

## **Analysis of hydrogen and fluorine in pyroxenes: I. Orthopyroxene**

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### **ABSTRACT**

Pyroxenes have the capacity to incorporate both hydrogen and fluorine in their structures, and accurate measurement of these volatile elements can be used to constrain geophysical and petrologic processes in planetary bodies. For example, pyroxenes may be used to constrain the volatile contents of melts from which they crystallized. However, the experimental determination of H and F in pyroxenes is difficult, particularly at the relatively low levels present in natural samples. Here we evaluate methods for determining both H and F in orthopyroxene.

We measured trace concentrations of H (~40–400 ppm H<sub>2</sub>O) and F (<1–17 ppm) in a suite of nine orthopyroxenes from varying geological environments, using secondary ion mass spectrometry (SIMS). The SIMS data for H (measured as <sup>16</sup>O<sup>1</sup>H, referenced to <sup>30</sup>Si and <sup>18</sup>O) are cross calibrated against Fourier transform infrared (FTIR) spectra, in turn calibrated against either manometry (Bell et al. 1995) or the frequency-dependent molar absorption coefficient derived by Libowitzky and Rossman (1997). Despite the fact that our samples exhibit a wide range of IR band structures, with varying percentages of absorbance split among low (2600–3350 cm<sup>-1</sup>) and high (3350–3700 cm<sup>-1</sup>) wavenumber bands, the SIMS data are fit with the same precision and virtually the same regression slope regardless of which IR calibration is used. We also confirm previous suggestions that the matrix effect for SIMS analyses between orthopyroxene and olivine is small (≤20%). Anomalously high yields of <sup>16</sup>O<sup>1</sup>H in some analyses can be attributed to the presence of amphibole lamellae, and these analyses must be filtered out with different criteria than for olivine due to differences in the geometrical relationship of host to inclusion. For F, our derived values are highly dependent on analytical uncertainties related to the use of silicate glasses as standards. Regardless of the accuracy of our calibration, we see systematic differences in F concentrations in orthopyroxenes and olivines depending on their geological context. Samples derived from crustal environments and from Colorado Plateau minette diatremes have very low F (≤3 ppm), while higher contents can be found in megacrysts from South African kimberlites (up to 17 ppm in orthopyroxene and 47 ppm in olivine) and in xenocrysts from the Rio Grande Rift (Kilbourne Hole, 7–9 ppm in orthopyroxene).

**Keywords:** FTIR, SIMS, mantle, calibration, nominally anhydrous minerals