

Oxidation of arc magmas by hydrogen incorporation in mantle orthopyroxene

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The high water contents and oxygen fugacities of magmas formed at subduction zones are fundamental characteristics which have shaped the petrology and chemistry of Earth's continents. The mechanism through which the oxidised signature is acquired, and how it relates to the elevated water contents, remains unclear. Here, we apply Fourier transform infrared spectroscopy to orthopyroxene from a suite of arc mantle peridotite xenoliths to trace the spatial and temporal modification of mantle wedge fO_2 during interaction with primary arc melts.

Samples span a range of textures and equilibration conditions, from cold, reduced, protogranular peridotites representative of the ambient mantle, to hot, oxidised peridotites reflecting modification of the ambient mantle by melt-rock reaction. Total orthopyroxene H contents correlate positively with calculated fO_2 and peridotite texture, with samples showing textural evidence for melt-rock reaction yielding the highest H and fO_2 . This increase in H content is accommodated entirely by a subset of "redox-sensitive" point defects, identified following deconvolution of the infrared spectra. High resolution mapping of individual orthopyroxene crystals reveals an increase in redox-sensitive hydrous point defects towards the rims, whereas H stored in redox-insensitive point defects decreases in concentration towards the rims. Single orthopyroxene crystals thus uniquely preserve cryptic modification of both mantle H and fO_2 , capturing the transition from reduced ambient mantle, to oxidised reacted mantle.

Our data provide new evidence that primary melts are already oxidised in the uppermost mantle wedge, and that their oxidised nature facilitates the transfer of H from melt to ambient mantle minerals. A consequence of this observation is that H can be efficiently fractionated from O in hydrous melts. This mechanism would result in progressive melt oxidation during migration away from the source of melting and continuous reaction with the surrounding peridotite. Such a process would help to reconcile discrepant geochemical evidence for the origin of oxidised arc magmas.