The role of the Mid-Atlantic Ridge for chemical fluxes in the Atlantic: Clues from Ra and Ac isotopes

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We present data on the distribution of short-lived radium isotopes ^{223}Ra and ^{224}Ra, as proxies for their parent isotopes ^{227}Ac and ^{228}Th, from the deep South Atlantic (GEOTRACES cruises GA10E and GA10W), together with ^{228}Ra and ^{226}Ra data from the same samples. Samples were collected in-situ using submersible autonomous pumping systems (SAPS) equipped with two MnO_2-coated acrylic fibers in series. We use a new evaluation method to determine Ra adsorption efficiencies of this sampling technique with a Ra delayed coincidence counter (RaDeCC), avoiding the determination of the efficiency based on the decrease of Ra from the 1st to the 2nd absorber (1-B/A). Instead, we have individual efficiencies for each absorber. Efficiencies of the new sampling method are on average 30% (±8%) for two absorbers combined, with an average sample volume of 381 L.

Elevated ^{227}Ac values at ~3000m across the Atlantic basin, with a maximum at the mid-Atlantic Ridge (MAR), suggest a potential effect of the MAR on the distribution of chemical species in various ways: As a source for elements that can be modeled as analogues of ^{227}Ac; as a a barrier between ocean basins; and by enhancing isopycnal mixing with long-distance effects.

Hematite/Water Interfaces Probed by Second Harmonic Generation

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The Fe(III)/Fe(II) redox couple is a fundamental transformation pathway for iron oxides, however, the study of iron oxide surfaces in aqueous solution by powerful spectroscopic techniques has been limited due to "strong absorber problem". Here, we overome this issue using atomic layer deposition (ALD) of thin films of polycrystalline α-Fe_2O_3 which were analyzed using the Eisenthal chi$^{(3)}$ technique, a variant of second harmonic generation (SHG) that reports on interfacial potentials. The point of zero charge was found to be 5.5 ± 0.3. The interaction of aqueous Fe(II) at pH 4 and in 1 mM NaCl with ALD-prepared hematite was found to be fully reversible and to lead to about 4 times more ferrous iron ions adsorbed per square centimeter than on fused-silica surfaces under the same conditions. The data are consistent with a recently proposed conceptual model for net Fe(II) uptake or release that is underlain by a dynamic equilibrium between Fe(II) adsorbed onto hematite, electron transfer into favorable surface sites with attendant Fe(III) deposition, and electron conduction to favorable remote sites that release and replenish aqueous Fe(II). Additional work carried out under flow conditions at pH 4 with 10 mM NaCl resulted in partially irreversible adsorption of Cr(III), the extent of which was found to depend on Cr(III) concentration, as confirmed by X-ray photoelectron spectroscopy. The interaction of Cr(III) with hematite was compared with the adsorption of Cr(III) to the silica/water interface, which is the substrate for the ALD-prepared hematite films, and found to be fully reversible under the same experimental conditions. The observed binding constant for Cr(III) interacting with the silica surface was found to be $4.0(6) \times 10^3$ M^{-1}, which corresponds to an adsorption free energy of $-30.5(4)$ kJ/mol when referenced to 55.5 M water. Cr(III) surface coverages were calculated to be 1.0×10^{12} ions/cm^2 assuming a +3 charge for chromium. The observed binding constant for Cr(III) interacting reversibly with the hematite surface was calculated to be $2(2) \times 10^4$ M^{-1} (adsorption free energy of $-35(2)$ kJ/mol). Maximum metal ion surface coverages 8.3×10^{11} reversibly bound ions per cm^2, again assuming a +3 charge of chromium. The data also allows us to estimate that about 6.7×10^{12} Cr(III) ions are irreversibly bound per cm^2 hematite at saturation coverage. The results of this investigation are discussed in the context of surface passivation in permeable reactive barriers.