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Enhanced H and F incorporation in borian olivine

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ABSTRACT

B-containing olivine from the Tayozhnoye Fe deposit (Siberia, Russia) has unusually high H and F contents of 0.012 H and 0.026–0.043 F per formula unit of four O atoms. There are a minimum of eight infrared O-H absorption bands, none of which correlates with the known O-H band frequencies of hydrous magnesium silicates. The O-H band at 3672 cm^{-1} has not been observed in previously published olivine spectra. Transmission electron microscopy indicates substantial replacement of olivine by clinohumite and disordered mixtures of olivine and humite-group minerals near the rims of the olivine grains, whereas the interiors of the olivine grains contain regions of unaltered olivine structure. H_2O contents calculated from the defect stoichiometry and defect density are approximately one-tenth of the total H_2O content estimated from the infrared data. The O-H bands, therefore, are believed to reflect the presence of OH within the olivine crystal structure. Infrared-active stretching vibrations at 758, 1164, and 1257 cm^{-1} are consistent with the presence of $^{[4]}BO_4$ groups within the olivine structure. Our data represent the first direct evidence of the coupled substitution $B(F,OH)Si_{-1}O_{-1}$ in orthosilicate minerals. As a potential carrier of B, F, and H in the subducted oceanic lithosphere, olivine may play a key role in recycling these elements into the mantle.

INTRODUCTION

The occurrence of H in nominally anhydrous minerals has been documented in several investigations (Kats, 1962; Wilkins and Sabine, 1973; Beran and Putnis, 1983; Aines and Rossman, 1984; Smyth et al., 1991; Bell and Rossman, 1992a). H_2O contents on the order of parts per million have been measured in most mantle phases, with pyroxenes, in general, more hydrous than olivines or garnets (Miller et al., 1987; Skogby et al., 1990; Smyth et al., 1991; Bell and Rossman, 1992a, 1992b). Infrared spectra of these nominally anhydrous minerals have strong absorption maxima in the O-H stretching region, suggesting that H_2O is in the form of OH and incorporated into the mineral structure by means of extended or point defects (Beran and Putnis, 1983; Bai and Kohlstedt, 1993).

An alternative mechanism for incorporating OH is a coupled substitution with another component. An unusually B-rich olivine sample from the Tayozhnoye Fe deposit (Russia) led Grew et al. (1991) to suggest that a coupled substitution involving B should be considered. To examine this possibility, we obtained IR and transmission electron microscopy (TEM) data from the Tayozhnoye olivine. The results were used to test whether the substitution of B by Si coupled with the substitution of F and OH for O in 1:1 correspondence, that is, $B(F,OH)Si_{-1}O_{-1}$, could be a viable mechanism for incorporating OH, F, and B in olivine and other orthosilicate minerals.

SAMPLE

Olivine was separated from a single drill core (no. 485, depth 858.4 m), kindly provided by N. N. Pertsev, from the Tayozhnoye deposit, which is located in the Precambrian Aldan shield of central Siberia, Russia. This core consists of an unusual orthosilicate-hosted magnetite ore enriched in B (Pertsev and Boronikhin, 1986; Grew et al., 1991). The major constituents are olivine, magnetite, and spinel. Olivine forms colorless, subequant grains 0.5–7.0 mm across and commonly is clouded with opaque dust. Clinohumite is locally abundant; generally, it is subordinate to olivine, finer-grained (≤1.0 mm across), and interstitial to it. Alteration of the orthosilicate minerals to serpentine is rare. Trace constituents include serendibite, pargasite, phlogopite, tourmaline, pyrrhotite, chalcopyrite, zircon, ludwigite, and sinhalite. The ore was affected by several metamorphic cycles from upper

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amphibolite to granulite facies conditions (4–5 kbar, 650–850 °C).

METHODS

To collect IR absorption data, colorless olivine grains were separated from the host material by crushing the sample and removing individual grains by hand. The host rock was obtained from a section of the core a few centimeters away from the sections analyzed by Grew et al. (1991). The chemical data reported by Grew et al. (1991) indicate that the olivine in this portion of the core is relatively homogeneous: Fo = 86–89 mol%, and, in weight percent, MnO 0.27–0.30, B_2O_3 1.11–1.35, F 0.33–0.55, TiO_2, Al_2O_3, Cr_2O_3, and CaO 0.0–0.08. Two of the mineral grains were oriented using a universal microscope stage; they were then mounted in acrylic resin and polished on two parallel surfaces perpendicular to one of the principal crystallographic axes.

Infrared spectra were collected using a Nicolet 60SX Fourier-transform infrared spectrophotometer. Reflectance infrared spectra were collected and compared with a synthetic single-crystal forsterite standard to determine and confirm the crystallographic orientations of the two samples initially obtained from interference figures. Transmission spectra of the polished specimens were taken using a 100-μm aperture through crack- and inclusion-free regions of the samples. Areas near grain boundaries were avoided. Sample thicknesses were 200 and 314 μm. The spectra were normalized to a thickness of 1 mm to facilitate comparison between the two samples and with previously published spectra. Transmission spectra were also collected on pressed disks, prepared by grinding 1.25 mg of the sample with approximately 280 mg KBr, to obtain spectral information in the silicate and borate stretching regions.

TEM samples were prepared by ion milling disks cut from petrographic thin sections and lightly coating the thinned specimens with C. Electron microscopy and selected-area electron diffraction (SAED) were performed with a Philips 420ST microscope operated at 120 keV, as described by Veblen and Bish (1988). Energy-dispersive X-ray spectra were obtained with a Link ATW ultrathin-window Si(Li) detector, a Link 2040 pulse processor, and a 4pi Spectral Engine analyzer board installed in a Macintosh Quadra 950 computer. Electron energy-loss spectroscopy (EELS) was performed with a Gatan parallel EELS spectrometer mounted on a Philips 430 electron microscope.

Molecular orbital calculations were performed to compare the theoretical IR spectrum of a $^{[4]}BO_4$ group with the IR spectrum of the Tayozhnoye olivine. The molecular optimization was carried out on the $[H_4BO_4]^{1-}$ molecule using 3-21G** basis sets.The use of small molecular clusters to model the vibrational modes of minerals was based on the assumption that short-range forces play a dominant role in determining the bonding and vibrational properties of minerals (Lasaga and Gibbs, 1988). The H atoms in the $[H_4BO_4]^{1-}$ molecule terminate the B-O bonds to provide charge compensation and to mimic the effects of next nearest neighbor cations on the vibrational modes of the BO_4 group. We are not implying that there is an H_4BO_4 entity within the olivine structure. The $[H_4BO_4]^{1-}$ molecule was chosen because it is the simplest model of $^{[4]}BO_4$ group, with a small associated charge, that, when optimized at the 3-21G** level, can provide a significant correlation of the theoretical vibrational modes with those observed experimentally.

Hartree-Fock molecular orbital calculations were performed with the program Gaussian 92 (Frisch et al., 1992) on the Cray Y-MP at the San Diego Supercomputing Center. All parameters were varied until a minimum-energy configuration was found within a tolerance of 1×10^{-7} H (H = Hartrees). A frequency analysis of the optimized geometry calculated no imaginary frequencies for the configuration, indicating that the optimized geometry represents a true minimum in the potential energy surface.

RESULTS AND DISCUSSION

Electron microscopy

Previous TEM studies have demonstrated that several kinds of structural disorder can occur in olivine: (1) Slabs of humite-group structure may be intergrown parallel to (001) (Kitamura et al., 1987; Drury, 1991). Such defects are of particular interest in the present study because they result in the structural incorporation of H and F. (2) Slabs of oxidized olivine-like structure (laihunite) also can occur parallel to (001) (Banfield et al., 1990, 1992). (3) Slabs of the olivine, spinel, and β-phase structures can mutually intergrow (Price, 1983; Green, 1992). To evaluate the possibility that the chemical composition and spectroscopic characteristics of the Tayozhnoye olivine are strongly affected by such extended defects, the sample was examined with TEM methods.

The interiors of the Tayozhnoye olivine crystals contain regions of pure olivine structure up to a few micrometers in diameter, as evidenced by sharp olivine SAED patterns (Fig. 1a) and the absence of planar defects in TEM images. In contrast, near grain boundaries there has been substantial replacement of olivine by ordered clinohumite and disordered mixtures of olivine and (001) slabs of humite-group minerals (Fig. 1b). Most of the borian olivine, however, is intermediate between these extremes, containing scattered (001) planar defects and producing SAED patterns with streaks parallel to **c*** (Fig. 1c). The humite-type defects are commonly observed to terminate at partial dislocations, as described by Drury (1991), and free dislocations also are present.

Because humite-group defects introduce H and F into olivine, and because spectroscopic data were collected from the clear interiors of olivine crystals, the interior defect densities were measured for two Tayozhnoye olivine crystals. Planar defects intersecting the ion-milled specimen edge were counted from bright-field TEM images; 648 defects were observed over 264 μm of the sam-

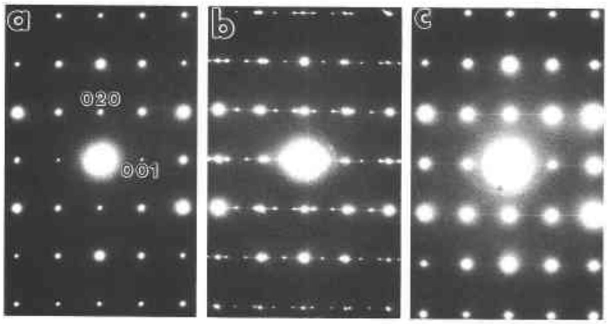

Fig. 1. SAED patterns from Tayozhnoye olivine. (**a**) Olivine free of planar defects, crystal interior. (**b**) Intergrown clinohumite, olivine, and disordered olivine, from near the grain boundary. (**c**) Olivine with planar defects, crystal interior.

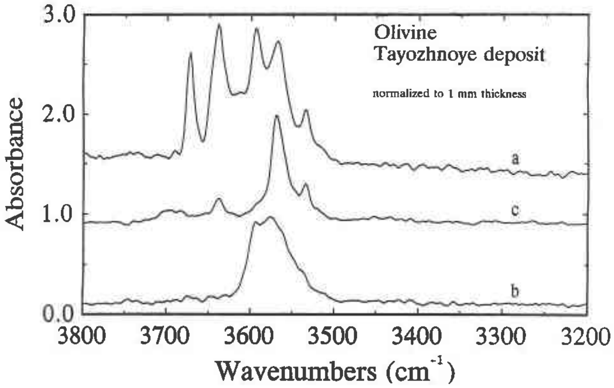

Fig. 2. Infrared absorption spectra, in the principal O-H stretching region, for each of the principal crystallographic axes of olivine.

ple parallel to the **c** axis. This measurement yielded an average distance between defects of 0.41 μm, or a defect density of approximately 2450 mm^{-1}.

High-resolution TEM images of numerous planar defects indicate that most defects consist of two N (norbergite) slabs intergrown within the O-slab olivine matrix, although some defects contain either an isolated N slab or more than two N slabs (see Thompson, 1978, or Veblen, 1991, for the definition of polysomatic N and O slabs). We therefore assumed an average of two N slabs per defect. Given that each O slab has the stoichiometry $(Mg,Fe)_2SiO_4$ and that each N slab has the stoichiometry $(Mg,Fe)_2SiO_4 \cdot (Mg,Fe)(OH,F)_2$ and given the observed defect density, the humite-type defects could contribute approximately 0.00294 (OH,F) pfu of $(Mg,Fe)_2SiO_4$. Therefore, the observed defect density can account for only about 5–10% of the total amount OH and F indicated by other experiments. Furthermore, this defect density could not account for the large B content in this olivine, even if all the tetrahedral sites in humite-group slabs were completely filled with B.

Repeated attempts to analyze the olivine between defects directly for B and F with X-ray emission spectroscopy and EELS were unsuccessful because of poor peak to background ratios for B and interference with the FeL lines for F.

Infrared spectroscopy and theoretical calculations

Figure 2 presents the near-infrared absorption spectra for each of the principal crystallographic axes. The spectra corresponding to the **b** ($E\|\mathbf{b}$) and **c** ($E\|\mathbf{c}$) axes are similar to the spectra of olivines from Vesuvius and Tanzania, respectively, reported by Miller et al. (1987). The spectrum for the **a** axis ($E\|\mathbf{a}$) is distinct; the absorption maximum at 3672 cm^{-1} has no counterpart in any other published olivine spectra. Furthermore, the frequencies of most of the absorption bands do not correlate with the known O-H band frequencies associated with talc, serpentine, or humite-group minerals, although the peak at 3688 cm^{-1} could be the 3685-cm^{-1} peak of lizardite. We suggest that the seven (possibly eight) unique O-H bands do indeed reflect the presence of OH within the olivine crystal structure of the samples.

The O-H absorption intensities (13 per cm) are significantly higher than the absorption intensities (1–5 per cm) previously reported for mantle-derived olivine specimens (Miller et al., 1987; Bell and Rossman, 1992a). H_2O contents were calculated by three methods. In the first method, we calculated the H_2O content to be 714 ppm by taking ratios of our integrated intensities to the integrated intensities of an olivine for which the H_2O content was independently determined with nuclear resonance analysis (Endisch et al., in preparation). Using Beer's law, we calculated the H_2O content to be 1980 ppm, assuming an average molar absorptivity of 180, whereas, using the Paterson (1982) method, we calculated it to be only 210 ppm. These concentrations are significantly higher than previous determinations reported for olivine minerals (Beran and Putnis, 1983; Miller et al., 1987; Bai and Kohlstedt, 1993). In the absence of a more suitable calibration for determining H_2O contents in olivines, we find the 714 ppm value to be the most reliable determination for the Tayozhnoye olivine. This corresponds to 0.012 H apfu, so that (OH + F) = 0.038–0.055 and B = 0.047–0.057 apfu for the three olivines analyzed by Grew et al. (1991), a remarkable agreement considering the ambiguities in both the ion microprobe and spectroscopic data.

Figure 3 compares the IR spectra of a B-bearing olivine from Tayozhnoye, Russia, and a B-free olivine (Fo$_{91}$) from Kilbourne Hole, New Mexico. The spectra are similar, except for three bands at 758, 1164, and 1257 cm^{-1} in the spectrum of the B-containing olivine. The peak at 758 cm^{-1} is close to the 800- and 780-cm^{-1} peaks observed in the infrared spectrum of synthetic sinhalite ($MgAlBO_4$, olivine-type structure: Tarte et al., 1985). Tarte et al. (1985) assigned the doublet at 780–800 cm^{-1} to the ν_1 symmetric stretching mode of the BO_4 tetrahedron. The frequency analysis of the optimized $[H_4BO_4]^{1-}$ molecule predicts a frequency of 796 cm^{-1} for the symmetric stretching mode (Fig. 4), which supports the assignment

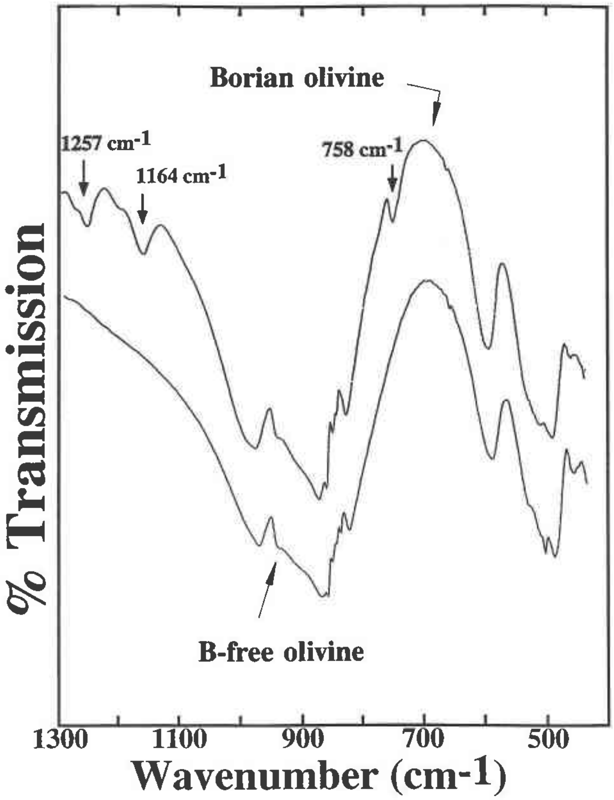

Fig. 3. Infrared transmission spectra, in the principal Si,B-O stretching regions, of borian olivine from Tayozhnoye, Russia, and B-free olivine (Fo_{91}) from Kilbourne Hole, New Mexico.

of the 758-cm^{-1} band in the borian olivine to ν_1. The substitution of B for Si may result in a distortion of the tetrahedral site because either the substitution mechanism involves the formation of terminal B-(OH) or B-F bonds or it results in a perturbation of the B-O-M linkage (where M = octahedral cation) from the polarization of the O atom by H providing the charge balance. The splitting between the 1257- and 1164-cm^{-1} bands in the borian olivine is similar to the observed ν_3 splitting (1100 and 930 cm^{-1}) in sinhalite (Tarte et al., 1985), but the peaks are approximately 200 cm^{-1} higher in frequency than the ν_3 peaks in sinhalite. Splitting of the ν_3 mode is consistent with a distortion of the tetrahedral groups. Trigonal BO_3-group stretching modes, which have frequencies between 1300 and 1500 cm^{-1}, were not observed.

CONCLUSIONS

The TEM and spectroscopic data presented here constitute the first direct confirmation of B = Si substitution coupled with OH = O and F = O substitution, i.e., $B(F,OH)Si_{-1}O_{-1}$, which was originally suggested by Christ (1965) and later proposed by Hinthorne and Ribbe (1974) for chondrodite and by Grew et al. (1991) for B-containing olivine. The $B(F,OH)Si_{-1}O_{-1}$ substitution is distinct from other substitutions involving B = Si, which is either coupled with another substitution, e.g., Al = Si (kornerupine: Grew et al., 1990), or results from B-Si disorder on a single site (synthetic $KBSi_3O_8$: Kimata, 1993). These substitutions involving B = Si are restricted to more polymerized silicates, whereas $B(F,OH)Si_{-1}O_{-1}$ is also possible in orthosilicates, in particular, olivine and humite-group minerals.

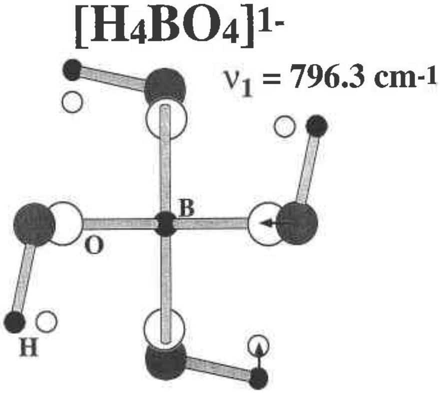

Fig. 4. Fully optimized geometry (3-21G**) of the $[H_4BO_4]^{1-}$ molecule. The solid circles represent equilibrium positions; open circles represent the displaced positions associated with the vibrational mode. The arrows illustrate the direction of displacement associated with the vibrational mode. The frequency of the symmetric stretching mode, ν_1, is calculated to be 796 cm^{-1}.

The $B(F,OH)Si_{-1}O_{-1}$ substitution has implications beyond crystal chemistry. Given the extensive interaction between oceanic crust and sea water, olivine is potentially a carrier of B, F, and H in subducted oceanic lithosphere and may play a key role in recycling these volatile elements back into the mantle. For example, if this substitution were operative in mantle as well as metamorphic olivine, the incorporation of 1–24 ppm B could explain the 1–20 ppm H_2O reported to be characteristic of most mantle olivine (Bell and Rossman, 1992a). Although such B contents exceed the concentrations of 0.3 ppm or less that have been reported for mantle olivine (Seitz, 1973; Steele et al., 1981), these B measurements are too sparse to be definitive or representative. The potential of olivine to incorporate volatiles such as B and F remains virtually unexplored, and any discussion of mantle volatiles must consider the role of olivine and the coupled substitution $B(F,OH)Si_{-1}O_{-1}$.

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