

Dissolved organic matter composition across a coastal-open ocean gradient in the eastern Pacific Ocean

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Dissolved organic matter (DOM) in marine systems is an important component of the global carbon cycle whose molecular-level composition is determined by a combination of abiotic and biotic factors related to sources, sinks and transformations. Molecular-level characterization of this heterogeneous mixture has become practical only recently with the advent of ultrahigh resolution mass spectrometry (ESI FT-ICR MS). To date, systematic surveys of DOM composition in the surface and deep oceans are rare, but those conducted to date have highlighted the potential of this tool to identify new marker compounds for different biological processes. Here we examine the DOM composition along Line P in the eastern Pacific Ocean, collected during the interdisciplinary GEOMICS cruise in May 2012. We explore the shifts in DOM composition from the coast to the open ocean as well as down the depth profile at selected locations. We further explore the source of surface DOM through comparison with culture-based investigations of metabolites exuded by phytoplankton and heterotrophic bacteria. Using multivariate statistical tools, we observe significant changes in compound distributions along the primary spatial gradients of Line P, notably an increase in N:C and S:C ratios with depth. We hypothesize that microbial activity is responsible for these changes and leads to the sequestration of N and S in increasingly recalcitrant molecules. These data will provide important chemical contexts for other omics-based analyses undertaken by GEOMICS colleagues and are an integral component of an emerging systems-biology view of the ocean.

New experimental data on TiO₂ solubility in hydrous rhyolite melts: Implications for titanium-in-quartz thermobarometry

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Application of the titanium-in-quartz (TitaniQ) thermobarometer to natural magmas requires estimation of the activity of TiO₂ because most natural magmas are not TiO₂-saturated. However, currently available methods to calculate TiO₂ activities in silicate melts return highly inconsistent results that commonly differ by a factor of up to two, which introduces large uncertainties in the calculated TitaniQ temperatures or pressures. In order to further constrain TiO₂ solubility in silicic melts we conducted experiments at 800-900 °C and 2 kbar in H₂O-saturated haplogranite melts with molar Al/(Na+K)-ratios ranging from 0.81 to 1.2.

Due to the slow diffusivity of Ti in silicate melts at these conditions we developed a new method to determine TiO₂ solubility. In a first step, anhydrous glasses with smooth TiO₂ concentration gradients over several millimeters were produced in an 1 atm high-temperature furnace. Pieces of these glasses were then hydrated for 3 days at 750 °C and 2 kbar at H₂O-saturated conditions in cold-seal pressure vessels, which caused crystallization of rutile in the TiO₂-rich parts of the samples. Finally, the recovered pieces were welded together with untreated ones (plus H₂O) into new Au capsules and were equilibrated at 800-900 °C and 2 kbar for 7 days, after which time the samples were rapidly quenched. In this way, forward and reverse runs could be conducted within single experiments. TiO₂ concentrations measured at the contact between rutile-bearing and rutile-free glass agree well between forward and reverse runs, suggesting that equilibrium was obtained.

An empirical best-fit model to our data predicts TiO₂ solubilities that are similar to those measured by [1], thus validating the TitaniQ model and corresponding tests on natural samples published in [2].

[1] Hayden&Watson (2007) *Earth Planet. Sci. Lett.* **258**, 561-568. [2] Huang&Audétat (2012) *Geochim. Cosmochim. Acta* **84**, 75-89.