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Data Analysis 1: Alkenone Paleothermometry - Uk'37

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JoVE Science Education Series: Earth Science

Title: Data Analysis 1: Alkenone Paleothermometry – $U^{k'}_{37}$

Throughout this series of videos, natural samples were extracted and purified in search of organic compounds, called biomarkers, that can relate information on climates and environments of the past. One of the samples analyzed was sediment. Sediments accumulate over geologic time in basins, depressions in the Earth into which sediment flows through the action of fluid (water or air), movement, and gravity. Two main types of basins exist, marine (oceans and seas) and lacustrine (lakes). As one might guess, very different types of life live in these settings, driven in large part by the difference in salinity between them. Over the last few decades, organic geochemists discovered a toolbox of biomarker proxies, or compounds that can be used to describe climate or environment, some of which work in marine environments and some of which work in lacustrine. We turn our attention here to the marine realm and alkenone paleothermometry using the $U^{k'}_{37}$ sea surface temperature proxy.

The most well-established and widely applied open-ocean biomarker sea surface temperature (SST) proxy is $U^{k'}_{37}$.

$$U^{k'}_{37} = (C37{:}2) / (C37{:}2 + C37{:}3)$$ (see HERBERT, 2003 for a review)

The index is based on the ratio of two polyunsaturated long-chain alkyl ketones, called alkenones, produced by some classes of haptophyte algae (CONTE *et al.*, 1994; VOLKMAN *et al.*, 1995). Culture (PRAHL *et al.*, 1988; PRAHL and WAKEHAM, 1987) and core-top sediment (MÜLLER *et al.*, 1998) calibration studies led to the development of the $U^{k'}_{37}$ Index as a quantitative SST proxy. Amazingly, the culture-based calibration of Prahl *et al.* (1988):

$$U^{k'}_{37} = 0.034(SST) + 0.039,$$

And the core-top calibration of Müller *et al.* (1998),

$$U^{k'}_{37} = 0.033(SST) + 0.044,$$

are statistically identical.

Reconstructed $U^{k'}_{37}$ temperatures correlate best with mean annual SST for a variety of climate and haptophyte production regimes in the global ocean (CONTE *et al.*, 2006). Alkenones are detected in marine sediment cores of early Eocene to modern age (MARLOWE *et al.*, 1990), and in exposed outcrops of uplifted marine sediment (CLEAVELAND and HERBERT, 2009) suggesting they are very stable over geologic time, and thus useful as a paleoclimate tool. $U^{k'}_{37}$ has been used to document paleo sea surface temperature changes at decadal (Sicre *et al.*, 2008) to orbital (Brassell *et al.*, 1986; Herbert *et al.*, 2010) timescales and are therefore very versatile.

In the open ocean, the coccolithophores *Emiliania huxleyi* and *Gephyrocapsa oceanica* are responsible for most alkenone production. It is not yet known why these haptophytes alter the unsaturation ratio of alkenones based on growth temperature. It was initially thought that alkenones were components of haptophyte cell walls and that their unsaturation was adjusted in order to keep the membrane fluid, much like saturated fats are solid at room temperature, while unsaturated fats are fluid. However, experiments aimed at this question found that instead of being associated with the cell membranes, alkenones were associated with energy storage structures inside the cell. Thus, their use inside the cell remains an open question.

Recently, alkenones have been found in lacustrine environments. However, their utility has so far been limited. Different alkenone producers than those in the marine realm dwell in lakes and thus the calibration between water temperature and unsaturation ($U^{k'}_{37}$) is different. Moreover, this calibration is different between lakes, making the creation of a 'global' calibration unlikely. Unfortunately, the creation of local calibrations is expensive and time consuming and so the future for $U^{k'}_{37}$ in lakes is also currently limited.

Alkenones are usually extracted from marine sediments. Very often the same organisms that produce alkenones produce fatty acid methyl esters of those alkenones called alkenoates. These compounds co-elute with the alkenones on a gas chromatograph and complicate their quantification. Therefore, these extracts will often undergo a saponification to remove alkenoates. Because the saponification produces carboxylic acids that are not gas chromatograph amenable, a silica gel column must be performed after the saponification to remove the carboxylic acids from the extract. The alkenones come out in the middle polarity ketone fraction that elutes in dichloromethane while the acids are left on the column. Lastly, in extreme cases, such as in sediments acquired from highly polluted areas, like estuaries near industrial centers, a urea adduction may also be required to remove unknown compounds that coelute with the alkenones on the gas chromatograph.

Once the total lipid extract is purified, the extracted and purified sample is run on a gas chromatograph coupled to a flame ionizing detector. The relative concentration of the two alkenones is determined by obtaining the area under the curve for each of the compounds on computer software designed for just this purpose (such as Agilent Chemstation). These areas are then put into the $U^{k'}_{37}$ ratio equation shown above to get a $U^{k'}_{37}$ value that ranges between 0 and 1. These $U^{k'}_{37}$ values are then mapped to sea surface temperature value using a calibration such as those described above.

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