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Sulfate in the mantle wedge: The oxidising agent in subduction zones.

K. Klimm (1), A. Bénard (2), S.C. Kohn (3), R.E. Botcharnikov (4), D.I. Ionov (2), and P.Y. Plechov (5)

(1) Goethe-Universität Frankfurt, Germany (klimm@em.uni-frankfurt.de), (2) Université Jean Monnet, Saint Etienne, France, (3) University of Bristol, UK, (4) Leibniz Universität Hannover, Germany, (5) Moscow State University, Russia

In subduction zones the fO_2 increases from the subducted slab to lavas erupted at the Earth's surface from reducing (log fO_2 = QFM-1) to oxidising conditions (log fO_2 = QFM+3). This increase of fO_2 is generally manifested and determined by an increase of Fe^{3+}/Fe^{2+} of mantle wedge derived xenoliths [1] or arc lavas [2]. The mantle wedge, which is the source region of all arc magmas where slab derived liquids trigger melting of mantle rocks, is more oxidised compared to normal mantle and the fO_2 range from log fO_2= QFM to QFM+2. This fO_2 is also in the range where the S speciation in silicate melts change from only S^{2-} present at QFM<0 to only S^{6+} present at QFM>2, according to the S speciation data on basaltic melts [3]. The increase of fO_2 is commonly explained by ingress of water released from the subducted slab [1]. However, a simple water addition does not provide a full oxidation mechanism as hydrogen is released as a reaction product, which is a highly reducing agent. In addition large quantities of water are required to increase both, Fe^{3+}/Fe^{2+} and S^{6+}/S^{2-}.

Here we present evidence from Raman and XANES measurements on synthetic and natural glasses that sulfate may be present in the mantle wedge and a redox exchange reaction between S and Fe during melt generation may cause the observed increase of Fe^{3+}/Fe^{2+} and therefore fO_2 within the mantle wedge.

The systematic correlation of features in Raman and XANES spectra of experimentally equilibrated sulfur-bearing, hydrous silicate glasses allows the identification of at least four different S-species in the glasses depending on fO_2 and Fe/S of the system. In Fe-free melts S is dissolved as SH^-, H_2S and/or SO_4^{2-} depending on the prevailing fO_2. Adding Fe results in the formation of Fe-S-complexes at the expense of SH^- and H_2S, which are still observed up to Fe/S $\sim$ 2.6. The S^{6+}/S^{2-} equilibrium in Fe-free/poor systems is at $\sim$1.5 log units lower fO_2 than observed for Fe-rich basalts [3]. Thus, for a fixed fO_2 at QFM sulfur 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 sulfate opposed to sulfide into the mantle wedge. The validity of this assumption is further confirmed by the presence of S^{6+} as anhydrite in melt inclusions determined by Raman measurements on mantle xenoliths from the Avacha volcano, Kamchatka, Russia. Interaction with the iron-rich wedge will cause reduction to sulfide. 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 via the reaction H_2SO_4 + 9FeO = FeS+ $4Fe_2O_3$ + H_2O. This mechanism is quite efficient because only 1000 to 3000 ppm of sulfur are required to increase the fO_2 of a basalt melt by two log units.

[1] Parkinson & Arculus (1999) *Chem Geol* 160, 409-423

[2] Carroll & Rutherford (1985) *Am Mineral* 73, 845-849.

[3] Jugo et al. (2010) *GCA* 74, 5926-5938.