

The redox state of convergent margin magmas and peridotites

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Thirty-five years ago, the view prevailed that the upper mantle sources of basalts is homogenous lherzolite with a constant oxidation state, close to the values defined by the synthetic fayalite-magnetite-quartz (FMQ) oxygen buffer. Trace element and isotopic geochemistry has demonstrated in the intervening years that the mantle is heterogeneous geochemically consequent to melt extraction, lithosphere recycling via subduction zones, and variable extents of subsequent whole-mantle mixing and exchange. Subduction of supracrustal materials for example raises the possibility that the mantle could be, at least locally, oxidised. Measured $\text{Fe}^{3+}/\text{Fe}^{2+}$ of island arc compared with mid-ocean ridge basalts in combination with much higher S abundances in the former than the latter have been interpreted to reflect more oxidised sources of convergent ($\text{FMQ} + 1$ to $2 \log_{10}$ units $f\text{O}_2$) versus divergent magmas. Sulfur for example is much more soluble in basalt as sulfate at these oxidised conditions than the sulfide prevailing at FMQ. Oxidised mantle sources in the asthenospheric wedge overlying subducted lithosphere seem to be confirmed by thermobarometric calculations of redox conditions reflected in wedge-derived olivine-orthopyroxene-spinel (peridotite-harzburgite) assemblages. The similarity of V/Sc ratios of arc and ridge basalts on the other hand has been interpreted to reflect a mantle source redox constancy independent of tectonic environment, given the relative incompatibility during peridotite partial melting of higher valence states of V compared with V^{3+} and redox-invariant Sc^{3+} . However, an assumption of compositional similarity of mantle sources is likely incorrect; the ensemble of island arc wedge sources is more depleted (i.e., lower V/Sc) than those tapped beneath ridges because of the fluxing potency of slab-derived fluids. A coincidence of V/Sc ratios reflects a combination of lower V/Sc in relatively refractory arc sources allied to increased incompatibility of V during partial melting of these sources due to the influx of an oxidised slab-derived component. The nature of this component and its redox characteristics are currently a matter of debate. While H_2O alone seems inadequate, the possibility that low-Fe, sulfate-rich, slab-derived fluids interacting through redox-exchange with mantle wedge peridotite could be the oxidising agent has acquired considerable observational support over the past few years. A corollary is that the redox state of convergent margin magmas has undergone secular change with consequences for base and precious metal occurrences.