

Compositional characteristics of kinoshitalite from the Sausar Group, India

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ABSTRACT

Ba-rich and Ba-poor micas with varying Mn and Mg content in octahedral sites coexist in isolated pockets in braunite-bixbyite-hausmannite ores that have been invaded by late silicic pegmatite and carbonate veins in the Sausar Group, India. The micas are secondary in nature and are pseudomorphs after carbonates and alkali feldspars. One of the micas approaches closely synthetic end-member kinoshitalite, $\text{BaMg}_3\text{Al}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$. The present study shows a complete solid solution between the K (phlogopite) and Ba (kinoshitalite) end-members. Compositional diversities in these micas are attributable to the different minerals that the micas replaced.

INTRODUCTION

Kinoshitalite, $\text{BaMg}_3\text{Al}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$, was defined by Yoshii et al. (1973a) as the Ba and Mg trioctahedral brittle mica. As an end-member, it is known only as a synthetic phase obtained hydrothermally at 600 °C and 2 kbar (Fron del and Ito, 1967). Naturally occurring kinoshitalite has been reported with considerable amounts of K and Mn (Yoshii et al., 1973b; Yoshii and Maeda, 1975; Matsubara et al., 1976). Yoshii and Maeda examined Mn-bearing kinoshitalite and phlogopite and found a break in optical and physical properties near the ratio Ba:K = 0.5. Crystal-structure studies of kinoshitalite have been made by Kato et al. (1979) and Guggenheim and Kato (1984). A Mn-free kinoshitalite was recently reported by Solie and Su (1987). They did not describe the material as kinoshitalite apparently because they misinterpreted the original definition of kinoshitalite to include Mn as a required component.

Data are presented here for a near-end-member kinoshitalite, in addition to samples with considerable variations in occupancy in interlayer and octahedral cation sites, from the Precambrian Sausar Group, India. Compositional variations are inferred to be the result of the chemistry of the minerals that the micas replaced. No evidence was found for a possible solvus.

GEOLOGICAL BACKGROUND

The Ba-bearing micas described here occur in pockets in manganese oxide-rich rocks at Netra, Balaghat District, India. These rocks are conformably enclosed in metapelites belonging to the Precambrian Sausar Group. Garnet-biotite thermometry indicates the temperature of metamorphism as 650 ± 25 °C at an estimated pressure of 6 kbar (Roy et al., 1986). This estimate is consistent with the development of sillimanite in the metape-

lites. Micas have developed in manganese oxide-rich rocks where the latter have been invaded by late silicic pegmatite and carbonate veins. In these pockets, the manganese oxide-rich rocks exhibit the following mineral assemblage: braunite + hausmannite + bixbyite + Ba-bearing mica + alkali feldspar + hematite + calcite + dolomite + quartz. The oxides collectively account for over 80% of the rock. Braunite, the most abundant phase, occurs as polyhedral grains, showing sharp boundaries with associated phases. Hausmannite and hematite also form polyhedral aggregates, and bixbyite is poikiloblastically enclosed in braunite.

CHARACTERISTICS OF THE MICAS

Three types of micas can be distinguished optically in the manganese oxide-rich rocks. One is colorless ($\beta = 1.632$), another is yellow ($X = \text{light yellow}, Y = Z = \text{deep yellow}$ with a brownish tinge, absorption $X < Y = Z, \beta = 1.628$), and a third is brown ($X = \text{light brown}, Y = Z = \text{deep brown}$, absorption $X < Y = Z, \beta = 1.610$). All the varieties are optically negative. Because of their low modal abundance and the difficulty of separation, it was not possible to obtain X-ray powder-diffraction data for these micas. The three varieties may coexist in a single hand specimen. Petrographic study further shows that the micas have diffuse grain boundaries and pseudomorphous relationships with the associated phases. Colorless micas are closely associated with dolomite, yellow micas with manganite, calcite, and the brown variety with alkali feldspars, manganese oxides, and quartz.

Chemical compositions of the micas and the associated phases were determined with a JEOL-JXA 733 EPMA operated at 15-kV accelerating voltage and 1- to 2- μm electron-beam diameter. The standards used were synthetic CaSiO_3 (Si, Ca), rutile (Ti), corundum (Al), hematite (Fe),

TABLE 1. Chemical analyses of the micas from Netra, Sausar Group, India and their recalculated structural composition on the basis of 12(O,OH)

	1	2	3	4	5	6†	7†	8
SiO ₂	37.00	40.13	38.20	37.71	24.13	23.03	24.68	23.43
TiO ₂	0.33	0.21	0.57	0.20	—	—	—	—
Al ₂ O ₃	14.73	10.54	13.99	14.38	16.98	16.16	18.26	19.25
Fe ₂ O ₃ *	2.71	1.51	3.43	3.29	3.46	6.45	2.79	1.87
MnO*	4.37	6.65	7.07	4.22	9.66	14.11	2.52	2.62
MgO	22.16	23.93	20.64	21.52	16.78	10.97	22.26	21.95
CaO	—	0.03	0.05	0.07	—	0.01	—	0.05
Na ₂ O	0.04	0.10	0.18	0.22	0.09	0.05	—	0.11
K ₂ O	8.48	7.70	8.43	7.88	0.60	0.51	0.72	0.24
BaO	3.95	0.78	1.36	4.25	25.60	24.32	27.01	27.60
H ₂ O	4.24	4.36	4.27	4.24	3.40	3.22	3.55	3.50
Total	98.01	96.01	98.19	97.98	100.70	98.83	101.79	100.62
Ca	—	0.002	0.004	0.006	—	0.001	—	0.005
Na	0.006	0.014	0.026	0.032	0.015	0.009	—	0.018
K	0.808	0.732	0.801	0.755	0.067	0.061	0.078	0.026
Ba	0.116	0.023	0.040	0.125	0.884	0.887	0.893	0.926
Total	0.930	0.771	0.871	0.918	0.996	0.958	0.971	0.975
Mn ²⁺	0.276	0.420	0.446	0.268	0.721	1.112	0.180	0.190
Mg	2.446	2.659	2.290	2.408	2.203	1.521	2.800	2.800
Fe ³⁺	0.153	0.003	0.214	0.207	0.144	0.417	0.096	0.081
¹⁰ Al	0.059	—	0.072	0.103	—	—	—	—
Ti ⁴⁺	0.018	0.012	0.032	0.011	—	—	—	—
Total	2.972	3.094	3.054	2.997	3.068	3.050	3.076	3.071
Si	2.763	2.992	2.844	2.831	2.126	2.143	2.083	2.005
¹⁴ Al	1.237	0.926	1.156	1.169	1.763	1.772	1.816	1.942
Fe ³⁺	—	0.082	—	—	0.111	0.085	0.101	0.053
Total	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000

Note: The specimens represented by analyses are as follows: (1–4) brown mica, (5–6) yellow mica, (7–8) colorless mica.

* Total Fe as Fe₂O₃ and total Mn as MnO.

† 6 and 7 coexist.

manganosite (Mn), periclase (Mg), jadeite (Na), orthoclase (K), and natural barite (Ba). The F content of the micas was not determined. Microprobe data (ZAF corrected) and structural formulas are given in Table 1. Total Fe is considered as Fe₂O₃. The presence of hematite (rather than magnetite), bixbyite, hausmannite, and braunite in the assemblage indicates that f_{O_2} was well above the HM buffer, which justifies the assumption of computing total Fe as Fe₂O₃. Admittedly, Mn in the micas may occur in the trivalent state, but this could not be determined and total Mn was thus computed as MnO.

The colorless mica approaches closely the synthetic Ba-Mg phase of Frondel and Ito (1967), with Ba occupying ~95% of the interlayer sites and Mg >91% of the octahedral sites. The yellow micas show appreciable substitution of Mn (23.6–36.4%) and Fe³⁺ for Mg in the octahedral sites. However, they also contain more than 90% of Ba in interlayer positions. Thus, both types of mica qualify as kinoshitalite on the basis of their Ba:K ratios. Their variable Mn:Mg ratios in octahedral sites are significant. The brown micas, on the other hand, are typically manganian phlogopites, where K far exceeds Ba in the interlayer positions. These are characterized by limited variation in Mn (8.9–14.6%), Mg (75–86%), and Fe³⁺ (~0–7%) in octahedral sites, but are consistently enriched in Si and depleted in Al as compared to the Ba-rich micas.

The Ba:K ratios of the micas studied, as well as those of the previously reported phases (Fig. 1), show a nearly

complete range of substitution in the interlayer sites. All samples were collected from formations metamorphosed at 600 ± 100 °C. That the major substitution linking Ba-poor micas with Ba-rich micas is governed by Ba + ¹⁴Al

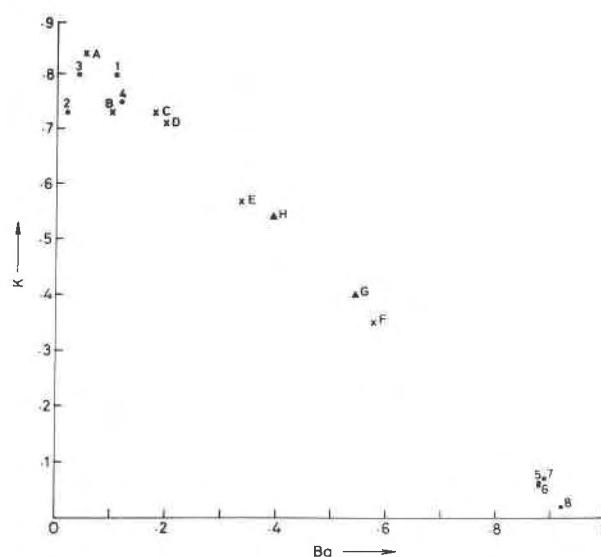


Fig. 1. Atomic content of Ba plotted against K in Ba-rich and Ba-poor micas. Data points A–F (×) are from Yoshii and Maeda (1975). Data points G–H (Δ) are from Solie and Su (1987). Data points 1–8 (●) are from the Netra area.

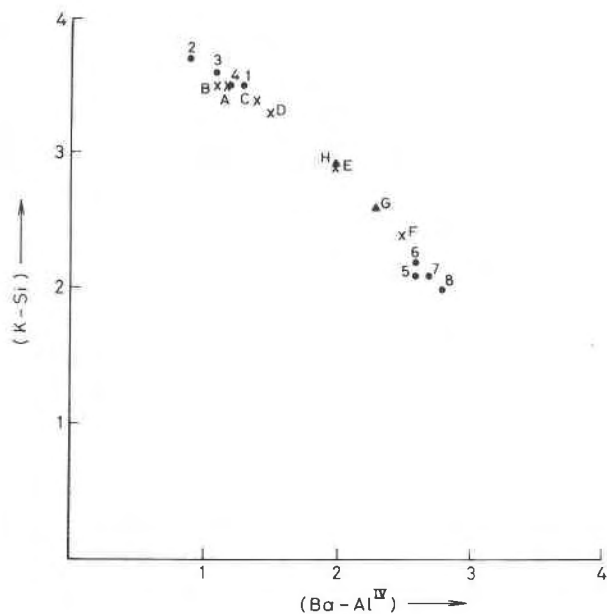


Fig. 2. $(\text{Ba} + \text{Al}^{\text{IV}})$ plotted against $(\text{K} + \text{Si})$ of the micas. For references, see Fig. 1.

$\approx \text{K} + \text{Si}$ exchange is evident from Figure 2, in accordance with the suggestion of Yoshii et al. (1973b). However, substitution of Fe and Mn in octahedral sites in the micas studied are not correlatable with variations in either X_{Ba} or $X_{\text{Al}^{\text{IV}}}$. The color of the micas could be closely related to variations in these transition-metal contents (cf. Nassau, 1978).

Of the associated phases, braunite, bixbyite, and hausmannite contain 6.5%, 25.5%, and 4.8% Fe_2O_3 , respectively, and the carbonates 3–4% MnO.

DISCUSSION

The colorless micas that contain only minor Mn and Fe in octahedral sites are the most Ba-rich micas described. They closely approach the end-member composition $\text{BaMg}_3\text{Si}_2\text{Al}_2\text{O}_{10}(\text{OH})_2$ and conform to the definition of kinoshitalite. Because kinoshitalite contains both Ba in the interlayer site and an Al_2Si_2 tetrahedral composition per formula unit, it is neither precisely analogous to phlogopite (which has an AlSi_3 tetrahedral composition per formula unit) nor to magnesian anandite (which has an $\text{Fe}^{3+}\text{Si}_3$ tetrahedral composition per formula unit). Our study shows nearly complete solid solution in the phlogopite-kinoshitalite series at temperatures of about $600 \pm 100^\circ\text{C}$.

Petrographic studies reveal that the different types of micas in the manganese oxide-rich rocks are late replacements of such diverse phases as calcite, dolomite, and

alkali feldspar in the presence of manganese oxides. The formation of high-Mg colorless micas on dolomite and brown micas on alkali feldspar clearly demonstrates the influence of the nature of the replaced minerals on the composition of the micas. Solie and Su (1987) advocated two possibilities to account for the variation in Ba:K ratios of their specimens, namely the presence of a solvus and/or variations in the fluid composition in microdomains. The data presented here do not indicate the presence of a solvus in the phlogopite-kinoshitalite series. Moreover, variations in chemical composition within a single grain (cf. Solie and Su, 1987) cannot be easily explained by fluid composition. As the micas described by Solie and Su occur in a contact metasomatic zone, it is likely that those micas are a result of nucleation on different substrates also.

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