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The redox state of the Primitive Helium Mantle

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Today, ocean island basaltic (OIB) volcanoes with high thermal anomalies and buoyancy fluxes sample parcels of mantle which preserve isotopic signatures of the early Earth. This "primitive" mantle is thought to be relatively unperturbed by the effects of plate tectonics for as long as ~4.5 billion years. Known as the focus zone (FOZO), or the primitive helium mantle (PHEM), it is identified by high $^{3}He/^{4}He$ ratios reflecting abundant stable and non-radiogenic ^{3}He despite ingrowth of ^{4}He through the radioactive decay of ^{235}U, ^{238}U, and ^{232}Th. Some portions of this reservoir also have negative $\mu^{182}W$ and positive $\mu^{142}Nd$ (μ = the deviation of $^{182}W/^{184}W$ and $^{142}Nd/^{144}Nd$ from terrestrial standards)created through the radioactive decay of the short-lived parent isotopes ^{182}Hf ($t_{1/2}$ = ~8.9 million years) and ^{146}Sm ($t_{1/2}$ = ~103 million years). The W and Nd anomalies are indicators of processes which occurred in the first ~50-500 million years of Earth formation. Kama'ehuakanaloa seamount, the youngest Hawaiian Island chain volcano, samples FOZO/PHEM. To determine the oxidation state of this primitive, ancient mantle component, we present $Fe^{3+}/\sum Fe$, and $S^{6+}/\sum S$ ratios (XANES) of pristine glassy pillow basalts erupted at Kama'ehuakanaloa that have $^{3}He/^{4}He$ ratios 20-30 times greater than the same ratio in air and $-\mu^{182}W$.

Kama'ehuakanaloa glasses are recovered between ~950-2400 mbsl, and have 5.18-8.25 wt% MgO and 850-2570 ppm S. These glasses have 0.158-0.206 $Fe^{3+}/\sum Fe$ and 0.00-0.384 $S^{6+}/\sum S$, corresponding to calculated fO_2 from $Fe^{3+}/\sum Fe$ of ΔQFM = +0.12 to +0.60. These $Fe^{3+}/\sum Fe$ overlap with ranges in XANES-determined values in other OIB, including at nearby Hawaiian volcanoes Mauna Kea and Kilauea. After accounting for the effects of low-pressure differentiation, we find that Kama'ehuakanaloa lavas with the highest $^{3}He/^{4}He$ ratios can be produced from modeled primary melts with $Fe^{3+}/\sum Fe$ and fO_2 similar to that of the mantle sources of mid-ocean ridge basalts. This suggests that the fO_2 of FOZO/PHEM is no different than the depleted upper mantle that feeds mid-ocean ridge spreading centers today. Any OIB with elevated fO_2 have not inherited this characteristic from FOZO/PHEM, but more likely through varied proportions of recycled materials subducted into the interior of Earth.