American Mineralogist, Volume 63, pages 490–498, 1978

The site distribution of iron and anomalous biaxiality in osumilite[1]

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Abstract

Osumilites from Sakkabira, Japan, Obsidian Cliffs, Oregon, and Nain, Labrador have been studied by optical, infrared, and Mössbauer spectroscopy. Osumilite is an anhydrous mineral. A major proportion of the Fe^{2+} occurs in the channel-like cavities. Biaxial Nain osumilite is X-ray hexagonal, and does not show infrared spectroscopic evidence for Al/Si ordering. The biaxiality arises from the channel contents.

Introduction

Osumilite, $K(Mg,Fe,Mn)_2(Al,Fe^{3+})_3(Si,Al)_{12}O_{30}$, is found in rhyolite or rhyodacite volcanic rocks and high-grade metamorphic rocks in contact aureoles. Its crystal structure (Brown and Gibbs, 1969) is similar to that of cordierite and beryl, because it contains channel-like cavities that are formed by the tetrahedral framework. In cordierite and beryl the channels are formed by a superposition of six-membered tetrahedral rings, whereas the channels in osumilite are formed by a superposition of double hexagonal rings (Fig. 1). The tetrahedral rings in these minerals are linked by octahedra and additional tetrahedra.

Osumilite is generally deep blue and displays uniaxial optics. However, Berg and Wheeler (1976) reported a pink biaxial osumilite from Nain, Labrador. The cause of the difference between uniaxial and biaxial optical behavior has not been established.

Water, as 1.73 percent H_2O^+, was found in the initial analysis of the Sakkabira osumilite by Miyashiro (1956). Brown and Gibbs found electron density in the center of cavities *between* the double hexagonal ring groups and attributed it to (Na,K,Ca) ions. They also found electron density near the center of the cavity *within* the double hexagonal rings and attributed it to H_2O hydrogen-bonded to the channel-wall oxygens. Olsen and Bunch (1970) found that the weight percent of the oxides in microprobe analyses of osumilites summed near 100 percent, and concluded that natural osumilites are virtually anhydrous. This conclusion has not been tested by independent means.

The results of the spectroscopic study of cordierite (Goldman *et al.*, 1977) are applied to the study of osumilite, because of the structural and spectroscopic similarities between both minerals. Goldman *et al.* concluded that (1) Fe^{2+} occurs in both the octahedral and channel sites, and (2) the blue color of cordierite originates at least primarily from intervalence charge-transfer between octahedral Fe^{2+} and channel Fe^{3+}. They also established the calibration for quantitatively determining the water content from infrared absorption spectra. These interpretations provide the basis for the study of osumilite.

This paper reports the findings of a combined electronic absorption and Mössbauer study of three osumilite samples to examine the site distribution of iron and the origin of color. Changes in the electronic absorption spectra are compared to variations in $2V$ and inferences are made regarding structural state. In addition, infrared spectra have been taken to examine the water content in osumilite, and to see if spectral differences exist between the uniaxial and biaxial samples.

Experimental details

Samples of osumilite from the type locality in Sakkabira, Japan (Miyashiro, 1956) (Stanford University #7753); Obsidian Cliffs, near McKenzie Pass, Oregon (Caltech #7396); and Nain, Labrador (Berg and Wheeler, 1976) are used in this study. The former two samples occur in silicic volcanic rocks, are dark blue,

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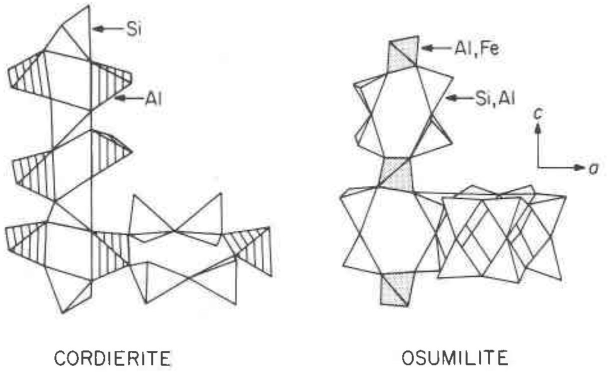

Fig. 1. The tetrahedral framework in cordierite and osumilite proposed by Brown and Gibbs (1969).

exhibit uniaxial positive optics, and are inferred to contain Fe^{3+} in tetrahedral coordination based on stoichiometry (Olsen and Bunch) and X-ray (Brown and Gibbs) considerations. Their polarized electronic absorption spectra were taken on polished slabs cut to contain c. The Nain osumilite occurs in a granulite, is pink, and exhibits biaxial positive optics with $2V$ ranging from 13 to 40° as measured with a universal stage for different crystals in one hand specimen. γ is parallel to the c axis; the orientation of the α and β indicatrix directions in the plane normal to c is not known. The γ direction for spectroscopic measurement was obtained by first orienting a slab to center the *Bxa* figure and then rotating this slab 90° about α to obtain a centered flash figure. After obtaining the γ spectrum, the sample was rotated 90° to reproduce the centered *Bxa* figure, and thinned for measurement of the α and β spectra. Electron microprobe data, obtained at Caltech with a MAC-V automated electron microprobe, were taken on slabs used for the optical spectra (Table 1). Microprobe data for Nain osumilites having $2V$'s of 24, 30, and 36° were taken to see if variations in $2V$ can be related to compositional differences, but no such correlation is evident. Microprobe analyses of a Nain osumilite heated at 700°C in air for 13 hours did not differ from the analyses of the unheated samples. 494, 561 and 520 μg of the Sakkabira, Obsidian Cliffs, and Nain samples, respectively, were each ground with 200 mg of KBr and pressed into a pellet for infrared spectra. The pellets were heated *in vacuo* at 80°C overnight, and repressed to minimize adsorbed H_2O on the KBr. All infrared spectra were taken against a KBr reference pellet. Concentrations for the Obsidian Cliffs and Nain samples used in the Mössbauer experiments are about 2.3 and 1.3 mgFe/cm^2 with the off-resonance regions having about 2.9×10^6 and 1.1×10^6 counts/channel, respectively. All Mössbauer spectra and parameters are reported relative to metallic iron. A Mössbauer spectrum of the Nain osumilite was also taken after heat treatment in air at 813°C for 13 hours, but significant Fe^{3+} resonance was not observed.

Site distribution of iron

Electronic absorption spectra

The electronic absorption spectra of the uniaxial osumilites from Sakkabira and Obsidian Cliffs are presented in Figures 2 and 3. They consist of absorption features at 10,280, 15,480, 22,220, and 24,150 cm^{-1} (973, 646, 450, and 414 nm) in ω polarization and 4650, 7020, and 10,280 cm^{-1} (2150, 1425, and 973 nm) in ω polarization. Faye (1972) attributed the asymmetry and breadth of the band at 15,480 cm^{-1} in the ω spectrum of an Obsidian Cliffs sample to a superposition of a dominant lower-energy band assigned to intervalence charge transfer between tetrahedral Fe^{3+} and octahedral Fe^{2+}, and a subordinate higher-energy band assigned to tetrahedral Fe^{3+}. Faye assigned the weak band near 22,220 cm^{-1} to tetrahedral Fe^{3+} and the band near 10,280 cm^{-1} to octahedral Fe^{2+}.

The electronic absorption spectra of an osumilite from Nain having a $2V$ of 40° (Fig. 4) clearly illustrate the three distinct optical directions. The γ spectrum (which has the same crystallographic orientation as ϵ in Figs. 2 and 3) consists of bands at 4686, 7020, and 10,280 cm^{-1} (2135, 1425, and 973 nm). Peak maxima differ slightly for the main band in α

Table 1. Electron microprobe analyses of osumilite

oxide	weight percent				
	Labrador 2V=36°	Labrador 2V=30°	Labrador 2V=24°	Japan	Oregon
SiO_2	60.3	61.2	60.8	60.6	60.7
TiO_2	0.2	0.2	0.2	0.0	0.1
Al_2O_3	22.0	22.2	22.4	22.0	21.8
MgO	5.7	5.7	5.6	3.0	3.0
FeO*	6.3	6.4	6.6	9.4	9.7
MnO	0.1	0.1	0.1	1.0	1.2
Na_2O	0.2	0.4	0.3	0.7	0.2
K_2O	4.0	4.3	4.2	3.2	3.2
	99.0	100.5	100.1	99.9	99.9

*total iron reported as FeO

A. A. Chodos and D. S. Goldman, Analysts

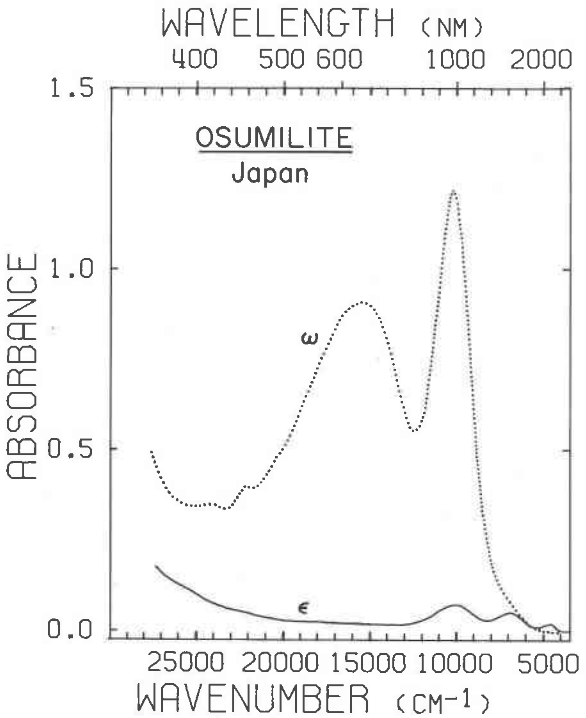

Fig. 2. Room-temperature electronic absorption spectra of an osumilite from Sakkabira. Crystal thickness = 0.10 mm.

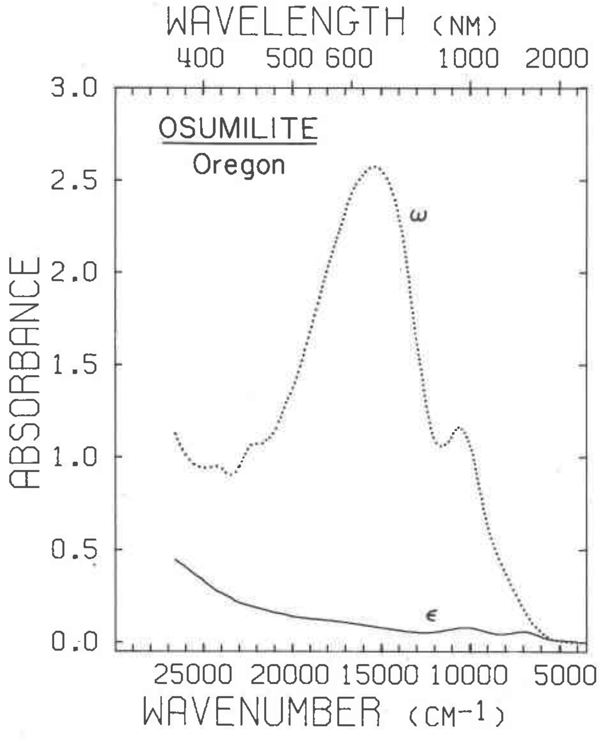

Fig. 3. Room-temperature electronic absorption spectra of an osumilite from Obsidian Cliffs. Crystal thickness = 0.10 mm.

and β polarizations and occur at 10,360 and 10,400 cm^{-1} (965 and 962 nm), respectively. The band in the visible region in α and β has a broad maximum between 18,000 and 21,000 cm^{-1}, and has a weak shoulder at 22,220 cm^{-1} (450 nm), corresponding to the position of the band observed in ω in the other samples. Some of the intensity of the 4686 cm^{-1} band occurs in α, but it is only observed in mm-thick sections.

Absorptions due to Fe^{2+} can be assigned using the criteria established for cordierite by Goldman *et al.* These criteria include absorption band positions, intensities, polarizations, and the energy difference between the components of split bands. Therefore, the bands at 10,280 and 7020 cm^{-1} in γ (or ϵ) are assigned to Fe^{2+} in the octahedral site. Bands in the 10,200–10,400 cm^{-1} region in α and β (or ω) and the 4650–4700 cm^{-1} region in γ (or ϵ) are assigned to Fe^{2+} in the channels. The two absorption bands arising from each type of Fe^{2+} are considered to represent electronic transitions to the components of the split ^5E_g state. The barycenter (median) energies of the two transitions for octahedral and channel Fe^{2+} are 8650 and 7590 cm^{-1}, respectively. For comparison, the barycenter energy for octahedral Fe^{2+} in cordierite is about 9200 cm^{-1} (Goldman *et al.*). The larger barycenter energy in cordierite reflects smaller average M–O distance of the octahedral site (2.12A; Gibbs, 1966) than in osumilite (2.15A; Brown and Gibbs, 1969). The barycenter energy can be used as an estimator of 10 Dq, the theoretical energy difference between the $^5T_{2g}$ and ^5E_g electronic states, if the splitting of the $^5T_{2g}$ state is small or similar among the samples compared (Faye, 1972). It should therefore vary as $(1/\bar{a})^5$, where $\bar{a}$ is the average metal–oxygen bond distance of the coordination site. Using the cordierite data, a barycenter energy of 8575 cm^{-1} is expected for octahedral Fe^{2+} in osumilite from the ideal $(1/\bar{a})^5$ dependence. These results support the assignment of the octahedral Fe^{2+} bands in osumilite spectra. In both minerals the two octahedral Fe^{2+} bands are polarized parallel to the c axis and have similar intensities.

The barycenter energy of channel Fe^{2+} in osumilite of about 7600 cm^{-1} is slightly larger than observed in cordierite (~ 7200 cm^{-1}). In both minerals the higher-energy band is polarized in the plane normal to the c axis and is much more intense than the lower-energy band, which is polarized parallel to the c axis. As in cordierite, heating experiments support the assignment to channel Fe^{2+} in osumilite. After an $\alpha\gamma$ slab was heated in air at 700°C for 13½ hours, it was cooled to room temperature and spectroscopically examined. The bands assigned to octahedral Fe^{2+} retained the same intensity after heat-treatment, whereas both bands assigned to channel Fe^{2+} were reduced to about 85 percent of their intensity prior to heating. Berg and Wheeler suggested, from the presence of graphite and pyrrhotite in the rock, that Fe^{3+} is "virtually absent" in the Nain osumilite. Using this assumption and the molar absorptivity determined for octahedral Fe^{2+} in cordierite of 3.5, the intensity of the octahedral Fe^{2+} band at 10,280 cm^{-1} indicates that only about 60 percent of the total iron in the Nain osumilite is in the octahedral site and 40 percent is in the channels. Spectroscopic evidence for tetrahedral Fe^{2+} is not observed. The site distribution of iron in the Nain and Obsidian Cliffs osumilites will now be analyzed using Mössbauer spectroscopy.

Mössbauer spectroscopy

The Mössbauer spectrum of the Nain osumilite (Fig. 5) supports the contention of Berg and Wheeler that Fe^{3+} is negligible in this osumilite. The Fe^{2+} resonant absorption is more intense in the low-velocity region, although both regions have asymmetry in their absorption profiles with the high-velocity absorption being broader. It is unlikely that the intensity asymmetry is produced by preferred orientation in the absorber, because these crystals do not possess good cleavage. These observations suggest that Fe^{2+} occurs in multiple environments.

A two-doublet fit to the spectrum is presented in Figure 5a and the resulting spectral parameters are listed in Table 2. The areas of the two lines of each doublet and the halfwidths of all peaks were constrained to be equal. The large halfwidths of the peaks (0.42 mm/sec) and the inability to fit the main peak intensities and the region near +0.6 mm/sec suggest that this fit is inadequately modeling the data. This poses a problem, because the electronic absorption spectra of osumilite suggest that Fe^{2+} resides in only two types of sites, the octahedral and channel sites. Although a three-doublet fit to the spectrum (Fig. 5b) provides a better overall spectral fit, a physically meaningful interpretation for each of the three doublets is unclear. In addition, the peak half-width in the three-doublet fit (0.38 mm/sec) is still broad for Fe^{2+} in a single site. Spectral broadening can result from variations in next-nearest-neighbor chemistry, as has been proposed in clinopyroxenes (Dowty and Lindsley, 1973), orthorhombic Mg–Fe amphiboles (Seifert, 1977), and calcic amphiboles (Goldman, 1978). We suggest that the outer doublet arises *mostly* from Fe^{2+} in the octahedral site, based on the similar quadrupole splitting and isomer shift found for octahedral Fe^{2+} in cordierite (Goldman *et al.*), and the inner two doublets are *mostly* due to Fe^{2+} in the channels. The smaller quadrupole splitting and isomer shift values of the inner doublet(s) are consistent for the more distorted channel environment. The results from the two- and three-doublet fits indicate that about 68 and 53 percent of the total iron is octahedral Fe^{2+}, respectively. Considering that the three-doublet fit probably underestimates octahedral Fe^{2+} content because of increased peak overlap, and *vice versa* for the two-doublet fit, an approximate value of 60 percent of the iron in the Nain osumilite being in the octahedral site is reasonable, and agrees with the site distribution predicted from the electronic absorption spectra.

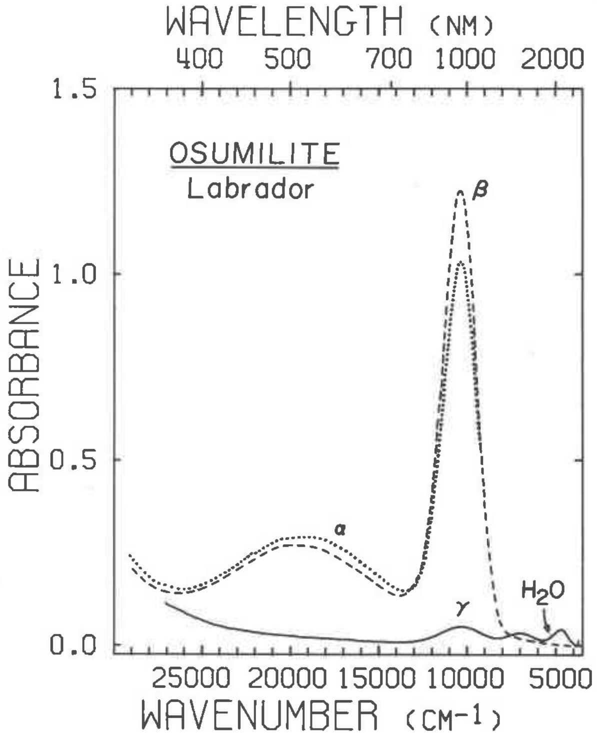

Fig. 4. Room-temperature electronic absorption spectra of an osumilite from Nain. Optic orientation: $\gamma = c$; α and β occur in the plane normal to the c axis. Crystal thickness = 0.10 mm.

The Mössbauer spectrum of the Obsidian Cliffs osumilite (Fig. 5d) also shows asymmetry in the profile and intensity of the Fe^{2+} resonance, which is again fitted with three doublets. The three doublets are only moderately similar to the quadrupole splitting and isomer shift values (Table 2) found in the Nain sample, and the area ratio of the outer doublet to the total Fe^{2+} resonance is 56 percent, which is also

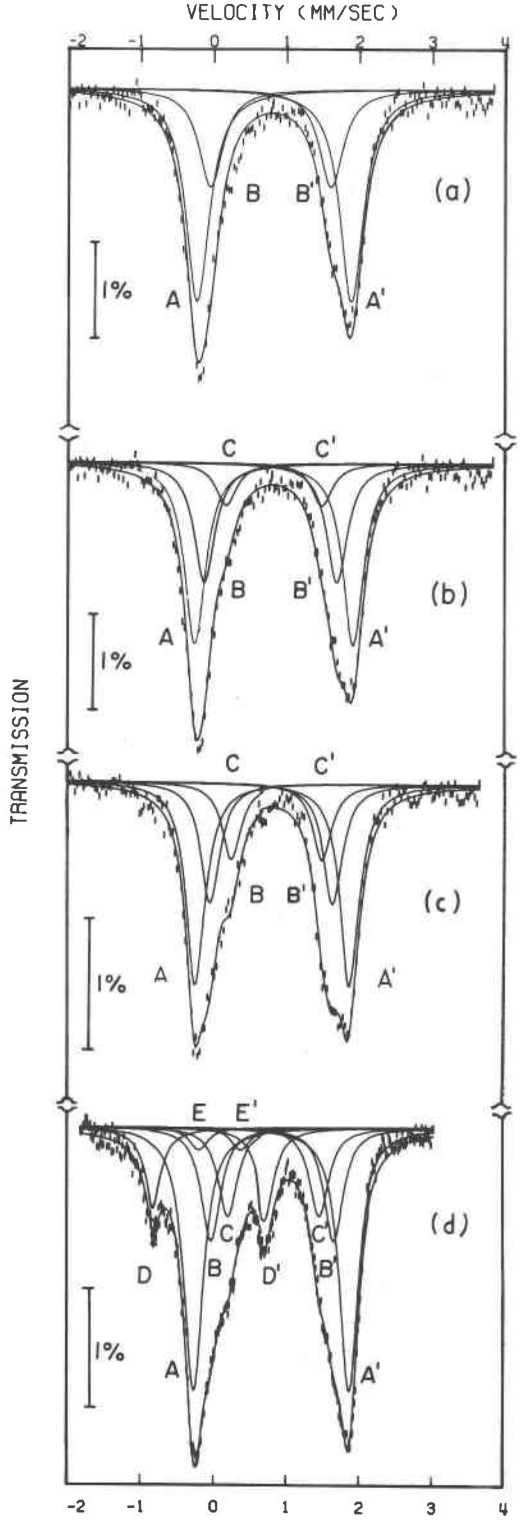

Fig. 5. Room-temperature Mössbauer spectrum of osumilite from Nain: (a) fitted with two Fe^{2+} quadrupole doublets, (b) fitted with three Fe^{2+} quadrupole doublets, and (c) heated to 813° for 15 hours; (d) osumilite from Obsidian Cliffs.

similar to that found in the Nain osumilite. In addition, octahedral Fe^{2+} (the outer doublet) accounts for about 45 percent of the total iron, in agreement with value predicted from the electronic absorption spectra (41 percent). The Obsidian Cliffs Mössbauer spectrum contains two additional peaks not found in the Nain spectrum, that occur near +0.9 and −0.8 mm/sec and have equal intensities. Fitting a doublet to these peaks results in isomer shift and quadrupole splitting values of 0.25 and 1.71 mm/sec, respectively. The isomer shift is indicative of high-spin Fe^{3+}, but this value is much smaller than expected for Fe^{3+} in octahedral coordination (~ 0.4–0.5 mm/sec). This doublet is assigned to Fe^{3+} in tetrahedral coordination, based on the similar parameters reported for tetrahedral Fe^{3+} in ferri-diopside (Hafner and Huckenholz, 1971) and sapphirine (Bancroft *et al.*, 1968), although this assignment is not consistent with the data reported for iron orthoclase (Brown and Pritchard, 1969). Peaks placed at +0.5 and −0.1 mm/sec for "octahedral" Fe^{3+} improve the fit, but their physical significance is not certain.

The ϵ values (molar absorptivity) from the electronic absorption spectra for octahedral and channel Fe^{2+} in osumilite from the site distribution determined from the Nain sample are 3.5 and 130 respectively.

Water

Infrared absorption spectra of single crystals of osumilite indicate that it is virtually anhydrous. The fundamental stretching modes of water occur in the 3300–3700 cm^{-1} region, but this region is free of absorption features in the Sakkabira and Obsidian Cliffs osumilites. Although the initial analysis reported by Miyashiro found H_2O^+, all subsequent electron microprobe analyses of the Sakkabira osumilite (Olsen and Bunch, 1970; G. Brown, personal communication, 1977; this work) have failed to find evidence for water. Recognizing the possibility that the batch of osumilite used by Miyashiro could differ in water content from that used by other investigators, we nevertheless conclude that osumilite is correctly formulated as an anhydrous mineral. The Nain osumilite does have weak water absorptions in the infrared region (Fig. 6); however, the water content is calculated to be less than 0.01 percent (by weight), using the molar absorptivity for water determined in cordierite by Goldman *et al.* The presence of the combination modes near 5250 cm^{-1} (1905 nm), barely visible in Figure 4 in γ, indicate that the molecular species H_2O is present, although these data do

Table 2. Mössbauer parameters

Sample	Peaks	Isomer Shift	Quadrupole Splitting	Half-Width	% Area	χ^2
Nain Labrador	AA'	1.20	2.35	0.42	68	392*
	BB'	1.14	1.86	0.42	32	
Nain Labrador	AA'	1.21	2.41	0.38	53	313*
	BB'	1.16	2.03	0.38	35	
	CC'	1.17	1.48	0.38	12	
Nain Labrador Heated‡	AA'	1.22	2.34	0.34	51	255*
	BB'	1.19	1.88	0.34	30	
	CC'	1.26	1.41	0.34	19	
Obsidian Cliffs Oregon	AA'	1.19	2.33	0.33	45	539**
	BB'	1.20	1.86	0.33	20	
	CC'	1.21	1.40	0.33	15	
	DD'	0.25	1.71	0.33	16	
	EE'	0.40	0.60	0.33	4	

*200 channels fitted **330 channels fitted ‡813° 15 hours

not exclude the simultaneous presence of the OH^- ion. The complexity of the spectra in the fundamental region indicates that water (or OH^-) occurs in multiple environments. The spectra display anisotropic differences between E⊥*c* and E||*c*, but in the plane perpendicular to *c* the water bands fail to display anisotropy (< 4 percent). This result was verified for 8 samples with $2V$ ranging from 19 to 36°. This result contrasts strongly with cordierite, for which the water features are highly anisotropic, and indicates that the water in the Nain osumilite is structurally ordered according to the "pseudo" hexagonal symmetry of the crystal. It seems unlikely that the water would cause the biaxial optics if it is hexagonally ordered. This conclusion is further substantiated by the poor correlation between water concentration and $2V$ (Fig. 7).

Origin of color

Heating experiments on cordierite (Goldman *et al.*) suggested that its blue color originates from intervalence charge transfer between octahedral Fe^{2+} and channel Fe^{3+}. A similar result has been obtained with osumilite. The Nain osumilite was heated for one hour at 813° and then one hour at 869°C. Intensities of the octahedral features remained the same after heat treatment, but significant change occurred in the spectrum normal to the *c* axis (Fig. 8). The channel Fe^{2+} band near 10,400 cm^{-1} reduced in intensity, and the sample turned from pink to blue. Analogous to the results for cordierite, this suggests that a portion of the channel Fe^{2+} oxidizes upon heating, and that the blue color in osumilite is at least in part due to intervalence charge transfer between octahedral Fe^{2+} and Fe^{3+} in the cavities between the double hexagonal ring groups. The origin of the pink color in the Nain osumilite is unclear. The possibility that an intervalence charge transfer between octahedral Fe^{2+} and Fe^{3+} in the adjacent tetrahedral site is responsible for some of the blue color in the Sakkabira and Obsidian Cliffs osumilites cannot be excluded. It may be a possible cause for the asymmetry of the main charge-transfer band.

The concentration of water in the channels appears to correlate with the ease at which channel Fe^{2+} will oxidize upon heating. Channel Fe^{2+} was not oxidized at 869°C in the anhydrous Obsidian Cliffs osumilite. About 15 percent of the channel Fe^{2+} was oxidized at 700°C in the Nain osumilite, which contains minor amounts of water. Nearly 45 percent of the channel Fe^{2+} is oxidized at these temperatures in water-bearing cordierites. Ninety percent of the water in the Nain osumilite was lost from the sample heated to 869°C, as determined by the infrared spectra, yet the value of $2V$ did not change, further indicating that water does not cause the biaxial optics.

The Mössbauer spectrum of the heated Nain osumilite shows no change in the intensity asymmetry, but does show broadening of both components of the Fe^{2+} doublet in the inner region (Fig. 5). The spectrum changes to resemble that of the Obsidian Cliffs osumilite but without the Fe^{3+} doublet. The half-widths of the three-doublets fit (Table 2) are still broad for Fe^{2+} in a single site.

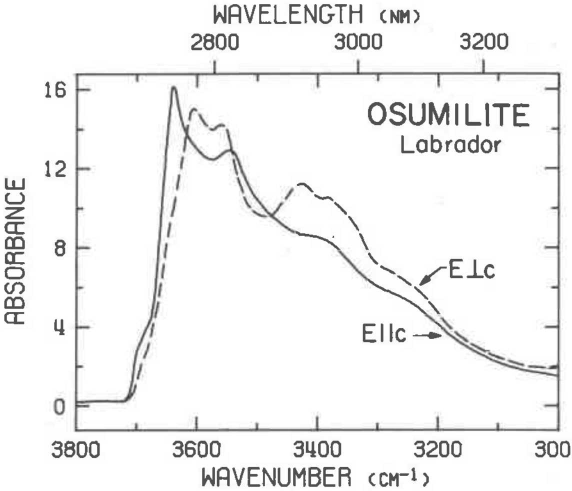

Fig. 6. Infrared absorption spectra of a crystal of Nain osumilite ($2V$ = 40°) taken at 78 K. These spectra exhibit only moderately better spectral resolution than the room-temperature spectra, and are about 40 percent more intense. Data presented for 1.0 cm-thick sample.

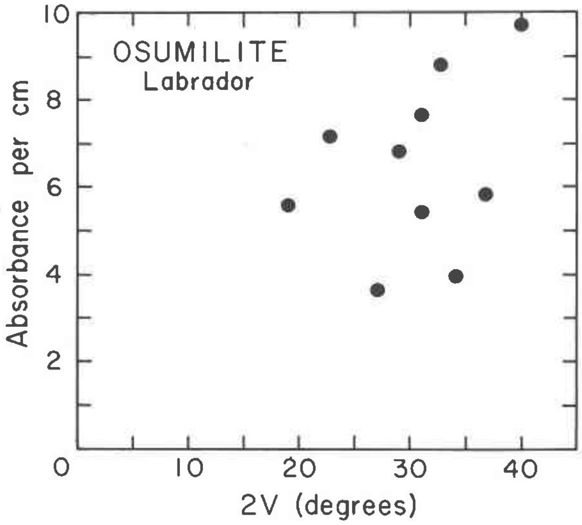

Fig. 7. Correlation of the $2V$ angle with water content as measured by the intensity of the E⊥c band at 3600 cm^{-1}.

Structural state

There remains a discrepancy between the electronic absorption and X-ray data concerning the structural symmetry of the Nain osumilite. Zero and upper-level X-ray precession photographs of a crystal of Nain osumilite with $2V = 30°$ are consistent with a hexagonal *P6/mcc* space group. This result has been independently confirmed by Professor Gordon Brown (personal communication) at Stanford University. However, the biaxial optics and three distinct absorption directions indicate that the overall symmetry must be lower than hexagonal. In the Sakkabira sample there are only two absorption directions and the $2V$ is zero. Therefore, if the Nain osumilite were truly hexagonal the bands in α and β due to channel Fe^{2+} near 10,400 cm^{-1} would have equal intensities, both being in the plane normal to the c axis.

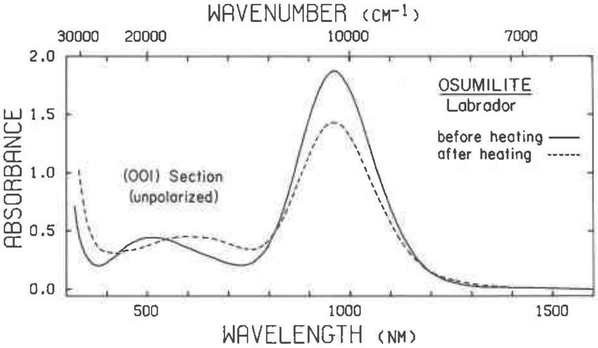

Fig. 8. Electronic absorption spectra of an osumilite from Nain before heat treatment and after heating at 813° for 1 hour and then for 1 hour at 869°C. The sample turned from pink to blue after heating.

Because the Nain samples exhibit a wide range of $2V$, the relationship between $2V$ and the β/α intensity ratio of the channel Fe^{2+} bands was explored, and the results are presented in Figure 9. The hexagonal Sakkabira and Obsidian Cliffs osumilites are also included in this correlation, which shows that the intensity asymmetry in the plane normal to c increases as $2V$ increases. The trend is not linear and appears to have an upward curvature. This trend intersects typical values for cordierite which have asymmetry values near 2.0 with $2V$ values of 80–90°.

The correlation in Figure 9 was not expected initially, because the band intensity differences are due to the effect of the coordination about the channel Fe^{2+} ion on its electronic structure, whereas $2V$ is determined by differences in refractive index along the different crystal directions in the visible region, which are controlled by the electron distribution of the entire structure. Cordierite has a completely ordered Al/Si tetrahedral framework, a large $2V$, and a large band-intensity difference, whereas the Sakkabira osumilite has a disordered tetrahedral framework, $2V$ equal to zero, and no difference in band intensity. This suggests that the Nain osumilite may have variable degrees of Al and Si order in the double hexagonal rings which control the overall optics of the crystal. A greater degree of order is expected in the slowly-cooled Nain osumilite compared to the quickly-cooled volcanic osumilites from Sakkabira and Obsidian Cliffs.

The infrared spectra of the three osumilites have been taken to see if differences exist between the Nain sample and the hexagonal osumilites from Sakkabira and Obsidian Cliffs (Fig. 10). Although differences exist in the band near 1150 cm^{-1} and in the 800–500 cm^{-1} region among these samples, major differences in band complexity in the Nain sample are not apparent. Systems which show a high degree of Al/Si ordering, such as feldspars, show a major loss of resolution of the fine structure in this region as the sample becomes disordered. We conclude that if differences in the Al/Si ordering exist in these osumilites, they are subtle.

Stoichiometry considerations

The average of the three electron microprobe analyses of the Nain osumilite (Table 1) has been normalized to the theoretical 30 oxygens, in which all iron is considered to be Fe^{2+} based on the Mössbauer data. Using our best estimate from optical and Mössbauer data that 60 percent of the Fe^{2+} is in the octahedral site, the following formula results:

$$(Na_{0.10}K_{0.89}Fe^{2+}_{0.37})^{XII}(Mg_{1.43}Fe^{2+}_{0.53}Mn_{0.01})^{VI}$$
$$(Al_{2.66})^{IV}(Si_{10.30}Al_{1.70})^{IV}O_{30}$$

There is clearly more Fe^{2+} and Mg available than can be accommodated in the octahedral site. The observation that natural osumilites have more than 2.0 formula units of Mg and Fe^{2+} suggested the presence of these ions in tetrahedral coordination. Berg and Wheeler placed the excess in the tetrahedral (*T*2) site with Al. They based this interpretation from a plot of osumilite formulas with regard to two coupled substitutions: the first involves (Mg,Fe) replacing Al in tetrahedral coordination and Si replacing Al, and the second involves (Na,K) entering the channels with Al replacing Si. However, the results of our study indicate that tetrahedral Fe^{2+} does not occur, and therefore Fe^{2+} should not be included in the first coupled substitution. In this case, natural osumilite compositions would plot in the field (Mg <2), which does not necessitate tetrahedrally-coordinated Mg. The 0.34 vacancies in the *T*2 site only amount to 2 percent vacancies in the 15 tetrahedral sites.

The resulting formula of the Obsidian Cliffs osumilite, using an Fe^{3+}/Fe^{total} ratio of 0.20 determined from the Mössbauer spectrum, is:

$$(Na_{0.06}K_{0.69}Fe^{2+}_{0.10})^{XII}(Mg_{0.75}Fe^{2+}_{1.01}$$
$$Fe^{3+}_{0.06}Ti_{0.01}Mn_{0.17})^{VI}(Al_{2.66}Fe^{3+}_{0.23})^{IV}(Si_{10.30}Al_{1.70})^{IV}O_{30}$$

The resulting site distribution of Fe^{2+} from this formula does not agree with the distribution expected from Mössbauer and electronic absorption spectra, and the reason for the discrepancy is unclear. Again, there appear to be vacancies in the *T*2 site containing the Al and Fe^{3+} ions, which is in general agreement with the findings of Olsen and Bunch for natural osumilites. The formula for the Sakkabira osumilite may be found in Olsen and Bunch, and will not be analyzed herein without knowledge of the Fe^{3+}/Fe^{2+} ratio.

Conclusions

This study has shown that osumilite should be formulated as an anhydrous mineral. Evidence also indicates that an appreciable proportion of the iron occurs in the channels. Other ions for which direct spectroscopic probes do not exist may also be located in these sites and may relate to the unresolved problem of the stoichiometry and site occupancy of os-

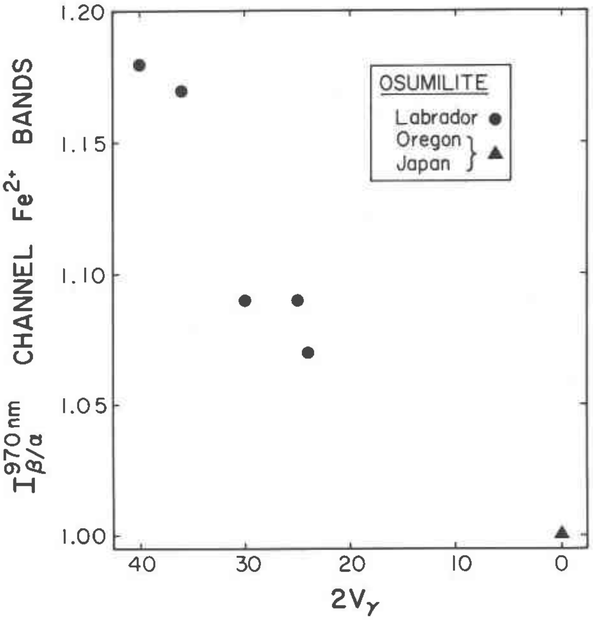

Fig. 9. Correlation between $2V$ and the intensity ratio of the channel Fe^{2+} absorption bands in the plane normal to the *c* axis in osumilite.

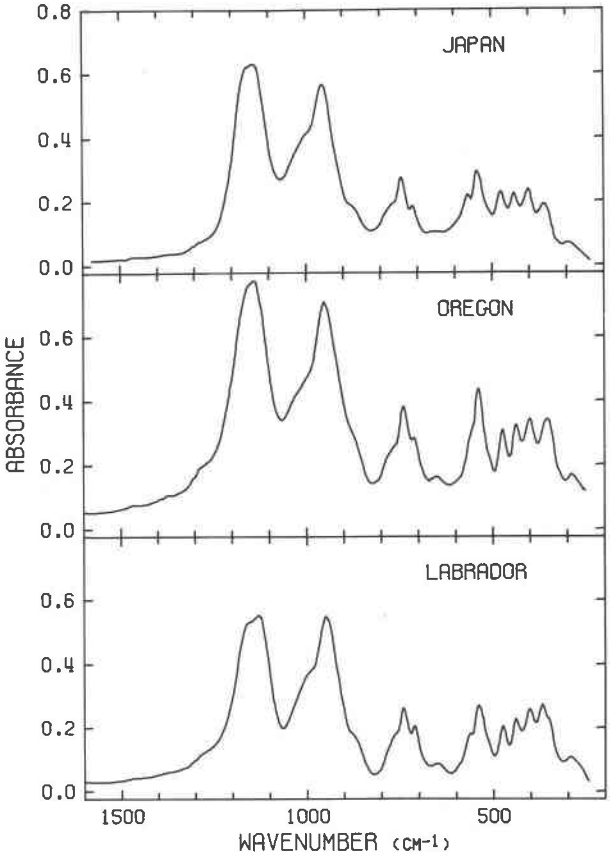

Fig. 10. Room-temperature infrared spectra of osumilites from Nain, Sakkabira, and Obsidian Cliffs.

umilites. Trace water in the Nain osumilite may be important in the color changes which accompany heating but appears not to be a direct cause of its biaxiality. Of all the features examined, only the iron spectra show biaxial characteristics. In particular, it is the spectra of the channel Fe^{2+} which show this to the greatest extent. We conclude that the ions in the channel are associated with the biaxiality, but have not established if they are the cause of the biaxiality, or if they are merely responding in turn to the influence of a more fundamental feature of the osumilite structure.

Acknowledgments

Wayne Dollase (University of California, Los Angeles) took the Mössbauer spectra used in this study and fitted the spectrum of the Obsidian Cliffs sample. Jonathan Berg (Northern Illinois University) provided the Nain osumilite, Gordon Brown (Stanford University) provided the crystals of the Sakkabira osumilite and several discussions concerning osumilite crystal chemistry, and Jack Huneke (California Institute of Technology) provided Obsidian Cliffs osumilite. Portions of this research were supported by NSF Grant EAR76-02014.

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Manuscript received, August 26, 1977; accepted for publication, December 5, 1977.