Geochemical modelling of triple oxygen isotope composition of seawater using high precision $\Delta^{17}O$ analyses of oceanic crust

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The evolution of $\delta^{18}O$ of seawater over geologic time has been repeatedly assessed by studying the ancient rock record. Dispute remains over whether ocean $\delta^{18}O$ is buffered at 0 ± 2‰, and is practically invariable [1], or evolved from very low values like -13‰ to the present value over geologic time [2]. Here we present the first geochemical mass balance model for evolution of both $\delta^{18}O$ and $\delta^{17}O$ of seawater over time.

Modern seawater has $\delta^{18}O$ of 0‰ and $\Delta^{17}O$ of -5ppm [3] ($\Delta^{17}O$ is defined relative to a line with slope 0.5305 and zero intercept [4]), whereas the Earth mantle has $\delta^{18}O = 5.6‰$ and $\Delta^{17}O = -101 \pm 2$ ppm [4]. The oxygen isotope composition of seawater is controlled by high- and low-temperature interactions with oceanic and continental crust. We have analyzed high- and low-T altered oceanic crust samples from the DSDP/ODP Hole 504B and IODP Hole U1383C. Hydrothermally altered dolerites from the sheeted dike complex have $\delta^{18}O = 4.6 \pm 0.1‰$ and $\Delta^{17}O = -49 \pm 7$ ppm, whereas low-T altered basalts from the uppermost crust have $\delta^{18}O = 10.7 \pm 0.4‰$ and $\Delta^{17}O = -130 \pm 6$ppm.

We use these data for box modeling of present and past oxygen fluxes between the different reservoirs. Using modern flux values from [1] and [2] we obtain, within uncertainty, the present-day seawater values for ice-free world: $\delta^{18}O = -1.5‰$ and $\Delta^{17}O = -5$ppm. The model yields $\delta^{18}O = -11‰$ and an increased $\Delta^{17}O = 62$ppm if the high-T alteration is switched off (i.e., much lower high-T to low-T alteration ratio than today; cf. [2]). We will discuss the results with respect to changing $\delta^{18}O$ of ancient chemical sediments [5] and suggest possible reasons for these changes.

[1] Muehlenbachs (1998) *Chem. Geol.* **145**, 263-273. [2] Jaffres et al. (2007) *Earth-Science Rev.* **83**, 83-122. [3] Luz & Barkan (2010) *GCA* **74**, 6276-6286 [4] Pack & Herwartz (2014) *EPSL* **390**, 138-145. [5] Sengupta et al. (2014) *Goldschmidt Conference, abstract* 2248.