Triple Oxygen Isotope Geochemistry

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Triple oxygen isotope geochemistry debuted in 1973 in work by Clayton's group where it was applied exclusively in the extra-terrestrial realm. In 1983 Thiemens' group expanded its application into terrestrial atmospheric chemistry. In the last several years, the triple oxygen isotope approach has been used to address a growing spectrum of Earth and planetary science problems. One of the most notable recent lines of development is the study of subtle changes in the triple oxygen isotope relationship in otherwise totally mass-dependent processes. With regard to this growing field, we make the following three statements and argue that they are not at all as outrageous as they sound.

1. To clear up a prevailing conceptual confusion, we must sacrifice the beloved Greek symbol λ. The most important parameter in triple oxygen isotope studies is the mass exponent, symbolized as θ, β, γ, or most commonly as λ. There is also this phenomenological correlation in $\delta'^{17}O$-$\delta'^{18}O$ space where points lining up with a slope confusingly also symbolized as θ, γ, or commonly λ. Further confusing things, the subtle deviation of the $\delta'^{17}O$ value from an expected $\delta'^{17}O$ is evaluated, the $\Delta'^{17}O$ is measured using a slope value of θ, C, or λ. We advocate that only three symbols are necessary, θ, S, and C. And eliminating the use of the most confused symbol, λ, will facilitate a universal reference frame and dissolve confusions.

2. The α_{eq} values determined using the three-isotope method may be all incorrect. A critical assumption for the three-isotope method is that the evolution trajectory to an equilibrium point in $\delta^{17}O$-$\delta^{18}O$ space is strictly a straight line. This assumption is fundamentally wrong (see an abstract in this volume by Cao *et al* for details). One additional yet independent requirement is that the secondary fractionation line has a slope value of 0.52 or other predefined value, a value that cannot be known a priori before α_{eq} is determined.

3. It is the triple oxygen isotopes not clumped isotopes that may ultimately resolve the issue of warm or cool Archean oceans. While clumped isotopes' anticipated geothermometer potential for the distant past has faded away, the triple-oxygen geothermometer, based on different θ-α temperature sensitivity in different mineral-water systems, may bring new hope to one of the classical geological problems: Was Archean seawater as warm as 70°C or was the early seawater $\delta^{18}O$ as low as -10‰?

Triple isotope geochemistry and clumped isotope geochemistry have their own strength and weakness, but both share their true potentials in the exploration of geochemical kinetics.