

The stability and structure of Mg²⁺ bicarbonate and carbonate ion pairs – An experimental and theoretical study

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The chemistry of Mg²⁺ in aqueous CO₂ solutions is of fundamental importance, both with respect to the reaction mechanism of magnesium carbonate precipitation and in relation to sequestration of CO₂ by carbonate mineralization.

In order to get insight into the coordination and stability of Mg²⁺ bicarbonate and carbonate ion pairs, a combined experimental and theoretical study was conducted. Potentiometric titration and UV-Vis-IR spectrophotometric measurements on dilute solutions were conducted and the stability constants for the MgHCO₃⁺ and MgCO₃ (aq) complexes derived *in situ* at 10-100°C. In addition, density functional calculations were conducted on the hydration environment around the Mg²⁺, HCO₃⁻ and CO₃²⁻ and on the respective complexes.

The aquated Mg²⁺ ion is octahedral coordinated. Upon substitution of HCO₃⁻ or CO₃²⁻ with first shell waters, the coordination changed to five fold with important implication for further reactions and magnesium carbonate mineralization. At neutral to alkaline pH values, the MgHCO₃⁺ and MgCO₃ (aq) ion-pair contribute significantly to the CO₂ speciation in magnesite saturated to supersaturated solutions. Moreover, with increasing temperature, their stabilities increase. However, under alkaline conditions and with increasing temperatures, the solutions become brucite saturated limiting the availability of Mg²⁺ in solution for carbonate mineralization and ion-pair formation.

Fluids on the loose – Capturing meaningful geochronology in sulfides

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For generations, economic geology students have been taught to tackle the world's giant ore deposits. If you aren't studying an economically important deposit at an operational mine, the value of your work may be perceived as less important. This approach to understanding the non-unique pandemic phenomenon of metal-carrying, sulfur-bearing, and sulfide-precipitating fluids in the crust has stymied our progress in ore geology. We cannot glean crucial and fundamental relationships by simply acquiring more and more data from massively chaotic environments fraught by full-time chemical and physical disequilibrium. If we want to understand *how* fluids are transferred in the Earth's crust, *where* fluids originate and *why* they migrate, and how these fluids relate to the observed and unseen rock record, we must turn our attention to locations where fluids have left their simple and indelible mark in the geologic history. This is readily accomplished through study of small metallic-mineral occurrences, and in particular by application of Re-Os geochronology and tracer studies. Dating of many small sulfide-bearing deposits gives us detailed histories of terrane-scale fluid migration events, be they external additions or metamorphic rearrangements of existing volatiles.

As geoscientists we have no truly robust means to correlate through space without the component of time. Without absolute dating, we have no frame of reference beyond immediately visible stacking or cross-cutting relationships. Re-Os studies of sulfides in the Earth's crust have taught us that (1) the duration of large porphyry-style mineralization is an unimportant question as it is different for every deposit and every district and will not help us find ore, (2) the age of sulfide mineralization should not be shoe-horned to agree with associated U-Pb ages for obvious reasons, and (3) excluding true porphyry-style deposits, the mineralization process, in its entirety, commonly spans tens of millions of years.

If you want to understand the ore giants in the world, step back and be sure you understand the less complicated varieties first. Less is more. Good questions demand the right analytical approach. Though easy access to geochemical data tempts us to adopt the get-more-data approach, this will not lead to clarity of understanding.