Fluid-mediated element cycling recorded by orogenic Atg-serpentinite and Chl-harzburgite from Almirez, Spain

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Serpentinites are central to water (re)cycling in subduction zones and thus effect fluid-mediated element transfer between the exosphere and the deep Earth. Diverse and often controversial models exist on the relevance of various source contributions to the budget of fluid mobile elements of hydrous peridotites and how these evolve during the subduction cycle. This work offers novel constraints on ongoing debates. We present a comprehensive bulk rock and silicate mineral major to trace element study covering the antigorite dehydration reaction recorded at Cerro del Almirez, Spain, including the systematics of As, Sb, B, W, Li, In, Tl, Bi, Cd, and Sn (Vieira Duarte *et al.*, 2021; Pettke & Bretscher, 2022).

Pre-hydration magmatic processes produce strong compositional variations on centimetre to metre to kilometre scales. Serpentinisation via seawater and sediment-equilibrated pore fluids produces highly variable fluid-mobile element (FME) bulk rock enrichments in B, As, Sb, W, Cs, ±Li, ±Bi, ±Pb, ±U exceeding primitive mantle concentrations. We introduce the concept of hydration enrichment numbers (HEN) to quantify such hydration-mediated FME enrichment. Highest HEN are observed for Sb and As (up to 650) and lowest for Ba and Rb (down to 0.06) for Almirez data, quantifying fractions of minimal enrichment (values >1) and minimal prograde subduction loss (values <1). Antigorite dehydration produces Chl-harzburgite rocks that still preserve an FME signal representative of original hydration element enrichment. Prominent fractions of As, Sb, B, Rb, Sr, Cs, Ba, Pb, Zn, Cl, Br, Li, Na, K, and Ca are lost to the fluid upon serpentinite dehydration including the antigorite-out reaction, as also suggested by LA-ICP-MS measurements of fluid inclusion relics in olivine of Chl-harzburgite. We find no evidence in support of significant fluid-mediated element addition (e.g., Th, U, Ta, Sr, Pb, Cs, Rb, Li) upon antigorite dehydration as has been postulated in literature by simple comparison between Atg-serpentinite and Chl-harzburgite coexisting at Almirez. Variable extents of magmatic refertilisation prior to serpentinisation can account for the differences in HFSE between individual Atg-serpentinite and Chl-harzburgite samples.

Oxide and sulphides minerals are not relevant sinks for FME on bulk rock scale. Magnetite shows variable enrichments in Cr, Ni, V, Mg, Mn, and Ti, and pentlandite displays strongly variable enrichments in Co, As, Se, Sb, Tl, Pb, and represents the sink for the light PGE. Antigorite is recognized as the main sink for B, As, Sb, Bi, ±W.

We conclude that oceanic serpentinisation dominates the FME imprint of subducting slab serpentinites and that progressive subduction goes along with successive FME loss. We propose that serpentinites from fluid-dominated, highly hybridised and oxidised plate interface melange materials displaying spectacular FME enrichments with a sedimentary flavour are overrepresented in the published sample record. Thus, the combined data set of hydrous peridotites from Almirez may offer a more representative compositional estimate of the bulk mass of subducted serpentinite.

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