Standardizing high precision Δ₁⁷O data from silicate rocks and minerals

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The Δ₁⁷O value of O₂ gas (the analyte for nearly all oxygen triple isotope measurements) can currently be measured to a precision of about 6 ppm; significantly better than the precision of the corresponding δ₁⁷O and δ₁⁸O data. However, reporting Δ₁⁷O measurements of silicate rocks to this degree of accuracy, relative to (for example) the VSMOW-SLAP line on the ln(1 + δ₁⁷O) versus ln(1 + δ₁⁸O) plot, poses practical challenges. Regardless of the reference line assigned, Δ₁⁷O values are still inextricably linked to the δ₁⁷O and δ₁⁸O calibration of the ‘working standard’ O₂ on the VSMOW–SLAP scale. Yet few laboratories have the capability to make such measurements on waters and on silicates. Even when direct calibration to VSMOW and SLAP is possible, there is not yet consensus on the Δ₁⁷O values of widely used silicate standards such as UWG-2 garnet or San Carlos olivine, when reported to a common reference line.

Fluorination of silicate rocks and minerals, to produce O₂ for isotope ratio measurements, requires a different procedure from that used for the fluorination of waters. Thus, there is the possibility of systematic errors being introduced by using a water reference material for reporting δ₁⁷O and δ₁⁸O data of silicates. Furthermore, fractionation arrays of natural silicates on the three-isotope plot are generally offset from VSMOW, which introduces an additional complication. To eliminate such potential sources of error, some authors have chosen to report δ₁⁷O and δ₁⁸O data relative to San Carlos olivine (as representative of Earth’s mantle) rather than to VSMOW, in conjunction with a reference line of assigned slope, for characterizing Δ₁⁷O values. However, a two-point scale, such as VSMOW–SLAP for waters, is preferable to a single point calibration.

We have therefore characterized Δ₁⁷O values (and with inter-laboratory comparison) of two silicates spanning a greater δ₁⁸O range than VSMOW–SLAP and suggest that these materials may be used for accurate determinations of silicate Δ₁⁷O values. Our high-δ₁⁸O standard is a flint, designated SKFS, with δ₁⁸O = 33.93 ± 0.08 ‰ (standard error) and Δ₁⁷O = −69 ± 3 ppm relative to the VSMOW-SLAP reference line. This material can therefore be used to calibrate the position of an assigned reference line such that it passes through VSMOW. Alternatively, in combination with our low-δ₁⁸O silicate standard, designated as KRS (δ₁⁸O = −25.20 ± 0.03, Δ₁⁷O = −114 ± 2 ppm relative to the VSMOW-SLAP reference line), an empirical two-point silicate reference line may be defined from high precision δ₁⁷O and δ₁⁸O measurements of these proposed standards. Δ₁⁷O data of...
silicate rock and mineral samples reported relative to this reference line are independent of whether the δ¹⁷O and δ¹⁸O measurements are reported relative to VSMOW or to the 'working standard' O₂, of any isotopic composition. This confers significant advantages for inter-laboratory comparisons.