Growth rate effect on fractionation of elements and Li isotopes during calcite and aragonite growth

RINAT GABITOV

Department of Earth and Space Sciences, University of California, Los Angeles, Los Angeles CA 90095-1567 (gabitr@ucla.edu)

The interest in microscale distributions of elements and isotopes in calcium carbonate has increased in recent decades due to problems emerging from diverse disciplines such as paleoclimatology, paleoceanography, biomineralization, and geochemical cycling at the Earth's surface. Naturally occuring and synthetic calcium carbonates are, in many cases, heterogeneous in trace or minor elements and stable isotopes. Often these variations cannot be explained by temperature variability or composition of the growth medium thus suggesting nonequlibrium crystal growth. Such disequilibrium is especially significant during growth of carbonate minerals under ambient conditions.

An experimental approach was employed to study the effects of mineral growth rate on the fractionation of ^{7}Li/^{6}Li, Li/Ca, Mg/Ca, Sr/Ca, and U/Ca between Ca carbonates and fluid at 25°C. This work is unique because it evaluates linear mineral growth rates (V=distance/time), rather than bulk mass precipitation rates, through introducing chemical spikes as time markers during the experiment, and analyzing experimental carbonates *in situ* by sencondary ion mass spectrometry (SIMS) and electron microprobe (EMP).

EMP data from this work show that partition coefficients of Sr between calcite and fluid (K_d^{Sr}=[Sr/Ca]$_{mineral}$/[Sr/Ca]$_{fluid}$) increase with V, extending the existed K_d^{Sr}-V trend to the faster growth region [1, 2, 3]. K_d^{Mg} and K_d^{U} in aragonite increase with increasing of the growth rate of spherulite (hemispherical bundles of thin aragonite crystals) [4]. In contrast to calcite, K_d^{Sr} in aragonite does not show significant correlation with V. The recent SIMS data on Li/Ca suggest that Li behaves similarly to Mg during aragonite growth. ^{7}Li/^{6}Li yielded single sample variability that exceed those between two aragonite samples precipitated at different rates. Additional ^{7}Li/^{6}Li, Li/Ca, and Li/Mg data will be presented.

[1] Lorens (1981) *GCA,* **45**, 553–561. [2] Tesoriero & Pankow (1996) *GCA*, **60**, 1053–1063. [3] Gabitov & Watson (2006) *G-3*, **7**, Q11004. [4] Gabitov *et al.* (2008) *GCA,* **72**, 4058–4068.

Quantifying boron in natural type IIb blue diamonds

E. GAILLOU[1]*, D. ROST[2], J.E. POST[1] AND J.E. BUTLER[3]

[1]Department of Mineral Sciences, Smithsonian Institution, Washington, DC 20560, USA (gailloue@si.edu, postj@si.edu)
[2]The University of Manchester, SEAES, Oxford Rd., Manchester, M13 9PL, UK (detlef.rost@manchester.ac.uk)
[3]US Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375, USA (james.butler@nrl.navy.mil)

Natural, type IIb blue diamonds are known to get their color from B impurities. Although many studies have reported B concentrations for laboratory doped diamonds (up to 1000 ppm; [1]), only a few values have been determined for natural diamonds. It is generally accepted, however, that the B concentration in natural diamonds is ~1 ppm [e.g. 2], which is a detection limit difficult to achieve for most analytical methods. More commonly, spectroscopic methods are used [3, 4] to obtain estimations of only the B that is not compensated in the structure by N. The goal of this study was to develop a direct and quasi non destructive method to measure total B concentration in what are typically high value blue diamonds, even in the most precious ones, such as the Hope diamond. For that purpose, B-implanted diamond standards were created, and several measurements on each of 8 natural, type IIb diamonds were acquired with a Time-of-Flight SIMS. Because of the high sensitivity of this method, a volume of sample only 50 x 50 μm wide and few nm deep was consumed for each analysis. The total B concentrations vary from 0.07 (±0.02) to 8.4 (±1.2) atomic ppm over all of the samples, and also appears to be heterogeneous within individual samples. These B values will be presented, and compared to results obtained by FTIR (i.e. total versus non-compensated B) and phosphorescence spectroscopy.

[1] Thonke (2003) *Semicond. Sci. Technol.* **18**, S20-S26. [2] Collins (1982) *J. Gem.* **18**, 37–75. [3] Collins & Williams (1971) *J. Phys. C, Solid St. Phys.* **4**, 1789–1799. [4] Fisher, Sibley & Kelly (2009) *J. Phys, Condens. Matter* **21**, 1–10.