X-ray absorption spectroscopy of silicates for in situ, sub-micrometer mineral identification

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ABSTRACT

We present X-ray absorption near-edge structure (XANES) spectroscopy of 11 silicate and aluminosilicate minerals and two glasses at the SiK and SiL_{2,3}, and OK edges. The similar nearest-neighbor environments lead to similar spectral lineshapes at each edge, but the fine-structure differences allow individual and groups of structurally similar minerals to be distinguished. By combining spectra and their first energy derivative from three absorption edges, we show that every mineral studied is distinguishable with XANES. This background work, combined with X-ray PhotoElectron Emission spectroMicroscopy (X-PEEM), allows non-destructive in situ, sub-micrometer (to 35 nm) X-ray analysis of materials, including silicate inclusions, which has not been possible previously. Images and spectra from a 7 µm x 3.5 µm quartz inclusion in zircon are presented as a test of this novel technique in geology.

INTRODUCTION

The rock-forming silicate minerals exhibit a rich diversity of crystal structure, obtained through patterns of Si-O linking (pure SiO_2 alone exhibits eight polymorphs and many more glassy phases) and cation incorporation, such as Al, Fe, and the alkali metals. Electron diffraction, X-ray diffraction, and electron microprobe analysis are firmly established as robust methods of silicate mineral identification, but the latter two techniques do not allow sub-micrometer resolution. Selected-area electron diffraction has higher resolution, but it requires destructive ion milling. X-ray absorption near-edge structure (XANES) is element-specific and is used both as a probe of bonding and as a fingerprint for certain local coordination geometries (Wilke et al. 2001). Here we explore the potential for X-ray absorption spectroscopy to provide an absolute method of silicate mineral identification. XANES can be coupled with high resolution X-ray photoelectron emission spectroMicroscopy (X-PEEM) (Bauer 2001), for spatially resolved chemical analysis of mineral inclusions on the micrometer and submicrometer scale, with optimum resolution of 6 nm (De Stasio et al. 2001). XANES spectroscopy is equivalent to electron energy-loss spectroscopy (EELS) (Garvie and Buseck 1999), but allows analysis of thick samples, is surface sensitive, and non-destructive to polished grains or thin sections.

The sensitivity of XANES to crystal structure is strongly dependent on the nature of the final states of the X-ray absorption process, which may vary at different absorption edges of an element. For example, transition metal L edge absorption is frequently sensitive to atomic charge and nearest-neighbor coordination (Grush et al. 1996; Wang et al. 1997). The sensitivity of X-ray absorption to structural modifications beyond the nearest-neighbor environment has not been fully explored. We have previously shown that L_{2,3} edge X-ray absorption is sensitive to cubic-hexagonal polymorphism in II-VI semiconductors, for which the nearest-neighbor positions are unchanged, and that this modification is not detectable with K-edge absorption (Gilbert et al. 2002). Si occurs within SiO_4 tetrahedra in all the minerals analyzed in this study.

Evidence already exists that XANES spectroscopy of silicates may allow species identification. Using large cluster molecular orbital calculations, other authors have concluded that the unoccupied states are more sensitive than the valence band to the details of SiO_4 tetrahedral linkage in silicates (Tanaka et al. 1995). A recent large study of SiL_{2,3} EELS showed excellent discrimination between and within nesosilicate, inosilicate, and sorosilicate classes (Garvie and Buseck 1999). By contrast, lineshapes within the tectosilicate and phyllosilicate classes were far less distinct. The present study addresses this problem. We use X-ray absorption spectra at the SiK and SiL_{2,3} edges, and the OK edge of selected silicates to observe the relative sensitivity of each absorption edge to different silicate structures. The minerals in this study were selected to distinguish feldspar, quartz, or silicate glass inclusions in zircons (Peck et al. 2001).

EXPERIMENTAL METHODS

Portions of the silicate samples listed in Table 1 have been chemically analyzed and imaged by electron microprobe analysis (Table 2). In separate preparations, pieces were powdered and pressed into soft indium metal. X-ray absorption spectra were acquired in the total electron yield (TEY) mode at the University of Wisconsin Synchrotron Radiation Center, on the HERMON beamline (SiL_{2,3} edge, OK edge, CaL_{2,3} edge; < 0.1 eV resolution), the 6m TGM beamline (SiL_{2,3} edge; 0.1 eV resolution), and the DCM beamline (SiK edge; < 0.5 eV resolution). SiL_{2,3} edge spectra acquired on both 6 m TGM and HERMON beamlines are presented. SiL_{2,3} XANES from quartz taken on the two beamlines were compared to ensure that there are no detectable differences in energy resolution and absolute

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