Boron K-edge XANES of borate and borosilicate minerals

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ABSTRACT

Synchrotron radiation B K-edge XANES spectra are reported for 19 borate and borosilicate minerals. The spectra are characterized by three prominent features; a sharp peak (A) at ~194 eV (the edge feature of trigonal B; $^{11}$B), a broader peak (B) at 197–199 eV (the edge feature of tetrahedral B, $^{13}$B), and a broad peak (C) at 200–201 eV for tetrahedral B and 203–204 eV for trigonal B. The area of peak A is very sensitive to content of $^{11}$B and its position yields information on B-O bond length and linkage of the BO$_3$ group. The area of peak B is proportional to content of $^{13}$B but quantification is limited by overlap with peak C. The width of peak B increases with increasing divergence of B-O bond lengths, responding to splitting of $\sigma^*(t_2^*)$ antibonding orbitals. The tetrahedral component of peak C appears to be a $\sigma$-shape resonance. For trigonal B minerals, the relative intensity of peak C and its satellite peaks increases with increase in mean size and/or atomic number of next-nearest-neighbor cations. C being most intense in vonsenite (Fe$^{3+}$Fe$^{2+}$BO$_4$). Pricite (Ca$_2$B$_2$O$_7$·7H$_2$O), of unknown structure, has 80% $^{13}$B, and an isolated BX$_3$ group with $^{13}$B-O = 1.373(5) Å. Comparison of B K-edge XANES spectra collected using total electron yield (sampling depth <60 Å) and fluorescence yield (sampling depth <1100 Å) shows that borates and borosilicates readily reconstruct in surface and near-surface environments. More profound structural damage involving conversion of $^{13}$B to $^{11}$B occurs in minerals with high contents of $^{13}$B, and hydrous Mg borates with interstitial H$_2$O are unstable in the high vacuum of the spectrometer.

INTRODUCTION

As is evident in the recent comprehensive review (Grew and Anovitz 1996), the mineralogy of B is diverse and complex, with 208 naturally occurring compounds. Although B is a trace element, with an abundance in the Earth’s upper continental crust of 15 ppm, it is concentrated by igneous, fluid-rock, and sedimentary fractionation processes to the extent that it forms essential minerals in pegmatites, contact metamorphic and hydrothermal ore (borosilicates) and evaporite (borates and borosilicates) deposits. The crystal chemistry of boron minerals is reasonably well understood (Burns et al. 1995; Hawthorne et al. 1996). Boron is a relatively strongly bonded, complex-forming element in oxy compounds and has an analogous role to Si in mineral structures, forming polymerized BX$_6$ and BX$_4$ (X = O,OH) anion clusters, chains, sheets, frameworks, etc. However, unlike tetrahedrally coordinated Si, trigonally and tetrahedrally coordinated B (hereafter referred to as trigonal and tetrahedral B or $^{11}$B and $^{13}$B, respectively) readily form bonds with hydroxyl groups; e.g., the complexes BO$_3$ (OH)$_2$, BO(OH)$_3$, B(OH)$_4$, BO$_4$, BO$_3$(OH)$_2$, BO$_2$(OH)$_2$, and B(OH)$_4$, all occur in borate compounds (Wells 1984). The weaker B-O bond and more exotic chemistry of B result in a much greater divergence of individual bond distances and angles in trigonal and tetrahedral B-oxygen complexes than in tetrahedral Si-oxygen complexes (cf. Hawthorne et al. 1996). Boron is also an important component in granitic and pegmatitic magmas (e.g., London et al. 1996) and, of course, borosilicate glasses are of considerable commercial and technological interest for their heat and chemical resistance, strength, and light weight (e.g., Pyrex, vycor, and optic fiber glasses).

The known structures of B minerals were determined by conventional X-ray and neutron diffraction procedures, but these methods are not applicable to amorphous materials and difficult to apply to either very fine grained or poorly crystalline minerals (e.g., priceite in this study). Chemical spectroscopic methods have important application in such cases and, more generally, provide complementary information to diffraction methods on chemical state and bonding. Solid state $^{11}$B NMR spectroscopy has been extensively used for information on the structure of alkali borate and borosilicate glasses (e.g., Yun and Bray 1978; Dell et al. 1983; Turner et al. 1986; Prabakar et al. 1990; Gan et al. 1994). The chemical state and sterochemistry of B is also reflected in B K-edge spectra. In early studies, Hallmeier et al. (1981) obtained B K-edge X-ray absorption near-edge structure (XANES) spectra of some borates and B oxides, fluorides, and hydrides using synchrotron radiation (SR), and assigned their features using multiple scattering $\chi\alpha$ calculations of BF$_3$ and isoelectronic CF$_3$ and BF$_4$ systems, and Ishiguro et al. (1982) reported B K-edge XANES of B trihalides and interpreted them with ab initio molecular orbital (MO) calculations. Electron energy-loss near-edge structure (ELNES) spectroscopy yields spectra equivalent to XANES. This technique was extended to the B K-edge by Brydson et al. (1988) and Sauer et al. (1993) and applied to several borate and borosilicate minerals by Sauer et al. (1993), Garvie et al. (1995a, 1995b) and Garvie and Buseck (1996). We have recently reported application of high-resolution SR B K-edge...