Distinguishing arc, backarc, and hotspot affinities using helium isotope and C/^{3}He ratios

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The northern Lau Basin is host to a complicated pattern of volcanic activity, including the volcanoes of the Tofua Arc and several back-arc spreading centers. Farther west along the NW Lau Spreading Center, elevated ^{3}He/^{4}He ratios in the seafloor lavas suggest that an OIB or mantle plume signature, possibly from Samoa, has influenced this extensional zone. Helium isotope and C/^{3}He ratios have proved useful for differentiating between arc vs. back-arc influences. True back-arc systems are similar to mid-ocean ridge (MOR) systems with ^{3}He/^{4}He of ~ 8 Ra (R = ^{3}He/^{4}He and Ra = Rair) and C/^{3}He of ~10^9. In contrast, arc volcanoes typically have lower ^{3}He/^{4}He ratios and higher C/^{3}He ratios ($\geq 10^{10}$), presumably due to downgoing slab components. For example, the recently erupting West Mata submarine volcano in the NE Lau Basin has 7.3 Ra and C/^{3}He of ~10^{10}, indicating strong arc affinities. In contrast, lavas and hydrothermal fluids from the NELSC have 8.0 – 8.6 Ra and C/^{3}He of 1 – 3 x 10^9, typical MOR or back-arc signatures. Other volcanic centers in the region show varying degrees of arc or downgoing slab influence based on their ^{3}He/^{4}He - C/^{3}He fingerprint. A broader view of the entire northern Lau Basin indicates that elevated ^{3}He/^{4}He ratios indicative of an OIB signature are confined to the Northwest Lau Spreading Center, and that the NE Lau Basin is characterized by both arc and back-arc signatures.

Thermodynamics of one and two electron transfer steps: Implications for iodide oxidation and iodine environmental cycling

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In oxygenated waters, chloride and bromide are the thermodynamically stable halogen species that exist whereas iodate, the thermodynamically stable form of iodine, and iodide can co-exist. The stability and oxidation of halides in the environment is related to the unfavorable thermodynamics for the first electron transfer with oxygen to form X· atoms. However, reactive oxygen species (ROS) such as $^1O_2$, H_2O_2 and O_3 can oxidize the halides to X_2 and HOX in two electron transfer processes; these reactions become less favorable with increasing pH. Fe (III) and Mn (III, IV) solid phases can oxidize halides with similar patterns as ROS.

The best oxidants in aqueous solution appear to be the one electron oxidant, ·OH, and the two electron oxidants, $^1O_2$, H_2O_2 or O_3. However, thermodynamic favorability depends on the halide with iodide being the easiest to oxidize as well as on pH with thermodynamic favorability decreasing with increasing pH. In sediments, Mn (III) (oxy)hydroxides are possible oxidants at near neutral pH for iodide; however, chloride and bromide reactions can only occur at pH values ≤ 2-3. I_2 and HOI form on iodide oxidation and can react with natural organic matter with formation of organo-iodine (R-I) compounds. During the treatment of drinking water, unwanted R-I disinfectant byproducts can form when the oxidant is not capable of quantitatively converting iodide to iodate.

In the atmosphere, halogen oxidation reactions are more likely due to photodecomposition of C-X bonds to X atoms, which react with O_3, NO, XO and other species by O atom transfer, a two electron transfer process. In the case of iodine, iodine oxide species form aerosol nanoparticles leading to cloud condensation nuclei.