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Gorceixite in topaz greisen assemblages, Silvermine area, Missouri

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Abstract

Gorceixite [$(Ba,Sr)Al_3(PO_4)_2(OH,F)_5 \cdot H_2O$] occurs in the final stage of mineralization in greisenized breccias at the Ozark mine, Silvermine area, Missouri. The greisen assemblage consists of quartz-topaz-sericite with wolframite and minor cassiterite. Base metal sulfides were deposited after greisen development, and the assemblage gorceixite–fluorite–apatite–barite is the latest breccia cement.

The Ozark mine gorceixite is chemically unique in several respects. It is a gorceixite–goyazite solid solution [$(Ba_{.78-.60}Sr_{.15-.35}Ca_{.07-.05})Al_3(PO_4)_2F_{1.12-1.26}(OH)_{3.88-3.74} \cdot H_2O$] nearly devoid of calcium and rare earth elements. Zoning, from Sr-rich cores to Ba-rich rims, occurs in individual crystals. It contains significant amounts of fluorine, indicative of deposition from fluorine-rich hydrothermal fluids. Unlike previously analyzed gorceixites, its composition fits the crandallite group stoichiometry exceptionally well. Hexagonal unit cell dimensions determined from X-ray diffraction data are a_0 = 7.02Å and c_0 = 17.29Å.

Gorceixite in the greisen assemblage contrasts with reported occurrences in diamondiferous sands, merumite, carbonatites, pegmatites, and marl. The Silvermine area occurrence appears to be a variation in the suite of late carbonates and rare phosphates that are universally present in tin–tungsten type mineralization.

Introduction

Topaz-bearing greisens, which occur with tungsten/base metal sulfide mineralization in the Silvermine area, Madison County, Missouri, were described by Singewald and Milton (1929). Mineralization occurs in unmetamorphosed rhyolite and monzonite (Silvermine Granite–Scully, 1979) of Precambrian age (Bickford and Mose, 1975). The greisen assemblage of quartz–topaz–sericite is restricted to regular veins in the monzonite (Pomerene, 1947) and to veins and breccias in the rhyolite (Hayes, 1947). Mineralization consists of the greisen stage, which includes wolframite, zinnwaldite, and minor cassiterite, and a later sulfide stage comprised of pyrite, arsenopyrite, chlorite, fluorite, sphalerite, chalcopyrite, and argentiferous galena (Lowell and Gasparrini, 1982).

Gorceixite in the greisen assemblage

Gorceixite is a hydrated barium aluminum phosphate of the crandallite group (Palache et al., 1951). In the Silvermine area, it occurs as an open-space-filling cement in brecciated rhyolite at the Ozark mine. Masses of mottled white to salmon-colored gorceixite (identified by X-ray diffraction—Table 1) coat quartz and fluorite crystals (Fig. 1). In thin section, colorless, lath-shaped crystals and clusters of crystals are seen to be intergrown with fluorite, apatite, and barite. The gorceixite is length-fast, and exhibits low birefringence with parallel, undulose extinction. These intergrowths were the final minerals deposited in the paragenetic sequence.

Chemical composition

Chemical analyses, by wavelength-dispersive microprobe techniques, of gorceixite from the Ozark mine are reported in Table 2. A wide (30 μm) probe-beam diameter was used to minimize the effect of water loss on the analyses (gorceixite contains >10 wt.% H_2O). As a consequence, it was impossible to fully distinguish compositional differences within the individual crystals that were indicated on backscattered electron images.

The crandallite group of minerals has the general formula (Fleischer, 1975):

$$AB_3(PO_4)_2(OH,F)_5 \cdot H_2O \text{ in which}$$
$$A = Ca, Sr, Ba, Pb, Bi, Ce, Th; \text{ and}$$
$$B = Al, Fe^{3+}.$$

In gorceixite from the Ozark mine, barium and strontium are the major cations in the A site; minor amounts of calcium and cerium were also detected. Aluminum occupies the B site, and a significant amount of fluorine occurs in hydroxyl sites. Compositional zoning of individual crystals reflects variations in the proportions of barium and strontium in a gorceixite–goyazite solid solution. Zoned crystals have goyazite-rich cores with near-end-member gorceixite rims. The observed variation in com-

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Table 1. X-ray powder diffraction data for gorceixite from the Silvermine area, Missouri

hkℓ	d Å(obs)	I/I_0	hkℓ	d Å(obs)	I/I_0
101	5.72	63	300	2.031	15
110	3.51	55	303	1.907	44
113	2.988	100	220	1.753	37
202	2.875	42	223	1.679	39
024	2.479	15	312	1.647	21
211	2.282	75	315	1.514	10
122	2.216	39	226	1.501	32
hexagonal		a_0=7.02 Å		c_0=17.29 Å	

X-ray data for gorceixite-goyazite solid solution ($Ba_{.67}Sr_{.28}Ca_{.06}Al_3(PO_4)_2F_{1.21}(OH)_{3.79}\cdot H_2O$) obtained with a variable-slit diffractometer, Cu K_α radiation, 0.008° 2θ/sec, internally standardized with fluorite. Indexed by comparison to JCPDS Card No. 19-535, corrected where necessary. Cell parameters calculated using Cohen's method (Cullity, 1978, Ch.11).

Table 2. Average electron microprobe analyses in oxide weight percent and normalized to dehydrated crandallite stoichiometry ($AB_3(PO_4)_2O_{2.5-x}F_{2x}$). A is high-strontium gorceixite, B is low-strontium

	A		B	
Al_2O_3	30.47		30.02	
Fe_2O_3	0.02		0.03	
P_2O_5	27.81		27.71	
CaO	0.61		0.73	
SrO	7.61		2.95	
BaO	19.16		24.00	
CeO_2	0.06		n.d.	
F	4.74		4.19	
TOTAL	90.51		89.63	
Ba	0.63	1.05	0.80	1.02
Sr	0.37		0.15	
Ca	0.05		0.07	
Al	3.01	3.01	3.00	3.00
Fe^{3+}	0.002		0.002	
$PO_4{}^{3-}$	1.97		1.99	
F	1.26		1.12	

A: $Ba_{.60}Sr_{.35}Ca_{.05}Al_3(PO_4)_2F_{1.26}(OH)_{3.74}\cdot H_2O$

B: $Ba_{.78}Sr_{.15}Ca_{.07}Al_3(PO_4)_2F_{1.12}(OH)_{3.88}\cdot H_2O$

n.d.-not detected

position was from 8 mole% to 43 mole% goyazite in gorceixite.

Chemical formulas normalized to dehydrated crandallite stoichiometry are also shown in Table 2. The calculated formulas are in excellent agreement with the ideal gorceixite–goyazite formula. This agreement contrasts with previously reported analyses (Palache et al., 1951; Milton et al., 1958) which indicated an excess of aluminum and water in gorceixite. The analyses presented in this study are unique in several other respects. The absence of calcium and rare earth elements is noteworthy (cf. Palache et al., 1951; Milton et al., 1958). In addition, the gorceixite analyzed in this study has a higher fluorine content than previously reported for gorceixite (Milton et al., 1958).

Unit cell parameters

Unit cell dimensions for the Ozark mine gorceixite (Table 1) differ from those reported on JCPDS Card No. 19-535. The a_0 value of 7.02Å is similar to that of other members of the crandallite family. The value of c_0 (17.29Å) is substantially larger than that reported on JCPDS Card No. 19-535. This discrepancy probably results from compositional differences between the two. The gorceixite reported on Card No. 19-535 is Ca-rich [($Ba_{.50}Ca_{.32}Ce_{.05})Al_{3.41}P_{1.60}O_{14}H_8$] and non-stoichiometric. The Ozark mine gorceixite is a stoichiometric solid solution between the Ba- and Sr-endmembers.

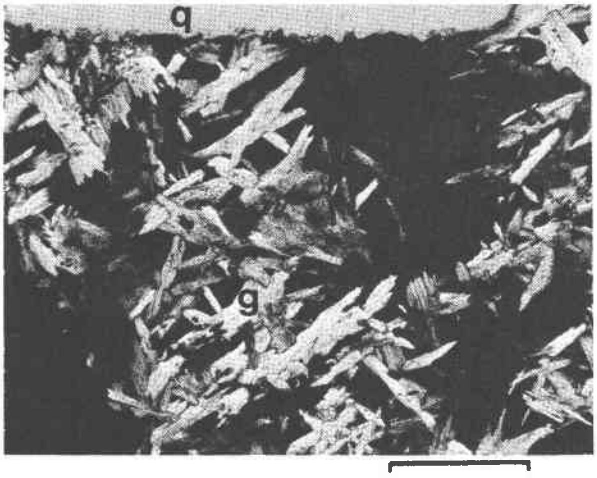

Fig. 1. Photomicrograph of gorceixite (g) and fluorite (black) filling open space between large quartz (q) and fluorite (black, lower left) crystals. Crossed nicols; bar = 0.5mm.

Other occurrences of gorceixite

Gorceixite is found with other members of the crandallite group in diamondiferous sands near Minas Geraes, Brazil, and in diamondiferous sands in Africa (Palache et al., 1951). It occurs in placers with merumite (complex mixtures of many unusual chromium minerals), rutile, and tourmaline in Guyana (Milton and Narain, 1969). Primary sources for these detrital accumulations were not identified.

Gorceixite has been reported from pegmatites (Bhaskara and Cunha, 1968) and carbonatites (Serdyuchenko and Chayka, 1967; Kapustin, 1971). In sedimentary rocks, it occurs as nodules in the Bashi marl in Alabama (Milton et al., 1958) and along fractures in the Arkansas novaculite (Young, 1958). Gorceixite is clearly a secondary mineral in the novaculite, but Milton et al. (1958) were unable to determine if the nodules in the Bashi marl were of primary, diagenetic, or secondary origin.

Discussion

The occurrence of gorceixite with greisen–sulfide mineralization in the Silvermine area contrasts with the carbonatite, pegmatite, and sedimentary occurrences cited in the preceeding section. The Silvermine area greisens have been interpreted as tin–tungsten type mineralization, genetically related to the emplacement of "tin-type" granites during the final stages of igneous activity in the St. Francois Mountains (Lowell, 1976; Kisvarsanyi, 1980). Tin–tungsten mineralization is characterized by a late, post-sulfide stage of deposition involving carbonates (Landis and Rye, 1974; Kelly and Rye, 1979; Collins, 1981) and rare phosphates (Kelly and Turneaure, 1970). Barite gangue occurs in the upper veins of the Cornwall district, U. K. (Sainsbury, 1969).

Gorceixite and minor fluorite, apatite, and barite, occupy this late stage of the tin–tungsten mineralization at the Ozark mine. Wavellite and vivianite (Al- and Fe-phosphates) occur in the Bolivian deposits; an alkali earth phosphate is unusual in this respect. The intergrowths of barite, however, are suggestive of the Cornwall district. Gorceixite in the Silvermine greisen–sulfide assemblage adds another variation to the suite of late carbonates and phosphates associated with tin–tungsten type mineralization.

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