

## COMPOSITIONS OF NATURAL OSUMILITES

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### ABSTRACT

Osumilite from the type locality, Sakkabira, Japan, has been analyzed by electron microprobe and major differences are observed contrasted with the original wet-chemical analysis. The other two known world occurrences, Sardinia and Oregon, were analyzed. Comparison of all three shows a variation in the number of Na ions per formula accompanied by variations in the percentage of vacancies in the alkali position. Because of the analytical totals no constituent water can be inferred in these osumilites.

One occurrence (Oregon) exhibits a paragenesis which offers the first field evidence of the type of breakdown of (metastable) osumilite observed in laboratory experiments.

The rare mineral osumilite was analyzed during a study of the meteoritic mineral yagiite (Bunch and Fuchs, 1969). Repeated electron microprobe analyses revealed major discrepancies with the analysis which accompanied the original description (Miyashiro, 1956). Communication with A. Miyashiro indicated that the original analysis is in error probably due to impurities, which were difficult to separate from the relatively large quantity required for the wet-chemical analysis.

This paper reports the new electron microprobe analysis of pure osumilite from the type locality, Sakkabira, Japan, with microprobe analyses of heretofore unanalyzed osumilites from the only other known world occurrences, Monte Arci, Sardinia (Rossi, 1963), and Obsidian Cliffs, Lane County, Oregon, U.S.A. (Walker, personal commun.). Establishment of the composition and compositional variations is especially important in view of the recent refinement of the structure by Brown and Gibbs (1969).

Analyses were carried out with an ARL-EMX electron microprobe using wet-chemically analyzed mineral standards (albite for Na and Al, andesine for Si and Ca, orthoclase for K, olivine for Fe and Mg). All analyses were run at 15 kv and 0.03 microamperes sample current. Corrections were made for drift, deadtime, background, mass absorption, fluorescence, and atomic number.

The new analyses are given in Table 1 with the original wet-chemical analysis. In addition, a microprobe analysis by S. J. B. Reed (personal commun.) is given. His analysis was performed completely independently using a different instrument, different reference standards, etc.

TABLE 1. OSUMILITE ANALYSES

Locality	Sakkabira, Japan	Sakkabira, Japan	Sakkabira, Japan	Monte Arci, Sardinia	Obsidian Cliffs, Oregon
Method:	Wet chemical	Microprobe	Microprobe	Microprobe	Microprobe
Analyst:	Minato, 1956	Bunch, 1968	Reed, 1968	Bunch, 1968	Bunch, 1968
SiO <sub>2</sub>	50.78	61.6	61.6	61.2	61.8
TiO <sub>2</sub>	0.01	0.11	—	0.12	0.11
Al <sub>2</sub> O <sub>3</sub>	24.85	21.4	21.4	22.0	21.8
Fe <sub>2</sub> O <sub>3</sub>	1.95	1.9 <sup>a</sup>	1.9 <sup>a</sup>	1.7 <sup>a</sup>	1.5 <sup>a</sup>
FeO	9.97	6.8	6.9	8.4	6.9
MnO	0.40	0.80	0.90	0.74	0.98
MgO	6.68	3.7	3.0	2.9	3.5
CaO	0.61	0.12	0.07	0.14	0.11
Na <sub>2</sub> O	1.00	0.96	0.7	0.35	0.27
K <sub>2</sub> O	1.42	3.0	3.4	3.0	3.0
H <sub>2</sub> O+	1.73	—	—	—	—
H <sub>2</sub> O—	0.27	—	—	—	—
Sum	99.67	100.4	99.9	100.6	100.0

<sup>a</sup> Inferred from structural requirements (see Table 2 and text).

The agreement between our respective analyses is excellent with the exception of the two elements Na and Mg, for which the agreement is only good. These elements have the lowest atomic numbers of the elements analyzed and as such may be subject to lower precision by the microprobe method. Structural formulae calculated from these analyses are given in Table 2.

#### DISCUSSION OF ANALYSES

The structural formulae indicate that the 12-coordinated position takes from 1.00 to 0.75 atoms. As the filling of this position drops from 1.00 to 0.75 the mole fraction  $K/(K+Na+Ca)$  increases approximately linearly from 0.65 to 0.87 (Fig. 1). In the structural formulae of all three osumilite samples the numbers of K and Ca atoms in this position are approximately constant at about 0.65 and 0.02, respectively. The mole fraction drops because the position adds Na, finally bringing the total to unity. This suggests that by extrapolating the line in Figure 1 to  $K/(K+Na+Ca) = 1.00$  the position would be only about 60 percent occupied. Nevertheless, pure potassium osumilite has been synthesized (Schreyer and Seifert, 1967) that contains one full atom of K in this position. This raises the question, for which we can offer no explanation,

TABLE 2. STRUCTURAL FORMULAE OF OSUMILITES<sup>a</sup>

Locality	Coordination		IV	IV	K/(K+Na	Si/(Si
	XII	VI	T(2)	T(1)	+Ca)	+Al)
Sakkabira	$K_{0.68}Na_{0.33}Ca_{0.02}1.00(Mg_{0.93}Fe^{2+}_{0.96}Mn_{0.11})_{2.00}(Fe^{3+}_{0.21}Al_{2.63})_{2.87}(Si_{10.32}Al_{1.62})_{12}O_{30}$				0.65	0.86
Monte Arci	$(K_{0.66}Na_{0.12}Ca_{0.03})_{0.81}(Mg_{0.72}Fe^{2+}_{1.13}Mn_{0.10})_{2.00}(Fe^{3+}_{0.22}Al_{2.73})_{2.93}(Si_{10.34}Al_{1.66})_{12}O_{30}$				0.81	0.86
Obsidian Cliffs	$(K_{0.68}Na_{0.08}Ca_{0.02})_{0.78}(Mg_{0.88}Fe^{2+}_{0.98}Mn_{0.11})_{2.00}(Fe^{3+}_{0.13}Al_{2.75})_{2.94}(Si_{10.41}Al_{1.59})_{12}O_{30}$				0.87	0.87

why these three natural occurrences should show such consistent K deficiencies.

In terms of the two tetrahedral positions determined by Brown and Gibbs the *T*(1) tetrahedron is only moderately distorted and twelve of them comprise the double hexagonal rings. Brown and Gibbs noted that the mean oxygen-cation bond length of 1.627 Å agrees well with an average of  $Si/(Si+Al^{4+})=0.85$  in this position. The three osumilite analyses presented here yield 0.86 to 0.87, in close agreement with Brown and Gibbs. The fact that they are all three nearly identical suggests that 0.86 may represent saturation of the *T*(1) position with respect to Al for the temperature and pressure conditions in which they formed.

Brown and Gibbs determined that the very distorted *T*(2) position

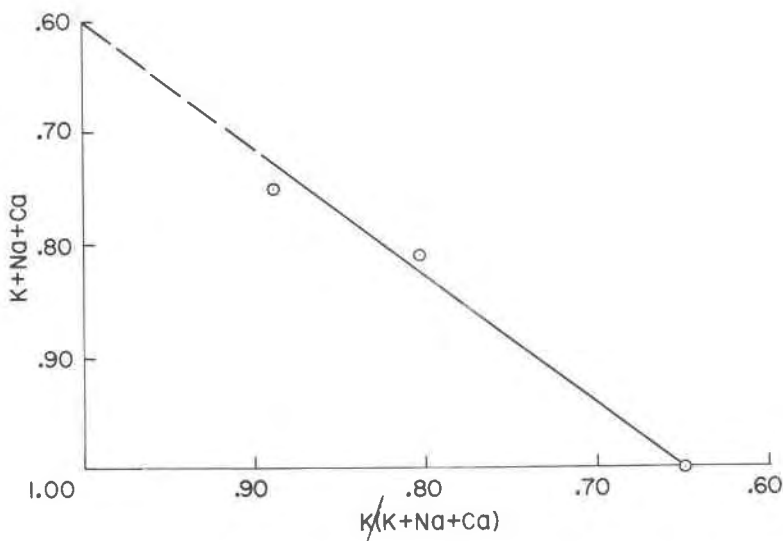


FIG. 1. Filling of the 12-coordinated position in osumilites.

is occupied by  $(Al_{2.61}Fe^{3+}_{0.37})$ . This required they infer about 2.7 weight percent  $Fe_2O_3$  from their probe analysis, which was not directly determined. In the analyses presented in this paper the same kinds of inferences are made and  $Fe_2O_3$  is reported. The amount, however, was computed to maintain overall charge balance of the whole formula and the octahedral position total at exactly two. This results in implied vacancies in the  $T(2)$  position. This choice was arbitrary; we might have filled the  $T(2)$  position to three exactly, leaving the octahedral position at a total of less than two, and with a somewhat higher  $Fe^{3+}/Fe^{2+}$  ratio. On the other hand some combination might be the actual case. On this basis, however, the structural formulae in Table 2 show a reciprocal relationship between the atom totals in the  $T(2)$  tetrahedra and the 12-coordinated alkali position such that a rise in one nearly balances the charge change of a decrease in the other.

Analytical totals are close to 100 percent, which does not permit the inference of any significant structural water. This is at variance with the results of Brown and Gibbs. They reported only 56.8 percent  $SiO_2$ , which caused their analytical total to fall almost 2.9 percent short of 100 percent permitting them logically to infer about 2 wt. % water, which is equivalent to two water molecules per unit cell. The original analysis (Miyashiro, 1956) (Table 1) contains 1.73 percent constituent water. Miyashiro concluded, however, that it might not be necessary in the structure. In the structural position to which it is assigned by Brown and Gibbs, within the double hexagonal rings, its absence would have no effect upon the structure. Finally, a newly corrected microprobe analysis by Brown and Gibbs (personal commun.) gives silica as 59.7 percent, with an analytical total of 100.6 percent without the inference of any water. We must conclude that water is not a constituent of osumilite, although absorbed water or zeolitic water may be present in small amounts.

#### STABILITY RELATIONS

All three world occurrences of osumilite are quite similar. Prominent hexagonal prisms occur within vesicles within rhyolite or rhyodacite. Some anhedral, fine-grained osumilite also occurs in the largely aphanitic ground-mass except at Monte Arci. The associated prominent coarse crystals within the vesicles are tridymite, fayalitic olivine, and some quartz. In the Obsidian Cliffs specimen prominent reddish-brown, paper-thin plates of hematite occur with osumilite. A few of these plates were observed girdling osumilite crystals and apparently growing through them. A number of powder diffraction patterns of this material showed only poorly defined hematite peaks, however, in one case a sharp mica pattern was present with hematite lines as well. It was impossible to ob-

tain a specimen of this mica free of considerable hematite and of a size large enough for analysis by microprobe. An analysis was made of the contaminated material to obtain an approximate composition. The analysis is close to that of phlogopite, with an atom ratio Si/Al of 3/1. The powder diffraction pattern agrees with that of natural phlogopite.

Schreyer and Seifert (1957) determined that natural osumilite breaks down into biotite, iron-rich cordierite, and quartz, at 2 kbar water pressure, 650°C. In their study of the metastability of synthetic osumilite they observed that initial partial breakdown produced only a mica phase with relict osumilite of (presumably) a modified composition. The mica phase observed in the Obsidian Cliffs occurrence may be a partial breakdown product of natural osumilite. Absence of any cordierite indicates that breakdown was indeed only partial. Abundant hematite plates may be interpreted as pseudomorphs after phlogopite resulting from the partial breakdown of small crystals of osumilite. Conversion of phlogopite to hematite can be attributed to leaching by escaping volcanic gases, principally water.

#### ACKNOWLEDGMENTS

We are grateful to Dr. A. Miyashiro for his comments and aid in obtaining osumilite specimens from Sakkabira. We also thank Drs. W. Schreyer, G. E. Brown, and G. V. Gibbs for critically commenting on the manuscript, and Dr. R. J. Davis for helpful comments on osumilites. We thank Dr. S. J. B. Reed for his analysis of the Sakkabira specimen, Dr. G. Rossi for providing specimens of the Monte Arci osumilite, and Dr. George Walker for information on the Obsidian Cliffs occurrence.

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*Manuscript received, October 3, 1969; accepted for publication, January 14, 1970.*