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Deciphering the archive of methane-related venting activity and chemical changes in authigenic carbonates of a cold seep environment

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Large carbonate blocks from the SE-Knoll (Hydrate Ridge, Cascadia) were investigated in order to decipher the geochemical archive of a methane-related massive carbonate build-up, supplied by a long lasting 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. Geochemical and isotopic signatures of these often laminated carbonates are regarded as tool for the reconstruction of changes in fluid composition and precipitation conditions.

The first block (hr-sek1) from the upper part of the steep wall of the SE-Knoll is characterized by three distinct units, reflecting the succession of different phases of venting activity at least on local scale. In detail we have determined U-Th ages of 65 - 60 ky in the lowermost unit (carbonate dominated, with structural indicator for high

fluid dynamics), 59 ky for a fossil-rich sediment layer above (gastropode shells of the cold seep related species Provannidae, implying decreased venting intensity) and 55 ky for the uppermost unit (partially massive to fine laminated carbonate, pointing to increased methane supply).

The second block (hr-sek2-1), sampled from the sediment surface at the NW-base of the SE-Knoll, contains vertical carbonate veins in a consolidated 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 already recognized in sample hr-sek1.

The age data set implies an episodic reactivation of a fluid pathway over a time interval of at least 100 ky. In general the age distribution points to a close correlation with periods of sea level low stands, known from palaeoceanographic reconstructions.

Applying high-resolution LA-ICP-MS, a set of 40 elements was quantified by single spot (80μm) 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. 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).