Experimental study of carbonate aqueous solutions at high pressure and high temperature

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The behaviour of carbonate solutions and the solubility of carbonate minerals in aqueous fluids are of major importance for modelling transfers of matter in subduction zones. We have carried out diamond-anvil cell experiments for in-situ monitoring of carbonate solutions at elevated pressures and temperatures using Raman spectroscopy and synchrotron x-ray micro-fluorescence.

Vibrational properties of carbonate ions in aqueous fluids at high pressures and temperatures

Raman spectra of aqueous carbonate ions have been recorded up to 30 GPa and 400°C in liquid water, ice VI and ice VII. Pressure induced shifts of vibrational frequencies of the carbonate symmetric stretching mode were found significantly larger in liquid water than in ice VII and in crystalline carbonates. Quantitative anharmonic parameters have been derived for these ions in solution

Solubility of strontianite ($SrCO_3$) in aqueous fluids at high pressures and temperatures

In-situ x-ray fluorescence spectra were obtained on aqueous solutions, close to strontianite crystals (i.e. within 100 micrometers), loaded in an externally heated diamond anvil cell (beamline ID 22, ESRF). Using a high-resolution monochromatic beam of 3x8 µm and 18 keV, respectively, allowed avoiding x-ray pollution emanating from the adjacent crystal and optimising the sensitivity for Sr. Collection geometry at 20° from the transmitted beam resulted in quantitative analyzis of the strontium-bearing solution down to 0.001 mol/l. A strong increase in solubility of strontianite in water was recorded between 1 bar and 2 GPa. At 1.8 GPa and 100°C, solubility was found to be 0.2M, that is two orders of magnitude higher than at 1 bar, 25°C. The specific effect of increasing carbonate solubility with increasing pressure persisted up to the highest pressures and temperatures investigated (3.5GPa, 250°C). Preliminary kinetic data of the dissolution reactions showed equilibration times of the order of 1 hour within the diamond cell sample volume at 1 GPa and 100°C.

Geochemical evidence for enhanced productivity and paleoclimate reconstruction during S1 sapropel deposition in the Mediterranean

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The enhanced Ba concentration in sapropel layers suggests that their deposition may be derived from increased productivity. The use of this proxy assumes that the Ba in the sapropel layer is associated with marine barite (non-diagenetic and non-detrital) that precipitates in the water column. The characteristics of the barite separated from the S1 layer in the eastern Mediterranean confirmed that marine barite is indeed responsible for the excess of Ba, which supports the suggestion that S1 deposition resulted from enhanced productivity. Detrital-element ratios in this sapropel layer, such as Zr/Al, imply that increased precipitation/runoff may be responsible for higher nutrient supply, hence increased productivity. In contrast, in the western-most Mediterranean (Alboran Sea basin, ODP Site 976) sapropel deposition is difficult to detect because organic carbon concentrations are diluted by high terrigenous input. During the S1 sapropel time interval, the Ba content is also not high. Although anoxic diagenesis may have led to poor barite preservation, significant differences in productivity across Mediterranean basins are also suggested by this record. Further east, in the north-western South Balearic basin (37º 15.96‘ N/ 00º 02.99’ W, 2587 m), an excellent sediment interval containing a visible sapropel layer (with an associated Ba enrichment) older than S1 was recovered during the Basacalb cruise (TTR-9). At this site, greater depth, oxic conditions and lower sedimentation rates than in the Alboran Sea basin could have also led to the development of a record of the S1 time interval comparable to that of the eastern Mediterranean. However, increased organic carbon or Ba content during S1 time interval are not evident, and Ba content is not as high as in eastern Mediterranean sapropels or older sapropels recovered at the same site. These differences between the eastern and western basins suggest that mechanisms that resulted in sapropel deposition may have been different in different Mediterranean basins and may have also varied through time.