Quantitative mapping of the oxidation state of iron in mantle garnet

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The garnet structure can accommodate both Fe^{2+} and Fe^{3+} and $Fe^{3+}/\Sigma Fe$ of garnets in garnet peridotite can be used to determine the oxygen fugacity (fO_2) of the cratonic lithosphere. This is important as an indicator of diamond (versus carbonate) stability. Post-formation metasomatic processes in the upper mantle, or during transport in kimberlites, may impose high fO_2s that result in diamond breakdown or resorption. Such events will usually be recorded by the coexisting garnet.

$Fe^{3+}/\Sigma Fe$ of garnets has traditionally been determined by Mössbauer spectroscopy of powdered samples. This lacks spatial resolution and the data for each measurement take several days to acquire. X-ray absorption near edge structure (XANES) spectroscopy is now commonly being used to determine $Fe^{3+}/\Sigma Fe$, is capable of micron spatial resolution and spectra can be recorded in ~15 minutes. We have recently reported a new method for quantifying $Fe^{3+}/\Sigma Fe$ from the XANES spectra of mantle garnets with an accuracy and precision comparable to Mössbauer spectroscopy [1].

XANES spectra were recorded in fluorescence mode from garnets prepared as either polished thin sections or electron probe mounts. A calibration curve relating the XANES spectra to $Fe^{3+}/\Sigma Fe$ of mantle garnets previously analysed by Mössbauer spectroscopy allowed garnet unknowns to be quantified. By recording the fluorescence intensity at a small number of energies as a function of position $Fe^{3+}/\Sigma Fe$ maps could be produced. It is possible to quantitatively map the oxidation state of Fe with a spatial resolution and acquisition time comparable to elemental mapping using the electron microprobe. This allows zonation of $Fe^{3+}/\Sigma Fe$ due to metasomatic processes to be identified.

[1] Berry *et al.* (2010) *Chem. Geol.* **278**, 31-37.

Carbonation of Steel Slag I

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Mineral carbonation provides a durable and environmentally inert method of sequestering CO_2 emissions. Larnite (Ca_2SiO_4), a major constituent of steel slag, is highly reactive with aqueous CO_2 [1]. Consequently, carbonation of steel slag offers an opportunity to reduce CO_2 emissions while recycling an industrial by-product. This study investigates the reactions taking place during the dissolution and carbonation of steel slag, and is part of a larger study designed to determine the conditions under which conversion of larnite and other calcium silicates to calcite is optimized.

Experiments were conducted on 2 – 3 mm diameter steel slag grains supplied by Tata Steel RD&T. A H_2O-CO_2 fluid mixture ($XCO_2 = 0.05$) was pumped through a flow-through reactor containing these grains. Temperature ranged from 120°C to 200°C, the pressure was 250 bar and the flow rate was 3.00 mL/min. The duration of experiments varied from 3 to 7 days.

The slag grains reacted to form Ca-carbonate and –phosphate phases upon contact with the CO_2-saturated fluid. These phases subsequently dissolved, forming a porous aluminium and iron oxide framework around the edges of the grains. The compositions of the reacted fluid reflect the observed dissolution of Ca-bearing phases and the buffering of Si by the formation of quartz. These results are in good agreement with predictions from thermodynamic calculations, indicating that the system achieved local equilibrium.

[1] Santos et al. (2009) *Journal of Hazardous Materials* **168**, 1397-1403.