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Analysis of hydrogen and fluorine in pyroxenes: II. Clinopyroxene

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ABSTRACT

Studies of coexisting, nominally anhydrous minerals in mantle samples show that clinopyroxene is an especially important host for hydrogen. Recent experimental studies have also shown that clinopyroxene may contain significant amounts of fluorine, which has implications for the F budget of the mantle. More accurate quantification of H and F is therefore a desirable goal.

We measured H in 13 natural clinopyroxenes using Fourier transform infrared (FTIR) spectroscopy. $^{16}O^{1}H/^{30}Si$ and $^{19}F/^{30}Si$ were also measured in the samples using secondary ion mass spectrometry (SIMS). H data were compared between the two techniques and F was calculated with reference to F-bearing silicate glass standards. Four of the clinopyroxenes are used as standards for SIMS calibration in multiple laboratories, and three have been measured previously using hydrogen manometry and/or elastic recoil detection analysis. Compared to clinopyroxenes in previous surveys comparing FTIR and SIMS, the 13 samples cover a broader range in chemistry and band positions in the O-H vibrational spectrum. They also all lack detectable amphibole lamellae, which are otherwise commonly present in this mineral group. In contrast to orthopyroxene, the SIMS and FTIR data for clinopyroxene show significantly better correlations ($r^2 = 0.96$–0.98) when the frequency-dependent IR calibration of Libowitzky and Rossman (1997) is applied, as opposed to the Bell et al. (1995) calibration ($r^2 =$ 0.92–93). We derive a frequency-dependent molar absorption coefficient with parameters different from those of Libowitzky and Rossman's calibration, which was established using data on stoichiometric hydrous phases and gives poor agreement with the manometrically determined value for PMR-53. Comparison of data for PMR-53 to our SIMS calibrations for orthopyroxene and olivine suggests that the matrix effect among these phases is less than 20% relative. Fluorine concentrations vary depending on geological context, with the highest concentrations (up to 214 ppm) found in diopsides from crustal metamorphic environments. Mantle samples follow similar geographic trends as olivines and orthopyroxenes, with higher F in xenocrysts from Kilbourne Hole (46 ppm) and South African kimberlites (up to 29 ppm) compared to the Colorado Plateau (8 ppm). On the basis of chemical correlations, we propose two different incorporation mechanisms for F: (1) coupled subsititution with Al^{3+} and/or Fe^{3+} in tetrahedral sites; and (2) coupled substitution with monovalent cations (Na and K) in the M2 site. The second substitution is more relevant to mantle augites than crustal diopsides. Our measured F concentrations are much lower than those in some clinopyroxenes synthesized in recent high *P*-*T* studies. Nevertheless, our data support suggestions that the F budget of the mantle can be entirely accommodated by incorporation in nominally anhydrous/fluorine-free minerals.

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