Tracing the triple isotope composition of air by high-precision analyses of meteorites, rocks and fossils

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High-precision measurements of the triple oxygen isotope ratios ($\delta^{18}$O and $\Delta^{17}$O) in terrestrial waters, rocks and minerals opened new and exciting applications in the field of stable oxygen isotope geochemistry. After giving a short overview over measurement techniques and various applications, it will be emphasized on tracing the atmospheric composition in rocks and minerals.

Atmospheric samples from ice cores only date back ~1 Myrs. To obtain information about the atmosphere for the 99.98% of Earth history that is not covered by ice cores, we need to look for rocks. The oxygen isotope composition of the atmosphere younger than 2.4 Gyrs is dominated by molecular oxygen ($O_2$). Molecular $O_2$ is one of few components on Earth that has a mass-independent oxygen isotope signature. The anomaly in $^{17}$O provides information about the presence of an ozone layer, the global biosphere primary production, or the atmospheric CO$_2$ mixing ratio. A few rocks and fossils provide information about the $^{17}$O anomaly of air $O_2$. Sedimentary sulfates may form by precipitation from SO$_4^{2-}$ that formed by subaerial oxidation of pyrite. In that process, a part of the oxygen in the sulfate originates from air $O_2$. Mobilizing of the sulfate oxygen can carry this anomaly over to other minerals like Fe oxides. The isotope signature of fossil tooth enamel also provides information about the atmospheric composition. Air $O_2$ is inhaled and used to oxidize carbohydrates and fat to (mainly) CO$_2$ and H$_2$O, which equilibrate with body water. Tooth apatite then precipitates from body water and inherits an anomaly in $^{17}$O from the inhaled air $O_2$. Manganese oxides are known to form by oxidation of Mn under participation of $O_2$. If the isotope composition of dissolved $O_2$ in the aqueous environment, in which the manganese oxides form is controlled by air, manganese oxides can be used to trace the composition of air $O_2$. It has been shown that some meteorite impact melts (tektites) have exchanged with ambient air $O_2$. As result of that exchange, they carry a $^{17}$O anomaly that may be used to trace the composition of air $O_2$. Also, I-type cosmic spherules have been shown to be indicators for the isotope anomaly of air $O_2$. These spherules form by aerial oxidation of asteroidal metallic Fe,Ni particles and thus can carry the anomaly of air $O_2$. Such recent discoveries open insights into the composition of the Earth atmosphere beyond the 1 Myrs limit from the ice core record.