Early diagenetic alteration of zeolites in subseafloor sediment of the South Pacific Gyre

BRYCE HOPPIE* AND ALYSSA WITT

Department of Chemistry and Geology, Minnesota State University, Mankato, Minnesota 56001 USA (*correspondence: bryce.hoppie@mnsu.edu)

Zeolite minerals are distributed throughout much of the subseafloor sediment of the South Pacific Gyre (SPG). Previous studies of deep-sea zeolites suggest that they form through the early diagenetic alteration of volcanic debris within the first meter of the subseafloor and subsequently undergo dissolution at burial depths exceeding 50 m. In SPG subseafloor sediment, porosities frequently exceed 80% and pore water residence times are greater than 10^5 years. Consequently, substantial opportunities exist for zeolites beneath the SPG to undergo post-depositional mineral-to-pore water interactions.

For this study, over 1,200 randomly selected zeolite crystals were isolated from clay-rich samples of SPG subseafloor sediment obtained during IODP Expedition 329. Crystals were analyzed using optical microscopy, SEM-EDS, and X-ray diffraction techniques. Strata were found to include the zeolite minerals phillipsite, $(Na, K)_2 (Mg, Ca) Al_6Si_{10}O_{32} \bullet 12H_20$, and harmotome, $(Na, K)_2 (Ba, Mg, Ca) Al_5Si_{11}O_{32} \bullet 12 H_2O$. The zeolites generally exhibit up to 100x increases in prismatic length within the first 4 to 15 m below the seafloor. Larger mean diameters of the phillipsite crystals correspond to elevated $[K^+]$ and $[Si^{4+}]$ whereas increased $[Ba^{2+}]$ corresponds to smaller harmotome crystals. Individual crystal volumes exhibit no consistent trend versus burial depth and do not correlate to euhedralism, a proxy for crystal dissolution; sub- and anhehdral crystals are found at all depths and are particularly prevalent in the upper 10 to 25 m of the western study sites. All crystals maintain overall charge balance; however, none of the alkali or alkaline earth elements within the zeolites vary consistently with the other cations of similar electron valence or with $[Al^{4+}]$ or $[Si^{4+}]$.

These results show that SPG subseafloor zeolite minerals are not uniform or predictably variable with respect to their textural attributes or composition. Furthermore, they do not readily corroborate previous explanations of deep-sea zeolite diagenesis. Although the observed mineral characteristics could derive from local, shallow subsurface environmental disparities, they are also suggestive of cation-change and non-uniform interactions among zeolites and pore water within the SPG subseafloor environment.

A comparison of geothermometers for shallow silicic magmas

J.M. HORA[1]*, G. WÖRNER[1], A. KRONZ[1], AND A. K. SCHMITT[2]

[1]GZG-Abt. Geochemie, Georg-August Universität, 37077 Göttingen, Germany (* correspondence: jhora@gwdg.de)
[2]Department of Earth and Space Sciences, University of California, Los Angeles, CA 90095, USA

Several geothermometers can be applied to silicic systems. Aside from 'traditional' two phase thermometers, recent calibrations involving partitioning of Si, Ti, and Zr among quartz, titanite, and zircon offer the promise of being able to extract T-t paths from zoned crystals. Recognition of P, a_{TiO2} a_{SiO2} dependence have resulted in some controversy and revisions to these thermometers over the past few years. Difficulty in testing calibrations of these thermometers lies in having to assume values of input variables such as P and activities of components when comparing to only one or two other thermometers. Another complication is that the chemical species involved in various thermometers diffuse at different rates, and may result in comparing temperatures locked in at different times during a cooling history.

By choosing a natural system where there are more applicable thermometry equations than free variables (e.g. P, component activities), we can evaluate consistency of results among thermometers in the contexts of (a) differing diffusivities, (b) testing various calibrations of the same thermometer, and (c) a magmatic thermal history. We compared Fe-Ti oxide, amhibole, amphibole-plagioclase, two-feldspar, Zr-in-titanite, Ti-in-zircon, and Ti-in-quartz thermometers in rhyodacite dome lavas at Parinacota volcano, Chile. This also includes thermometry of U-Th-dated zircon with crystallization ages ranging from >350 ka to near-eruption (~47 ka), and oxide inclusions in titanite. This comparison indicates: (a) good agreement (T = 740-760°C) among phases where diffusion is slow when $P = 3.5$kbar, $a_{TiO2} = 0.85$, $a_{SiO2} = 1$, interpreted as conditions of crystallization, (b) progressively lower temperatures with increase in diffusivity (quartz ≈ 720°C, oxides ≈ 710°C), likely reflecting latest storage and syn-eruption temperatures, respectively; and (c) both the pressure-dependences of the Ti-in-zircon thermometer suggested by [1] and [2] agree with other thermometers, whereas the calibration of Ti-in-quartz by [3] produces the most consistent results at the low pressures and temperatures experienced by these magmas.

[1] Huang & Audetat (2012) *GCA* **84**, 75-89. [2] Ferry & Watson (2007) *CMP* **154**, 429-437. [3] Ferriss *et al* (2008) *Eur. J. Mineral.* **20**, 745-755.

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