

Growth rate effect on oxygen isotope fractionation between aragonite and fluid at 24°C by *in situ* analysis

RINAT I. GABITOV^{1*}

¹University of California, Los Angeles, USA, gabitr@ucla.edu (* presenting author)

Introduction and Methodology

Oxygen isotope compositions ($\delta^{18}\text{O}$) of biogenic and inorganically precipitated calcium carbonate minerals are being used to reveal marine and terrestrial temperatures from the past. However, experimental and natural observations show that factors other than temperature control $\delta^{18}\text{O}$ in CaCO_3 via disequilibrium fractionation [1,2, etc.]. Among these factors are crystallization rate, solution pH, and saturation state of the fluid with respect to CaCO_3 phase (Ω). Previous experimental assessments of disequilibrium effects for $\delta^{18}\text{O}$ were focused on controlling pH and Ω of the experimental solution, followed by bulk analysis of $\delta^{18}\text{O}$ in multicrystalline precipitates. The precipitation rates in those works are usually being reported as amount of precipitated CaCO_3 per surface area and time (or simply amount per time) [3,4]. Because of this, inter- and intra-crystal isotopic variability has remained unknown.

In this work, I used the alternative approach of *in situ* Secondary Ion Mass Spectrometry (SIMS) at lateral spatial resolution of $\sim 10\ \mu\text{m}$ to determine isotopic and chemical variability of precipitated aragonite. The standard deviation of ten SIMS analyses of clear-beige natural aragonite (Belice, Bohemia) was 0.3 ‰ (1 σ); the bulk $\delta^{18}\text{O}_{\text{VPDB}}$ in this reference aragonite was determined by stable isotope mass spectrometry as -7.79 ‰. Hemispherical bundles of aragonite crystals (spherulites) were precipitated by diffusion of CO_2 from ammonium carbonate into $\text{NH}_4\text{Cl-MgCl}_2\text{-CaCl}_2$ solution at 24°C. Spherulite growth (extension) rate (V) was monitored by sequentially spiking the growth medium with rare earth element (REE) dopants. After performing $\delta^{18}\text{O}$ analyses with a Cs^+ primary beam the same spots were revisited to determine their REE/Ca using an O⁻ beam. pH was measured in periodically sub-sampled fluids where aragonite nucleated and crystallized between starting and terminal pH of 8.3 ± 0.1 and 8.63 ± 0.02 , respectively.

Results

SIMS spot analyses demonstrate that nucleation centers of aragonite spherulites are depleted in $\delta^{18}\text{O}$ relative to their edges by as much as 4 ‰. REE/Ca profiles show decreasing V in the spherulites with time (i.e., spherulites edges advanced at slower rates than centers). $\delta^{18}\text{O}$ increases by 2.4 ‰ with decreasing V between 3 and 0.1 $\mu\text{m/hr}$. Because of a large fluid to crystal molar ratio (~ 4000) $\delta^{18}\text{O}$ of the fluid unlikely changed significantly during aragonite crystallization. Analysis of fluid sub-samples for $\delta^{18}\text{O}$ is ongoing and will permit to accurately calculate the dependence of the fractionation factor ($\alpha^{18}\text{O}$) on aragonite growth rate.

- [1] McConnaughey (1989) *Geochim. Cosmochim. Acta* **53**, 151-162. [2] Rollion-Bard et al. (2003) *Coral Reefs* **22**, 405-415.
 [3] Kim et al. (2006) *Geochim. Cosmochim. Acta* **70**, 5790-5801.
 [4] Dietzel et al. (2009) *Chem. Geol.* **268**, 107-115.

Phase equilibrium constraints on the genesis of wehrlite cumulates at mid-ocean ridges and the origin of the clinopyroxene paradox

GLENN A GAETANI^{1*}, JOHN MACLENNAN²

¹Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA, 02543, USA (ggaetani@whoi.edu)

²Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, UK (jcm1004@cam.ac.uk)

A longstanding gap in our understanding of ocean crust accretion is the occurrence of pyroxene-bearing ultramafic cumulates near the base of the crust in ophiolites [1]. A similarly unresolved issue in the evolution of mid-ocean ridge basalts (MORB) is a compositional signature for clinopyroxene crystallization in abyssal tholeiites that are pyroxene saturated only at upper mantle conditions (the clinopyroxene paradox) [2]. Melting experiments conducted on lava from the Borgarhraun flow in the Theistareykir segment of Iceland's Northern Volcanic Zone provide new insights into both of these issues. Our results, combined with those of Winpenny and MacLennan [3], indicate that wehrlite nodules in the Borgarhraun flow crystallized at moderate pressures and relatively low temperatures from highly depleted magmas. This is consistent with an origin for wehrlite cumulates by crystallization of late-stage melts generated in the upper portions of the ascending mantle. The eventual mixing of these magmas with melts formed deeper the melting column imparts a clinopyroxene crystallization signature on erupted MORB.

Experiments were carried out on primitive (Mg# ~ 0.72) Borgarhraun lava at 1 bar and 1190 to 1320°C by suspending rock powder from Re loops in a vertical gas-mixing furnace, with oxygen fugacity controlled at ~ 1.5 log units below the fayalite-magnetite-quartz buffer. Experiments were also conducted at 1.0 to 1.4 GPa and 1260 to 1370°C, in graphite capsules, using a solid-medium piston-cylinder device. All run products were analyzed for major elements by electron microprobe. Trace elements were analyzed in a subset of the experiments by secondary ion mass spectrometry.

The 0.1 MPa liquid line of descent for Borgarhraun lava is typical of MORB, with olivine on the liquidus at $\sim 1310^\circ\text{C}$, followed by olivine + plagioclase at $\sim 1220^\circ\text{C}$. Clinopyroxene appears at $\sim 1205^\circ\text{C}$. At 1.2 GPa Olivine + clinopyroxene crystallize together on the liquidus at $\sim 1360^\circ\text{C}$. Clinopyroxenes in the wehrlite nodules studied by Winpenny and MacLennan [3] are compositionally distinct from those in our high-pressure experiments. The former are characterized by higher Mg# and CaO, and are strongly depleted in incompatible elements. A likely parent magma for the wehrlite cumulates is, therefore, a late-stage partial melt formed at relatively shallow depths. Dantas et al. [4] proposed a similar origin for pyroxenite cumulates from the Southwest Indian Ridge, suggesting that this process may be common at mid-ocean ridges.

References:

- [1] Elthon et al. (1982) *J Geophys Res* **87** 8717-8734.
 [2] Francis (1986) *Nature* **319** 586-589.
 [3] Winpenny and MacLennan (2011) *J Petrology* **52** 1791-1812.
 [4] Dantas et al. (2007) *J Petrology* **48** 647-660.