Experimental constraints on HFSE partitioning and Ti mobility in saline fluids

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High field strength elements are important geochemical indicators in many geological settings, and in particular in subduction zones. The HFSE signature of arc magmas is depleted relative to MORB, and there is much debate about the cause of this. Interaction between crustal and mantle rocks, and fluids liberated during metamorphism are critical for the transport of elements within the Earth, and the generation of diverse geochemical signatures, such as those at subduction zones. A fundamental premise of many mass-flux calculations in fluid transport is that Ti is essentially immobile in metamorphic fluids. Indeed, previous experimental data supports this 'constant Ti' frame of reference, demonstrating quite low rutile (TiO_2) solubility in aqueous fluids. However, we have performed novel experiments in saline fluids, which indicate that F (and Cl) greatly enhances the solubility of rutile, and hence increases the mobility of Ti. We will show that this has implications for the mobility of the other HFSE, which are strongly sequestered into Ti-phases such as rutile [1,2]. The experimental run products have been analysed using isotope dilution ICP-MS techniques [3,4] to estimate rutile/fluid partition coefficients which may be used to determine the relative mobility of HFSE in some potential metamorphic fluids. These new partition coefficients may aid us in unravelling the processes behind the observed HFSE depletion in subduction zone magmas, and may help to address the high field strength element budget of the Earth's crust and mantle.

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Secular trends in $\delta^{11}B$ and prospects for determining the direction of paleo-pCO_2 change

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The B isotopic composition of seawater is significantly heavier than average river input, which is the primary flux to the oceans. In fact today, a time of low pCO_2, the $\delta^{11}B$ of seawater is near a high end-member of measured isotopic values at 39.6 per mil. The 30 per mil offset between river water and seawater is controlled by sorption of $B(OH)_4^-$, which is at least 17 per mil lighter than $B(OH)_3$ and dominates B output flux out of the ocean. The speciation of B is controlled by pH, which has a quantifiable relationship to pCO_2, such that at lower pH less $B(OH)_4^-$ is available. Therefore, times of low pH and high pCO_2 should be times of significantly lighter seawater $\delta^{11}B$. Geologic intervals of high pCO_2 that approach the residence time of B, estimated to be between 8-20 Ma, should lead to $\delta^{11}B$ that approaches the river input value. Thus, we predict that to first order the secular variability in $\delta^{11}B$ through the Phanerozoic will give the direction of change in pCO_2. This hypothesis is supported by currently published $\delta^{11}B$ values of brachiopods, which report low values during greenhouse times and high values during icehouse times. Secular variability in B isotopes has been suggested to be the main problem for using the boron pH proxy for deep time. Our working hypothesis suggests that while it is true that obtaining absolute pH/ pCO_2 values may not be possible, we can obtain a high-resolution record of the change in direction. The use of B isotopes, especially when coupled with other indicators of ocean and atmosphere change, has tremendous potential for improved temporal resolution of climate change and its relationship to the processes that drive these changes.