

Gatehouseite, a new manganese hydroxy phosphate from Iron Monarch, South Australia

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Abstract

Gatehouseite is a new manganese hydroxy phosphate from Iron Monarch, South Australia. The new mineral occurs as radiating clusters of pale yellow, and yellow to pale brownish orange bladed crystals up to 100 μm in length. The crystals are elongated along [010] and the principal forms are {102}, {110} and {001}. Gatehouseite also occurs as overgrowths on prismatic arsenoclasite crystals. Associated with gatehouseite are baryte, shigaite, manganose ferroan calcite, hausmannite and hematite. Gatehouseite appears to have formed at low temperature by the interaction of phosphorus-rich fluids on hausmannite in carbonate-rich fractures in the hematite ore. Electron microprobe analysis yielded: MnO 64.42, FeO 0.19, CuO 0.03, ZnO 0.03, PbO 0.05, Al₂O₃ 0.10, P₂O₅ 22.18, V₂O₅ 0.38, As₂O₅ 3.58, H₂O (6.44%). These data gave an empirical formula of Mn_{5.09}Fe_{0.01}Al_{0.01}(P_{1.75}As_{0.17}V_{0.02})_{Σ1.94}O₈(OH)_{4.00}, calculated on the basis of 12 oxygen atoms. The simplified formula is Mn₅(PO₄)₂(OH)₄. The mineral is transparent with a pale yellow streak, an adamantine lustre and an estimated Mohs hardness of 4. The crystals exhibit a distinct cleavage on {010} and have a splintery fracture. The strongest lines in the X-ray powder pattern are (*d*_{obs}, *I*_{obs}, *hkl*) 4.48 (10) (004); 4.03 (10) (104); 2.900 (100) (115); 2.853 (70) (106); 2.801 (50) (021); 2.702 (80) (303); 2.022 (15) (322); 1.608(15) (330). These data were indexed on an orthorhombic cell, with *a* = 9.097(2), *b* = 5.693(2), *c* = 18.002(10) Å and a volume of 932.4(8) Å³; the space group is probably P2₁2₁2₁. For Z = 4 and using the empirical formula, the calculated density is 3.74 g/cm³. Optical properties could not be determined in full; two refractive indices are 1.74(1) and 1.76(1) (white light); pleochroism is distinct from brown to near colourless. The crystals are length slow with parallel extinction. The name is for Dr. Bryan Michael Kenneth Cummings Gatehouse (1932–), crystal chemist of Monash University, Melbourne, Australia.

KEYWORDS: gatehouseite, new mineral, manganese hydroxy phosphate, arsenoclasite, Iron Monarch, South Australia.

Introduction

IN May 1987, Mr. Glyn Francis, Quality Control Officer at the Iron Monarch iron ore deposit, submitted a group of specimens from the mine to one of the authors (AP) for identification. One specimen contained a few very small pale brownish orange crystals which were unfamiliar. Energy dispersive X-ray analyses showed that the mineral contained manganese, phosphorus and a minor amount of arsenic. Electron microprobe analysis indicated that the mineral had a formula

of the type $M_5(XO_4)_2(OH)_4$, similar to arsenoclasite and pseudomalachite. However there was insufficient material to enable the powder X-ray diffraction pattern to be recorded. Also in one group of specimens submitted for study was one which contained prismatic crystals up to 5 mm long of a dark orange brown mineral which proved to be arsenoclasite. The crystals were overgrown by rims of what appeared to be the undescribed phosphorus analogue of arsenoclasite (Pring *et al.*, 1989). Several years later Mr. Francis located further specimens containing

the small brownish orange crystals with enough material to obtain an X-ray diffraction pattern. The diffraction pattern showed that the small brownish orange crystals and the overgrowths were the same mineral; this mineral was subsequently confirmed as the new phosphorus analogue of arsenoclasite.

The new species, gatehouseite, has been named for Dr. Bryan Michael Kenneth Cummings Gatehouse (1932–) a crystal chemist of Monash University, Melbourne, Australia, in recognition of his outstanding contribution to the understanding of the crystal chemistry of oxides and oxysalts. The mineral and the name were approved by the Commission on New Minerals and Mineral Names in 1992 (92-016). Type specimens are held in the collections of the South Australian Museum, Adelaide, and the Museum of Victoria, Melbourne.

Occurrence

Iron Monarch (32°45'S, 137°08'E) is situated at the northern end of the Middleback Ranges on Eyre, Peninsula, South Australia, some 500 km northwest of Adelaide. The Ranges contain a number of large sedimentary iron ore deposits of Precambrian age, including Iron Monarch, which are currently worked by Broken Hill Proprietary Limited as a source of high grade iron ore. The Iron Monarch orebody also contains pods of high-grade manganese ore and the presence of iron and manganese with small amounts of copper, zinc, phosphorus and other elements has led to an unusually diverse secondary mineralogy. To date approximately 100 mineral species have been identified from the Iron Monarch deposit (Pring *et al.*, 1992a).

The mine sequence at Iron Monarch consists of a series of massive bands of hematite which grade into siliceous iron formation (Miles, 1954). The sequence also contains a number of pods of manganese mineralisation. In the upper part of the deposit the manganese minerals are principally pyrolusite and cryptomelane, whereas lower in the sequence hausmannite is the dominant manganese mineral. During its geological history the deposit has been folded gently and intruded by dolerite dykes. It is known that the iron-manganese ore contains small but significant amounts of elements such as Zn and P, and lesser amounts of other elements such as Cu, As, V and Bi. These elements were mobilised into groundwaters during weathering processes. The secondary minerals precipitated from these fluids into fractures and joint planes in the orebody.

The new mineral occurred in cavities in a

matrix consisting of hematite, hausmannite, baryte and carbonates from the 130-metre level on the eastern side of the Iron Monarch open-cut. Shigaite, baryte, arsenoclasite, manganiferous ferroan calcite, hausmannite and hematite are found in close association with gatehouseite. Metaswitzerite–switzerite, sussexite, pyrobelonite, and triploidite have also been identified on specimens from the same immediate area of the open-cut but these minerals have not been noted in direct association with gatehouseite (Pring *et al.*, 1989, 1992a, b).

Ruszala *et al.* (1977) prepared $\text{Mn}_5(\text{PO}_4)_2 \cdot (\text{OH})_4$ in sealed gold tubes at 400°C and 3.7 kbar from a mixture of $\text{Mn}_3(\text{PO}_4)_2$ and KOH and they noted that under less basic conditions triploidite was produced. While the geological evidence at Iron Monarch suggests a much lower temperature and pressure regime it seems likely that gatehouseite and triploidite were formed from the interaction of basic fluids with hausmannite under changing pH conditions.

Physical and optical properties

Gatehouseite occurs as radiating to divergent groups of individual blade-like crystals up to 100 $\mu\text{m} \times 20 \mu\text{m} \times 5 \mu\text{m}$ and elongated parallel to [010]. The principal forms observed are {102}, {110} and {001} (Figs. 1 and 2). Contact twinning on {001} is sometimes observed. The crystals have a splintery fracture and a distinct cleavage on {010} (arsenoclasite has a perfect cleavage on {010}; Moore, 1967). The crystals are transparent and the colour ranges from pale yellow through yellow to pale brownish orange with a pale yellow streak. The lustre is adamantine and the Mohs hardness is estimated to be 4. The density could not be measured because of the small crystal size, however the calculated density with $Z = 4$ is 3.74 g cm^{-3} , based on the empirical formula, or 3.85 g cm^{-3} for the simplified formula $\text{Mn}_5(\text{PO}_4)_2(\text{OH})_4$.

Gatehouseite is biaxial but the sign could not be established. Because of the morphology it was possible to measure only two of the three refractive indices, which were 1.74(1) and 1.76(1) (measured in white light). The 2V could not be measured or calculated, nor could the dispersion be observed. The crystals are length slow with parallel extinction. Gatehouseite exhibits distinct pleochroism with the colour changing from brown to near colourless.

Gatehouseite also occurs as overgrowths on arsenoclasite crystals up to 5 mm in length. In this mode of occurrence gatehouseite forms the outer rims of arsenoclasite crystals.

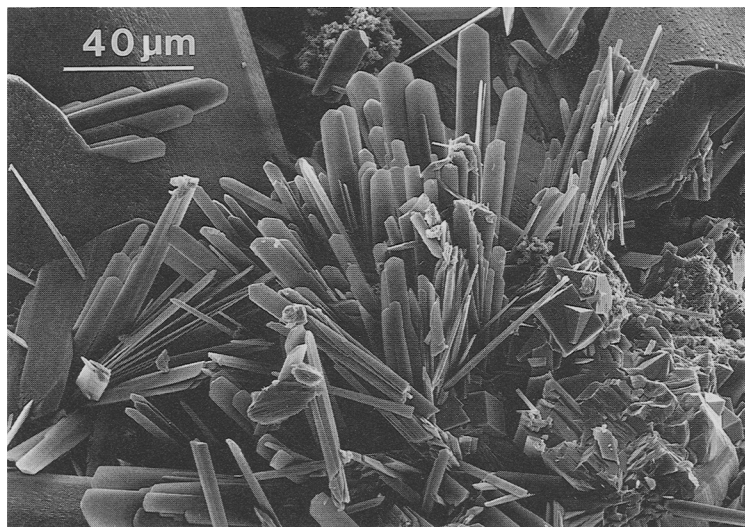


FIG. 1. (left) SEM photomicrograph showing a group of blade-like crystals of gatehouseite with baryte.

Chemistry

Gatehouseite was analysed using a JEOL electron microprobe at 15 kV with a nominal specimen current of 0.020 μ A. The standards used were pure metals (Mn, Cu, V), fluorapatite (P), arsenopyrite (As), sphalerite (Zn, S), hematite (Fe), galena (Pb) and corundum (Al). No other elements with an atomic number greater than eight were detected by wavelength spectroscopy. Water could not be determined directly as there was insufficient material; thus in the analyses below, water was calculated to give 4(OH) by analogy with arsenoclasite. A total of four analyses were obtained for the small blade-like crystals, for which the average is given in Table 1. The empirical formula, calculated on the basis of 12 oxygens, is $Mn_{5.09}Fe_{0.01}Al_{0.01}(P_{1.75}As_{0.17}V_{0.02})\Sigma_{1.94}O_8(OH)_{4.00}$ and the simplified formula is $Mn_5(PO_4)_2(OH)_4$. The analyses of gatehouseite rims and the arsenoclasite crystals are also presented in Table 1. The empirical formula for the rims and cores are $Mn_{4.78}Al_{0.03}(P_{1.74}As_{0.16}S_{0.01})\Sigma_{1.91}O_8(OH)_{4.00}$ and $Mn_{4.74}Al_{0.02}(As_{1.80}P_{0.12}S_{0.02})\Sigma_{1.94}O_8(OH)_{4.00}$ respectively. These analyses suggest that there is only limited solid solution between gatehouseite and arsenoclasite and that the two forms of gatehouseite have similar compositions.

Electron microprobe analysis gave consistently low totals for the formula $Mn_5(PO_4)_2(OH)_4$ and suggested rather a formula $Mn_{5.2}(PO_4)_{1.8}(AsO_4)_{0.2}(OH)_{4.2} \cdot 1 \cdot H_2O$ (when calculated on the basis of (P + As = 2)) or $Mn_5(PO_4)_{1.71}$

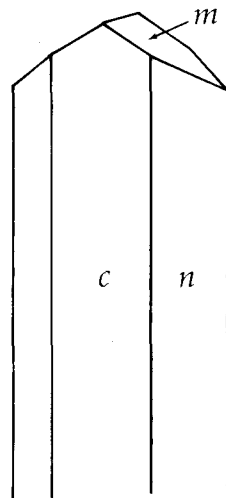


FIG. 2. (right) Schematic diagram showing the principal forms of gatehouseite: c, {001}; m, {110}; and n, {102}.

TABLE 1 Electron microprobe analysis of gatehouseite.

Wt% Oxide	1.	2.	3.	4.
MnO	64.42	63.34	55.74	66.59
FeO	0.19	-	0.03	-
CuO	0.03	0.04	0.05	-
ZnO	0.03	-	0.11	-
PbO	0.05	0.05	0.15	-
Al ₂ O ₃	0.10	0.32	0.17	-
P ₂ O ₅	22.18	23.05	1.37	26.65
V ₂ O ₅	0.38	-	-	-
As ₂ O ₅	3.58	3.32	34.10	-
SO ₃	-	0.10	0.23	-
H ₂ O*	6.44	6.43	5.85	6.76
Total	97.40	96.65	97.80	100.00

* H₂O calculated for 2 H₂O

1. Fine brownish orange crystals, Iron Monarch, S. Aust.
 $Mn_{5.09}Fe_{0.01}Al_{0.01}(P_{1.75}As_{0.17}V_{0.02})\Sigma_{1.94}O_8(OH)_{4.00}$
calculated on the basis of 12 oxygens.
2. Rim of arsenoclasite crystals, Iron Monarch, S. Aust.
 $Mn_{4.78}Al_{0.03}(P_{1.74}As_{0.16}S_{0.01})\Sigma_{1.91}O_8(OH)_{4.00}$.
3. Core of arsenoclasite crystals, Iron Monarch, S. Aust.
 $Mn_{4.74}Al_{0.02}(As_{1.80}P_{0.12}S_{0.02})\Sigma_{1.94}O_8(OH)_{4.00}$.
4. $Mn_5(PO_4)_2(OH)_4$.

(AsO_4)_{0.19}(OH)_{4.09} · H₂O (when calculated on the basis of 13 oxygen atoms). The formula and the analytical total may be improved if it is assumed one of five Mn cations is trivalent rather than divalent and thus there are five rather than four OH groups. This is in some ways a reasonable proposition in that gatehouseite occurs with

hausmannite and bermanite, both of which contain divalent and trivalent Mn. However there is no independent evidence for this suggestion. The light colour of gatehouseite suggests that the absence of significant amounts of trivalent Mn and the X-ray diffraction data confirm that gatehouseite is isostructural with the synthetic $Mn_5(PO_4)_2(OH)_4$ of Ruzsala *et al.* (1977) and that the unit cell contains 48 not 52 oxygens. The low totals for the electron microprobe analyses may be due to problems with ZAF correction procedures or microscopic fluid inclusions in the crystals.

X-ray crystallography

The powder X-ray diffraction pattern was recorded using a 100 mm diameter Guinier-Hägg camera with monochromated $Cr-K\alpha_1$ radiation ($\lambda = 2.2896 \text{ \AA}$) and with silicon employed as an internal standard. Line intensities were estimated visually by comparison with a set of standard reflections. The powder pattern for gatehouseite (blade-like crystals) is given in Table 2. The

TABLE 2. Powder X-ray diffraction data for gatehouseite.

I/I_0	$d_{obs.} (\text{\AA})$	$d_{cal.} (\text{\AA})$	hkl
10	4.483	4.500	004
10	4.034	4.034	104
5	3.540	3.531	014
100	2.900	2.886	115
70	2.853	2.849	106
50	2.802	2.811	021
80	2.702	2.707	303
5	2.586	2.601	122
10	2.291	2.293	216
10	2.265	2.269	117
5	2.186	2.184	108
15	2.022	2.022	322
10	2.014	2.013	126
10	1.784	1.784	502
5	1.774	1.775	113
2	1.767	1.765	028
10	1.722	1.722	318
10	1.709	1.707	326
10	1.699	1.702	512
15	1.608	1.609	330

Cell parameters refined from the data above:

$$a = 9.097(2), b = 5.693(2), c = 18.002(10) \text{ \AA}$$

$$\text{Volume} = 932.4(8) \text{ \AA}^3$$

pattern was indexed by analogy with arsenoclasite and gave an orthorhombic cell. Least squares refinement was undertaken using 20 reflections with $2\theta < 80^\circ$. The final parameters obtained were $a = 9.097(2)$, $b = 5.693(2)$, $c = 18.002(10) \text{ \AA}$, $V = 932.4(8) \text{ \AA}^3$. The axial ratios calculated from the unit cell parameters are $a:b:c = 1.5979:1:3.1618$. This unit cell is within experimental error of that reported by Ruzsala *et al.* (1977) for synthetic $Mn_5(PO_4)_2(OH)_4$. Ruzsala *et al.* (1977) established that synthetic $Mn_5(PO_4)_2(OH)_4$ has the space group $P2_12_12_1$ and is isostructural with arsenoclasite. The assignment of the unit cell for gatehouseite was confirmed by electron diffraction patterns obtained using a Philips EM400 transmission electron microscope fitted with a double tilt holder.

Relationship to other minerals

Gatehouseite is a new member of the compositional group $M_5(XO_4)_2(OH)_4$, which includes minerals such as arsenoclasite, pseudomalachite, reichenbachite, ludjibaite, cornwallite and cornubite. The structural relationships between these minerals are yet to be fully established; however Shoemaker and Kostiner (1981) have compared the structures of the three polymorphs of $Cu_5(PO_4)_2(OH)_4$ —pseudomalachite, ludjibaite and reichenbachite. They found that the structures are based on common structural elements but differ in the topography of the layers of edge-sharing CuO_6 polyhedra. Cornwallite is isostructural with pseudomalachite (Berry, 1951), while cornubite is structurally distinct from the $Cu_5(PO_4)_2(OH)_4$ polymorphs. Moore and Molin-Case (1971) determined the structure of arsenoclasite and suggested that it was distinct from the $Cu_5(PO_4)_2(OH)_4$ polymorphs in that manganese was present in trigonal bipyramidal coordination, in addition to the octahedral coordination found in the structures in this chemical family. Ruzsala *et al.* (1977) showed that synthetic $Mn_5(PO_4)_2(OH)_4$ is isomorphous with arsenoclasite. However they argue that Moore and Molin-Case's trigonal bipyramids are in fact highly distorted octahedra, and that while structures differ in topological detail from the $Cu_5(PO_4)_2(OH)_4$ polymorphs, they are nevertheless part of the same structural group.

Arsenoclasite is a rare mineral and its distribution in nature, until its discovery at Iron Monarch, was restricted to Långban in Sweden. At Långban it occurs in fissures in hausmannite-impregnated dolomite with sarkinite and adelite (Aminoff, 1931). Arsenoclasite is one of a series of basic

manganese arsenates, with the general formula $Mn^{2+}_n(OH)_{2n-3x}(AsO_4)^{3-x-}$, which have been found at Långban, Sweden. This series includes allactite, $Mn_7(AsO_4)_2(OH)_8$, synadelphite, $Mn_4(AsO_4)(OH)_5$, eveite, $Mn_2(AsO_4)(OH)$, and sarkinite, $Mn_2(AsO_4)(OH)$. With the exception of arsenoclasite, sarkinite, which is isostructural with triploidite, is the only one of these minerals for which a phosphate analogue is known. The occurrence of triploidite and gatehouseite together at Iron Monarch suggests that analogues of allactite, eveite and synadelphite may also be found at Iron Monarch.

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