

Oxide minerals in miarolitic rhyolite, Black Range, New Mexico

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Abstract

Crystals of hematite, pseudobrookite, bixbyite, and cassiterite occur in cavities within miarolitic, lithophysal rhyolite in the Black Range of southwestern New Mexico. Compositional and paragenetic relationships are compatible with the results of pertinent phase equilibrium studies, and suggest that these oxides crystallized at temperatures of 500° C or higher, probably from a gas phase present during late stages of rhyolite crystallization.

Introduction

Tertiary flow-layered Taylor Creek rhyolite is exposed along the walls of Paramount Canyon in the northern part of the Black Range, New Mexico. A distinctive facies of lithophysal, miarolitic rhyolite, as exposed on the north rim of Paramount Canyon 5.3 km west of Boiler Peak, contains an unusual suite of oxide minerals including hematite, bixbyite, pseudobrookite, and cassiterite (Lufkin, 1972, 1974; Lufkin and Jahns, in preparation). They appear to have crystallized penecontemporaneously within cavities and lithophysae of the rhyolite, where they are associated primarily with quartz and sanidine, and locally with topaz, monazite, fluorite, and silica polymorphs. No single cavity containing all four oxides has been observed, but pairs such as hematite–cassiterite, hematite–pseudobrookite, and bixbyite–pseudobrookite, are common. This suite of oxide minerals is of particular interest because estimates of temperature and pressure of tin mineralization can be made, based on the uncommon association of cassiterite with these high temperature Fe–Ti–Mn oxides.

Hematite

Hematite, the most abundant of the oxide minerals, occurs both in cavities and in veinlets of cassiterite and hematite. It is invariably specular, appearing as thin hexagonal plates 1–3 mm in diameter. These plates are fresh and generally weakly corroded. The hematite commonly is intergrown with cassiterite, which also forms crystalline encrustations on some hematite plates and aggregates of plates.

Hematite contains as much as 3 percent SnO₂, on

the basis of electron probe analyses of six crystals associated, but not intergrown, with cassiterite. All of the analyzed grains appear homogeneous in polished section, and the tin content appears to reflect true differences in composition of the hematite.

Bixbyite

Bixbyite, (Fe,Mn)₂O₃, is a rare mineral first described from the Thomas Range, Utah, by Penfield and Foote (1897). Specimens were later recognized from the Black Range, and were discussed by Fries *et al.* (1942) and Mason (1944). Bixbyite occurs in the Paramount Canyon area, most commonly as cubes 2.7 mm or less on an edge (Fig. 1). Both individual cubes and penetration twins have been found in heavy-mineral separates. Some of the cubes are modified by octahedral (111) faces. On one rhyolite fracture surface encrusted by several crystals of bixbyite, octahedral crystals are modified by dodecahedral (110) faces.

The larger crystals are generally sharp and fresh in appearance. Edges of the smaller cubes commonly are corroded, or rounded. Inclusions of quartz and alkali feldspar are common. Both oscillatory growth and sector zoning are observed in the majority of crystals. Growth layers generally are parallel to cube faces and are expressed by narrow bands of contrasting reflectivity, commonly delineated by linear pits in the polished surface (Fig. 2).

Compositions of five bixbyite crystals are recorded in Table 1. The microprobe analyses, which are based on averaged probe traverses across whole crystal surfaces, reflect a broad compositional range with re-



FIG. 1. Bixbyite cube in lithophysal rhyolite, Paramount Canyon.

spect to major elements. Of the five analyzed specimens, Fe_2O_3 ranges from 35.0 to 48.9 percent, while Mn_2O_3 varies from 45.6 to 61.7 percent. In a single scan of a zoned crystal, the Fe content may vary as much as 34 percent. Bixbyite rims are generally Mn-rich. Bixbyite from the Black Range is more Mn-rich than analyzed material from the Thomas Range (Fries *et al.*, 1942; Staatz and Carr, 1964). In addition, the content of Sn (0.4–0.9 percent) is signifi-

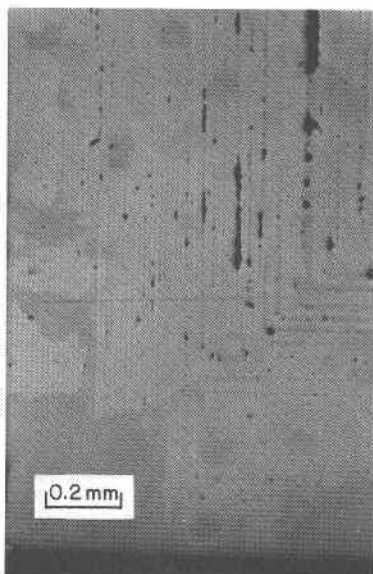


FIG. 2. Photomicrograph of growth zoning in bixbyite. Polished section in air, crossed nicols.

TABLE 1. Electron probe analyses of bixbyite, Paramount Canyon

	1	2	3	4	5	Mean
Al_2O_3	0.6	0.1	0.2	0.2	0.1	0.2
Fe_2O_3^1	48.9	35.0	44.5	38.0	37.8	40.8
Mn_2O_3^2	45.6	61.7	55.0	60.2	59.1	56.3
TiO_2^3	1.3	1.4	1.3	1.1	0.9	1.2
SnO_2	1.2	0.5	0.8	0.5	0.5	0.7
Total	97.6	98.7	101.8	100.0	98.4	99.2
¹ Total Fe as Fe_2O_3						
² Total Mn as Mn_2O_3						
³ Total Ti as TiO_2						

cantly higher than that of Utah bixbyite (.05–0.1 percent Sn), which is associated with beryl, garnet and topaz, but not with cassiterite (Staatz and Carr, 1964).

Pseudobrookite

Pseudobrookite (Fe_2TiO_5) occurs as black, acicular crystals $\frac{1}{2}$ to 2 mm long, generally in association with bixbyite. These crystals are present as individuals and as tiny semi-radial clusters (Fig. 3). Many are striated longitudinally, parallel to the c-axis. Some appear to have been corroded, but most are characterized by sharply defined, lustrous faces.

Of the thirty grains of pseudobrookite that were separated and mounted for special study, about one-third contain vermicular intergrowths of hematite 0.4 mm or less wide (Fig. 4). This feature appears to be most common among the grains forming semiradial clusters. Hematite commonly is enclosed at the base of pseudobrookite crystals, where they join to form these clusters.

The origin of these intergrowths is enigmatic. Solid solution and exsolution phenomena in the system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$ (Buddington and Lindsley, 1964) are well known between crystallographically compatible members of each series, *e.g.*, hematite-ilmenite (hexagonal), magnetite-ulvöspinel (isometric), but have not been documented experimentally between members of crystallographically different series, *e.g.*, pseudobrookite (orthorhombic) and hematite. And, if hematite intergrowths were produced by exsolution, one might expect a more uniform distribution of hematite throughout the body of pseudobrookite, or a concentration of hematite near grain boundaries.

Pseudobrookite is stable at high temperature, but

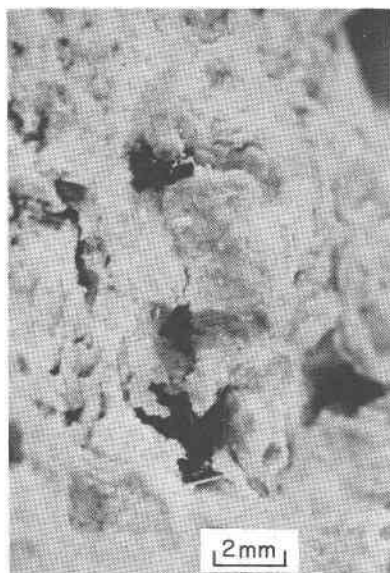


FIG. 3. Clusters of pseudobrookite crystals in lithophysal rhyolite. Same hand specimen as Fig. 1.

breaks down to form hematite and rutile at $585 \pm 10^\circ$ C and 2 kbar pressure, as demonstrated experimentally by Haggerty and Lindsley (1970). The instability of pseudobrookite with respect to the binary oxides at low temperatures is also predicted from its positive entropy of formation (Navrotsky, 1975). Rutile, however, is not present with hematite, although the hematite intergrowths are titaniferous.

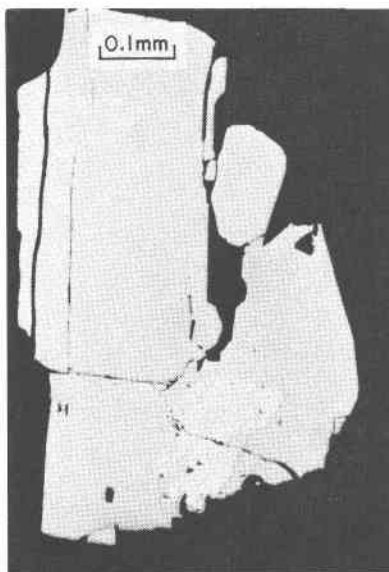


FIG. 4. Photomicrograph of hematite intergrowth (white) near base of pseudobrookite cluster. Polished section in air, plane polarized light.

TABLE 2. Electron probe analyses of pseudobrookite, Paramount Canyon

	1	2	3	4	5	Mean
Al ₂ O ₃	0.3	0.4	0.3	0.3	0.4	0.3
Fe ₂ O ₃ ¹	66.3	66.2	65.7	66.4	66.1	66.1
MnO ₂ ²	2.2	2.4	2.5	1.8	2.3	2.2
TiO ₂ ³	30.8	31.3	30.8	30.6	31.1	30.9
SnO ₂	1.5	1.5	1.5	1.3	1.5	1.5
Total	101.1	101.8	100.8	100.4	101.4	101.0
¹ Total Fe as Fe ₂ O ₃						
² Total Mn as MnO ₂						
³ Total Ti as TiO ₂						

Ti-rich members of the pseudobrookite-ferropseudobrookite series are found most commonly as oxidation products of titanomagnetite or ilmenite in subsilicic rocks (e.g., Buddington and Lindsley, 1964; Carmichael, 1967; Haggerty and Lindsley, 1970). If the Fe-rich pseudobrookites at Paramount Canyon resulted from oxidation of an Fe-Ti oxide parent, there is no direct evidence of this in the lithophysal rhyolite. If present originally, ulvöspinel might yield hematite and pseudobrookite under more oxidizing conditions with decreasing temperature. Magnetite (-ulvöspinel?) is noted in amounts generally less than 1 percent in non-lithophysal sections of the Taylor Creek rhyolite.

Microprobe analyses of pseudobrookite crystals from the Paramount Canyon locality yielded the values recorded in Table 2. The pseudobrookites, both with and without intergrowths, are relatively homogeneous; in individual crystals, Fe and Ti vary ≤ 0.5 percent. The tin content, about double that in bixbyite, probably represents a substitution of Sn⁴⁺ for Ti⁴⁺. The mean Fe₂O₃ content of 66.1 percent in pseudobrookite is close to the calculated composition of 66.6, while TiO₂ is deficient by about 2.5 percent. It is reasonable to assume that the Ti sites are occupied in part by Mn⁴⁺ and Sn⁴⁺. Specimens from Utah are relatively rich in titanium, but this may be due to rutile intergrowths (Palache, 1935).

Attempts to analyze the hematite intergrowths in pseudobrookite were unsuccessful, due primarily to their fine grain size. Because the pseudobrookite is practically of end-member composition, the composition of coexisting hematite relative to pseudobrookite, in the absence of rutile, cannot be predicted from the known phase relationships.

Cassiterite

Cassiterite occurs in cavities with hematite, and in veinlets with quartz, topaz, hematite, and alkali feldspar. In the cavities it forms stubby to platy crystals that are ruby-red in color and rarely exceed 1 mm in maximum dimension. Twinning commonly is recognizable in polished section. Most of the twin lamellae are parallel, whereas others intersect to form wedge-shaped patterns. Internal reflection generally is expressed in shades of yellow, violet, and green.

In its close association with specular hematite, the cassiterite occurs as both overgrowths and intergrowths. In some veinlets it appears to comprise numerous growth plates, stacked one upon the other and commonly parallel to underlying plates of hematite. Cassiterite has not been observed coating or intergrown with bixbyite or pseudobrookite. Both the limited amount and the fine-grained nature of cassiterite have prohibited economic recovery of tin at Paramount Canyon, although small tonnages of wood-tin concentrate have been produced elsewhere in the district.

Temperature of formation

In view of the broad thermal stability of cassiterite, the close spatial and paragenetic association of cassiterite with bixbyite and pseudobrookite in Para-

mount Canyon provides important information for estimation of the P-T environment of tin deposition in silicic volcanic rocks.

Phase relations pertinent to occurrences of bixbyite and pseudobrookite have been investigated experimentally during the past thirty years. Principal phases were first established by Mason (1943) for the system $\text{Fe}_2\text{O}_3\text{-Mn}_2\text{O}_3$ from 400 to 1000°C at a pressure of 1 atm. This study was later improved and extended to 1585°C (Muan and Sōmiya, 1962).

The range in composition of five bixbyite crystals from Paramount Canyon is 35.0 to 48.9 percent Fe_2O_3 , averaging 40.8 percent (Table 1). Considering bixbyite as pure $(\text{Mn,Fe})_2\text{O}_3$ by normalizing to 100 percent the average amounts of Fe_2O_3 and Mn_2O_3 for these five crystals, the composition becomes approximately 42 percent Fe_2O_3 , 58 percent Mn_2O_3 . Referring to the data of Muan and Sōmiya (Fig. 5), this compositional mixture would yield hematite and bixbyite at about 640°C and above 950°C would form spinel and bixbyite; this establishes a "stability range", for equilibrium conditions, of 310° at 1 atm ($X_{\text{O}_2} = 0.25$).

Pseudobrookite, a mineral of widespread occurrence, is found in volcanic rocks ranging in composition from basalt to rhyolite. Akimoto *et al.* (1957) first demonstrated the existence of a complete solid-

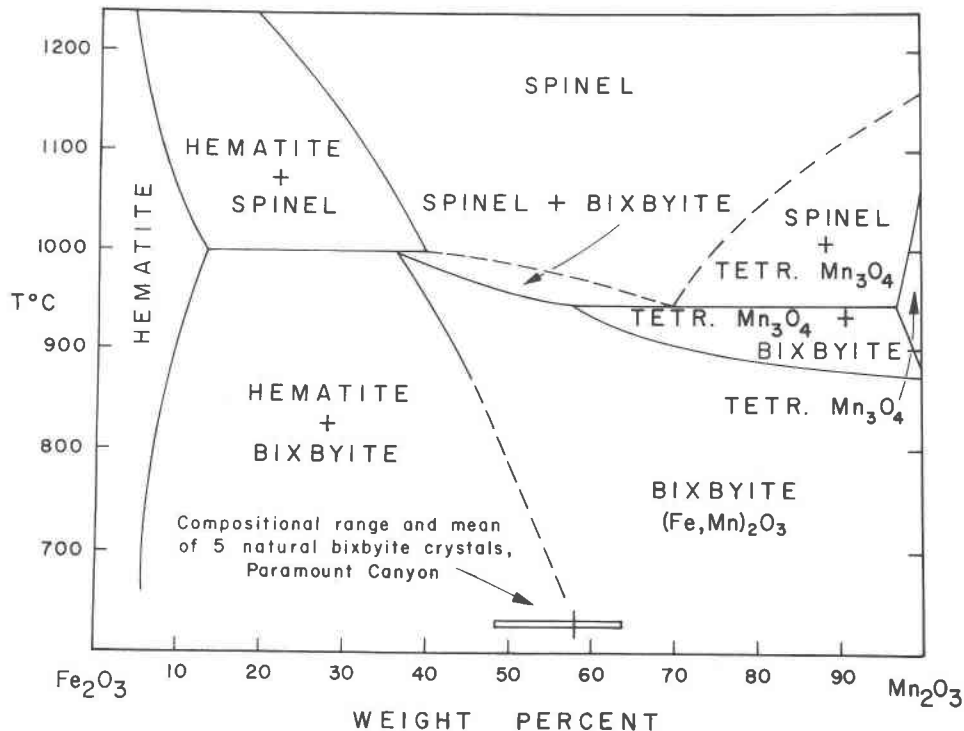


FIG. 5. Phase relations in the system iron oxide-manganese oxide in air (after Muan and Sōmiya, 1962).

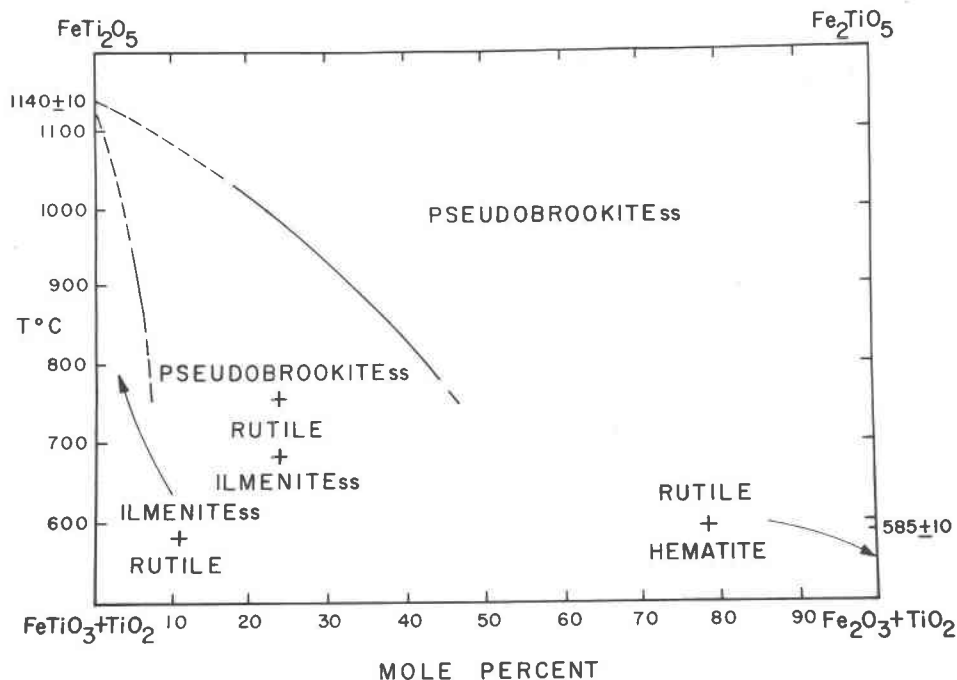


FIG. 6. Phase relations in the ferropseudobrookite-pseudobrookite series, projected through TiO_2 onto the composition plane $\text{FeO}-\text{Fe}_2\text{O}_3$ (after Haggerty and Lindsley, 1970).

solution series between pseudobrookite (Fe_2TiO_5) and ferropseudobrookite (FeTi_2O_5) at temperatures above 1150°C . The limits of solid solution have not been closely established at most lower temperatures, however, owing in part to sluggish reactions in this thermal range (Haggerty and Lindsley, 1970). Phase relations above 1400°C are known to be complex (MacChesney and Muan, 1959).

In determining stability relations from 750° to 1150°C (Fig. 6), Haggerty and Lindsley (1970) showed that the solution series is not linear as formerly assumed. The pseudobrookite end-member breaks down to form hematite and rutile at $585 \pm 10^\circ\text{C}$, as determined by hydrothermal experiments at 2 kbar and f_{O_2} controlled by hematite + hydrogen peroxide buffer. The pseudobrookite from the Black Range is similar in composition to the calculated end-member if allowances are made for the substitutions of Mn and Sn for Ti.

Discussion and conclusions

The association of bixbyite and pseudobrookite with cassiterite in miarolitic cavities in the Taylor Creek rhyolite of Paramount Canyon probably reflects crystallization from a gas phase, and it establishes a genetic relationship between tin mineralization and the primary cooling history of the

rhyolite. Furthermore, crystallization temperatures of these oxide phases can be estimated through comparisons with known phase equilibrium relationships.

If data from experimental studies of comparable synthetic systems are rigorously applied, a minimum crystallization temperature of 585°C can be assigned to the pseudobrookite and a minimum temperature of 640° to the bixbyite with a composition corresponding with the averaged microprobe analyses of five natural crystals (Table 1). Several complicating factors are immediately apparent, however. Natural crystal inhomogeneities, particularly Mn-Fe zoning in bixbyite, complicate any application of results from synthetic studies based on phase homogeneity. Nor can the effects of Sn and/or Ti substitution for Fe on the ranges of phase stability of bixbyite and pseudobrookite be determined.

Despite the complications inherent in comparing the natural and synthetic systems, it seems reasonable to conclude that the oxide minerals, pseudobrookite and bixbyite, crystallized from a gas phase at temperatures of 500°C or higher, and a pressure near 1 atm. A similar environment of crystallization may apply to cassiterite and hematite as well, although direct evidence for this is lacking, due to the absence of cassiterite-pseudobrookite or cassiterite-bixbyite assemblages.

Acknowledgments

This study is a continuation of part of a Stanford doctoral research project completed in 1972 and funded in part by the New Mexico Bureau of Mines and Mineral Resources, G.S.A. Grant 1325-69, and by the Stanford Shell-Esso Research Fund.

High purity cassiterite was kindly provided as a tin standard by C. L. Sainsbury and George A. Desborough, U.S. Geological Survey. Sincere appreciation is extended to my colleagues, Douglas Smith and Susan Levy, who instructed me in the use of the ARL electron microprobe and data reduction procedures. Professors Richard H. Jahns (Stanford University), Kenneth L. Williams (University of Sydney), and Douglas Smith are thanked for their constructive criticisms of an earlier version of this manuscript.

The Geology Foundation, University of Texas at Austin, is gratefully acknowledged for defrayment of publication.

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Manuscript received, September 29, 1975; accepted for publication, January 7, 1976.