Title: Meteorite Classification Using Triple Oxygen Isotopes

Authors: Riley Havel [1,2] (riley_havel@brown.edu; https://orcid.org/0000-0002-7161-9236) and
Daniel E. Ibarra [1,2] (daniel_ibarra@brown.edu; https://orcid.org/0000-0002-9980-4599)

Affiliations: 1 Department of Earth, Environmental and Planetary Sciences, Brown University, Providence, USA;
2 Institute at Brown for Environment and Society, Brown University, Providence, USA

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For decades, measurements of all three isotopes of oxygen have been made in a handful of specialized laboratories around the world. These measurements either confirm meteorite classifications or prevent misclassification of terrestrial materials. Isotope geochemists making these measurements, in collaboration with meteorite enthusiasts and scientists, frequently receive questions regarding best practices for sample preparation and data interpretation. In this *Toolkit*, we provide guidance for those interested in soliciting oxygen isotope measurements of suspected meteorite samples with the goal of expanding and diversifying meteorite collections, which enable studies at the frontier of planetary science.

Meteorite Classification

Meteorites are classified according to their petrology, mineralogical compositions, and triple oxygen isotope compositions[1]. It is always recommended that petrological and mineralogical analyses of suspected meteorites be conducted prior to soliciting oxygen isotope measurements, as they more often than not clearly distinguish between terrestrial and extraterrestrial materials and reliably classify meteorites. However, in instances where those analyses are not able to accomplish the latter, oxygen isotopes serve as a secondary classification tool.

Triple Oxygen Isotopes

Analytical Methods

Oxygen is a major element with three isotopes: ^{16}O, ^{17}O, and ^{18}O, making up approximately half the mass of silicate-rich meteorites. To make oxygen isotope measurements using conventional[2] or laser fluorination techniques[3], samples are heated in the presence of a highly reactive fluorine compound (typically BrF_5 or F_2). As the reaction proceeds, oxygen is released from minerals and forms O_2. Triple oxygen isotope compositions of the O_2 gas are then determined by measuring mass-to-charge ratios of 32, 33, and 34 produced by samples and standard reference materials using dual inlet gas source isotope ratio mass spectrometry (IRMS)[3].

Notation

Variations in the ratios of ^{17}O and ^{18}O to ^{16}O in samples and standard reference materials, which are used to quantify isotopic variations in planetary materials, are on the order of parts per thousand and reported in per mil (‰) using δ- notation (Eq. 1)[4]. For studies which take advantage of high precision measurements, a linearized version of δ- notation, referred to as *prime* notation, is used[5,6]. In a plot of $\delta^{18}O$ versus $\delta^{17}O$, isotopically heavy materials *(i.e.*, those with higher relative abundances of ^{17}O or ^{18}O) plot in the upper right region and isotopically light materials in the lower left (Fig. 1). These terms can also be used to describe the composition of materials in relation to one another (*e.g.*, CO chondrites are isotopically light compared to CI chondrites).

Deviations from the Terrestrial Fractionation Line (TFL), a line on which most terrestrial materials plot, are quantified using $\Delta^{17}O$ values. The $\Delta^{17}O$ value depends on $\delta^{17}O$, $\delta^{18}O$, and the slope, λ, which varies for different isotope fractionation processes (Eq. 2). One must be mindful of the λ used to calculate $\Delta^{17}O$ when making comparisons to literature data; 0.52, 0.5247, or 0.528 are typically used in planetary science[3,7,8]. In a plot of $\Delta^{17}O$ versus $\delta^{18}O$, terrestrial rocks typically have $\Delta^{17}O$ values from approximately -0.4 to 0.1‰[9], whereas meteorites span a wider range from approximately -6 to 3‰[1,3].

$$\delta^{x}O = \left(\frac{(^{x}O/^{16}O)_{sample}}{(^{x}O/^{16}O)_{reference}} - 1\right) \times 10^{3} \ (x=17,18;\ ‰)\ \text{(Eq. 1)}$$

$$\Delta^{17}O = \delta^{17}O - \lambda \times \delta^{18}O\ (‰)\ \text{(Eq. 2)}$$

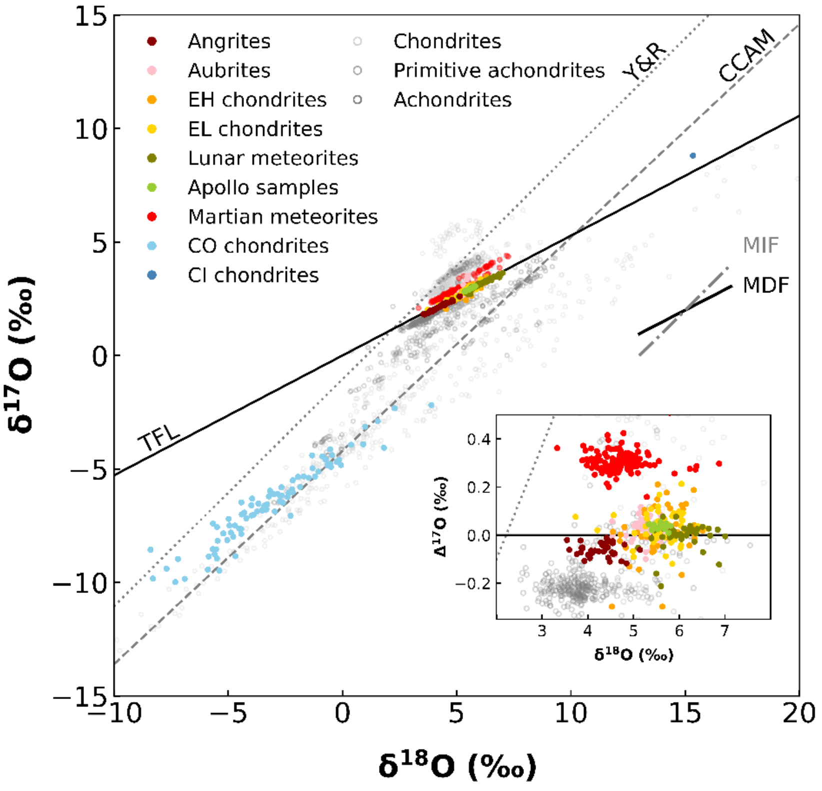

Figure 1. Triple oxygen isotope compositions of bulk meteorites. All data besides those for Apollo samples[10] were compiled from the Meteoritical Bulletin; $\Delta^{17}O$ values plotted in the inset were recalculated using λ=0.52. The Terrestrial Fractionation Line (TFL), Carbonaceous Chondrite Anhydrous Mineral Line (CCAM), and the Young & Russell Line (Y&R) are shown[1,3,8,11]. Example fractionation lines resulting from mass-dependent fractionation (MDF) and mass-independent fractionation (MIF) are shown.

Isotope Fractionation and Mixing

When isotopes in a system evolve, they either do so in a way that depends on the differences in their masses, mass-dependent fractionation, or in a way that does not, mass-independent fractionation. Evidence of mass-dependent fractionation is observed in meteorites whose parent body fractionation lines are approximately parallel to the TFL[7,8]. Mass-dependent fractionation is caused by processes such as melting, differentiation, or alteration[8]. Evidence of mass-independent fractionation and isotopic mixing is also observed in many meteorites as mixing lines between isotopically light and heavy endmembers along slopes not parallel to the TFL (*e.g.*, those that plot along slopes of ~1 in a plot of $\delta^{18}O$ versus $\delta^{17}O$). Mass-independent fractionation is caused by processes like photochemistry[11]. In some cases, when meteorites have experienced significant terrestrial weathering, their original isotopic composition can be difficult to determine as mixing with terrestrial weathering products, which plot near the TFL, can shift compositions to higher or lower $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ values.

Sample Preparation

There are several sample preparation choices to be made in advance of making triple oxygen isotope measurements. Though each laboratory may have a preferred sample preparation procedure, it is important that those soliciting the data are aware of how these choices might impact data interpretation. Here, we aim to demystify these options.

Bulk material or mineral separates? Chips or powders? How do I choose?

Meteorites are classified using measurements of bulk material to best represent the average composition of the meteorite parent body. Mineral separates, however, might be better suited to address specific science questions. Though sample mass requirements vary across laboratories, each replicate measurement requires ~0.5-3.5 mg of silicate-rich material[3,6]. Measurements on bulk chips are prone to sampling mineralogically, and therefore isotopically, heterogenous material. Consequently, measurements on chips might not be representative of the bulk meteorite composition. Conversely, measurements on bulk powders are more likely to be representative of bulk meteorite compositions, as they can sample much larger masses. Homogenizing large chips to produce powders also simplifies the process of removing metal chunks from metal-rich meteorites. If metal chunks are not separated from the silicate fraction, the amount of oxygen-rich material weighed for a measurement will not be a reliable indicator of oxygen content, which can result in low apparent yields and reduce measurement precision. Moreover, when measuring hydrated meteorites like CM chondrites, powders can be mixed efficiently with LiF to combat the reactive nature of hydrous phases during laser fluorination - the primary modern analytical method for these measurements.

Leaching? Does it really make a difference?

Though leaching in dilute hydrochloric acid (HCl) or ethanolamine thioglycollate (EATG) solutions has been used with some regularity in an effort to remove terrestrial weathering products from meteorites, it has recently been shown that these treatments likely also remove indigenous oxygen, and therefore, compromise how accurately a measurement represents the bulk meteorite[3]. Carbonaceous chondrites are particularly susceptible to the removal of indigenous oxygen by leaching procedures. Differences in the oxygen isotope compositions of untreated and leached sample replicates can be as large as ~5‰ in $\delta^{18}O$ and ~1‰ in $\Delta^{17}O$[3]. In most cases, EATG leaching shifts oxygen isotope compositions more than HCl, illustrating a potential range of compositions. Oftentimes, tielines drawn between untreated and leached replicates have similar slopes to parent body fractionation or mixing lines, and therefore have the potential to help address specific science questions. If one does choose to leach samples, treatments require 10-20 mg of powdered material. It is recommended that untreated and leached replicates always be measured in tandem. Notably, even if the effects of terrestrial weathering are substantial, they are unlikely to influence meteorite classification when using triple oxygen isotope compositions as a secondary tool.

Data Interpretation

What can Δ^{17}O actually tell us?

The Δ^{17}O parameter has great utility. For most parent bodies where oxygen has undergone mass-dependent fractionation, Δ^{17}O values are consistent across the meteorites they produce and, in combination with δ^{18}O values, can be used to classify meteorites. This is observed in samples from planetary bodies like Earth, Mars, and the Moon (Fig. 1 inset). The utility of the Δ^{17}O parameter differs for chondrites and primitive achondrites, where meteorites of the same classification might have a wide range of Δ^{17}O values that are controlled by variable abundances of isotopically light or heavy minerals whose isotope compositions are inherited from mass-independent fractionation processes (Fig. 1). As such, the Δ^{17}O parameter can be used to estimate relative abundances of minerals in a sample or constrain alteration fluid compositions[3].

Common Misconceptions

Terrestrial materials commonly confused for meteorites (*e.g.*, slag, rocks with black rinds mistaken for fusion crust, high density and magnetic materials) and several meteorite groups (*e.g.*, lunar materials, angrites, aubrites, and enstatite chondrites) have Δ^{17}O values very close to, but not exactly, 0. Unfortunately, these extraterrestrial materials also have a narrow range of δ^{18}O values which overlap fields defined by various terrestrial materials[9]. Therefore, if a sample has a Δ^{17}O value that is close to, but not exactly 0, it does not mean that it is a meteorite, nor does it necessarily mean that it is not one. The typical precision of Δ^{17}O measurements is <0.01‰[3] but in many cases, is not sufficient for differentiating between terrestrial materials and meteorite groups that have similar Δ^{17}O values.

Because of these nuances and limitations, suspected meteorite samples that have not undergone the appropriate petrological and mineralogical characterization are aspirationally, and commonly, misinterpreted to be meteorites based solely on their non-zero Δ^{17}O values. As such, the Δ^{17}O parameter cannot be used independently of δ^{18}O values, petrology, or mineralogy to determine whether a sample is a meteorite. To state it plainly, petrological and mineralogical characterization are essential for meteorite classification as even triple oxygen isotope compositions can be inconclusive when trying to parse terrestrial materials from meteorites.

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