fO_2 and *p*H during subduction zone metasomatism: Challenges and opportunities

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Deep aqueous fluids play a key role on the long term Earth differentiation. Carbon-iron redox coupling at lithological interfaces from the shallow to deep subduction zones, *e.g.* manifest in the reduction of carbonates to graphitic C in blueschist oceanic units from Alpine Corsica (*1*), challenged long held views about the role of redox and fluids on C transfers at depth. However, the role of charge distribution, *i.e.* *p*H, on metasomatism has not been fully considered in these studies. We show that this can now be accomplished by merging conventional phase-equilibrium modeling with non-electrolyte molecular fluids, and electrostatic modeling of dissolved electrolytes to 3 GPa and 900 °C (*2*). This approach is applied to constrain activity ratios and composition of aqueous solutes, fO_2 and *p*H of a fluid at equilibrium with a model pelite lithology. Disparities between solubility predictions and independent experimental solubility measurements acquired on pelitic systems point to the importance of alkali-Al-Si polymers in controlling pelitic fluid compositions. We find that *p*H is within *c.a.* 1-2 log units above neutrality, indicative of alkaline conditions, over the investigated *P* and *T* (0.5 – 3 GPa, 400-900 °C) and in the absence of anions such as halogens. C-saturated COH fluids (X_O=1/3) exhibit *p*H lower than C-free fluids by ~1 *p*H units, in part due to the presence of additional C bearing ligands. Their nature and abundance as a function of solvent properties and phase assemblages along selected geotherms will be discussed. The causes and implications of *p*H fluctuations on the interpretation of metasomatic patterns in field and experimental systems will be discussed, with special reference to the fate of volatiles at depth.

[1] M. E. Galvez et al.. Contributions to Mineralogy and Petrology **166**, 1687-1708 (2013) [2] M. E. Galvez, C. E. Manning, J. A. D. Connolly, D. Rumble. Earth and Planetary Science Letters, (revision)