

Sulphur speciation and the oxidation state of the mantle wedge

Klimm, Kevin¹ Kohn, Simon C.² Botcharnikov, Roman³

¹Institut für Geowissenschaften, Universität Frankfurt, Germany ²Department of Earth Sciences, University of Bristol, UK ³Institut für Mineralogie, Universität Hannover, Germany

Recycling oceanic crust in subduction zones via fluids or melts through the overlying mantle and to the volcanoes on top of the lithosphere involves successive oxidation. The mantle wedge, which is the source region of all arc magmas, is known to be more oxidised relative to normal mantle or oceanic crust by one to two orders of magnitude (Brandon & Draper, 1996). The oxidation of the mantle wedge was previously attributed to an interaction with water released from the subducting slab, but a simple water addition does not provide the full oxidation mechanism, because water can only oxidise rocks if hydrogen is released as a reaction product. Other possible volatile agents, presumably affecting redox conditions, should be considered. For instance, the flux of sulphur from subducted slab can be responsible for the oxidation of the mantle wedge, because the speciation and solubility of S in magmas largely depend on its oxidation state.

We have performed well constrained high-pressure and high-temperature experiments on iron-free melts with controlled oxygen fugacities (fO_2) and measured the oxidation state of S in the quenched glasses using X-ray absorption near edge structure (XANES). Glass compositions include soda-lime-glass, $K_2Si_4O_9$, albite and a trondhjemite-glass representing a residual liquid during partial melting of subducted oceanic crust. Experiments were performed in CSPV and IHPV at 850 and 1000°C, 200 MPa and at fO_2 's ranging from QFM-2.5 to QFM+4.

The $S^{6+}/\Sigma S$ ratio in the glass is a function of fO_2 . At $fO_2 > QFM+1.5$ sulphur is dissolved as S^{6+} . At $fO_2 < QFM-1.5$ sulphur is dissolved as S^{2-} . In between sulphur is dissolved as a mixture of S^{6+} and S^{2-} . The relatively steep change of S^{6+}/S^{2-} ratio with fO_2 is therefore at two orders of magnitude lower fO_2 than previously reported for Fe-bearing systems (QFM+1; Jugo et al., 2005). Thus, for a fixed fO_2 at ~QFM sulphur is dissolved as mostly S^{2-} in Fe-bearing systems and as S^{6+} in Fe-free systems. We propose that Fe-poor slab liquids carry sulphate opposed to sulphide into the mantle wedge. Interaction with the iron-rich wedge will cause reduction to sulphide. The oxygen released during this reduction causes an increase of the prevailing ferrous to ferric ratio ($Fe^{3+}/\Sigma Fe$) and subsequently fO_2 in the mantle wedge. This mechanism is quite efficient because only 1000 to 3000 ppm of sulphur are required to increase the fO_2 by two log units. In addition these amounts of sulphur match the sulphur content of primitive melt inclusions in rocks from arc volcanoes.

References

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