Geophysical Research Abstracts, Vol. 9, 08169, 2007
SRef-ID: 1607-7962/gra/EGU2007-A-08169

$Sr^{2+}/Ca^{2+}$and $^{44}Ca/^{40}Ca$ Fractionation During Crystallization of $CaCO_3$ Polymorphs – Experimental study at Low Temperature

J. Tang (1), S. J. Köhler (1), M. Dietzel (1), A. Eisenhauer (2), F. Böhm (2), and A. Leis (3)

(1) Institute of Applied Geosciences, Graz University of Technology, Rechbauerstrasse 12, 8010 Graz, Austria, (2) Leibniz-Institut für Meereswissenschaften, Dienstgebäude Ostufer, 8D/104, Wischhofstr. 1-3, 24148 Kiel, Germany, (3) Institute of Water Resources Management, JOANNEUM RESEARCH Forschungsgesellschaft mbH, Elisabethstrasse 16/11, 8010 Graz, Austria (Tang@tugraz.at)

Trace elements and isotopes fractionate during $CaCO_3$ crystallization. The degree of fractionation is commonly influenced by $CaCO_3$ crystallization environments and may be used as a proxy to reconstruct paleoenvironments (such as T and solution chemistry). In this study, CO_2 Diffusion Technique (CDT; e.g. Dietzel et al., 2004) and Double Diffusion Technique (DDT; e.g. Prieto et al., 1997) are used to crystallize $CaCO_3$ polymorphs. The aim is to assess the impact of temperature, precipitation rate, solution chemistry, cation diffusion, and $CaCO_3$ polymorphs on Sr^{2+}/Ca^{2+} and calcium isotope fractionation in inorganic systems.

The experimental results indicate that at a temperature range from 5º to 40ºC, single type of $CaCO_3$ polymorphs (calcite and aragonite) can be produced by controlling the aqueous Mg^{2+}/Ca^{2+} molar ratio and the precipitation rate, $R_{calcite}$ (μmol m^{-2} h^{-1}), in the reaction solution. For example, for CDT a Mg^{2+}/Ca^{2+} molar ratio less than 0.01 yields calcite as sole precipitate, whereas a ratio of about 2 exclusively induces aragonite formation. Most calcite crystals exhibit rhombohedral habit. Aragonite occurs as fibrous crystals, usually in radiating groups.

The Sr^{2+}/Ca^{2+} distribution between aqueous solution and $CaCO_3$ minerals is very sensitive to polymorphs due to the respective crystal type. Under all experimental conditions, Sr^{2+}/Ca^{2+} molar ratios in aragonite are typically higher than that in calcite at analogous experimental conditions. Accordingly, e.g. for calcite a continuous enrichment of aqueous Sr^{2+} vs. Ca^{2+} in the reaction solution is observed, caused by Sr^{2+} discrimination in the crystal lattice, which can be followed by a Rayleigh fractionation process.

The results show that the distribution coefficient of Sr^{2+}into calcite, D_{Sr} = $(Sr^{2+}/Ca^{2+})_{calcite}$/ $(Sr^{2+}/Ca^{2+})_{aq}$ is positively correlated to the precipitation rate $(R_{calcite})$ at a constant temperature of 5º, 25º, and 40ºC. Elevated precipitation rates usually lead to lower discrimination effects during the precipitation (see also Lorens, 1981; Tresorio and Pankow, 1996**)**.

However, the value of D_{Sr} for calcite is also influenced by temperature. At an identical precipitation rate D_{Sr} values show a negative temperature dependence (also Dickson, 1985 and Rimstidt et al., 1998). In general, slopes for $\log(D_{Sr})$ vs. log(R) decrease from high temperature to low temperature, which indicates that precipitation rate effect is enlarged at lower temperatures. At very low precipitation rates the overall temperature effect might be small. In this case, Sr discrimination in calcite may be controlled by slow precipitation kinetics or even by equilibrium fractionation. Further experiments at low precipitation rates have to be carried out by using CDT with seed crystals to verify this behavior.

Distribution of $^{44/40}Ca$ into calcite seems to be negatively related to D_{Sr} and precipitation rates when comparing all experimental data (5º, 25º, and 40ºC) and the temperature effect seems not to be significant. At similar precipitation rates, the degree of $^{44/40}Ca$ isotope fractionation only slightly changes at 5º, 25º, and 40ºC. Comparing our data to the literature e.g. Lemarchand et al. (2004) is complicated by the various approaches to estimate instantaneous in-situ precipitation rates and different experimental setups. Our experiments were done at much lower ionic strength and different solution composition (i.e., Sr presence in reaction solution). Since we notice that there is a strongly negative relationship between Sr distribution and $^{44/40}Ca$ isotope fractionation in the precipitating calcite, the presence of Sr might be a critical factor which accounts for Ca isotope behavior in our experiments. More studies have to be carried out to identify the main factors on $^{44/40}Ca$ isotope fractionation into calcite.

Experiments using DDT show that cation diffusion in gel follows the order of Ba>Ca>Sr>Mg and ^{40}Ca diffuses faster than ^{44}Ca at 25˚C. The degree of fractionation may be caused by individual diffusion coefficients, ion exchange, and the structure of the gel. In terms of the overall Ca isotope fractionation by calcite crystallization, diffusion effect is highly significant. Measured overall Ca isotope fractionation for calcite, $\Delta^{44/40}Ca_{calcite-Ca2+}$, from DDT is for example about -1 ‰, whereas $\Delta^{44/40}Ca_{Ca2+diffusion}$ due to calcium diffusion without $CaCO_3$ formation ranges from -0.4‰ to -1.5‰, depending on the diffusion length and concentration gradient.

References

Dickson, J.A.D., 1985, pp173-188.

Dietzel, M., Gussone, N., and Eisenhauer, A., 2004. *Chemical Geology*, **203**, 139-151.

Lemarchand, D., Wasserburg, G.J., and Papanastassion, D.A., 2004. *Geochim. Cosmochim Acta*, **68**, 4665-4678.

Lorens, R.B., 1981. *Geochim. Cosmochim. Acta* **45**, 553-561

Prieto, M., Fernández-González, A., Putnis, A., and Fernández-Díaz, L., 1997. *Geochim. Cosmochim. Acta* **61**, 3383-3397.

Rimstidt, J.D., Balog, A., and Webb, J., 1998. *Geochim. Cosmochim. Acta* **62**, 1851-1863.

Tesoriero, A. and Pankow, J.F., 1996. *Geochim. Cosmochim. Acta* **60**, 1053-1063.