# Methane cycling at Lost City: A biological view of geochemistry

ALEXANDER S. BRADLEY[1]*, PENGFEI SONG[1], ROGER E. SUMMONS[2] AND PETER R. GIRGUIS[1]

[1]Biological Laboratories, Harvard University, 16 Divinity Avenue, Cambridge MA 02138 (*correspondence: bradley@fas.harvard.edu)
[2]Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139

The Lost City Hydrothermal Field [1] is an ecosystem in which vent fluid chemistry is controlled by serpentinization reactions. These conditions are conducive to abiotic methane production [2] as well as the support of biological methane producing archaea [3]. Both aerobic and anaerobic microbes mediate the consumption of methane [3], and possibly of other volatile hydrocarbons, in this system. With multiple sources and sinks, deconvoluting the dynamics of methane cycling in this system is inherently complex.

This difficulty is magnified by the isotope systematics. Methane at Lost City has $\delta^{13}C$ ranging from -13.6‰ to -8.8‰ [1]. In most environments, this range of $^{13}C$ content would suggest a dominantly abiotic methane source. But evidence from lipid biomarkers suggests that biologically produced methane at Lost City should be similarly enriched in $^{13}C$, due to vanishingly small concentrations of inorganic carbon [4].

Carbon limitation in vent fluids is likely due to an abundance of $H_2$ – nearly 15 mM – that is sufficiently high for near quantitative reduction of inorganic carbon to biomass and methane. High pH (9 to 11) ensures that most remaining inorganic carbon is $CO_3^{2-}$, which is generally thought to be biologically unavailable.

Under these conditions it is not yet clear how methanogenic archaea cycle energy and carbon. While hydrogenotrophy is an attractive hypothesis, the limited supply of inorganic carbon may pose difficulties for autotrophy. Another possibility is that serpentinization drives the inorganic synthesis of organic compounds that can be used by microbes as carbon sources. A range of biologically produced molecules, including lipids, nucleic acids, and proteins, can be queried to better understand the physiology of microbes at Lost City and shed light on their interactions with the geochemical environment.

[1] Kelley *et al.* (2005) *Science* **307**, 1428-1434. [2] Proskurowski *et al.* (2008) *Science* **319**, 604-607. [3] Brazelton *et al.* (2006) *AEM* **72**, 6257-6270. [4] Bradley *et al.* (2009) *GCA* **73**, 102-118.

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# The distribution of $^{231}$Pa and $^{230}$Th in paired water column and surface sediment samples

LOUISA I. BRADTMILLER[1]*, LAURA F. ROBINSON[1], JERRY F. MCMANUS[2], MAUREEN E. AURO[1] AND HELEN C. BOSTOCK

[1]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, USA (*correspondence: lbradtmiller@whoi.edu)
[2]Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY, USA
[3]National Institute of Water and Atmosphere Greta Point, Wellington, New Zealand

Both $^{231}$Pa and $^{230}$Th are produced in the ocean by the radioactive decay of dissolved uranium ($^{235}$U and $^{234}$U, respectively), and because uranium is uniformly distributed in the modern ocean the production of both isotopes occurs uniformly and at a constant rate. However, due to differences in particle reactivity, the residence times of these two isotopes differ by an order of magnitude. The combination of constant production and different residence times has been exploited in the use of $^{231}$Pa and $^{230}$Th as tracers for water column processes in the modern ocean (such as circulation and biological productivity), and in the use of the sedimentary $^{231}$Pa/$^{230}$Th ratio as a proxy for changes in those processes through time. Both of these applications require an understanding of the distributions of $^{231}$Pa and $^{230}$Th in the modern ocean, and of the fractionation between the dissolved phase and the particles that form the sedimentary record.

We present new water column profiles of total $^{231}$Pa and $^{230}$Th in the Southern Ocean, coupled with measurements of the immediately underlying sedimentary $^{231}$Pa/$^{230}$Th ratio. Seawater measurements were made on 7-10L samples using a new multiple-ion-counting array on the Neptune multi-collector ICP-MS at WHOI. Thorium concentrations in the water column increase linearly with depth, increase gradually with increasing latitude, and show no correlation to water mass structure. This result is consistent with previous measurements of dissolved $^{230}$Th in the Southern Ocean. Protactinium concentrations also increase with depth and towards the south, but show greater variation than $^{230}$Th. This variability likely reflects a combination of the influence of different watermasses and site-specific patterns of circulation, as expected due to the longer residence time of Pa in the water column. Sedimentary $^{231}$Pa/$^{230}$Th ratios are uniformly lower than watercolumn ratios, and in some cases do not vary significantly with sediment type despite known differences in the affinity of opal and carbonate for Pa.