

## Cold-seep carbonates as marine isotope geochemical archives: New insights comparing chronology and emplacement controlling processes of circum-Pacific settings

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Authigenic carbonates of cold-seep areas are potential high-resolution recorder of changes in vent activity and fluid composition through time. Crucial tools for the identification and the understanding of driving processes, mechanisms and sources of marine methane emanation are the investigation of age constrains of paleoactivity phases and the determination of related isotope geochemical signatures. Cold-seep carbonates are especially relevant for the reconstruction of marine methane emanation and the estimation of their contribution to the marine and global carbon cycle.

This study compares the U-Th geochronology in order to identify distinct precipitation stages and related isotope signatures of 3 different settings around the Pacific throughout the last 200 ka; covering the range from mature accretionary systems at Hydrate Ridge (Cascadia Margin, off Oregon) and the Hikurangi Margin (off New Zealand) to the mound dominated erosive subduction system of Central America (Costa Rica, Nicaragua).

The data set from Hydrate Ridge, based on profiles through large m-scale block samples of cruise So165, provides detailed insight into the multi-stage origin of precipitates of a focused fluid venting system. The data strongly indicate close relation of increasing venting with decreasing sea-level, coupled by major shifts of the hydrostatic balance between pore water buoyancy and water column height. TV-Grab samples (cruises M54 & So173) and exceptional drill-cores (BGS-Rockdrill-I, cruise M66) of mound and scarp structures from the central America subduction system point to significant tectonic controls on vent position and activation. The age systematic still implies influences of major sea-level changes on flux intensity and downward prograding precipitation inside mound structures.

Exceptional new TV-Grab samples from the Hikurangi margin (cruise So191) will be presented accompanied by actual results of on-going isotope geochemical investigation.

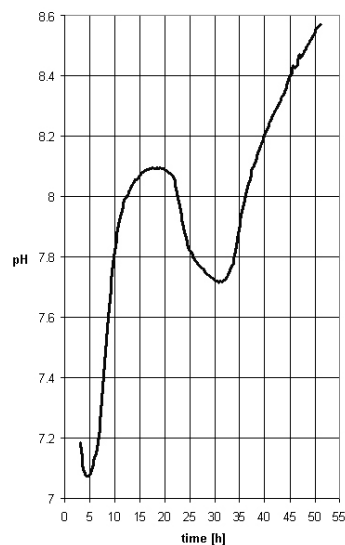
## Influence of metal cations on iron oxide formation

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Little information is available on the time-resolved formation of iron oxides and the influences of foreign metal cations during their formation. In this study, we examined the oxidation-hydrolysis reaction of FeSO<sub>4</sub> in the presence of Cu, Zn and Cd at nominal concentrations of 3.33-10 mol %. The pH was buffered with 1 M NaHCO<sub>3</sub> (HCO<sub>3</sub>:Fe = 2.5) near neutral pH. The ensuing suspensions were stirred at 350 rpm at open atmosphere and 25±0.5 °C. The pH, Fe<sup>2+</sup>, Fe<sub>total</sub>, Me<sub>total</sub> and S<sub>total</sub> were measured for 48 h. XRD patterns and DRIFT spectra were collected to determine which solid phases were dominating the suspensions. The reaction proceeds through distinct pH-periods (Fig. 1 with 10 mol % Zn under conditions described above).



**Figure 1:** pH vs time.

Green rust and siderite are the initial reaction products. Green rust dissolved over a 20 h period during which siderite became increasingly crystalline. Zinc partitions into solid phases within 2 h and cannot be measured in solution thereafter. The first crystalline goethite particles were recorded after 12 h. The pH reduction from 8.1 to 7.7 after 20 hours occurred due to the oxidation/hydrolysis of Fe<sup>2+</sup>/Fe<sup>3+</sup> dissolving from residual siderite and the concurrent production of H<sup>+</sup>. During the formation of goethite, the HCO<sub>3</sub><sup>-</sup> equilibrium shifts towards CO<sub>3</sub><sup>2-</sup> (pH = 9.2 after 100 h), because H<sup>+</sup> are required to balance negative charge on the colloids. Additional data concerning metal concentrations in the solid phases over time, final metal concentrations and the congruency of metal substitution in goethite will be presented for single, bi and a tri-metal system.