

Oxygen isotopes in hydrothermally altered ocean crust record seawater $\delta^{18}\text{O}$ evolving with continental growth and emergence

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The oxygen isotope composition of seawater underpins interpretations of Earth's climate and tectonic evolution. In a trio of papers characterized by a remarkable union of novel isotopic measurements, geochemical intuition and tectonic foresight [1-3], Karlis Muehlenbachs demonstrated how the oxygen isotope composition of seawater is buffered by fluid-rock interactions during high-temperature hydrothermal alteration of oceanic crust and low-temperature weathering of oceanic and continental crust. As tectonic style is the outward manifestation of Earth's thermal evolution, the oxygen isotope composition of seawater is robust monitor of the secular variation in plate tectonics on Earth over multi-million- to billion-year time scales. In pioneering efforts, Muehlenbachs and colleagues used the oxygen isotope compositions of ophiolites [4-5] to infer an invariant seawater $\delta^{18}\text{O}$ value for much of Earth's history and, by extension, uniformitarian plate tectonic style in state and rate (Figure 1). Here we build on these approaches and, by quantitatively enforcing isotopic and fluid mass-balance over multiple dimensions in altered rocks, we exploit the well-developed framework of geophysical inverse theory to estimate fluid $\delta^{18}\text{O}$ values (i.e., seawater) with an associated uncertainty. Given independent estimates of temperature from fluid inclusions, mineral-specific isotopic compositions, and/or chlorite geothermometry, we applied this approach to a series of hydrothermally altered oceanic-crustal rock sections from 0.2 Ma to 3.2 Ga to produce an expanded record of seawater $\delta^{18}\text{O}$ values through Earth history (Figure 1, [6]). We suggest that seawater $\delta^{18}\text{O}$ was high ($\approx 3\text{‰}$) until the Mesoarchean Era, after which it dropped in two discrete steps of $\approx 2\text{‰}$ each, between ≈ 3 and 2.5 Ga and ≈ 2 and 1.5 Ga, reaching modern, ice-free values of -1‰ between 1.5 and 1 Ga. These steps coincide with peaks in the number of preserved zircons, and may reflect a pulsed onset of widespread, continental crust generation at subduction zones and Wilson cycling.

[1-2] Muehlenbachs and Clayton (1972a, b), *Canadian Journal of Earth Sciences* 9, 172-184 & 471-478

[3] Muehlenbachs and Clayton (1976), *Journal of Geophysical Research* 81, 4365-4369

[4] Holmden and Muehlenbachs, (1993), *Science* 259, 1733-1736

[5] Muehlenbachs et al. (2003), *Geological Society, London*, 218, 401-414

[6] Muehlenbachs (1998), *Chemical Geology* 145 (3-4), 263-

