Micron-scale intrashell $\delta^{18}O$ variation in cultured planktic foraminifers

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Introduction

Recent studies have used *in situ* analyses via Secondary Ion Mass Spectrometry (SIMS) to document $\delta^{18}O$ heterogeneity within the shell walls of planktic foraminifers and shell microstructures [1,2] that may result from ontogenetic, ecologic, or diagenetic controls. Here we show that the rate of precipitation of shell calcite in the extant planktic foraminifer *Orbulina universa* is sufficiently rapid that 12h calcification periods in ^{18}O-labeled seawater can be resolved and accurately measured using SIMS with a 3 µm spot. *Orbulina universa* secretes a large, spherical shell that thickens over the course of 3-5 days. Live *O. universa* were collected via scuba diving and maintained at constant temperature (22°C). These individuals calcified continuously while they were transferred every 12h between ambient seawater ($\delta^{18}O_w$ = -0.4‰ VSMOW), and seawater with enriched barium (4x ambient seawater) and $\delta^{18}O_w$ = +18.6‰ VSMOW. Transfers produced geochemically distinct layers of calcite that were enriched in both Ba and ^{18}O, separated by layers precipitated in ambient seawater. We quantified the position of the Ba-spiked calcite in the shell wall of *O. universa* specimens via laser ablation ICP-MS depth profiling of trace element ratios, and then measured intrashell $\delta^{18}O$ in the same specimens using SIMS with a 3 µm spot and an average precision of 0.6‰ (±2 SD).

Results and Conclusion

Measured $\delta^{18}O_{calcite}$ values in *O. universa* shell layers are -2.0±0.5‰ VPDB (*n*=5) for ambient calcite and +16.4±0.4‰ VPDB (*n*=3) for ^{18}O-labeled calcite. These values agree well with predicted values of -2.2‰ and +16.8‰, respectively, computed using empirical $\delta^{18}O$-temperature calibrations from live culture of *O. universa* [3]. Elemental and oxygen isotope data show that LA-ICP-MS and SIMS measurements can be cross-correlated within the spatial resolution of the two analytical techniques. Precipitation of ^{18}O and Ba seawater tracers in planktic foraminifer shell calcite appears to be synchronous, with no measurable spatial offsets. These results demonstrate the capability of SIMS to resolve diurnal growth increments in foraminiferal shells, and highlight the potential to address paleoceanographic and biomineralization questions.

[1] Kozdon *et al.* (2009) *Chemical Geology* **258**, 327-337. [2] Kozdon *et al.* (2011) *Paleoceanography* **26**, PA3206. [3] Bemis *et al.* (1998) *Paleoceanography* **13**, 150-160.

Development of the MultiGAS for determining fumarole gas chemistry in geothermal systems

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Geothermal exploration relies on the gas geochemistry of fumaroles, bubbling/boiling springs and steaming ground to offer insight into the nature of the fluids at depth, procceses affecting them when rising to the surface, and provide estimates of the temperature of last equilibration of the gases within the reservoir. Traditional measurements involve direct sampling of the gases in pre-evacuated Giggenbach glass bottles before being sent to the lab for chemical analysis. Gas component analysis, combined with the isotope ratios of certain components (e.g., CO_2, He), provides insight into the proportion of magmatic, crustal, meteoric and atmospheric components in the fluid, and the state of equilibrium and temperature of these fluids at depth.

The Multi-component Gas Analyzing System (MultiGAS) was developed by the volcanological community over 10 years ago as a field-portable instrument for in-situ analysis of the major volcanic gas components in diffuse and dilute gas emissions. No two instruments are identical but all consist of various sensor types now capable of simultaneously analyzing for H_2O, CO_2, CO, SO_2 and H_2S.

In high-temperature (volcanic) geothermal systems, surface manifestations are often composed of gas emissions. In some cases, low temperatures and/or low flow rates make traditional sampling of fumaroles difficult, due to rapid vapor condensation and atmospheric contamination. The MultiGAS is best suited to these types of manifestations~~,~~ providing a tool that can be used at a wide variety of gas emmission styles.

The MultiGAS has been field-tested in a geothermal prospect area characterized by steaming ground and fumaroles at the boiling temperature of water. Results of the MultiGAS analysis ($H_2O/CO_2/H_2S$ ratios) are compared with the equivalent ratios obtained from traditional sampling and analytical procedures, in order to identify the advantages and disadvantages of this new technique, and allow for the characterization of the hydrothermal system from the gas phase. The MultiGAS also allows for the gas/steam ratio of fumaroles to be quickly assessed in the field, which can aid in mapping/targeting of fumaroles in a large field, and the selection of the most ideal fumaroles to sample using the traditional method.