



Oxygen three-isotope distributions in terrestrial carbonates, silicates and waters – Insights and inferences from high precision measurements and a ‘mass-independent’ fractionation process

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High precision measurements of oxygen three-isotope ratios in terrestrial silicates, waters and the fractionation of atmospheric O₂ during respiration, have demonstrated that the respective mass-dependent fractionation arrays are characterized by distinctive and reproducible slopes on the logarithmic form of the oxygen three-isotope plot. By re-examining data which demonstrated the generation of a mass-independent isotopic anomaly during carbonate thermal decomposition (under high vacuum conditions to minimize back-reaction), it is shown that – surprisingly – terrestrial carbonates appear to be in accord with the silicates line, rather than that of meteoric waters. Furthermore, the few published high precision measurements of both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in tropospheric CO₂ indicate that the oxygen three-isotope composition of this atmospheric constituent also fits on the carbonates fractionation array.

Small but significant departures from reference fractionation arrays may be indicative of unusual (but generally mass-dependent) processes. For example, terrestrial silicates which recrystallized under extreme P-T conditions ($> 700^\circ\text{C}$ and $\sim 3 \times 10^9$ Pa) plot on a distinctively steeper fractionation line than do other rock-forming silicates. Similarly, recently-published data indicate that the transition from snow firm to deeply

buried ice is also associated with a steeper fractionation line than that which characterizes meteoric waters (including polar precipitation). Several published studies have reported that the oxygen three-isotope relationship in meteoric waters, when characterized at very high levels of accuracy and precision, gives a fractionation array that is slightly offset (^{17}O -enriched) relative the VSMOW reference material. The extent to which this offset (<50 per meg) is a record of humidity conditions in the vapor source region, as has recently been proposed in the literature, or is simply a reflection of the fact that VSMOW is not a natural ocean water (but was prepared by distillation and mixing of different waters), is as yet unknown.