The quantitative determination of oxidation state ratios in minerals and melts

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Introduction: Many elements exist in more than one oxidation state at the oxygen fugacities, temperatures, and pressures of magmatic processes in the Earth and other planetary bodies. Different oxidation states of the same element behave geochemically as if they were different elements. This can result in differences in how an element partitions between co-existing crystals, melts, and fluids, producing enrichments and depletions that provide insight into geological conditions and processes. For example, the redox variability of Ce and Eu relative to the other REE results in anomalous abundances of these elements in the mineral zircon, crystals of which are the oldest known samples of the Earth. These anomalies record the oxygen fugacity of the melt from which the zircon crystallised, providing insight into ancient magmas and the evolution of the Earth.

Modern geochemical analytical techniques routinely determine the concentrations of many trace elements (and their isotopes) with high precision. However, oxidation states are rarely determined due to the limitations of traditional techniques such as redox titrations and Mössbauer spectroscopy. XANES spectroscopy is an ideal alternative that is enabling significant advances. For example, the oxidation state of Fe in mid-ocean ridge basalt, the most common rock on the surface of the Earth, has only recently been determined correctly, by XANES, after decades of previous work.

Methods: The quantification of oxidation state ratios requires the preparation of standards where the oxidation state of the element of interest varies systematically. In the case of melts, usually studied as glasses, samples can be prepared over 16 log units in oxygen fugacity. This is a much larger range than occurs in nature but the approach is to prepare samples for which the oxidation state varies from fully oxidised, through a transitional region, to fully reduced. Fitting data to this large range enables accurate results to be obtained for the range of interest. Melts are equilibrated in mixtures of gases that are used to control the oxygen fugacity. Samples can also be prepared at pressures up to 5 GPa using a piston-cylinder apparatus. Spectra can be recorded for glasses or of melts in situ using a home-built XAS furnace.

Results and Discussion: It is necessary to identify a spectral feature that is associated with a particular oxidation state. In many cases the energy or intensity of this feature can then be fit to a thermodynamic model to quantify the oxidation state ratio without the need for independently characterised standards. Such a "self-calibrating series" can then be used as standards for other studies. The accuracy and precision is usually better than 2% absolute. The oxidation state ratios in a melt are not always preserved on quenching to a glass due to redox exchange reactions. In this case, XANES spectroscopy is ideally suited to *in situ* experiments at the temperatures and pressures of geological processes. Results will be presented for Cr, Fe, Eu, and U.

Conclusions: Silicate melts or glasses containing a redox variable element can be prepared with almost any desired oxidation state ratio. XANES spectroscopy can be used to quantify the oxidation states and calibrate reference materials. Oxidation state ratios in melts and glasses record the oxygen fugacity at the time of melting and may be calibrated as oxybarometers.