Oxidation of the mantle wedge by H^+ in aqueous fluids: a new interdisciplinary approach

KAYLA IACOVINO[1], MEGHAN GUILD[2], CHRISTY B. TILL[2]

[1]Jacobs, NASA Johnson Space Center, 2101 E NASA Pkwy, Houston, TX 77058 kayla.iacovino@nasa.gov
[2]School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-6004

The observation that arc magmas are the most oxidized on Earth have led petrologists to question whether the subduction process might cause oxidation of the sub-arc mantle source. A strong correlation between the input of slab-derived aqueous fluid and $Fe^{3+}/\Sigma Fe$ in arc magmas [1] has led to the hypothesis that slab fluids may facilitiate the transfer of redox potential from oxidized slab material to mantle wedge and subsequently to primary arc melts. Despite this intuitive link, identifying an efficient and ubiquitous chemical process to transfer oxidation state in slab fluids has been challenging. Pure H_2O alone is an inefficient oxidizer in the mantle, necessitating another oxidant within the fluid. Commonly invoked components include S or C, which are likely heterogeneously distributed within subducting slabs, and direct transfer of Fe^{3+}, which is only possible in very solute-rich fluids.

Here we present a new mechanism to explain the oxidation of the sub-arc mantle by slab-derived aqueous fluid, wherein dissolved $H^+(aq)$ is reduced to $H_2(aq)$. Redox equilibrium is satisfied by electron transfer from $Fe^{2+}(s)$, which is oxidized in the rock to $Fe^{3+}(s)$ in the reaction: $2Fe^{2+}(s) + 2H^+(aq) = 2Fe^{3+}(s) + H_2(aq)$. This simple reaction was previously overlooked due to the assumption that all H must be bound by H_2O molecules (i.e., no dissolved H), applicable to a pure H_2O fluid, but not one with a solute load as addressed here. The application of thermodynamic modeling tools from aqueous geochemistry (DEW, EQ3/6) to mantle petrology predicts this reaction between mantle rock and slab fluid with our own experimentally constrained chemistry and fO_2 (QFM+2) [2]. Mass transfer model results show an increase in $Fe^{3+}/\Sigma Fe$ in mantle rock from MORB-like (0.15) to arc-like (0.2–0.3) values at reasonable fluid fluxes, co-incident with increasing H_2 activity in the fluid. This can explain the stark correlation between slab fluid input into the mantle wedge and the observed fO_2 of arc magmas. Moreover, it does not require diffusion of hydrogen out of the system. Instead, H_2 remains dissolved in fluid in equilibrium with oxidized mantle rock.

[1] Kelley and Cottrell (2009) *Science*
[2] Iacovino and Till (2017) *Goldschmidt*