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Determination of garnet oxidation state using Mössbauer, XANES and the flank method

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Introduction

Fe is the most common element in the Earth that exhibits a variable oxidation state occurring as both Fe^{2+} and Fe^{3+} in minerals and melts. The Fe^{3+}/Fe_{tot} ratio of geological samples can be used as an indicator of the redox conditions or oxygen fugacity (fO_2) at which a mineral formed.

Garnets are a mineral group which may contain both Fe^{2+} and Fe^{3+} . At depths below ~ 60 km where garnet bearing peridotites are stable, the Fe³⁺ component in garnet can be used to determine the fO_2 of the mantle (Gudmundsson and Wood 1995). In conjunction with data from geothermometers (e.g. two pyroxene or olivine-garnet) and geobarometers (e.g. Al in orthopyroxene) this allows the fO_2 of the mantle to be profiled as a function of depth (Woodland and Koch 2003). The fO_2 of the mantle is particularly important as an indicator of diamond (as opposed to carbonate) stability. For depths corresponding to pressures greater than the graphite to diamond transition the mantle fO_2 is, as expected, sufficiently reduced for diamond to be stable. However, post formation metasomatic processes may impose significantly higher fO_2 conditions leading to diamond breakdown or resorption. Such events will usually be recorded by the coexisting garnet as oxidised rims, which also exhibit differences in both major and trace element composition (McCammon et al. 2001). To enhance the use of garnet as a diamond indicator mineral in exploration and to predict the potential diamond grade of kimberlites, it is necessary to determine Fe^{3+}/Fe_{tot} with micron spatial resolution.

Due to the importance of Fe^{3+}/Fe_{tot} as a variable in geological systems significant effort has been devoted to refining methods for its determination. Chemical titrations are common although these involve dissolution and hence destruction of the sample and also lack spatial resolution. Mössbauer spectroscopy is arguably the most accurate method currently available, with a milliprobe technique allowing spectra to be collected from areas as small as $\sim 100 \text{ }\mu\text{m}$. In a recent study a 400 µm aperture was used to determine Fe³⁺/Fe_{tot} of metasomatised garnets, identifying the fO_2 of the rims as being two log units more oxidised than the core (McCammon et al. 2001). However, the spectra take days to acquire, which coupled with the poor spatial resolution, severely limit the ability to analyse large numbers of samples or to distinguish between rims and cores. An alternative technique involves use of the electron microprobe to determine Fe^{3+}/Fe_{tot} from the ratio of the $L\beta/L\alpha$ lines in the fluorescence spectrum (Höfer and Brey 2007). This "flank method" has the potential to provide routine determinations of Fe^{3+}/Fe_{tot} for garnets although careful calibration is required.

A further technique is X-ray Absorption Near Edge Structure (XANES) spectroscopy, undertaken at a synchrotron light source, which is capable of determining Fe^{3+}/Fe_{tot} to \pm 0.02 with sub-micron spatial resolution (Delaney et al. 1998). The method relies on systematic changes in the energy of spectral



features with Fe^{3+}/Fe_{tot} (Berry et al. 2003). Here we report XANES results for both synthetic and natural garnets.

Experimental

Synthetic garnets of the of the almandine-"skiagite" (Fe₃²⁺Al₂Si₃O₁₂-Fe₃²⁺Fe₂³⁺Si₃O₁₂) and andradite-"skiagite" (Ca₃Fe₂³⁺Si₃O₁₂-Fe₃²⁺Fe₂³⁺Si₃O₁₂) solid sultion series have been prepared previously (Woodland and O'Neill 1993, 1995; Woodland and Ross 1994). Fe³⁺/Fe_{tot} was determined by stoichiometry and Mössbauer spectroscopy. The samples form a suite of standards in which Fe³⁺/Fe_{tot} varies from 0 to 1.0. Fe³⁺/Fe_{tot} was also determined by Mössbauer spectroscopy for a number of natural garnets, which can be considered as secondary standards.

Fe K-edge XANES spectra were recorded in fluorescence mode, using a Si (111) channel cut crystal monochromator, at the Australian National Beamline Facility; Beamline 20B (bending magnet) at the 2.5 GeV Photon Factory (KEK, Tsukuba, Japan). Powdered garnet samples mounted on plastic film, prepared for transmission X-ray diffraction experiments, were oriented at 45° to both the excitation beam and detector. An Fe foil reference absorption spectrum was simultaneously acquired using the transmitted beam, allowing the energy of every sample to be individually calibrated by defining the first derivative peak of the Fe foil spectrum to be 7112.0 eV.

Results and Discussion

Fe K-edge XANES spectra of synthetic almandine and andradite are shown in Figure 1. The spectra exhibit an absorption edge and a pre-edge feature corresponding to the 1s \rightarrow 3d transition. The energy of both the edge and pre-edge increases with increasing Fe³⁺/Fe_{tot} (Berry et al. 2003). The pre-edge feature is shown in detail for andradite in Figure 2. It comprises transitions to the crystal field levels of Fe²⁺ and Fe³⁺ in the dodecahedral and octahedral garnet sites respectively. From crystal field theory two transitions are expected for Fe³⁺ in an octahedral site. The pre-edge spectrum was





Fig. 1 Fe K-edge XANES spectra of (a) almandine (Fe₃²⁺Al₂Si₃O₁₂) and (b) andradite (Ca₃Fe₂³⁺Si₃O₁₂). The pre-edge region of andradite, indicated by the box, is shown in more detail in Figure 2.



Fig. 2 Pre-edge region of andradite showing the raw data (symbols), the resultant fit, baseline, and pseudo-Voigt components.

thus fit to two peaks, with both the width and lineshape constrained to be equal. The resulting width of 2.1 eV and lineshape of 23% Lorentzian and 77% Gaussian (pseudo-Voigt) are in excellent agreement with that expected from the resolution of the beamline and the intrinsic width of the electronic transition (2.2 eV and 33% Lorentzian). The background under the pre-edge was fit simultaneously to the tail of a pseudo-Voigt function. For garnets containing both Fe^{2+} and Fe^{3+} it is difficult to theoretically model the multiple contributing components. Indeed, this is unnecessary and the intensity weighted energy, or centroid, of the background subtracted pre-edge can be used for calibrating and quantifying Fe^{3+}/Fe_{tot} (Berry et al. 2003).

The centroid energy of the garnet standards as a function of Fe^{3^+}/Fe_{tot} is shown in Figure 3. The centroids for both the almandine-skiagite and andradite-skiagite series are linearly correlated with Fe^{3^+}/Fe_{tot} . The slopes of the calibration curves for each series are constant although there is a discontinuity or offset near $Fe^{3^+}/Fe_{tot} = 0.3$. This strongly suggests a compositional effect on the centoid energy for a given value of Fe^{3^+}/Fe_{tot} . The natural garnets have similar Fe^{3^+}/Fe_{tot} values of ~ 0.1 but exhibit a range of centroids between the two calibration curves. This range may also reflect the effect of composition.



Fig. 3: Correlation between the XANES preedge centroid energy and Fe^{3+}/Fe_{tot} for standards (closed symbols) and natural garnets (open symbols). For $Fe^{3+}/Fe_{tot} < 0.3$ the standards belong to the almandine-skiagite series, and for $Fe^{3+}/Fe_{tot} > 0.3$ the standards are andradite-skiagite. The solid lines are curves of best fit for the three data sets.

In future work we will further investigate the effect of composition on the pre-edge centroid energy. The electron microprobe flank method has been calibrated using many of the same synthetic garnets as used for these XANES measurements (Höfer and Brey 2007) and compositional or matrix effects are also apparent. In this case, these have been

overcome by developing a self-absorption correction.

XANES analyses only require a polished surface (standard thin section or electron probe mount), can be undertaken in air, have a spatial resolution of ~ 3 μ m, and spectra can be acquired in as little as 10 min. The cubic structure of garnet makes this mineral ideal for the technique since XANES spectra are dependent on orientation for anisotropic materials. If correctly calibrated XANES and the flank method may provide new tools for determining the *f*O₂ of kimberlites.

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