

From natural UHP Fluid Inclusions to Thermodynamic-modelled speciation of subduction fluids

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Subduction fluids are a key component of long-term chemical cycles (i.e., H, C, S, N Cycles) and their reliable characterization is of primary importance to understand the processes related to mantle wedge metasomatism, oxidation and melting (e.g., Plank & Manning, 2019). H, C and S - due to their abundance - and C and S - due to their range of valence states - hold a great potential impact on the mantle wedge redox state. Both direct (fluid inclusion -FI- studies) and indirect (thermodynamic modelling, TM) approaches to study these fluids have reliability issues due to the complexity of the investigated processes. The chemical fingerprint of UHP FI can be easily modified by post-entrapment processes (Frezzotti & Ferrando, 2015), while TM of solute-bearing fluids at UHP conditions is in its infancy (Connolly & Galvez, 2018).

In this work, we apply and compare the data obtained by both these approaches on UHP FI trapped within peak diopside from a chemically simple marble (CMFS-COHS system), that experienced multiple carbonated dissolution-reprecipitation events (Ferrando et al., 2017), from the UHP Brossasco-Isasca Unit (BIU) of the Dora-Maira Massif (Western Alps). Classical molecular-fluid TM allowed to model post-entrapment reactions between FI and host diopside. Electrolytic-fluid TM allowed to model the chemical composition of the peak solute-bearing COHS aqueous fluid generated by progressive rock dissolution and dehydration reactions. The comparison between the modelled composition with that reconstructed by FI study allows to recognize the type and the extent of post-trapping chemical re-equilibrations occurred within UHP FI and to obtain the real composition of subduction fluid circulating in carbonate system at UHP conditions.

Building from these results, forward TM along the prograde UHP BIU PT-path (up to 4.3 GPa and 730°C), as a function of fO_2 , allowed to model the composition, speciation, and redox state of subduction fluids in the fO_2 range of $-2 < \log \Delta FMQ < +2$. The modelled fluid geochemistry allows to evaluate whether the redox potential, the transport mechanism and the solubility of C and S - as a function of P, T, and fO_2 - in H₂O-dominated subduction fluids, are coupled or not and the C and S potential redox impact on the mantle wedge.

Connolly, J. A., and Galvez, M. E. (2018) - Electrolytic fluid speciation by Gibbs energy minimization and implications for subduction zone mass transfer. *Earth Planet Sc Lett*, 501, 90-102.

Ferrando, S., Groppo, C., Frezzotti, M. L., Castelli, D., and Proyer, A. (2017) - Dissolving dolomite in a stable UHP mineral assemblage: Evidence from Cal-Dol marbles of the Dora-Maira Massif (Italian Western Alps). *Am Mineral*, 102(1), 42-60.

Frezzotti, M. L., and Ferrando, S. (2015) - The chemical behaviour of fluids released during deep subduction based on fluid inclusions. *Am Mineral*, 100(2-3), 352-377.

Plank, T., and Manning, C. E. (2019) - Subducting carbon. *Nature*, 574(7778), 343-352.