



Cold seep carbonates: Geochemical archives of marine methane emanation and gas-hydrate destabilization

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Cold seep ecosystems are often characterized by microbial mediated carbonate precipitation processes, due to interaction between methane-rich fluid and biological activity. Carbonates from these ecosystems provide unique archives of focussed marine methane emanation by their geochemical, geobiological, mineralogical and structural inventory. Beside geological setting and tectonic activity as general driving forces, oceanographic parameter like water temperature and sea-level changes are potential controls on episodic fluid flow. In this case study large carbonate blocks from Hydrate Ridge (Cascadia Margin, Oregon) were investigated in order to decipher the geochemical archive of methane-related massive carbonate build-ups, supplied by a long lasting and focused venting system. Applied methods are MIC-ICP-MS (multi ion counting - inductively coupled - mass spectrometry) for U-Th age data and Laser Ablation (LA)-ICP-MS for high spatial resolution element ratios and concentration data.

The precipitation of the investigated chemoherm carbonates is assumed to be due to the consumption of methane and sulfate by sulfate reducing and methane oxidizing bacteria. As a side product the released hydrogen carbonate forms calcium carbonate together with Ca predominantly out of the water column. Ages and growth rates of these carbonates are considered to be related to the methane supply and therefore as a tracer for changes in venting intensity and methane flux. Geochemical and isotopic signatures of these often laminated carbonates are regarded as tool for the reconstruction of changes in fluid composition and precipitation conditions.

An ex-situ drill core through a block from the upper part of a steep wall of the SE-

Knoll chemoherm (hydrate Ridge) provided a detailed view into a time interval of increased fluid flux from 65 to 55 ky. It is characterized by three distinct phases of venting activity. The lowermost unit is carbonate dominated and shows structural indicator for high fluid dynamics (65 - 60 ky). A fossil-rich sediment layer above could be dated on 59 ky (gastropode shells of the cold seep related species *Provannidae*, implying decreased venting intensity) and 55 ky are determined for the uppermost unit (partially massive to fine laminated carbonate, pointing to increased methane supply). In contrast, ex-situ drill cores through a block from the sediment surface at the NW-base of the SE-Knoll, sampled vertical carbonate veins in a consolidated Mg-carbonate-rich sediment matrix. The vein carbonate seems to be grown fine-laminated into open cavities which are interpreted as remnants of fluid pathways. The U-Th ages of these veins cluster around 140 ky close to the sediment. According to age data of the internal cavity surface the last precipitation occurred around 42 ky ago. In distinct zones ages of about 55 ky were determined pointing to the same phase of venting activity previously recognized.

The age data reflect an episodic reactivation of a fluid pathway over a time interval of at least 100 ky. The coincidence of massive carbonate build-up and glacial climatic intervals point to the possibility that the formation of the chemoherm carbonates and, hence, the activity of the cold seep vent sites are directly related to the height of sea level via the pressure difference between the height of the seawater column and the hydraulic head and buoyancy of the upward advecting fluids in the plumbing system of the sediments. The actual data set implies for the investigated glacials fluid advection rates in the order about 40 cm/a and up to more than 150 cm/a, respectively.

Applying high-resolution LA-ICP-MS, a set of 40 elements was quantified by single spot (0.08 mm) analysis with special emphasis on the correlation of element distribution pattern and ratios of U, Mg, Sr, Ba and Mo between and inside distinct growth bands of mm scale. First results document an anti-correlation of U when compared to the other four elements mentioned above. Furthermore, the U concentration varies on a sub-mm scale by up to a factor of four, what may result from frequent changes in the fluid / seawater mixing, fluid composition and redox conditions.

Sr and Ba profiles identify high-frequency changes between high and low fluid flow precipitation phases. First results imply a breakthrough of deep seated fluids from below the bottom simulating reflector (BSR) between 55 and 42 ky after a phase of extensive gas hydrate destabilization. A detailed interpretation of the high resolution element pattern is part of current research. In addition, a close accordance of high spatial resolution concentration and bulk solution ID (isotope dilution) data for U is determined and underlines the suitability of the applied method combination (LA-ICP-MS and MIC-ICP-MS).