

X-ray fluorescence microprobes using microfocusing mirrors

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High-energy synchrotrons are valuable sources of highly collimated, intense x-ray radiation for use in x-ray microprobe analysis including trace element quantification (x-ray fluorescence), chemical speciation determinations (x-ray absorption fine structure spectroscopy), mapping of internal element microdistributions (fluorescence microtomography) and phase identification (x-ray diffraction). Kirkpatrick-Baez mirrors (are being increasingly utilized for production of x-ray microbeams because of their achromaticity, photon density gains in excess of 10^4 , and long working distances (centimeters) (Eng et al. 1998). Spatial resolution near 1 micrometer is achievable with sub-100 ppb sensitivity. Major advantages of using x-rays for geochemical studies of trace elements include (1) applicability to virtually all elements with theoretically predictable sensitivities, and (2) capability for analyses of hydrated specimens (no vacuum chamber required). Two such instruments reside at the GeoSoilEnviroCARS sector at the Advanced Photon Source (Argonne, IL, USA) and at the National Synchrotron Light Source (Upton, NY, USA) (Sutton et al. 2003). These instruments are utilized primarily for research on problems in earth science related topics.

Applications are driven by the requirement for determination of the compositions, structures, oxidation states, and bonding characteristics of chemical species in materials with trace element sensitivity and micrometer spatial resolution. Example studies include: (1) Cu speciation in hydrothermal fluid inclusions (Mavrogenes et al. 2002); (2) arsenic sequestration by iron hydroxide plaques on plant roots (Blute et al. 2004); (3) redox studies of vanadium in basaltic glasses (Sutton et al. 2005); (4) trace element compositions of micrometeorites captured in aerogel (Flynn et al. 2001); and (5) halogens in micro-evaporites from the Nakhla meteorite (Sutton et al. 2002).

References

- Blute, N., et al., (2004), *Environ. Sci. & Technol.* 38, 6074-7.
Eng, P., et al., (1998), *SPIE* 3449, 145.
Flynn, G. J., et al., (2001), *Lunar Planet. Sci.* XXXII, 1398.
Mavrogenes, J.A., et al., (2002), *Am. Min.* 87, 1360-1364.
Sutton, S. R., et al., (2003), *RiMG* 49, 429-483.
Sutton, S.R., et al., (2002), *Lunar Planet. Sci.* XXXIII, 1278.
Sutton, S. R., et al. (2005) *GCA*, in press.

A XANES study of sulfur speciation in synthetic glasses and melt inclusions

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Natural basaltic glasses and melt inclusions may contain sulfur in a number of different forms including sulfate (S^{6+}), sulfide (S^{2-}), and intermediate (S^{4+}) species [1]. In order to determine the oxidation state and speciation of sulfur in silicate glasses, sulfur K-edge XANES spectra were recorded for a wide range of experimental samples. XANES experiments were performed at the European Synchrotron Radiation Facility (ESRF, France), using the X-ray microscopy beamline, ID21.

Glasses ranging from typical MORB-type basalts to Ca-(Na, Mg) rich compositions were synthesized under reducing conditions ($\log fO_2$ -8.79 to -10.92; $\log fS_2$ -1.91) at 1200-1400°C and 1 bar. The XANES spectra of all glasses show a main peak at 2476.3 eV (S^{2-}), while those of the Fe-bearing glasses also contain a shoulder on the absorption edge (2471.7 eV) and differ in their structure after the edge. High-pressure experiments saturated with FeS display a low energy peak at 2470.5 eV, indicating a contribution from sulfide microglobules. For glasses synthesized under oxidizing conditions ($\log fO_2$ -0.49 to -0.30; $\log fS_2$ -0.18 to -0.31; $\log fSO_2$ -1.47 to -2.06) at 1200-1400°C and 1 bar, all spectra are essentially identical despite large variations in composition. Sulfite (S^{4+}) species may co-exist with sulfate (S^{6+}) in Fe-free glasses under some conditions.

S^{2-} and S^{6+} were not found to coexist in the experimental glasses. The spectra of these samples differ significantly from those of melt inclusions in which the main peak occurs at 2476.5 eV (S^{2-}), in addition to the S^{6+} peak at 2482.2 eV, and an unassigned peak at 2469.4 eV. The presence of both S^{2-} and S^{6+} may reflect intermediate redox conditions, although this is unlikely given the very narrow fO_2 range over which the two oxidation states are expected to coexist. An alternative explanation is post-entrapment oxidation, which is supported by experiments on melt inclusions heated as a function of time.

Reference

- [1] Metrich N., Bonnin-Mosbah M., Susini J., Menez B. and Galois L. (2002), *Geophys. Res. Lett.* 29, 11.