

Sensitive, high-resolution measurement of volatile organic compounds dissolved in seawater using proton transfer reaction-mass spectrometry

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We developed an equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-MS) method for fast detection of volatile organic compounds (VOCs) including dimethyl sulfide (DMS) and isoprene dissolved in seawater. Dissolved VOCs extracted by bubbling pure nitrogen through the sample was continuously directed to the PTR-MS. DMS reached equilibrium with an overall response time of 1 min, and the detection limit was 50 pmol per Liter at 5-s integration [1]. The EI-PTR-MS instrument was deployed during a research cruise in the western North Pacific Ocean. Comparison of the EI-PTR-MS results with results obtained by means of membrane tube equilibrator-gas chromatography/mass spectrometry agreed reasonably well on average. EI-PTR-MS captured temporal variations of dissolved DMS and isoprene concentrations, including elevated peaks associated with patches of high biogenic activity. These results demonstrate that EI-PTR-MS was effective for highly time-resolved measurements of VOCs in the open ocean [2]. Further measurements will improve our understanding of the biogeochemical mechanisms of the production, consumption, and distribution of VOCs in the ocean surface.

[1] Kameyama, Tanimoto, Inomata, Tsunogai, Ooki, Yokouchi, Takeda, Obata, & Uematsu (2009) *Anal. Chem.* **81**, 9021–9026. [2] Kameyama, Tanimoto, Inomata, Tsunogai, Ooki, Takeda, Obata, Tsuda, & Uematsu (2010) *Marine Chem.* **122**, 59–73.

Oxygen isotope geochemistry beneath paleofumaroles

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Little is known about the chemical processes operating beneath fumaroles. However recent detailed documentation of sulfosalt assemblages has shown that mineral deposits such as El Indio, Chile and Summitville, Colorado contain quenched sulfosalt melt assemblages. Thus, these deposits provide a snapshot into the fracture-controlled plumbing systems hundreds of metres beneath paleo-solfataras. Independent temperature estimates suggest deposition of quartz and sulfosalts at ~ 675°C. This study focuses on the oxygen isotopic composition of euhedral quartz crystals (~200 microns in diameter) grown within sulfide/sulfosalt melt.

In situ stable isotope microanalyses of quartz separates from sulfosalt assemblages were performed using the SHRIMP II at the Australian National University. Intricate zonation of aluminium concentration in quartz (~2 micron growth bands) was mapped using the electron microprobe, and then targeted using a 20 micron spot on SHRIMP II.

Preliminary results indicate that the $\delta^{18}\text{O}$ of quartz crystals from the El Indio and Summitville deposits exhibit a wide range in isotopic compositions (3.7‰–17.1‰) – with variation of up to 11‰ within an individual crystal.

We interpret the heavy oxygen which exceeds the values of the ‘magmatic water box’ to be evidence of kinetic fractionation during hydrous silica deposition and subsequent dehydration.