Paleotemperature reconstruction using isotopic variations in speleothem fluid inclusion water

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Long-term records of paleotemperature are important in assessing how the global environment responds to changes in insolation and orbital parameters. The high precision Vostok temperature record extends over many glacial cycles, but is not absolutely dated and may not be applicable to continental climate change in mid- to low latitudes. The sea surface temperature records that are derived from trace element variations in foraminifera are highly buffered by the large oceanic reservoir and will not capture variability and sensitivity present on the continents. Methods based on ecological indicators give some indication of temperature fluctuation in the late Pleistocene, but often cannot be precisely dated.

Speleothems are ideal as paleoclimate proxies because they are well dated and form in caves that are protected from environmental factors that disturb other terrestrial proxies. However, calculation of temperature change from oxygen isotopic variation in speleothem calcite is complicated by the multiplicity of factors controlling $\delta^{18}O(ct)$. Paleotemperatures can be directly determined by using fluid inclusion water in speleothem calcite (c. 0.1 wt %) which is a sample of the drip water from which the speleothems grew. We measure δD and use the meteoric water line relationship $\delta D = 8\ \delta^{18}O + \delta D_o$, to eliminate the effects of post-depositional oxygen isotope exchange between calcite and fluid inclusions. Temperature of deposition is calculated from the equilibrium fractionation equation for calcite and water.

We extract water by crushing 0.5 - 1.5 g blocks of calcite, representing less than 1,000 years of growth. Agreement between coeval samples ranges from ± 1 to 5‰. The volume of water extracted from each sample ranges from trace amounts to 0.3 wt %. Holocene samples from California give calculated temperatures consistent with or warmer than modern site temperatures. Assuming δD_o=10‰, some Pleistocene samples from mid-continent sites give temperatures < 0 °C. Following Jouzel and Merlivat (1982), assuming δD_o = 4 ‰, we obtain $T \geq 0$°C for all samples. Two coeval speleothems from the Black Hills in South Dakota consistently record temperatures lower than modern for the Wisconsin glacial period.

References

Jouzel J., Merlivat L., and Lorius C. 1982. Nature 299:688-691

Hydrogen isotopic compositions of petroleum hydrocarbons

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To examine the processes which influence D/H ratios of petroleum, we measured δD of bulk oils, saturated, aromatic, and polar oil fractions, individual *n*-alkanes, formation waters and kerogen from source rocks. These data provide new insights into the H-isotopic variability of petroleum.

Relationships between compound classes. Comparison of 80 bulk oils and fractions indicates mean δD differences (±1σ) between fractions of: oil-saturate = 4.6 ± 8‰, oil-aromatic = –8 ± 10‰, and oil-polar = 0.4 ± 20‰. Although the polar fraction δD was similar to bulk oil on average, differences of up to 60‰ existed in some samples. Aromatic and saturate fractions should have different values so our data suggest that primary D/H ratios are not well-preserved in the aromatic fraction. Values of δD for bulk oils, saturate fractions, and weighted-mean values for individual *n*-alkanes were all typically within 10‰. In rare cases the saturate fraction was depleted in D by more than 20‰ relative to the *n*-alkanes, perhaps due to the abundance of isoprenoids.

Relationships between *n*-alkanes. *n*-Alkanes from a single oil can vary quite significantly in δD. The span of δD values covered by *n*-alkanes from a single oil ranged from 14 to 60‰. Moreover, some oils thought to derive from similar sources, and with similar alkane-abundance patterns, exhibited markedly different *n*-alkane isotopic patterns. For examples, two similar Cretaceous oils have *n*-alkane δD values ranging from –138 (n-C_9) to –109‰ (n-C_{27}) in one, and from –142 (n-C_9) to –147‰ (n-C_{25}) in the other. Values of δD typically increase with carbon number, but in some cases a maximum at n-C_{19} to C_{21} is observed. These patterns do not appear to be the result of simple mixing between two end members, and may be a direct result of oil generation.

Relationships to H sources. Non-exchangeable hydrogen in source rock kerogen is enriched in D relative to bulk oils and *n*-alkanes by 0 to 30‰. δD values of kerogens and oils are strongly correlated, so a large proportion of the D/H ratio of oils must be inherited from the source organic material. All of the studied oils have terrestrial source rocks, so the isotopic relationship between kerogen and environmental water is not yet clear. However, a series of 45 oils show no correlation between formation water and bulk oil δD values, indicating that exchange with reservoir water does not exert significant control over oil D/H ratios. Aromatic fractions and formation waters are slightly correlated (R^2 = 0.09).