

## **The Influence of Phase Separation on the Ca isotope Composition and Fluxes in Hydrothermal Systems**

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Calcium (Ca) is a key element for the understanding of the chemical history of the ocean and for the global climate on long geological time scales. This is because Ca is interacting with the carbon cycle and is a major constituent of the continental weathering. Beside the continental runoff the mid-ocean ridges are quantitatively important concerning marine Ca concentration and isotope budget. Variations of the hydrothermal circulation of seawater through oceanic crust have been recognized to play a significant role for the oceanic Calcium (Ca) mass and isotope ( $\delta^{44}/^{40}\text{Ca}$ ) balance. Hydrothermal activity leads to a chemical alteration of the circulating seawater during water-rock interaction, the formation of Ca-bearing minerals, and during phase separation. Within the framework of the subproject 'CARLA' in the 'Special Priority Program SPP1144' Ca isotope ratios ( $\delta^{44}/^{40}\text{Ca}$ ) in hydrothermal fluids sampled from the Logatchev hydrothermal field (15°N/45°W) have been investigated in detail. It could be demonstrated that the Ca isotope composition of the fluid endmember undergoes fractionation effects during the precipitation of anhydrite at high temperatures of up to 300 °C. The Logatchev hydrothermal field provides hydrothermal circulation without evidence for phase separation of the circulating seawater. However, with regard to the detected Ca isotope fractionation at high temperatures, the Ca isotopic compositions of phase separated hydrothermal fluids have still to be considered. This is if Ca isotopes become fractionated during phase separation, the global oceanic Ca isotope budget must be reconsidered. Phase separation leads to the formation of a low-salinity vapor and a high-salinity brine phase. The latter is enriched in metal cations that are mostly chloro-complexed. Experimental studies and theoretical models have shown that in aqueous NaCl solutions Ca occurs mainly as stable chloro-complexed species at sub- and supercritical conditions. Latter variation of complexation may influence the complex-sensitive Ca isotope composition of the vapor and the brine phase.