

An inversion-based self-calibration for SIMS measurements: Application to H, F, and Cl in apatite

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ABSTRACT

Measurements of volatile abundances in igneous apatites can provide information regarding the abundances and evolution of volatiles in magmas, with applications to terrestrial volcanism and planetary evolution. But measurement of volatiles in apatite (especially H) is challenging, and the most commonly utilized method—the electron probe—is often inadequate in precision and accuracy. Secondary ion mass spectrometry (SIMS) measurements can produce accurate and precise measurements of H and other volatiles in many materials including apatite. SIMS standardization generally makes use of empirical linear transfer functions that relate measured ion ratios (i.e., of an element of interest normalized to a reference element) to independently known concentrations or abundance ratios. However, this approach is often limited by the lack of compositionally diverse, well-characterized, homogeneous standards.

In general, SIMS calibrations are developed for minor and trace elements, and any two calibrations are treated as independent of one another. However, in crystalline materials, additional stoichiometric constraints may apply. In the case of apatite, the sum of concentrations of abundant volatile elements (H, Cl, and F) must closely approach 100% occupancy of their collective structural site (recognizing the possibility of trace substitutions or vacancies and other elemental species). Here we propose and document the efficacy of a method for standardizing SIMS analyses of abundant volatiles in apatites that takes advantage of this stoichiometric constraint. The principle advantage of this method is that it requires no independently known homogeneous reference standards, and under specific conditions it is effectively self-standardizing.

We define a system of independent linear equations relating measured ion ratios (OH^-/P^- , Cl^-/P^- , F^-/P^-) and unknown calibration slopes (i.e., the empirical transfer functions described above). Given sufficient range in the concentrations of the different elements among apatites measured in a single analytical session, solving this system of equations allows for the calibration slope for each element to be determined without standards, using only blank-corrected ion ratios. In the case that a data set of this kind lacks sufficient range in measured compositions of one or more of the relevant ion ratios, one can employ measurements of additional apatites of a variety of compositions to increase the statistical range and make the inversion more accurate and precise. These additional non-standard apatites need only be wide-ranging in composition. They need not be homogeneous nor have known H, F, or Cl concentrations.

Tests utilizing synthetic data and data generated in the laboratory indicate that this method should yield satisfactory results for a wide range of compositions provided apatites have “halogen” sites dominated by OH, F, and Cl. The inversion method is able to reproduce conventional calibration curves to within <2.5%, a level of accuracy comparable to—or even better than—the uncertainty of the conventional calibration, and one that includes both error in the inversion method as well as any true error in the independently determined values of the standards. Uncertainties in the inversion calibrations range from 0.1–1.7% (2σ), typically an order of magnitude smaller than the uncertainties in conventional calibrations (~4–5% for H_2O , 1–19% for F and Cl). However, potential systematic errors stem from the model assumption of 100% occupancy of this site by the measured elements. To a first order, each percent of deviation from 100% occupancy of this site by the measured elements results in a systematic error of 1% (relative) in all species. Carbonate-rich apatites appear to violate the assumptions of the model, and should not be used for calibration purposes—though their volatile contents can be accurately and precisely determined by an independent inversion calibration that omits the high-C data. Use of this method simplifies analysis of H, F, and Cl in apatites by SIMS, and may also be amenable to other stoichiometrically limited substitution groups, including $\text{P}+\text{As}+\text{S}+\text{Si}$ in low-C apatite, and $\text{Zr}+\text{Hf}+\text{U}+\text{Th}$ in non-metamict zircon.

Keywords: Apatite, SIMS, volatiles, inverse problems, calibration, uncertainties, trace elements, analytical methods