008	229
m	2.006	2.006	318
ms	1.727	1.728	415
		1.590	2.2.16
w	1.585	1.586	2.0.20
		1.584	4.1.10
w	1.560	1.560	3.1.16
w	1.494	1.492	426

Cell parameters: $a = 9.44(1)$ $c = 34.40(4)$ Å lawsonbauerite await a full single crystal structure determination which we hope shortly to initiate using crystals from Iron Monarch.

Acknowledgements. The authors wish to thank Mr. Stuart McClure of CSIRO Division of Soils, Adelaide, for taking the SEM micrograph. Microprobe analyses were obtained in the Department of Geology, University Melbourne.

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[*Manuscript received 16 September 1991*]

KEYWORDS: shigaite, Iron Monarch, South Australia, hydrated manganese aluminium sulphate, powder X-ray diffraction data, chemical analyses.

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MINERALOGICAL MAGAZINE, SEPTEMBER 1992, VOL 56, PP. 419–422

The occurrence of daqingshanite-(Ce) in the Nkombwa Hill carbonatite, Zambia

DAQINGSHANITE-(Ce), $(Sr,Ca,Ba)_3(Ce,La)(PO_4)(CO_3)_{3-x}(OH,F)_x$, was first found in 1976 in the margin of an altered pegmatite dyke in the Mont Saint-Hilaire alkaline intrusive complex, Quebec, Canada, and was recognised as a potential new species (Chao and Baker, 1979; Horváth and Gault, 1990). Daqingshanite was also identified in 1980 in low-grade meta-dolomite in the footwall zone of the Proterozoic Bayan Obo iron ore–rare earth element (*REE*) deposit in China and was subsequently described as a new species with the ideal formula $Sr_3RE(PO_4)(CO_3)_3$ (Yinchen *et al.*, 1983; Shigley, 1984). At Bayan Obo there may be some genetic links with carbonatite dykes. During a mineralogical study of the Nkombwa Hill carbonatite complex in northern Zambia, the present authors discovered daqingshanite in magnesiocarbonatite (Woolley and Kempe, 1989).

The Nkombwa Hill carbonatite (Turner *et al.*, 1989) is a 700 m wide and 1200 m long oval plug of dolomite carbonatite and subsidiary ferrocarbonatite occurring in northern Zambia as part of the late Proterozoic North Nyasa alkaline province