Variability of hydrogen defects in mantle orthopyroxene along a back-arc transect in Southern Patagonia

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In mantle xenoliths, the inter and intra-mineral distribution and speciation of H may record ambient mantle H budgets or interaction with the host magma. We measured H concentrations in orthopyroxenes from mantle xenoliths from eight different localities along a back-arc transect in Southern Patagonia, using Fourier transform infrared spectroscopy (FTIR). In these samples, we distinguish two different types of spectra, based on the relative absorbance of the 3590 cm⁻¹ peak in comparison to the 3570 cm⁻¹ peak: 1) Abs₃₅₉₀/Abs₃₅₇₀ > 1, 2) Abs₃₅₉₀/Abs₃₅₇₀ < 1. All groups have absorbance bands at 3515 cm⁻¹ and 3410 cm⁻¹, and sometimes, at 3310 cm⁻¹ and 3085 cm⁻¹. The results show variability between the different localities, within the same xenolith suites from a single locality, and also within the same xenolith sample, and the same crystal. The position of the different bands represents characteristic defects in which hydrogen is incorporated. Therefore, we used mineral major and trace elements contents to calculate thermodynamic parameters and indicators of metasomatism to investigate potential systematics related to the characteristic bands of the FTIR spectra. The combination of experimental peak attribution to defects and crystal scale observations suggests that a large concentration of R³⁺ (generic trivalent) cation defects relative to Si-vacancies due to intrinsic characteristics or external parameters could explain most of the differences in the FTIR spectra. At a larger scale, no clear correlation was observed between metasomatic indicators (Ti, Na, Th, Li, (La/Sm)ₐ), temperature or fO₂, but a correlation between the concentration of R³⁺, mostly Al³⁺, and the different types of spectra was observed, suggesting that a higher concentration of R³⁺ favors specific R³⁺-related absorption bands. The highly variable inter and intra-crystal H concentrations and H defects and lack of correlation with metasomatic indicators indicates rapid timescales of H modification prior to magma entrainment, with a dominant control from orthopyroxene solid solution composition. Our data indicates that combining crystal composition, total mineral H content and defect-specific H content are key to understanding the processes modifying mantle H concentrations.