A practical guide to clumped isotope geochemistry

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Clumped isotope geochemistry examines the spatial organization of rare isotopes within molecules and structural units of minerals. It principally focuses on the ordering, or 'clumping' of rare isotopes into bonds with or near each other rather than with isotopically normal atoms. Measurements of isotopic clumping encounter unique problems and limitations. Here, I discuss and illustrate the practical sides of this field, by way of a set of pithy aphorisms that should be followed when making such measurements by gas source isotope ratio mass spectrometry.

(1) *Cleanliness is next to godliness*: Abundances of clumped isotopic species (e.g., $^{13}C^{18}O^{16}O$) are influenced by isobaric interferences from contaminants (e.g., $^{12}C^{35}Cl$) making up as little as 1 ppb of the sample. This calls for aggressive sample purification procedures, often tailored to each sample type.

(2) *Water is root of all evil*: Even trace amounts of water can cause 'exchangeable' compounds (e.g., CO_2) to undergo isotopic re-ordering, even in the absence of measurable changes in bulk isotopic composition. This calls for strenuous efforts to dry samples, gas handling lines, etc.

(3) *Location, location, location*: The information content of clumped isotope geochemistry stems from isotopic ordering in specific bonds. Therefore, analytes must be extracted from samples with negligible, or minimal and controlled, extents of isotopic 'scrambling'. This generally rules out high-temperature processes and many heterogenous reactions.

(4) *You are only as good as your reference frame*: Clumped isotope measurements must be standardized against materials of known composition *and* known state of isotopic ordering, and must be very closely matched in composition to unknowns to avoid corrections for instrumental non-linearity. This calls for specialized approaches to standardization.

(5) *The devil is in the details*: The dynamic range of clumped isotope effects is less than 1 ‰ in most cases. Thus, this is a game that is only interesting when data have precision of hundredths of per mil.

(6) *Size matters*: Analytical precision is limited by exceptionally small relative intensities of ion beams for clumped isotopic species (ca. 10^{-5}x the major beam for most gases). Therefore, useful data generally require unusually large samples (ca. 10's or 100's of µmoles).

(7) *Time is on your side*: For the same reasons one strives for large samples, it is important to maximize counting times—generally an hour or more of analysis per gas is a minimum.