Silicon and oxygen isotopes: The maturation of lacustrine diatoms

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Oxygen and silicon isotope values of recent (antemortem, post-mortem) and Pleistocene lacustrine diatoms from the Valles Caldera (New Mexico) provide the opportunity to study 420 ka of opal maturation at the same location.

The $\delta^{18}O$ (SMOW) values, obtained by laser-fluorination [1], indicate significant reequilibration, with an increase in $\delta^{18}O$ value from <22‰ to >29‰ within 0.5 yrs after death. This is consistent with growth under oxygen isotopic disequilibrium followed by post-mortem equilibration with lake water. While no structural changes go with the alteration, differences in element compositions also imply exchange between water and diatom. Wholesale reequilibration of $\delta^{18}O$ ratios requires Si-O bond breaking. We measured the $\delta^{30}Si$ values of the same diatoms to see if Si also undergoes isotope exchange. $\delta^{30}Si$ values were obtained by MC-ICPMS [2].

The $\delta^{30}Si$ values (NBS-28) of all ante-mortem and post-mortem diatoms range from -1.0 to -2.6‰, and -0.4 to -1.9‰, respectively. A specific subset of diatoms was collected in spring, and the same population sampled 0.5 and 1.5 years post-mortem. The $\delta^{30}Si$ values increase from -2.4 to -1.9 to -0.4‰, indicating a possible maturation trend. The large ante-mortem range can also be explained by variable relative inputs from processes affecting the $\delta^{30}Si$ values of lake water (diatom [3] and clay [4] formation removes ^{28}Si from water).

Middle Pleistocene (interglacial) lacustrine diatoms from the Valles Caldera have even higher $\delta^{30}Si$ values of +0.3 to +0.7‰. The trend from low to high $\delta^{30}Si$ ratios mimics the $\delta^{18}O$ changes (at a smaller scale). Interglacials correlate with more positive $\delta^{30}Si$ values in marine diatoms [5]. We infer that Pleistocene Valles Caldera diatoms had higher initial $\delta^{30}Si$ values than modern ones, and additionally that exchange processes during burial caused further opal maturation.

The combined silicon and oxygen isotope study of such a system improves our understanding of the potential for using Si isotopes as paleoclimate proxies.

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Silicon and oxygen isotope values of cherts and their precursors

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We measured $\delta^{30}Si$ and $\delta^{18}O$ ratios in two sets of recent cherts and their precursors in order to evaluate the use of cherts as proxies for environmental conditions at their formation, and to constrain diagenetic transitions. This work has implications for models for Archean cherts formation.

In a handsample from the Miocene Monterey Formation [1, 2], both cristobalitic chert and biogenic, marine opal-A precursor are present. Magadi chert is modern, inorganic, quartzose chert formed from chemically precipitated magadiite [3, 4]. Both precursor-to-chert transitions are due to dissolution-precipitation processes. Monterey chertification is due to later diagenetic water [1, 2], and Magadi chertification occurs at the surface in the same system as magadiite [3, 4].

$\delta^{30}Si$ values were analyzed by MC-ICPMS (Neptune™), $\delta^{18}O$ values of cherts by ion microprobe (Cameca 1270), and precursor $\delta^{18}O$ values were taken from literature [1, 3].

The $\delta^{18}O$ values of the Monterey opal (37‰) and chert (28-34‰) suggest temperatures of 15°C and 48±8°C, respectively [1]. The $\delta^{30}Si$ values of the chert and opal are 0.0‰ and 1.4‰, respectively. Diatom formation increases the $^{30}Si/^{28}Si$ of the aqueous phase [5], and high diatom $\delta^{30}Si$ values are expected in highly productive oceans. Later chert-forming diagenetic water, equilibrated with Monterey Shale [1], is expected to have more negative $\delta^{30}Si$ values [6], and explains the lower $\delta^{30}Si$ value of the chert.

In contrast, the inorganic magadiite and magadi chert have similar $\delta^{18}O$ (33-38‰ [3, 4] and 38‰, respectively) and $\delta^{30}Si$ values (-0.2 and -0.5‰, respectively). The isotopic similarity demonstrates that no fractionation attends this chertification, as both phases form from the same silicon and oxygen source (hot springs [3, 4]).

$\delta^{30}Si$ ratios of cherts record the last chertification event, which can imprint different $\delta^{30}Si$ values onto its precursor. This needs to be considered for paleoclimate reconstructions.

We thank Jim Boles (UCSB) for providing the samples.

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