Pore water profiles in marine shallow-water hydrothermal systems: Natural laboratories to study redox gradients

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Several marine shallow-water hydrothermal vents discharge hot, slightly acidic, arsenic-rich, chemically reduced fluid into cool, slightly alkaline, oxygenated seawater. Mixing between the two aqueous phases generates redox gradients in sediment pore waters and in the water column. The marine shallow-water hydrothermal system in Tutum Bay, for example, discharged a fluid containing ~900 µg/L As, almost exclusively present as the reduced, trivalent arsenite (As^{III}), while local seawater measured between 1.2 and 2.4 µg/L As, with approximately equal levels of As^{III} and arsenate (As^{V}). Of particular interest in this study was As speciation and abundance in pore waters as a function of sediment depth and as a function of distance from the area of focused venting. With increasing distance, As^{T} concentration in the pore water decreased rapidly, but remained elevated up to 300 m from the area of focused venting when compared to a non-hydrothermal control site. The As^{T} concentration in the vertical pore water profiles increased with depth. Surprisingly, aqueous As^{V} far exceeded aqueous As^{III} at almost all distances and depths investigated, while at the control site the As^{III} concentration exceeded that of As^{V}. Thus, chemical disequilibria among As species provide potential energy for arsenite oxidizing microorganisms where hydrothermal fluid mixes with seawater near the vent orifice, and for arsenate reducing microorganisms with increasing distance and depth from the hydrothermal point source. In the Tutum Bay samples, As^{III} oxidation yields 70-90 kJ per mole electrons transferred with O_2 as the terminal electron acceptor, but only 25-55 kJ/mol e^- with NO_3^- or NO_2^-. Chemolithotrophic As^{V} reduction is less exergonic, yielding 0-25 kJ/mol e^- with sulfide or ferrous iron as the electron donor.

U-Pb zircon and $^{40}Ar/^{39}Ar$ hornblende ages of glaciogenic detritus around East Antarctica

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U-Pb ages of detrital zircon grains have provided an extrordinary tool for sedimentary provenance work, given that they are ubiquitous, resistant to damage and weathering, and that the U-Pb age records the crystallization age of the mineral. Although not as widely used, $^{40}Ar/^{39}Ar$ dating of detrital hornblende grains can also serve as a powerful sedimentary provenance tool, particularly in situations where chemical weathering is minor.

Certain natural biases exist between these two mineral chronometers. Zircon is an accessory mineral that is common to a wide variety of rocks, but occurs in particularly high concentrations in felsic crystalline rocks. Hornblende is a rock forming mineral, and it is particularly abundant in intermediate and mafic crystalline rocks and in amphibolites. In contrast to the resistance to resetting and destruction that characterizes zircon, hornblende is relatively susceptible to weathering and thus is not typically found in recycled sediments. Additionally, the $^{40}Ar/^{39}Ar$ system in hornblendes has a closure temperature (~500°C). Thus, for areas which have experienced a polymetamorphic history, e.g, East Antarctica, combining the two approaches can provide added detail to provenance studies.

$^{40}Ar/^{39}Ar$ and U-Pb ages of ice-rafted hornblende and zircon grains from proximal marine sediment cores around the East Antarctic perimeter reveal a generally similar picture of the subglacial geology, consistent with results of [1]. Although hornblende populations are slightly younger than dominant zircon populations from the same sample, both ages are consistent with limited on-land ages, showing dominant populations of 0.4-0.6 Ga, 1.0-1.3 Ga, 1.5-1.7 Ga, and ~3 Ga. Several cores illustrate the added value of the combined approach as they show age populations reflected by either zircons or hornblendes, but not both [1] Roy *et al*. (2007) Chem. Geol. 244, 507-519.