

## Quartz solubility and $\text{CO}_3^{2-}$ - $\text{HCO}_3^-$ equilibrium in $\text{H}_2\text{O}+\text{Na}_2\text{CO}_3$ and $\text{H}_2\text{O}+\text{NaHCO}_3$ fluids at high $P$ and $T$

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Alkali hydrogencarbonate and carbonate in aqueous fluids may play an important role in the mobilization of the REE and other elements at crustal conditions [1] and in subduction zones [2]. Here, the  $\text{CO}_3^{2-}$ - $\text{HCO}_3^-$  equilibrium and the quartz solubility in aqueous 4.65 molal  $\text{NaHCO}_3$  and 1.6 molal  $\text{Na}_2\text{CO}_3$  solutions were studied to 600 °C and 1.53 GPa using a hydrothermal diamond-anvil cell. The recorded spectra were normalized to the temperature dependence of the Stokes-Raman scattering intensity, the frequency and scattering factor, density, and reflection at the diamond-fluid interface [3,4]. The  $\text{HCO}_3^-$ (aq) and  $\text{CO}_3^{2-}$ (aq) concentrations were obtained from the integrated intensities of the Raman bands at  $\sim 1000$  and  $\sim 1060$   $\text{cm}^{-1}$  assuming that the ratio of the relative molar scattering factors  $J_{1000}/J_{1060}=0.1667/0.2434$  [3] is independent of pressure ( $P$ ) and temperature ( $T$ ). In the  $\text{Na}_2\text{CO}_3$  solution, the fraction of the species  $\text{CO}_3^{2-}$ (aq) did not show a significant dependence on pressure, but decreased with temperature from  $\sim 0.77$  at 100 °C to  $\sim 0.69$  at 200 °C to  $\sim 0.41$  at 600 °C. Before equilibration at 600 °C, the  $\text{CO}_3^{2-}$ (aq) fraction at vapor pressure was  $\sim 0.99$  at 100 °C and  $\sim 0.91$  at 200 °C. No  $\text{CO}_2$  or  $\text{CH}_4$  were detected. In the  $\text{NaHCO}_3$  solution, the  $\text{CO}_3^{2-}$ (aq) fraction increased with temperature and decreased with pressure along all studied isotherms from 200 to 600 °C, e.g. at 600 °C from 0.16 at 0.63 GPa to 0.1 at 1.5 GPa. Thus,  $\text{HCO}_3^-$  ions can be stable in lower crustal and upper mantle fluids. The only detectable Raman band from dissolved silica was at  $\sim 770$   $\text{cm}^{-1}$ , which indicates a predominantly monomeric silica speciation. The calibrated integrated intensity of this band was used to determine the  $\text{SiO}_2$ (aq) molality. The quartz solubility in 1.6 molal  $\text{Na}_2\text{CO}_3$  increased with  $P$  and  $T$ , but was always much higher than the solubility of quartz in water at the same  $P$ - $T$  condition. The quartz solubility in 4.65 molal  $\text{NaHCO}_3$  increased with  $T$ , decreased with  $P$  along the 500 and 600 °C isotherms to values below the solubility in water, and was approximately constant at 300 and 400 °C. For lower pressure isobars, there was a distinct drop in the solubility between 500 and 400 °C.

[1] Thomas *et al.* (2011) *Contrib. Mineral. Petrol.* **161**, 315–329. [2] Martinez *et al.* (2004) *Chem. Geol.* **207**, 47–58. [3] Rudolph *et al.* (2008) *Dalton Trans.*, 900–908. [4] Schmidt (2009) *Geochim. Cosmochim. Acta* **73**, 425–437.

## Molecular-level comparison of water-soluble sedimentary organic matter extracted by two methods

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Organic matter in marine sediments is a complex mixture of numerous individual molecules, which are central reactants in various biogeochemical processes and serve as a substrate for benthic organisms. The fate of organic matter and its bioavailability is largely controlled by composition, size and reactivity of the individual organic molecules. In this study, we aim at a molecular characterization of the easily mobilized and thus accessible fraction of organic matter in marine sediments. We compared the molecular composition of (i) the mobile dissolved organic matter (DOM) pool in interstitial waters, extracted with rhizons, with (ii) the organic matter that was extracted from the associated sediment with water in a Soxhlet apparatus. After solid phase extraction, both DOM fractions were subjected to molecular-level analysis by ultra-high resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS). We selected four different sediment horizons of a core from the Black Sea that represented different ages, depositional and geochemical conditions. FT-ICR mass spectra of the Soxhlet extracted DOM yielded 2- to 3-times higher numbers of molecules compared to the interstitial water DOM, with the former being distributed over a larger mass range and exhibiting higher abundances of heteroatom-bearing molecules. We related the molecular-level differences between both DOM pools to age and sediment geochemistry. The Soxhlet-extractable DOM pool was up to 30-times more concentrated than the DOM pool in the interstitial waters. Soxhlet extraction of sediments in combination with FT-ICR-MS analyses opens a window to studying a so far uncharacterized sedimentary organic matter pool that is potentially the major precursor of “traditional” DOM.