

An innovative paleotemperature proxy: clumped isotopes

Introduction

Clumped isotopes are used as paleotemperature proxy that can be measured on carbonates. It is a new and useful alternative to the commonly used $\delta^{18}\text{O}$ paleotemperature proxy, as measured clumped isotope values are independent from the isotopic composition of the waters it grew from or in most cases from biotic effects (Eiler, 2011).

Theory of clumped isotopes

Clumped isotopes, in this sense, are multiply substituted isotopologues of CO_2 molecules. Over 98% of all CO_2 molecules consist of one ^{12}C and two ^{16}O atoms, that together form a CO_2 molecule of mass 44. Molecules consisting of the same kind of atoms but with different isotopic composition are called isotopologues. For example, a CO_2 molecule consisting of one ^{13}C , one ^{16}O , and one ^{18}O forms an isotopologue of CO_2 of mass 47. This, in addition, is a multiply substituted isotopologue because two of the atoms (the ^{13}C and the ^{18}O) are heavier than in the most abundant molecule. Multiply substituted isotopologues form a more stable molecule than their lighter counterparts, because bonds between two heavy isotopes are slower vibrating and lower in energy than equivalent bonds between a heavy and a light isotope. Therefore, clumping is promoted by the thermodynamic driving force. The excess of CO_2 isotopologues of mass 47 compared to the stochastic distribution (all the stable isotopes are randomly distributed among all possible isotopologues) is dependent on the temperature (Eiler, 2007).

During clumped isotope measurements CO_2 gas derived from acid digestion of carbonates is analyzed. The excess of the mass 47 isotopologue is measured in the sample compared to a hypothetical reference with the same isotopic composition but with stochastic distribution. In other words, clumped isotope thermometry measures if rare isotopes clump together more or less than they would by random chance. Values of clumped isotope measurements are reported in per mil (‰), and noted with Δ_{47} . The higher the temperature, the less is the preference of heavy isotopes of clumping together, therefore the lower the Δ_{47} value gets. (Eiler & Schauble, 2004; Wang et al., 2004).

Clumped isotopes in practice

Clumped isotope measurements are very challenging and only a few laboratories can provide meaningful results. There are two factors that impact these measurements the most. One of them is that the isotopologue of mass 47 is very rare, only 45 ppm of CO_2 molecules consist of one ^{13}C , one ^{16}O , and one ^{18}O . For that reason, an advanced gas mass spectrometer equipped with an additional high-ohmic m/z 47 Faraday cup (besides the common m/z 44, 45 and 46 cups) is needed to measure geological samples that are usually small. Water is the source of the second difficulty of measuring clumped isotopes. Any minuscule trace amount of H_2O can

re-equilibrate the CO₂ gas or reaction intermediates. It is critical that the sample gas never meet with water.

In the lab at the Goethe-Universität the measurements are made on a ThermoFischer MAT 253 gas source mass spectrometer. Beforehand, any sample gas is purified on a self constructed, fully automated extraction line (Hofmann's Auto Line, HAL). Four milligrams of carbonate powder are needed for one measurement. At the start of the purification process, an auto sampler drops the silver capsule, containing the carbonate powder into 90°C warm, 105% phosphoric acid. An excess of phosphoric acid in the reaction vessel is needed so that H₂O molecules generated by the acid digestion reaction are immediately captured by the excess amounts of P₂O₅, so that no re-equilibration of the carbonate derived CO₂ occurs. The reaction vessel is connected to a glass U-trap submerged in liquid nitrogen, so that CO₂ gas can freeze out immediately. Water is frozen out in an intermediate U-trap cooled to -80°C. After the reaction is finished, the U-trap containing the solid CO₂ is submerged in -80°C ethanol, and an other U-trap submerges into the liquid nitrogen. This way the CO₂ sublimates and freezes out in the second trap, while the water stays frozen in the first trap. The process of CO₂ sublimation at -80°C is then repeated three times. During the purification process the CO₂ gas passes through a gas chromatograph where hydrocarbons and other contaminants are filtered out. After the end of the extraction process, the CO₂ gas enters the mass spectrometer, where it is analyzed alternately with a reference gas with known isotopic composition. One analysis consists of 11 acquisitions, each made up of 10 cycles and one pre measurement of the reference gas. In each cycle the peak intensities are measured for mass 44 through mass 49 for both the sample and the reference gas. From these data later the Δ_{47} value can be computed.

The clumped isotope measurements are prone to synthetic and analytical errors that have to be corrected. The 44 m/z ion beam in the mass spectrometer creates a negative background on the other collectors (Faraday cups). In the laboratory at the Goethe-Universität the 'pressure baseline correction' is done by measuring the negative background on m/z 49 (Bernasconi et al., 2013; Fiebig et al., 2016). For background correction quality control and for determining the degree of scale compression, reference gases with distinct isotopic compositions are equilibrated at 25°C and 1000°C temperatures and measured to create equilibrated gas lines. Additional corrections include the correction for fractionation during the acid digestion process and converting the Δ_{47} values to a standard reference frame (Dennis et al. 2011).

Clumped isotope measurements on brachiopods

Only a few clumped isotope studies have been made on modern brachiopods. Henkes et al. (2013) used modern brachiopods, collected from their natural environment to create a clumped isotope calibration (temperature to Δ_{47} relationship) for brachiopod calcites. Came et al. (2014) also conducted similar studies on brachiopods but they digested the carbonates in the phosphoric acid in 25°C instead of 90°C, therefore their calibration slope was steeper than of the previous study. Wacker et al. (2014), like Henkes et al. (2013) reacting at 90°C,

also used brachiopods, among other calcium carbonates, for their calibration study, and confirmed the $\Delta_{47}-1/T^2$ relationship obtained by Henkes et al. (2013).

Finnegan et al. (2011) studied Late Ordovician-Early Silurian carbonates (Brachiopods, Bryozoans, Corals, and Trilobites). Their results indicate a cooling of $\sim 5^\circ\text{C}$ during the Hirnantian and furthermore they made implications that there may not be a linear relationship between tropical ocean temperatures and continental ice volumes. Wacker (2014, PhD dissertation) studied Silurian brachiopods collected in Gotland, Sweden. SEM analyses revealed that samples were partly recrystallized. In consequence, Δ_{47} measurements yielded high temperatures. Cummins et al. (2014) also analyzed Silurian Brachiopods, which indicated warm ($33\pm 7^\circ\text{C}$) tropical temperatures. More recently Cusack et al. (2016) looked for biological effects in brachiopod shells using clumped isotope measurements.

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