

The coprecipitation of Mg and Si with calcium carbonate

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Introduction

Soil solutions and groundwaters are often supersaturated with respect to calcite. Saturation indices ($\log IAP/K_{sp}$ for soil solutions and shallow groundwaters average +0.5 and have been attributed to the slow precipitation kinetics of calcite as soil solutions concentrate due to evapotranspirational losses (Suarez, 1977; Suarez *et al.*, 1992). Calcite supersaturation has also been observed in soil-water equilibrations under controlled P_{CO_2} in the laboratory, however, such that evaporative concentration was not a factor (Suarez and Rhoades, 1982; Amrhein *et al.*, 1993). Under these conditions there must be a source of Ca^{2+} and/or HCO_3^- that has an effective solubility greater than calcite and the precipitation kinetics of calcite must be retarded. Slow calcite precipitation kinetics have been attributed to the presence of Mg, organic acids, and phosphate ions, but the identification of soluble sources of Ca and/or HCO_3^- has been more problematic. Elevated levels

of Ca and/or HCO_3^- are most often attributed to the presence of relatively unstable, Mg-substituted calcite (Miyamoto and Pingatore, 1992). The occurrence of low Mg-calcite is common to soils, however the extent of Mg-substitution is insufficient to explain the levels of supersaturation observed. This study was conducted to evaluate the effects of Si, as well as Mg, on the solubility of the precipitate formed from the evaporative concentration of a low salinity water.

Methods

A series of waters were prepared containing constant major ion concentrations with varying concentrations of Si and Mg (Table 1). Four L of each solution were slowly evaporated to a final volume of 0.40 L and then covered for 37 days to allow the solid, solution, and gas phases to reach equilibrium. The precipitated solids and the resulting brines were sampled, and the solids were redissolved in deionized water under

TABLE 1. Composition of initial solutions, saturation indices (SI) of the brines, and mole fraction of Mg in the solid phase precipitated from the brine

Water	Initial Solutions [†]		pH	Brines			Mole fraction Mg in solid [‡]	
	Mg mM	Si		Calcite SI	SiO ₂ (a) SI	sepiolite(a) SI	X-ray	T&P
7	0.4	0.0	8.4	+0.46	-1.31	-3.3	0.015	0.094
8	0.4	0.1	8.5	+0.49	-0.37	-0.39	0.025	0.094
9	0.4	0.5	8.4	+0.51	+0.13	+1.03	0.025	0.099
10	0.4	1.0	8.5	+0.81	-0.02	+0.87	0.020	0.132
11	0.0	0.0	8.3	+0.23	-1.71	< -11.7	0.000	< 0.050
12	0.0	0.1	8.2	+0.32	-0.31	< -7.8	0.000	< 0.050
13	0.0	0.5	8.3	+0.27	+0.12	< -6.4	0.000	< 0.060
14	0.0	1.0	8.4	+0.71	-0.04	< -6.5	0.010	< 0.090

[†]The balance of all initial solutions was Ca = 1.75 mM, Na = 10.8 mM, Cl = 8.1 mM, HCO_3^- = 3.4, SO_4 = 1.8 mM (solutions 7–10) and 1.4 mM (solutions 11–14).

[‡]Mole fraction of Mg in the calcite as determined by the shift in the d_{104} spacing measured by XRD and calculated from the Mg to Ca ratio and the calcite SI of the brines according to the work of Thorstenson and Plummer (1977).

TABLE 2. Solution composition of the redissolved solids and the mole fraction of Mg in the solids (X_{Mg}) based on solution analysis (sol'n) and the work of Thorstenson and Plummer, 1977 (T&P)

Water	pH	Ca	Mg	Na mM	Si	HCO ₃ ⁻	calcite SI	X_{Mg} sol'n	X_{Mg} T&P
7	8.2	0.62	0.02	0.57	0.03	1.30	+0.15	0.034	0.060
8	8.3	0.63	0.02	0.63	0.18	1.32	+0.20	0.026	0.063
9	8.4	0.56	0.04	0.94	1.00	1.52	+0.28	0.066	0.065
10	8.5	0.49	0.07	1.17	1.49	1.84	+0.41	0.123	0.080
11	8.2	0.58	0.00	0.48	0.01	1.20	+0.09	0.00	<0.02
12	8.3	0.52	0.00	0.75	0.17	1.32	+0.10	0.00	<0.03
13	8.3	0.46	0.00	0.92	0.87	1.36	+0.14	0.00	<0.04
14	8.7	0.40	0.00	1.89	1.19	1.84	+0.51	0.00	<0.07

controlled P_{CO_2} . The solids were characterized using X-ray diffraction analysis (XRD), infrared absorption spectroscopy (IR), and transmission electron microscopy (TEM). Ion activities of the brines were calculated with the geochemical speciation model MINTEQA2.

Results

The compositions of the resulting brines are summarized in Table 1. The data show that the level of calcite supersaturation generally increased with increasing Si and Mg concentrations in the initial solutions. Sepiolite supersaturation was observed in brines formed from Waters 9 and 10, and IR analysis indicated the presence of amorphous SiO₂ in samples 10, 13, and 14. Calcite and aragonite were identified in the solids precipitated from Mg containing solutions, whereas only calcite formed from the Mg-free solutions. Poorly crystalline sepiolite was identified with XRD, IR, and TEM in the solid from Water 9. Based on the shift in the d_{104} spacing of calcite, only low Mg-calcite had formed, and the shift in the calcite d_{104} spacing in the absence of Mg at the highest Si concentration (Water 14) indicates that Si coprecipitated with calcite. Dissolution of the solids resulted in increasing levels of calcite supersaturation with increasing Mg and Si contents of the precipitates (Table 2). Sodium was also released to solution due to adsorption of Na onto SiO₂. The amounts of Ca and Si released were inversely related due to Si inhibition of calcium carbonate dissolution. The increase in alkalinity with increasing Si content of the solid suggests that the dissolution of Mg- and/or Na-silicates was a source of HCO₃⁻ from the solid.

Discussion

Beckwith and Reeve (1963) reported no adsorption of Si(OH)₄⁰ on CaCO₃ precipitated in the laboratory, but found significant adsorption of Si onto natural calcium carbonates. There was a good correlation between the amount of Si in the original solid and the amount adsorbed. Lahav and Bolt (1964) reported that the self-diffusion of ⁴⁵Ca into calcium carbonates was blocked by soluble Si. These findings support an intimate association between CaCO₃ and Si that affects the reactivity of the CaCO₃. Thus, Mg in calcite may serve as a center for Si adsorption, or as a mechanism to distort the calcite structure allowing for Si incorporation.

Conclusions

Evaporative concentration of waters of varying Mg and Si concentrations resulted in a solid phase that was substantially more soluble than calcite. The stability of the precipitated solids was inversely proportional to the amount of Si and Mg present in the solid. In the waters containing Mg, the solid phases that formed consisted of a heterogeneous Mg-calcite containing coprecipitated Si, aragonite, a poorly crystalline Mg-silicate (protosepiolite), and a Na-silicate/amorphous SiO₂.

References

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