First Occurrence of Mandarinoite in China

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Abstract   This report describes the first occurrence of the rare mineral mandarinoite ($Fe^{3+}_2 Se_3 O_9 \cdot 6H_2O$) in China. It occurs in the Lower Permian Maokou Formation carbonaceous shale in Yutangba Village east of Enshi City in southwestern Hubei Province. The shale is selenium-rich and contains native selenium, V-Mo-Cr-bearing iron oxide, clay and quartz. Weathering of the selenium in the bedrock under moderate to high redox conditions in the presence of ferric iron has formed mandarinoite.

Key words: mandarinoite, selenium, carbonaceous shale (stone coal), Hubei, China

1 Introduction

Mandarinoite is a hydrated ferric iron selenite originally described by Dunn et al. (1978) and further studied in detail by Hawthorne (1984). In the type locality at the Pacajake Mine, Bolivia, the paragenetic association is various secondary selenium minerals. It is a rare species and has only been reported from four localities (Dunn et al., 1978; Hawthorne, 1984). Hawthorne (1984), on the basis of crystal structure analysis, modified the original formula to ($Fe^{3+}_2 Se_3 O_9 \cdot 6H_2O$). We found rare crystals of mandarinoite in a carbonaceous shale (known locally as stone coal) from Yutangba, a typical Se-rich area in China (Zheng et al., 1992; Wen and Qiu, 1999; Zhu et al., 2000), which is situated in the northern part of Shuanghe Town about 81 km east of Enshi City in southwestern Hubei Province. Mandarinoite was found during part of a detailed investigation of the mineralogy and geochemistry of selenium-rich carbonaceous shales. This paper reports the mineralogy of mandarinoite and discusses its paragenetic significance.

2 Geology of the Selenium-rich Area of Enshi, Hubei

A series of samples was collected in order to investigate the selenium geochemistry, speciation and mineralogy. The samples are from the Lower Permian Maokou Formation on a hill slope in Yutangba Village. Sample C1 contains mandarinoite, and represents a siliceous part of the Maokou Formation, which is mostly limestone. Wen and Qiu (1999) discussed the origin of selenium-bearing formations in China and indicated that the western Hubei region is an extensional fault basin. All of the selenium-bearing formations are closely related to rifts or syngenetic deep faults, whether they are developed at the margin of the
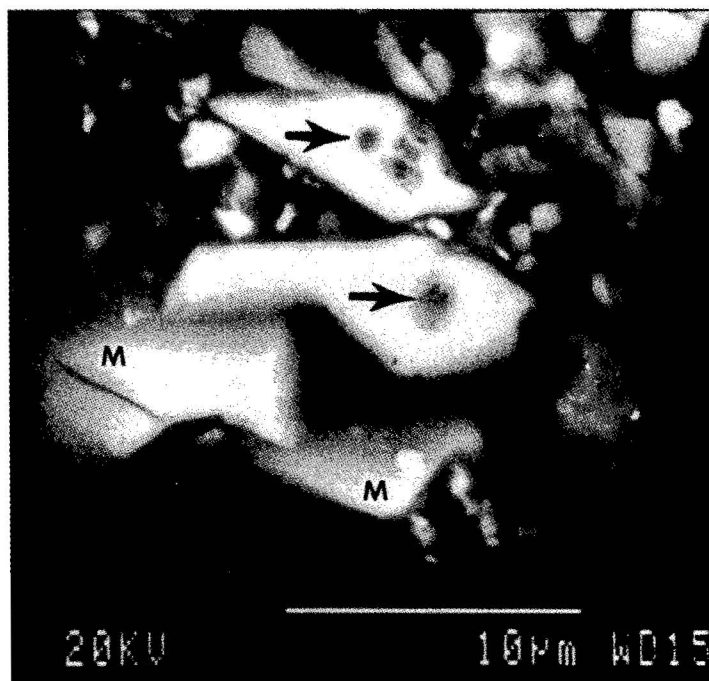

Fig. 1. Back-scattered, scanning electron microscope image of crystals of mandarinoite (M).
Arrows point to mandarinoite crystals that have suffered electron-beam damage.

Table 1   Chemical composition of host rock

SiO$_2$ (wt.%)	60.83	As (ppm)	3.54
TiO$_2$	0.185	Ba	89
Al$_2$O$_3$	4.29	Br	3.55
Fe$_2$O$_3$	0.67	Ce	22.3
MnO	0.031	Co	0.92
MgO	0.46	Cr	870
CaO	0.06	Cu	40
Na$_2$O	0.06	Hg	0.29
K$_2$O	0.67	Mo	883
P$_2$O$_5$	0.08	Ni	358
LOI	31.82	Sb	8.72
Total	99.16	Se	760
		Th	3.4
		U	58.4
Ash (wt. %)	68.2	V	3466
C (total)	26.6	W	1.66
S (total)	0.5	Au (ppb)	75.28

Notes: 1) major oxides, Ba, V by ICP analysis; 2) LOI = loss on ignition; 3) C, S by infrared spectroscopy; 4) Ce, Cu, Mo, Ni, Th and U by ICP-MS; 5) As, Br, Co, Cr, Sb, Se, W and Au by INAA; 6) Hg by cold vapor AA spectroscopy; 7) total iron as Fe$_2$O$_3$.

Fig. 2.   Energy-dispersive spectrum of mandarinoite showing the position of the major K_a peaks.
The minor K_β and L_a peaks of Fe are shown. Carbon is from the conductive coating. The y-axis is count intensity.

Table 2   Electron microprobe analyses of mandarinoite

Sample	C1p.1	C1p.3	C1p.1107	Average	Ideal formula
SeO$_2$ (wt.%)	55.53	57.98	57.40	56.97	55.68
Fe$_2$O$_3$	25.95	25.38	24.66	25.33	26.86
SO$_3$	0.25	0.00	0.13	0.13	-----
Total	81.73	83.36	82.19	82.43	82.84
H$_2$O by difference	18.27	16.64	17.81	17.57	17.16
Cations on the basis of 9 oxygens					
Se	3.007	3.090	3.103	3.067	3.000
Fe	1.953	1.880	1.843	1.892	2.000
S	0.019	0.000	0.010	0.010	-----
Total	4.979	4.970	4.956	4.968	5.000

Note: Total iron as Fe$_2$O$_3$; Total sulfur as SO$_3$; Ideal formula from Hawthorne (1984).

Yangtze craton or within it. Table 1 gives the chemical composition of the Se-rich carbonaceous shale that contains mandarinoite.

Endemic selenosis related to soils developed on Se-rich carbonaceous shales has been described in Yutangba Village (Zheng et al., 1992; Zhu et al., 2000). The circumstances of the ecotoxicity are related to Se bioavailability in the soil and uptake in plants, especially corn. The resulting selenosis was severe in some cases but limited to a small population.

3 Mode of Occurrence

Mandarinoite was found in carbonaceous shale containing native selenium, a vanadium, molybdenum-bearing iron oxide, various clays and quartz. It occurs as small crystals from 2 to 10 μm in size (Fig. 1). Two clusters of these crystals have been observed. It has a green color in incident light. No cleavage was observed. The hardness was not measured but is inferred to be low from the observed extreme electron-beam sensitivity.

4 Chemical Composition

Mandarinoite was first noted in the carbonaceous shale during a detailed examination by scanning electron microscope imaging aided by energy-dispersive X-ray analysis. Figure 2 shows an energy-dispersive spectrum of mandarinoite. It is important to note that oxygen was
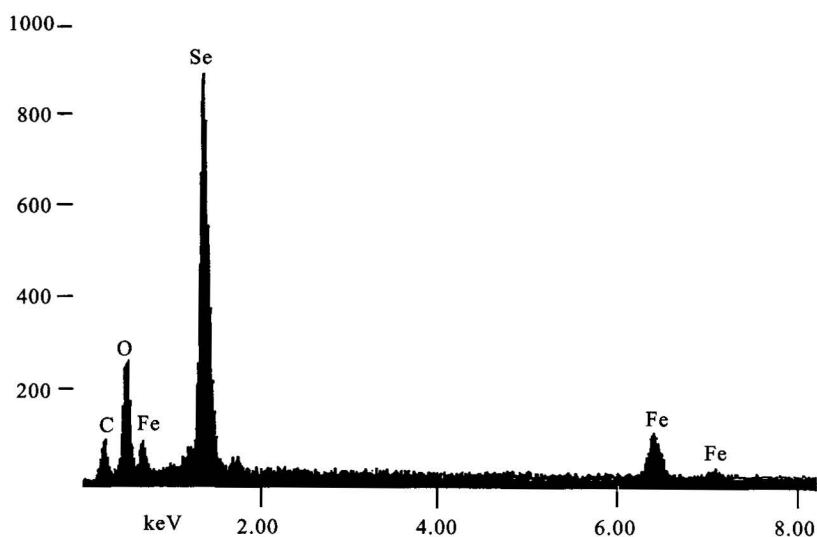
detected as a significant component of the phase. Mandarinoite was quantitatively analyzed using a JEOL JXA-8900R, fully-automated, five-spectrometer electron microprobe using wavelength-dispersive spectrometry. Operating conditions were 15 keV accelerating potential using 10 nanoampere beam current. The phase is very electron-beam sensitive (Fig. 1) and special care was taken during analysis. A 2 to 3 μm spot was used with counting times of 10 s on the peak and 10 s on background. Selenium metal, hematite and troilite were used as standards and the data were reduced using a Phi-Rho-Z (CITZAF) algorithm as supplied with the JEOL electron microprobe. Table 2 gives the results of representative electron microprobe analysis. The data in Table 2 are in good agreement with the structural formula as defined by Hawthorne (1984). The value of water determined by the difference is compatible with 6 waters of hydration, per formula unit.
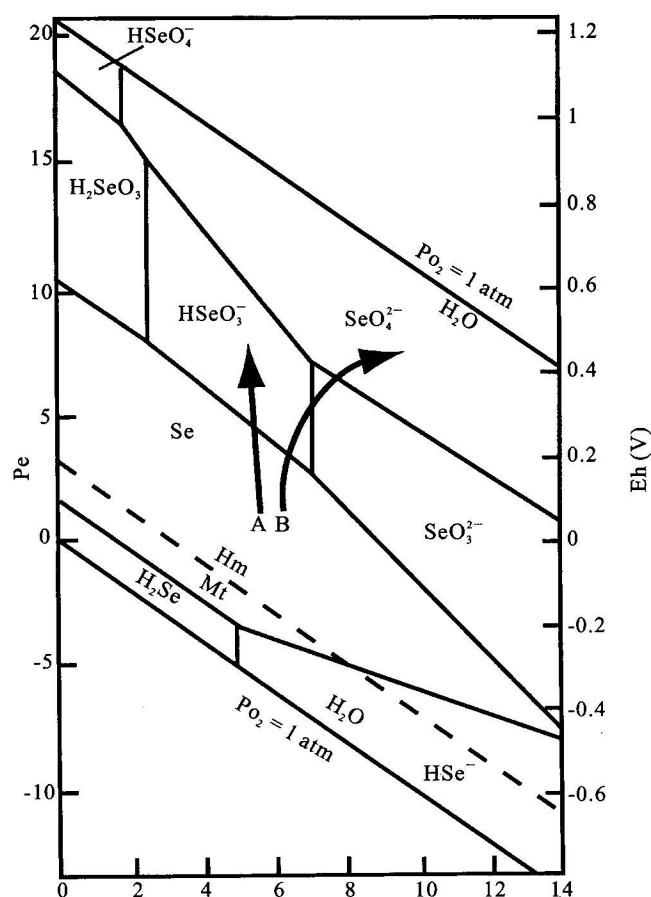
6 Discussion

Mandarinoite is a rare mineral resulting from the oxidation of more reduced selenium species. The bedrock in the Yutangba Village area contains extremely high selenium values, perhaps the highest in the world for shale (Zheng et al., 1992). The sample (C1) from which mandarinoite was found contains high Se and high values of the assemblage V-Mo-Cr (Table 1). Weathering of the Se-rich bedrock in this area has produced various insoluble and soluble Se species that are persistent in the soils. Selenium exists in four oxidation states in natural systems: +6 (selenate, SeO_4^{2-}), +4 (selenite, SeO_3^{2-}), 0 (elemental Se^0), and –2 (selenide, Se^{2-}). It can also be found in organic compounds such as amino acids or methylated compounds, and as metal-Se complexes. During chemical weathering of rocks, Se is easily oxidized. The oxidation state and pH of soils control the Se speciation in solution. Elrashidi et al. (1987) used the combined parameters of pe and pH (termed "redox") to model the chemical equilibria of selenium in soils. Selenate is the major species in solution at high pe + pH (> 15.0); at medium pe + pH (7.5–15) either SeO_3^{2-} or $HSeO_3^-$ species is predominant, depending on pH and at low pe + pH (< 7.5), HSe^- is the major species in solution. Figure 3 shows the selenium speciation as a function of pe and pH (Brookins, 1988; Thomson et al., 1986). The behavior of selenium during oxidation in natural environments is largely controlled by that of iron, when present, by association with Fe-oxides in adsorbed or precipitated forms (Howard, 1977). During the weathering of a carbonaceous shale in a near-surface oxidizing environment, the formation of organic acids will lower pH, leading eventually to the formation of various selenite species. Further increase in redox in either the weathered bedrock or soil will lead to the occurrence of selenate. We have suggested a tentative redox + pH path for this process in the Yutangba Village area as shown in Fig. 3. Any increase in pH, for example, by liming (adding calcium carbonate) of the soil, at relatively constant, pe will yield conditions significantly more favorable for the formation of selenate, a more soluble species (Fig. 3). The logarithm of the solubility product (K_{sp}) of mandarinoite,

$$Fe_2(SeO_3)_3 \cdot 6H_2O \rightleftarrows 2Fe^{3+} + 3SeO_3^{2-} + 6H_2O ,$$
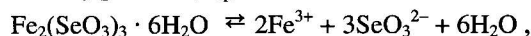
was found to be –41.6, which is less than any reported in the literature for a ferric selenite by more than 10 orders of magnitude (Rai et al., 1995). This shows the strong interaction between the aqueous ferric and selenite species, and suggests that the formation of mandarinoite will be strongly favored during partial oxidation of Se-rich rocks containing iron. However, mandarinoite is a rare species worldwide. This suggests either it is more abundant than recognized or the adsorption-desorption process of selenite

Fig. 3. Eh-pH diagram for the system Se-O-H modified from the literature (Brookins, 1988; Thomson et al., 1986).

Conditions are 1 atm pressure and 25°C for $10^{-6} M$ (0.08 mg/l) selenium. The hematite (Hm)-magnetite (Mt) boundary is drawn assuming a concentration of $10^{-6} M$ (0.06 mg/l) iron. Line A shows the probable pe + pH path for mandarinoite formation and line B indicates the effect of increased alkalinity from liming the soil. The paths are schematic and are used to illustrate general Se species evolution.

5 Crystal Structure

The original determination, based on limited data, by Dunn et al. (1978) assigned four molecules of water of hydration to the structure. Hawthorne (1984) on the basis of a detailed crystallographic study by direct methods observed that the formula unit contains six water molecules. Hawthorne (1984) reports that the space group is $P2_1/c$ with monoclinic cell dimensions of

a 16.810(4), b 7.880(2), c 10.019(2), β 98.26(2)°,

V 1313.4 Å, and Z=4.

The structure has large voids that are occupied by water molecules, which participate in a hydrogen-bonding scheme essential to the anion bond-valence requirements.

with ferric oxides, ferric hydroxides and/or clays plays a significant part in the weathering of selenium-rich shales.

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