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Testing X-ray and electron beam damage effects in apatite S-XANES

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Sulphur µ-XANES in apatite inclusions hosted by zircons from sanukitoids offers a reliable alternative to explore the redox-state evolution of the early Earth's upper mantle and its interactions with surface reservoirs. Pre-screening apatite S concentration via EPMA optimise Synchrotron time, but electron beam damage poses risks to S-speciation analyses. We have investigated apatite standards to assess the effect of X-ray beam and electron beam on S concentration and µ-XANES.

The effect of X-ray beam was evaluated by measuring XANES spectra in unfocussed (beam size = 200 × 200 µm, low dose) and in focused mode (beam size = 280V × 310H nm, high dose). Unfocussed beam caused no damages, while focused beam induced a progressive decrease of sulphate peak (S^{6+}) and the formation of sulphites (S^{4+}). Different beam attenuators were tested in order to define safe conditions for µ-XANES. The attenuated micro-X-ray beam was used to map regions exposed to EPMA. EPMA-exposed areas revealed minimal impact on sulphur and phosphorus concentrations. Conversely, the effect on sulphur speciation is important, even at low beam currents. Oxidised apatite crystals show a photo-reduction effect via the complexation of S, marked by a broad peak from 2.475 to 2.48keV, but do not appear to generate S^{2-}. Although reduced apatite standards are unavailable, a previously identified reduced apatite inclusion showed increased sulphate contribution in EPMA-exposed regions. These effects are interpreted as evidence for beam damage-induced redox change and the creation of S species that can significantly alter the primary S-XANES spectra. Moreover, as a result of a much larger beam size (and consequently interaction volume) in EPMA (~10 µm) compared to µ-XANES (<0.5 µm), finding hot-spots or high S pixels in apatite inclusions via µ-XRF maps remains a necessary approach, even after measuring their S concentration.

Understanding and mitigating these effects is crucial for obtaining accurate and reliable information from S-XANES experiments. However, the best approach so far remains to analyse a subset of apatite inclusions via EPMA so that an approximate concentration of the inclusions population is known and then perform µ-XANES analysis on representative apatite inclusions unaffected by prior electron beam damage.