

IR spectroscopic and quantum chemical study of metal bicarbonate and carbonate interaction in aqueous solutions

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Carbonate speciation are among the most important in aqueous systems. Carbonic acid deprotonates to form HCO_3^- and CO_3^{2-} , which further may complex with dissolved cations in solution. In this study, potentiometric and IR spectroscopic measurements were conducted as well as molecular simulation calculations to gain insight into the aqueous speciation of $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}\pm\text{MgCl}_2$ solutions. In $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ solutions $\text{CO}_2(\text{aq})$, HCO_3^- and CO_3^{2-} predominates, with addition to the $\text{NaHCO}_3(\text{aq})$ and NaCO_3^- ion-pairs. These ion-pairs are weak at low-temperatures but become increasingly important with increasing temperature under neutral to alkaline conditions in moderately dilute to concentrated NaCl solutions. With addition of MgCl_2 , MgHCO_3^- and $\text{MgCO}_3(\text{aq})$ ion-pairs form, these accounting for significant part of the carbonate species concentrations. The combined potentiometric and IR measurements demonstrate that these ion-pairs truly exist in solution and cannot solely be explained by non-ideal ion-ion interaction. Moreover, the coordination number of Mg^{2+} is reduced upon substitution of HCO_3^- and CO_3^{2-} to the hydration shell from six to a maximum number of five. These changes may have profound effects on further reactions of $[\text{MgCO}_3\cdot n\text{H}_2\text{O}]^0$ and $[\text{MgHCO}_3\cdot n\text{H}_2\text{O}]^+$ to form Mg-carbonate and bicarbonate clusters and minerals. No such coordination changes were observed associated with $\text{Na}^+ \text{HCO}_3^-$ and CO_3^{2-} ion pairing. Based on the experimental results the equilibrium ionization and ion-pair formation constants were retrieved that can be used to calculate aqueous speciation in $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}+\text{MgCl}_2$ containing solutions.

$\delta^{30}\text{Si}$ in early Archean cherts and implications for the silica cycle

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Si isotopes in Archean cherts offer insight into mass fluxes and mechanisms associated with silica concentration, precipitation, diagenesis and metamorphism. Previous studies have used Archean chert $\delta^{30}\text{Si}$ to estimate seawater $\delta^{30}\text{Si}$ [1-4], assuming a simple mass balance model with silica inputs from crustal weathering balanced by outputs of hydrothermal silicification and amorphous silica precipitation from seawater. This model relies on reservoir analogies, even though silicon reservoirs often have broad $\delta^{30}\text{Si}$ ranges resulting from low temperature dissolution and precipitation reactions. We propose that process analogies are more appropriate for the early Archean system.

To connect isotope composition to process, we used secondary ion mass spectrometry (SIMS) to compare $\delta^{30}\text{Si}$ and $\delta^{18}\text{O}$ in distinct silica phases present in cherts, including carbonaceous bands, pure chert bands and grains, early cavity-filling cements and later quartz-filled veins. Our results indicate that low temperature processes fractionated silicon isotopes in early Archean marine basins—behavior that probably precludes the application of chert $\delta^{30}\text{Si}$ as a paleothermometer. Relationships between $\delta^{18}\text{O}$ and petrographic textures are consistent with setting during early burial and diagenesis [5]. The average value we observe for petrographic textures we infer to be primary silica precipitates from seawater, $\delta^{30}\text{Si} +0.6\text{‰}$, is heavier than expected for bulk silicate Earth ($\delta^{30}\text{Si} -0.4\text{‰}$). This constraint is consistent with an isotope mass balance wherein contemporaneous iron formation deposits have negative $\delta^{30}\text{Si}$ composition and form a notable fraction of the mass balance of Si leaving seawater. Precipitation of authigenic clay minerals may have also comprised a large part of the required ^{30}Si -depleted sink, in addition to playing a role as an important non-carbonate alkalinity sink consuming cations released by silicate weathering. We present a new model for the Archean silica cycle based on process analogies and existing data sets.

[1] Robert & Chaussidon (2006), *Nature* **443**, 969-972. [2] van den Boorn *et al.* (2007), *Geology* **35**, 939-942. [3] van den Boorn *et al.* (2010), *Geochim Cosmochim Acta* **74**, 1077-1103. [4] Abraham *et al.* (2011), *EPSL* **301**, 222-230. [5] Lowe & Knauth (2003), *GSA Bulletin* **115**, 566-580.