P-T-fO_2 C and S speciation in subduction zone fluids as obtained by electrolytic-fluid thermodynamic modelling of impure carbonate system

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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 PTfO_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. However, dominant carbonate sediments (representing ~70% of the total subducted carbon; 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 from the Dora-Maira Massif (Western Alps). This marble experienced multiple carbonated dissolution-precipitation events during active subduction at HP-UHP conditions. 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 (Maffeis *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 of at different fO_2 (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 reduced conditions, C is additionally speciated as carboxylic compounds and hydrocarbons, while S is speciated as H_2S and HS^-. At oxidized conditions, C and S are speciated as HCO_3^- and SO_4^{2-}, respectively. 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.

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