

C and S speciation in HP-UHP fluids as obtained by electrolytic-fluid thermodynamic modelling of a UHP marble as a function of P-T- fO_2

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Element speciation in subduction fluids controls the transport efficiency of elements from the down-going slab to the overlying mantle wedge. Elemental speciation is controlled by P-T- fO_2 and bulk-rock composition (i.e., rock-buffered). Elements like C and S are characterised by a wide range of possible valance states, making them crucial in regulating the redox state of the arc mantle and the associated volcanism (e.g., Evans, 2012). However, dominant carbonate sediments (representing ~70% of the total subducted carbon, with up to 20% vol of organic C; Clift, 2017) are only marginally considered in the modelled subduction processes, mostly because of the lack of relevant decarbonation reactions at HP-UHP conditions. Similarly, because S is considered to be primarily subducted at UHP conditions as sulphides or sulphates within the altered oceanic crust (e.g., Walters et al., 2020), the S input from dominant carbonate sediments has been rarely considered.

To address the role of dominant carbonate sediments on the C and S long term cycles, we conducted electrolytic-fluid thermodynamic modelling of the fluid phase in equilibrium with a UHP impure marble (simple CFMS-COHS chemical system) from the Dora-Maira Massif (Western Alps). This marble experienced multiple carbonated dissolution-precipitation events during active subduction at HP-UHP conditions (Ferrando et al., 2017). The study of this natural sample allows linking the thermodynamically modelled HP-UHP evolution, of both rock and fluid, to the HP-UHP mineral assemblages and related fluid inclusions (Maffei et al., 2021). Using the bulk composition of the studied marble, we modelled the chemical evolution of the fluid along the prograde P-T path (from ~490°C-1.5 GPa to ~730°C-4.3 GPa) and at different fO_2 conditions (between +2 and -2 from the FMQ buffer). At changing P-T- fO_2 conditions, C and S speciation and concentration in the fluid are different. At oxidized conditions, C and S are predominantly speciated as HCO_3^- and SO_4^{2-} , respectively. At reduced conditions, C is additionally speciated as carboxylic acids and hydrocarbons, while S is speciated as H_2S and HS^- . The dissolution of carbonate dominated sediments is an effective process for the mobilisation of both C and S, with C being more easily released at reduced conditions and S at oxidised conditions instead. Thus, dissolution is a more effective process than decarbonation and desulphurisation reactions in releasing C and S during subduction at sub-arc depths.

References:

- Clift, P. D. 2017. A revised budget for Cenozoic sedimentary carbon subduction. *Reviews of Geophysics*, **55**(1), 97-125.
- Evans, K. A. 2012. The redox budget of subduction zones. *Earth-Science Reviews*, **113**(1-2), 11-32.
- Ferrando, S., Groppo, C., Frezzotti, M. L., Castelli, D., & Proyer, A. 2017. Dissolving dolomite in a stable UHP mineral assemblage: Evidence from Cal-Dol marbles of the Dora-Maira Massif (Italian Western Alps). *American Mineralogist*, **102**(1), 42-60.
- Maffei, A., Ferrando, S., Connolly, J. A., Groppo, C., Frezzotti, M. L., & Castelli, D. 2021. Thermodynamic analysis of HP-UHP fluid inclusions: The solute load and chemistry of metamorphic fluids. *Geochimica et Cosmochimica Acta*, **315**, 207-229.
- Walters, J. B., Cruz-Urbe, A. M., & Marschall, H. R. 2020. Sulfur loss from subducted altered oceanic crust and implications for mantle oxidation. *Geochemical Perspectives Letters*, **13**, 36-41.