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## **ACCEPTED MANUSCRIPT**

# Dehydroxylation and Diagenetic Variations in Diatom Oxygen Isotope Values

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#### **Abstract**

Numerous studies have documented changes in the dissolution and reactivity of biogenic silica as it is transferred from the water column to sediment archives; here we present the first experimental data that demonstrate a physical mechanism by which the oxygen isotope ( $\delta^{18}O_{sil}$ ) values of biogenic silica (diatoms) are altered during early diagenesis. The  $\delta^{18}O_{sil}$  value of diatom silica cultured at 19.3°C was +31.9%  $\pm$  0.2% (n = 6); the same silica experimentally aged in an artifical seawater media at near silica saturation at 85°C had an average  $\delta^{18}O_{sil}$  value of +27.1%  $\pm$  0.6% (n=20). The most significant change in the  $\delta^{18}O_{sil}$  value was coincident with an initial reduction in the total silanol abundance, indicating that the timing of dehydroxylation reactions in natural sedimentary environments is associated with diagenetic changes in the recorded  $\delta^{18}O_{sil}$  values. The rate of change in the experimental aging environment at 85°C was rapid, with significant changes in both silanol abundance and  $\delta^{18}O_{sil}$  values. Additionally, the silica-water fractionation relationship recorded by the

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