

## The chemistry of seawater-like fluids reacted with gabbro at conditions below and above the critical point of seawater

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Hydrothermal systems in water depths >3000 m can run at extreme pressure (p) and temperature (T) conditions above the critical point of seawater ( $CP_{SW} \sim 298$  bar and  $407^\circ\text{C}$  [1]), if enough heat from magma injections is provided. Exactly this type of submarine hydrothermalism has recently been discovered [2]: a high-pressure system in 3000 m water depth at  $5^\circ\text{S}$  on the Mid Atlantic Ridge (MAR) emanating extremely hot fluids ( $>400^\circ\text{C}$ ), which contain high to very high concentrations of transition metals (e.g., Cu, Fe) and exhibit an unique rare earth element (REE) chemistry with LREE and HREE depletion and no Eu-anomaly ('special REE-signature') [3]. Current hypotheses explain the chemical composition of the high p-T MAR  $5^\circ\text{S}$  fluids by either re-dissolution of anhydrite previously formed in the sub-seafloor, or deriving from a 'reaction zone fluid' leaching the oceanic crust at p-T conditions above the critical point of seawater [2, 3].

There is a large deficiency in experiments studying the REE distribution in fluids reacting with original rocks from the oceanic crust, e.g. MOR basalt and gabbro, in particular at p-T-conditions typical for deep water slow-spreading ridges. We experimentally investigated the effect of major mineral gabbro composition on the fluid chemistry using cold seal pressure vessels (CSPV) at 400 bar and at 375 and  $425^\circ\text{C}$  – conditions below and above  $CP_{SW}$ . Mixtures of plagioclase (plag) and clinopyroxene (cpx) grains sized 125-500  $\mu\text{m}$  reacted in gold capsules with 3.2 wt.%  $\text{NaCl}_{(aq)}$  fluid (similar to seawater salinity) containing in addition  $\sim 4$  ppm Ca and  $\sim 14$  ppm Mg at a fluid/rock ratio of  $\sim 10$  and at a run duration of 3, 10 and 30 d. The reacted fluids were extracted after quenching, and analysed by ICP-OES and ICP-MS. Significant chemical changes in the reacted fluid composition were observed for the major elements Mg, Na, and K varying systematically with starting mineral composition, run duration, and temperature. Only in cpx bearing systems Mg fluid concentration decreased, and Ca increased with both T and run duration. This suggests fluid-solid Mg-Ca exchange reactions during cpx alteration. Fluids reacting with plag are depleted in K, being independent on T or run duration and pointing towards K-Na exchange reactions. In all reacted fluids the concentrations of Rb, Sr, and Ba increased with decreasing Mg content resulting from cpx alteration. The concentration of REE- and transition metals were mainly below or close to the detection limit in fluids containing Cl but no sulfate.

First water-rock interaction experiments below and above  $CP_{SW}$  using natural sulfate bearing seawater (containing  $\sim 900$  ppm S) indicate that sulfur enforces gabbro alteration and enhances the REE and transition metal concentrations of reacted fluids accompanied by the formation of a 'special REE- fluid signature'. However, because of possible precipitation of REE- and transition metal bearing phases during/after quenching [4] more data are needed by *in situ* sampling of fluid phases, e.g. single phase fluid as well as coexisting liquid and vapor- or brine and vapor phases. Those experiments are in preparation by using a large volume hydrothermal reactor (PARR®) equipped with a flexible Au reaction cell system and two individual sampling tubes allowing *in situ* sampling of both, single or two phase fluids below or above  $CP_{SW}$ .

### References:

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