HUBEITE

●

A NEW MINERAL FROM THE DAYE MINE NEAR HUANGSHI, HUBEI PROVINCE, CHINA

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ABSTRACT

Hubeite, ideally $Ca_2Mn^{2+}Fe^{3+}[Si_4O_{12}(OH)](H_2O)_2$, is a new mineral from the Daye mine near Huangshi, Hubei province, China. It occurs as radiating aggregates of intergrown crystals with well-developed terminal faces. Aggregates are less than 5 mm across and individual crystals do not exceed 2 mm in size. Individual crystals are bladed and are slightly elongate along the *b* axis with a rhombic cross-section and the forms {100}, {001}, {101}, {$0\bar{1}1$} and {352}. Aggregates consist of divergent fan-like clusters of individuals that often repeat across ~{001} to form 'bow-tie' arrangements. Hubeite is dark brown to pale brown, depending on crystal size, with a pale orange-brown streak, a vitreous luster and no observable fluorescence under ultraviolet light. It is brittle with a conchoidal fracture, and has a good cleavage parallel to {001} and no observable parting. Mohs hardness is 5½, the observed density is 3.02(2) g/cm^3 and the calculated density is 3.01 g/cm^3. It is biaxial with an indeterminate optic sign and α 1.667(1), β 1.679(1), γ 1.690(1), $2V(obs)$ = 89(2)°, $2V(calc)$ = 87(5)°, strongly pleochroic with X = yellow-brown, Z = dark yellow-brown, Z > X, X ∧ *b* = 20° (in γ obtuse), Y ∧ *c* = 13° (in α acute), Z = *a*. Hubeite is triclinic, space group $P\bar{1}$, with the following unit-cell parameters refined from X-ray powder-diffraction data: *a* 9.960(6), *b* 13.87(2), *c* 6.562(7) Å, α 133.19(6), β 101.50(6), γ 66.27(5)°, *V* 601(1) Å^3, Z = 2. The ten strongest lines in the X-ray powder-diffraction pattern are as follows: *d* (Å), *I*, (*h k l*): 9.072,

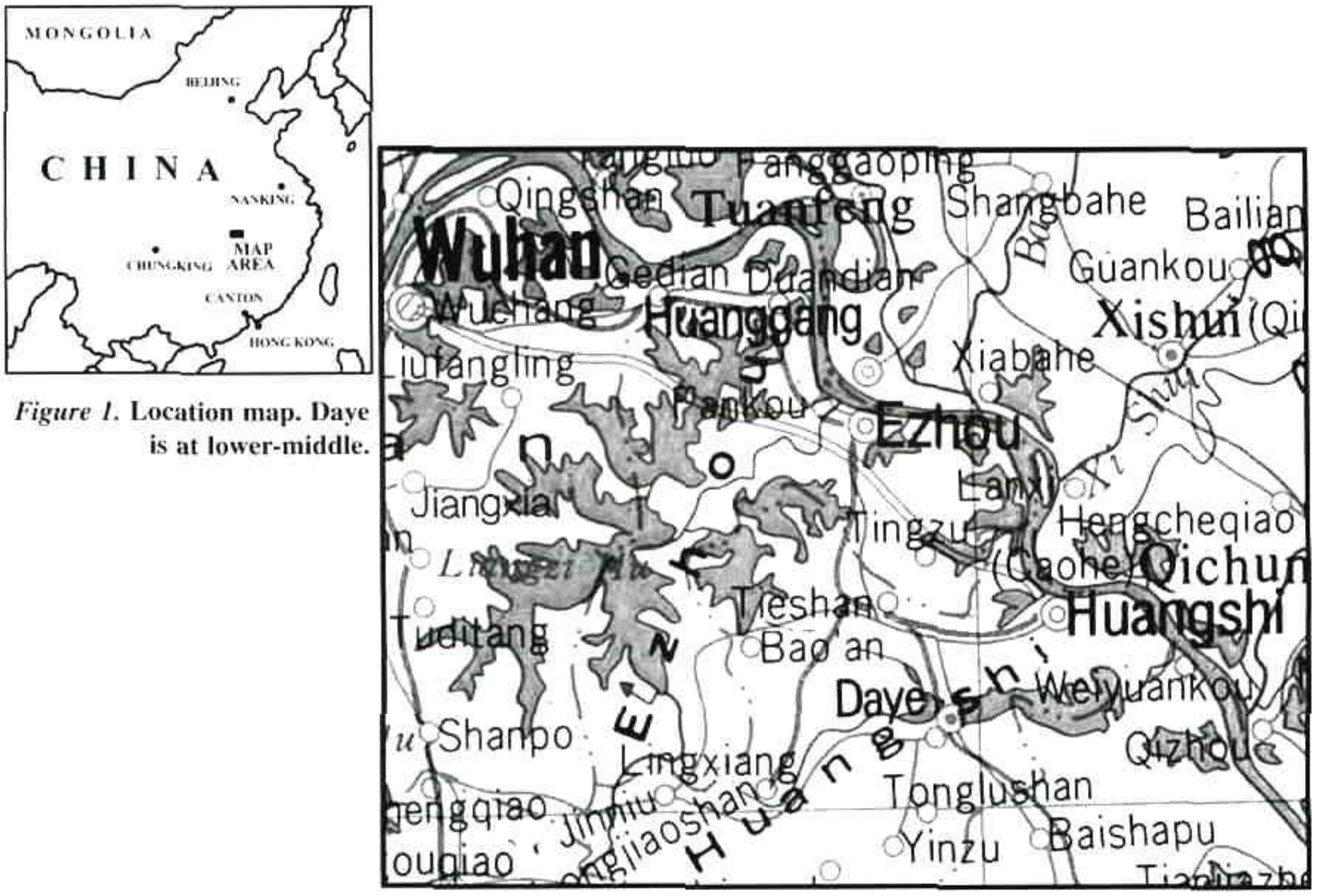

Figure 1. **Location map. Daye is at lower-middle.**

100, (1 0 0); 8.238, 90, (1 1 0); 5.000, 30, (1 2 0); 3.192, 30, (2 3 0); 3.126, 70, (3 2 0); 3.095, 70, ($\bar{1}42$); 2.781, 60, ($\bar{2}$ 2 0); 2.695, 30, ($\bar{1}52$); 1.993, 30, (3 3 1); 1.627, 30, ($\bar{1}54$, $\bar{1}73$). Chemical analysis by electron microprobe gave SiO_2 44.39, Al_2O_3 0.38, Fe_2O_3 13.94, MnO 11.34, MgO 0.29, CaO 21.91, H_2O(calc) 8.32, sum 100.57 weight %, where the amount of H_2O was determined by crystal-structure analysis. The resulting empirical formula, calculated on the basis of 15 anions, [including 1 (OH) and 2 (H_2O)] is $Ca_2(Mn^{2+}_{0.87}Ca_{0.12})_{\Sigma 0.99}(Fe^{3+}_{0.94}Al_{0.04}Mg_{0.04})_{\Sigma 1.02}Si_{4.00}O_{12}(OH)(H_2O)_2$; the end-member formula of hubeite is $Ca_2Mn^{2+}Fe^{3+}Si_4O_{12}(OH)(H_2O)_2$. The mineral is named for the province in China in which it was found. Hubeite has been approved by the Commission of New Minerals and Mineral Names of the International Mineralogical Association. Hubeite shows no close relationship to any other known mineral.

INTRODUCTION

At the 1998 Tucson Gem and Mineral Show, two of the authors acquired an intriguing brown mineral from The Rocksmiths and from Michel Jouty. Subsequent examination by X-ray powder diffraction suggested a new mineral, and this was confirmed by crystal-structure solution and refinement (Cooper and Hawthorne, 2002). The new mineral has the ideal chemical formula $Ca_2Mn^{2+}Fe^{3+}[Si_4O_{12}(OH)](H_2O)_2$ and was named **hubeite** (HÜ-BA-ĪT) after the geographical location of the type locality in the province of Hubei, China. The new mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association. The holotype specimen of hubeite *is stored in the Display Series of the National Mineral Collection of* Canada, housed in the Canadian Museum of Nature, Ottawa, Ontario, Canada (catalog # CMNMC 83268).

PHYSICAL AND OPTICAL PROPERTIES

Hubeite occurs as radiating aggregates of intergrown crystals with well-developed terminal faces. Aggregates are less than 5 mm across and individual crystals do not exceed 1 mm in size. Individual crystals are bladed and slightly elongate along the *b* axis with a rhombic cross-section. Dominant forms are {001} and {101} with minor {100}, {0$\bar{1}$1} and {35$\bar{2}$} (Fig.2). Aggregates consist of divergent fan-like clusters of individuals that repeat across ~{001}, or as "bow-tie" aggregates (Fig. 3). Hubeite is dark brown to pale brown (Fig. 4) depending on crystal size.

During the last two years, numerous hubeite-bearing specimens have come on the mineral market, representing at least two distinct parageneses. It occurs as isolated clusters of crystals, up to a few

Table 1. **Chemical composition (weight %)* and unit formula** of hubeite.**

SiO_2	44.39	Si	4.00
Al_2O_3	0.38		
Fe_2O_3	13.94	Fe^{3+}	0.94
MgO	0.29	Al	0.04
MnO	11.34	Mg	0.04
CaO	21.91	Σ	1.02
H_2O ***	(8.32)		
Total	100.57	Mn^{2+}	0.87
		Ca	0.12
		Σ	0.99
		Ca	2.00
		OH	1
		H_2O	2

* F, Na, K, Ti, Cr, V below detection limit; composition is the average of 25 points on 5 crystals

** calculated on the basis of 15 anions with OH = 1 and H_2O = 2 *pfu*

*** from the crystal-structure analysis of Cooper and Hawthorne (2002).

Table 2. **X-ray powder diffraction data for hubeite.**

$I_{est.}$	$d_{(meas.)}$ Å	$d_{(calc.)}$ Å	h	k	l	$I_{est.}$	$d_{(meas.)}$ Å	$d_{(calc.)}$ Å	h	k	l
100	9.072	9.059	1	0	0	3	2.460	2.467	2	$\bar{2}$	2
90	8.238	8.227	1	1	0	* 5	2.377	2.377	0	0	2
10	5.843	5.848	$\bar{1}$	$\bar{2}$	1	* 5	2.287	2.287	3	2	1
"	"	5.845	0	$\bar{2}$	1	3	2.196	2.195	$\bar{3}$	2	0
5	5.576	5.565	$\bar{1}$	1	0	* 20	2.164	2.164	$\bar{1}$	$\bar{5}$	3
5	5.374	5.411	$\bar{1}$	$\bar{1}$	1	5	2.116	2.122	$\bar{2}$	$\bar{5}$	3
* 30	5.000	4.997	1	2	0	"	"	2.120	2	$\bar{3}$	1
3	4.866	4.846	2	1	0	"	"	2.104	$\bar{2}$	$\bar{6}$	1
10b	4.723	4.753	0	0	1	* 3	2.088	2.088	0	$\bar{5}$	3
"	"	4.695	0	2	0	* 10	2.056	2.056	$\bar{1}$	$\bar{6}$	1
20	4.442	4.421	1	0	1	* 20	2.021	2.023	$\bar{2}$	2	1
* 20	4.013	4.024	$\bar{1}$	0	1	* 30	1.993	1.992	3	3	1
* 5	3.855	3.856	$\bar{2}$	$\bar{1}$	1	* 15	1.916	1.917	5	$\bar{1}$	0
* 10	3.655	3.650	$\bar{1}$	2	0	3	1.900	1.899	1	$\bar{6}$	2
* 10	3.581	3.590	$\bar{2}$	1	0	* 15	1.818	1.818	$\bar{4}$	$\bar{7}$	2
3	3.516	3.512	2	$\bar{1}$	1	3	1.784	1.788	$\bar{5}$	$\bar{1}$	1
3	3.453	3.452	1	1	1	"	"	1.783	2	$\bar{2}$	3
* 15	3.403	3.414	0	1	1	3	1.763	1.770	0	$\bar{1}$	3
* 30	3.192	3.189	2	3	0	"	"	1.767	5	1	1
* 70	3.126	3.123	3	2	0	* 3	1.747	1.746	$\bar{3}$	2	1
* 70	3.095	3.088	$\bar{1}$	$\bar{4}$	2	* 3	1.725	1.725	$\bar{4}$	$\bar{4}$	3
* 10	2.991	2.988	$\bar{1}$	1	1	3	1.693	1.697	5	$\bar{1}$	1
25	2.932	2.943	$\bar{2}$	$\bar{3}$	2	"	"	1.693	$\bar{2}$	3	1
"	"	2.923	0	$\bar{4}$	2	3	1.661	1.663	$\bar{5}$	$\bar{7}$	2
* 15	2.877	2.877	1	$\bar{2}$	2	5	1.648	1.652	4	1	2
* 60	2.781	2.783	$\bar{2}$	2	0	"	"	1.648	1	6	0
* 15	2.741	2.742	3	3	0	"	"	1.648	3	$\bar{5}$	2
* 30	2.695	2.694	$\bar{1}$	$\bar{5}$	2	"	"	1.647	3	$\bar{2}$	2
3	2.652	2.653	$\bar{1}$	$\bar{1}$	2	30	1.627	1.627	$\bar{1}$	$\bar{5}$	4
* 10	2.614	2.613	2	3	1	"	"	1.627	1	7	3
3	2.562	2.555	2	$\bar{2}$	1						
5	2.502	2.509	0	$\bar{5}$	2						
"	"	2.498	2	4	0						
"	"	2.495	$\bar{3}$	$\bar{3}$	2						

114.6 mm Debye-Scherrer powder camera: Co radiation, Fe filter (λ $CoK\alpha$ 1.79021 Å)
Intensities visually estimated: b = broad line; not corrected for shrinkage and no internal standard.
Indexed on the calculated intensities derived from crystal-structure refinement
* = reflections used for unit-cell refinement
refined unit-cell parameters: a 9.960(6), b 13.87(2), c 6.562(7) Å, α133.19(6), β 101.50(6), γ 66.27(5)°

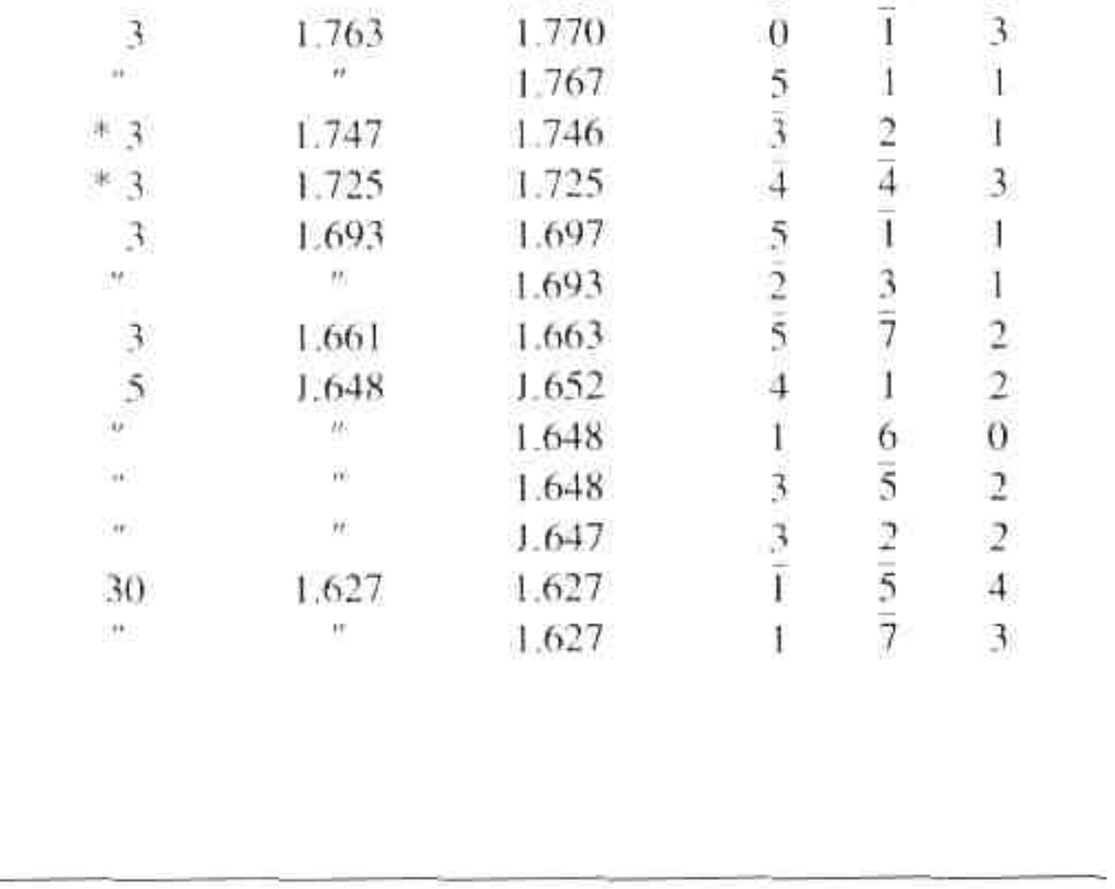

***Figure 2.* Idealized crystal drawing of hubeite. The setting of the axes is non-standard in order to maximize the number of forms visible; a = {100}, c = {00$\bar{1}$}, m = {101}, n = {0$\bar{1}$1}, x = {35$\bar{2}$}.**

millimeters across, perched on euhedral crystals of transparent to white quartz (Fig. 5). In some cases, these clusters are quite dense on a specimen (Fig. 6). A second association is as crystals covering both sides of flat, thin specimens (Fig. 7). Typically, one side is covered predominantly by hubeite with minor inesite and apophyllite, whereas the other side consists of approximately equal amounts of hubeite, pink inesite and white apophyllite (Fig. 8) or it can be dominated by pink inesite with only minor hubeite and apophyllite (Fig. 9). Hubeite can also occur with massive to radiating pink inesite that can be partly covered by a coating of honey-brown apophyllite and is associated with minor, small, equant, black prisms of ilvaite (Fig. 10).

Hubeite has a pale orange-brown streak, a vitreous luster and no observable fluorescence under ultraviolet light. It has a good cleavage parallel to {001}, no observable parting, and is brittle with a conchoidal fracture. Mohs hardness is 5½, the observed density is 3.02(2) g/cm³ (measured by suspension in methylene iodide) and the calculated density is 3.01 g/cm³. Optical properties

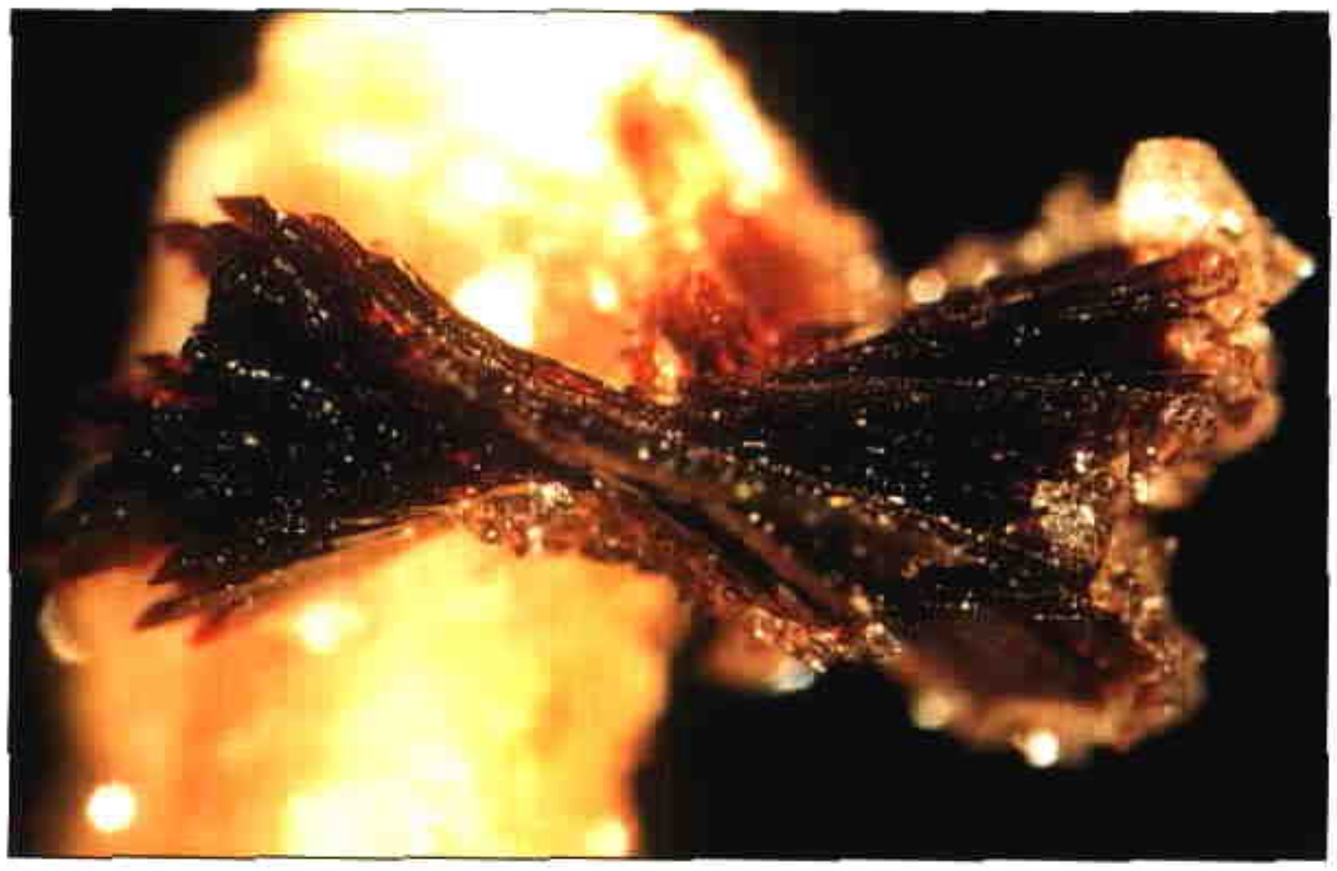

Figure 3. A bow-tie aggregate of hubeite crystals (~5 mm across) with white apophyllite coating the tips of the crystals; the out-of-focus pink crystal is inesite that is partly coated by apophyllite and quartz. Photography by Richard Green, Bill Cook specimen.

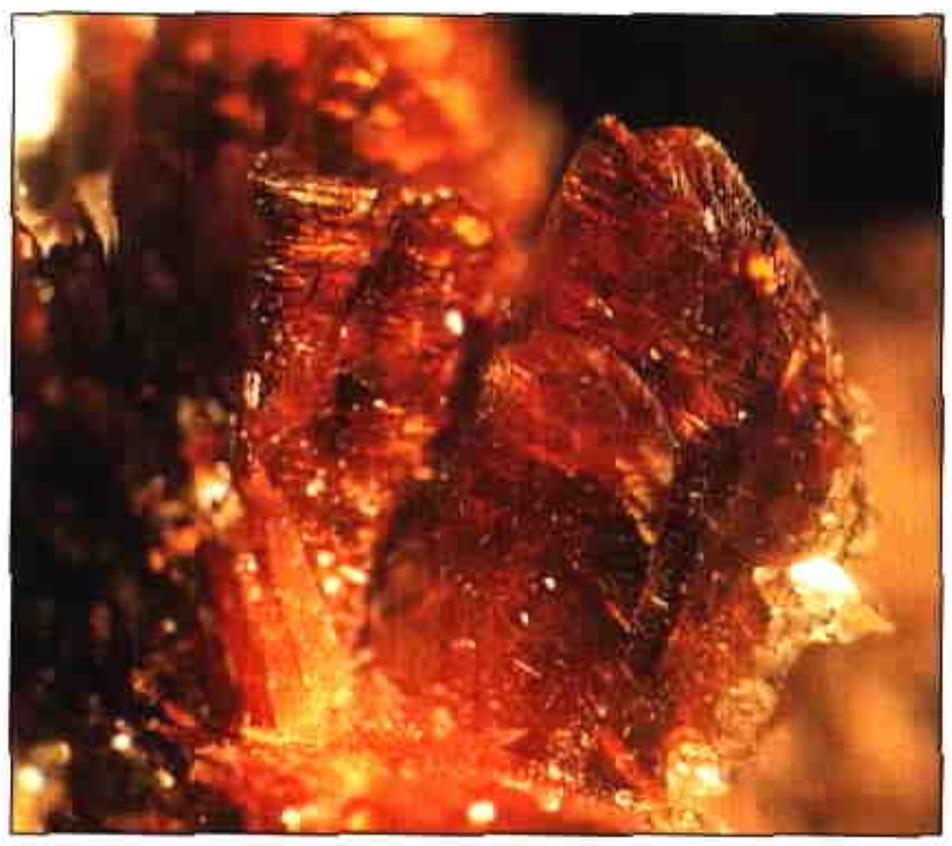

Figure 4. A single large aggregate of reddish brown hubeite (4 mm across). Photograph by Richard Green, Bill Cook specimen.

Figure 5. Clusters of hubeite on transparent to white quartz with minor pink inesite and pyrite; the specimen is 18.4 cm high. Photograph by Jeff Scovil, Ernesto Ossola specimen.

Figure 6. Quartz with abundant hubeite; the specimen is 9 cm wide. Photograph by Jeff Scovil, Bill Pinch specimen.

Figure 7. A small (4 cm tall) plate of hubeite (dark brown to black) with minor inesite and apophyllite. Photograph by Jeff Scovil, Ernesto Ossola specimen.

Figure 8. A small (7 cm wide) plate of pink inesite, white apophylite and brown hubeite in approximately equal amounts. Photograph by Jeff Scovil, Ernesto Ossola specimen.

Figure 9. A small (8.6 cm wide) plate dominated by pink inesite with minor hubeite and apophyllite. Photograph by Jeff Scovil, Ernesto Ossola specimen.

Figure 10. Massive pink inesite with a coating of honey-brown apophyllite crystals and minor hubeite and ilvaite (black crystals at the base of the specimen). Photograph by Jeff Scovil, Bill Pinch specimen (5.5 cm wide).

were measured with the Bloss spindle stage for the wavelength 590 nm using a gel filter. Hubeite is biaxial with an indeterminate optic sign due to the fact that 2V is close to 90°. The indices of refraction are α 1.667(1), β 1.679(1), γ 1.690(1), the calculated birefringence γ–α is 0.023, 2V(meas.) 89(2), 2V(calc.) 87(5)°; orientation $X \wedge b = 20°$ (in γ obtuse), $Y \wedge c = 13°$ (in α acute), $Z = a$. Hubeite is strongly pleochroic, X = yellow-brown (with a greenish tint), Z ≈ dark yellow-brown, with absorption Z > X.

CHEMICAL COMPOSITION

Crystals of hubeite were analyzed with a Cameca SX-50 electron microprobe operating in the wavelength-dispersion mode, with an accelerating voltage of 15 kV, a specimen current of 20 nA, and a beam diameter of 10 μm. The following standards were used: diopside (Si, Ca), spessartine (Mn), fayalite (Fe), andalusite (Al) and forsterite (Mg). The data were reduced and corrected by the *PAP* method of Pouchou and Pichoir (1984, 1985). The presence and quantity of OH and H_2O groups were established by crystal-structure solution and refinement (Hawthorne and Grice, 1990). The resultant chemical composition is given in Table 1, together with the formula unit based on 15 anions (including 1 OH and 2 H_2O groups) *pfu* (per formula unit). The end-member formula is $Ca_2Mn^{2+}Fe^{3+}[Si_4O_{12}(OH)](H_2O)_2$.

X-RAY POWDER DIFFRACTION

The powder-diffraction pattern was recorded with a 114.6-mm Debye-Scherrer powder camera using Fe-filtered Co$K\alpha$ X-radiation. Reflections were indexed by comparison of the observed pattern with the pattern calculated from the refined crystal-structure of hubeite (Cooper and Hawthorne, 2001). Table 2 shows the X-ray powder-diffraction data and the refined unit-cell dimensions of hubeite.

INFRARED SPECTRUM

The infrared spectrum was recorded according to the procedure described by Roberts *et al.* (1994) and is shown in Figure 10. There is a sharp peak in the principal (OH)-stretching region at ~3609 cm^{-1}, corresponding to an (OH) stretch. There is a broad envelope centered at ~3215 cm^{-1} with pronounced shoulders at 3455 cm^{-1} and 3115 cm^{-1} that may be assigned to stretching modes of one or more (H_2O) groups. The presence of (H_2O) groups is confirmed by the weak broad band at ~1609 cm^{-1} that corresponds to an H-O-H bending mode. All these bands are in accord with the results of crystal-structure solution and refinement that indicate the presence of both (OH) and (H_2O) groups. Lower frequency bands correspond to various modes of the (SiO_4) group.

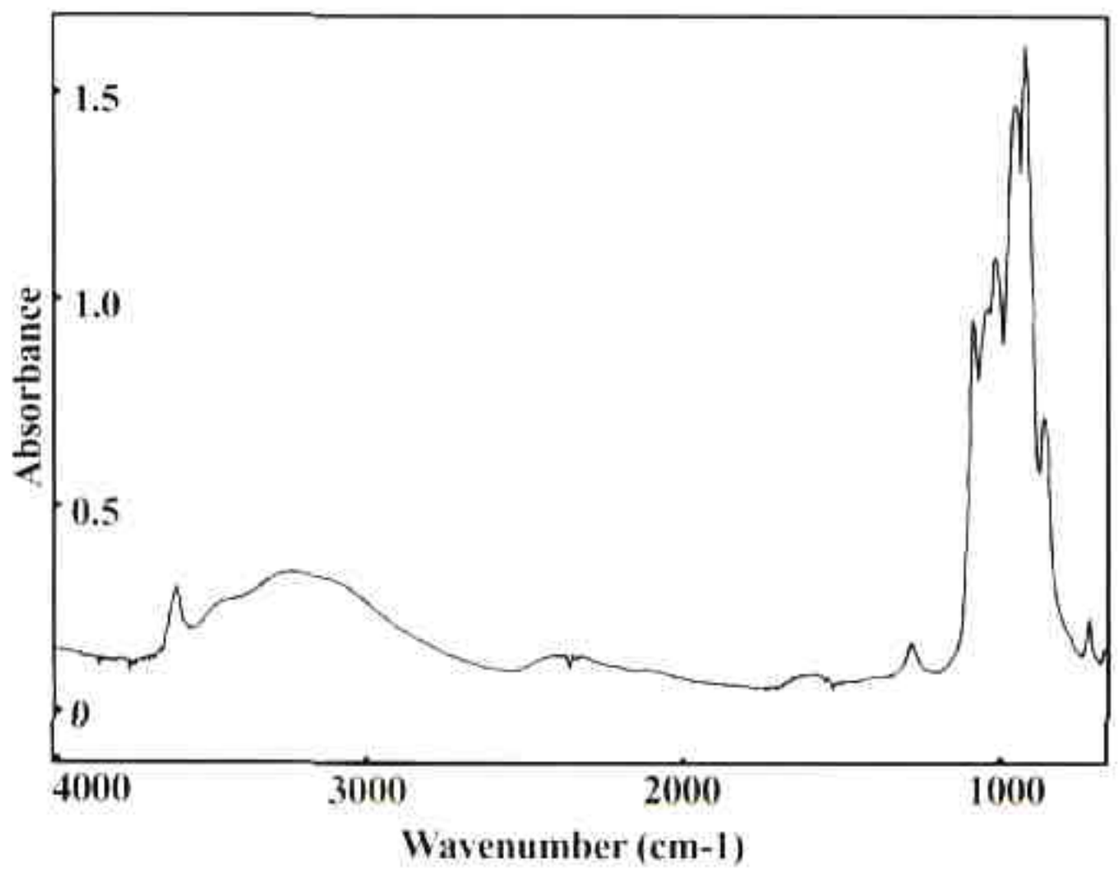

Figure 11. **The infrared spectrum of hubeite.**

PARAGENESIS AND RELATED MINERALS

Hubeite occurs at the Daye mine near Huangshi, Hubei province, China, where it is associated with pink inesite [with 0.93 weight % F: $(OH)_{1.4}F_{0.6}$], colorless apophyllite, quartz, pyrite and colorless-to-white calcite. The apophyllite is zoned from a core of natroapophyllite ($Na_{0.8}K_{0.2}$) to a rim of fluorapophyllite ($K_{1.0}$). There have been several verbal reports of manganbabingtonite from this locality. We have examined several specimens in detail with regard to associated minerals, but have not found manganbabingtonite. Of course, this does not preclude the occurrence of this mineral here, particularly in view of the variety of parageneses of hubeite.

Hubeite is a sorosilicate, as is apparent from the silicate part of the formula: $[Si_4\phi_{13}]$ (ϕ = unspecified anion) is the correct stoichiometry for a four-membered chain fragment of tetrahedra, and this has been confirmed by crystal-structure study (Cooper and Hawthorne, 2001). The only other sorosilicate mineral known to possess a four-membered chain fragment is ruizite: $Ca_2Mn^{3+}_2[Si_4O_{11}(OH)_2](OH)_2(H_2O)_2$ (Hawthorne, 1984; Moore *et al.*, 1985). Both hubeite and ruizite are Ca-Mn silicates; however, all Mn is divalent in hubeite and trivalent in ruizite. In addition, ruizite is Fe-free, whereas hubeite contains significant Fe^{3+}.

Ruizite is known from two localities: the Christmas mine, Gila County, Arizona, and Wessels mine, Kalahari Manganese Field, South Africa. At the Christmas mine, the ruizite assemblage consists of junitoite, smectite, xonotlite, sepiolite and apophyllite (*Williams and Duggan, 1977*). At Wessels mine, ruizite is found with quartz, datolite, pectolite, orientite, inesite and apophyllite (Wilson and Dunn, 1978). It is noteworthy that both of these assemblages are Fe-free. At Wessels mine, ruizite (Mn^{3+}) and apophyllite are interpreted to have formed after inesite (Mn^{2+}) and orientite (Mn^{2+} and Mn^{3+}), suggesting highly oxidizing conditions during crystallization of ruizite.

Hubeite also occurs with apophyllite, inesite and pyrite. We can infer that conditions during the crystallization of hubeite were mildly oxidizing, and that sufficient Fe was available for hubeite formation.

ACKNOWLEDGEMENTS

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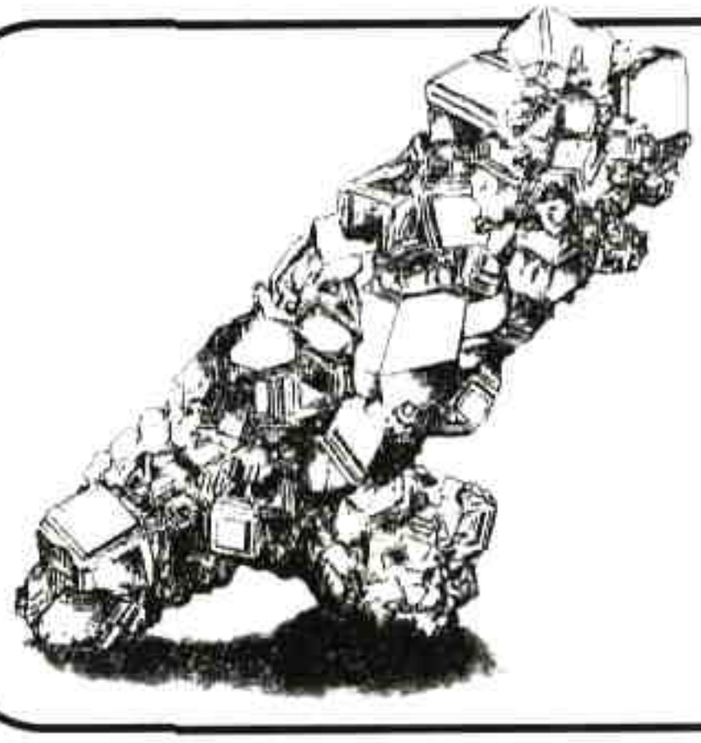

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