Subducted serpentinites are the boron reservoirs for arc magmatism

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Serpentinites are key players in volatile and fluid-mobile element cycles in subduction zones. Their dehydration represents the main event for fluid and element flux from slabs to mantle, though no direct proof of this fact yet exists. For this purpose, B isotopes are known markers of fluid-assisted element transfer during subduction. Until recently, the altered oceanic crust has been considered the main ¹¹B reservoir for arc magmas, which largely display positive $\delta^{11}B$. However, slab dehydration below fore-arcs transfers ¹¹B to the overlying hydrated mantle and leaves the residual mafic crust very depleted in ¹¹B below sub-arcs. The ¹¹B-rich composition of serpentinites candidate them as the heavy B carriers for subduction. Here we present high positive $\delta^{11}B$ of Alpine high-pressure (HP) serpentinites recording subduction metamorphism: we show a connection among serpentinite dehydration, release of ¹¹B-rich fluids and arc magmatism. In general, the δ^{11} B of these rocks is heavy (16% to + 24%) δ^{11} B). ⁸⁷Sr/⁸⁶Sr ranges from 0.7044 to 0.7065, i.e. lower than oceanic serpentinites formed from seawater. Our data suggest two implications. 1st, the analyzed HP serpentintes are ¹¹B reservoirs for subduction. They maintain high ¹¹B down to a first fluid release event, thus the $\delta^{11}B$ of olivine-veins, that fingerprint the composition of released fluids, justify the positive values observed in many arc lavas. Fluids released by dehydration of such HP serpentinites by full antigorite breakdown should have up to + 20% $\delta^{11}B$. The comparable ¹¹B fingerprint of serpentintes, their fluids and arc lavas provides a strong link between serpentinite subduction and arc magmatism. 2nd, the combination of δD , $\delta^{11}B$, ${}^{87}Sr/{}^{86}Sr$ of the HP serpentinite apparently favour their location above the subducting slab. This implies that serpentinites were formed by low-T fluids likely arising from a subducting lower plate.

A new Br isotope analytical protocol: Constraints on the global Br cycle

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Bromine possesses a chemistry broadly comparable to that of Cl and F, however its heavier mass and lower abundance results in slightly different behaviours in the geochemical cycling. Hence it is disproportionately enriched in sea water with respect to Cl, and unlike F possesses isotopes which may be fractionated by geological processes. These isotopes are ⁷⁹Br (50.686%) and ⁸¹Br (49.314%).

Br can be considered to be a 'hydrophile' element, and hence its behaviour is in many ways analogous to that of water. Therefore environmental (low temperature) aqueous processes, particularly transpiration, weathering and evaporation are likely to produce fractionations in δ^{81} Br of the order of ~3.5‰ [1]. These signatures may be inherited by hydrous fluids derived from subducted slabs in regions where extensive hydrothermal alteration and/or carbonate deposits are present in the downgoing slab.

This study has developed new chemical extraction, and most significantly, new mass spectrometric protocols for Br isotopes on silicates and waters using N-TIMS methodologies. Existing CF-IRMS methodologies offer internal precision of ~0.3% (1SD, [1]), whereas N-TIMS measurements of laboratory HBr and seawater standards produce external reproducibility of <0.07% (1SD) over a 6 month period with internal precision typically <0.06% (1SD) on single analyses.

Southern Hemisphere Pacific Ocean Water (SHPOW) records ${}^{81}\text{Br}/{}^{79}\text{Br}$ significantly lower (0.9627) than the IUPAC canonical ratio (0.9729; a difference of ~10‰).

Protocols for mitigation of PO_3^- polybaric interferences on $^{79}Br^-$ will also be presented, as will $\delta^{81}Br$ data for depleted Island Arcs Tholeiites.

[1] Shouaker-Stash et al. (2005) Anal. Chem 77, 4027–4033.

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