

## FT-ICR mass spectrometry of carbonate clusters: Magic clusters and pH effects

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The only experimental data on solute clustering for aqueous carbonate systems stem from a recent electrochemical study on CaCO<sub>3</sub> prenucleation-stage clusters, which suggested that nucleation of carbonates proceeds via cluster formation and aggregation [1]. However, there are no mass spectrometric studies that probe carbonate cluster distribution and composition in aqueous solutions as a function of pH or electrolyte concentration. Prompted by these recent experimental accounts of stable prenucleation carbonate clusters, we present results from Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometric experiments pertaining to the stability, distribution and mass composition of a range of different carbonate clusters. We also report theoretical geometries and thermodynamic data of the above carbonate clusters using DFT calculations as well as the G4 and CBS-QB3 multi-step ab initio methods. All carbonate cluster experiments have been conducted on a Bruker 7T FT-ICR mass spectrometer equipped with electrospray ionization (ESI) source and a precision leak-valve system used for solvation studies. Stable carbonate species obtained from electrosprayed solutions (0.05mM/pH=11.20) containing Na<sub>2</sub>CO<sub>3</sub> salts include the pure clusters [Na (Na<sub>2</sub>CO<sub>3</sub>)<sub>n</sub>]<sup>+</sup> ( $n \leq 12$ ), [Na<sub>2</sub> (Na<sub>2</sub>CO<sub>3</sub>)<sub>n</sub>]<sup>+2</sup> ( $n \leq 19$ ), [Na (NaHCO<sub>3</sub>)<sub>n</sub>]<sup>+</sup> ( $n \leq 9$ ) and [Na (NaOH)<sub>n</sub>]<sup>+</sup> ( $n \leq 11$ ) as well as the mixed clusters [Na (NaHCO<sub>3</sub>)(Na<sub>2</sub>CO<sub>3</sub>)<sub>n</sub>]<sup>+</sup> ( $n \leq 8$ ), [Na (NaHCO<sub>3</sub>)<sub>2</sub> (Na<sub>2</sub>CO<sub>3</sub>)<sub>n</sub>]<sup>+</sup> ( $n \leq 6$ ) and [Na (NaOH) (Na<sub>2</sub>CO<sub>3</sub>)<sub>n</sub>]<sup>+</sup> ( $n \leq 10$ ). Moreover, upon acid titration with HFor to 3.50, we were able to observe a strong pH dependence of cluster composition and size distribution, especially in the pH vicinity of bulk carbonate solution pK values, e.g. at pH=10.32. In addition, ion mass spectra exhibit several marked discontinuities or „magic clusters‘ indicative of highly stable carbonate clusters. Solvation energies for the stepwise attachment of water onto individual cluster species will also be presented and compared with results from ab initio calculations.

[1] Gebauer *et al.* (2008) *Science* **322**, 1819.

## OAE2 in marine sections at high Northern palaeolatitudes?

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The mid-Cretaceous world was characterised by unusually warm polar temperatures, extensive sea floor spreading and subsequent periods of major eustatic sea-level rise. At times volcanic outgassing increased the atmospheric pCO<sub>2</sub> and enhanced the terrestrial weathering. Weathering and rising sea level led to increased nutrient discharge and high organic productivity in the oceans. Associated increased decomposition of organic matter promoted the removal of oxygen, leading to anoxic conditions and elevated carbon burial in the sediments, a so called ‘oceanic anoxic event’.

One of the global oceanic anoxic events is the Cenomanian–Turonian boundary event (OAE2). The event is characterised by a major positive δ<sup>13</sup>C excursion (ca. 2–4 ‰) in marine carbonate and both marine and terrestrial organic matter, which indicates that a major disturbance of the global carbon cycle occurred in the ocean and atmosphere system. The OAE2 is thought to be a widespread event and evidence has been found all over the world, mostly at low and mid palaeolatitudes in the proto-Atlantic. However, records of the OAE2 from high palaeolatitudes are still scarce.

The ongoing work will establish the chemostratigraphy in different depositional environments in the Nuussuaq Basin in West Greenland and investigate the palaeoceanography that prevailed during the OAE2 in the basin. Three localities in a proximal–distal transect through the Nuussuaq Basin will be investigated for δ<sup>13</sup>C bulk from organic material and redox sensitive trace metals. These investigations should help to understand, if black shale deposition in the Nuussuaq Basin is linked to the widespread occurring OAE2.