# Clumped and magnesium isotopes in corals: a comparison with traditional paleothermometers

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Corals represent valuable paleoclimatic archieves that may record sub-annual sea surface temperature (SST) over many centuries. Despite strong correlations with SST, the interpretation of traditional proxies (i.e. $\delta^{18}$O, Sr/Ca) is not straightforward because variations in seawater composition and biological vital effects can overprint climatic signals. Evidence for vital effects include 1) proxy-SST calibrations that differ significantly from abiogenic relationships and 2) inter/intra-coral differences in proxy-SST calibrations. Carbonate clumped isotopes ($\Delta_{47}$) and magnesium isotopes ($\delta^{26}$Mg) have emerged as new paleotemperature proxies that may be less prone to seawater variability and vital effects.

Based on the temperature dependent "clumping" of $^{13}$C and $^{18}$O into a single bond, $\Delta_{47}$ temperatures, at equilibrium, do not depend on the composition of the solution from which a carbonate forms. Furthermore, similar $\Delta_{47}$-SST relationships in biogenic carbonates and inorganic precipitates argue against vital effects. However, early sub-annual coral $\Delta_{47}$ data deviates from the cannoical $\Delta_{47}$-SST relationship and may reflect a vital effect [1]. We present a survey of $\Delta_{47}$ shallow water corals from the Atlantic, Pacific and Red Sea. Sub-annual $\Delta_{47}$ in two *Porites* corals shows a temperature sensitivity similar to abiogenic calibrations, but offset toward higher $\Delta_{47}$ values that underestimate SST by ~9°C. This effect cannot be attributed to laboratory artifacts or environmental variables such as salinity, but may result from fast coral calcification. Possible mechanisms for this apparent link to calcification will be discussed.

Like $\Delta_{47}$, temperature dependent magnesium isotope fractionation [2] is unlikely to be affected by solution composition, suggesting it may also be a valuable paleo-thermometer. Sub-annual $\delta^{26}$Mg variability in two *Porites* corals shows obvious annual cycles that are in phase with $\delta^{18}$O and Sr/Ca, suggesting a temperature dependence not seen in previous bulk sampling [3]. However, the temperature sensitivity of coral $\delta^{26}$Mg appears to be larger than abiogenic experiments raising the possibility of a vital effect. Potential sources for this discrepancy will be discussed.

[1] Ghosh et al. (2006) *Geochim. Cosmichim. Acta* **70**, 1439-1456.
[2] Wang et al. (2011) *AGU Fall Meeting* **PP51E-07**.
[3] Wombacher et al. (2011) *Geochim. Cosmichim. Acta* **75**, 5797-5818.

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# Was Mineral Surface Toxicty an Impetus for Evolution of Bacterial Extra-cellular Polymeric Substances (EPS)?

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Bacterial community-living at the mineral-water interface is enabled by an extracellular, polymeric, biofilm matrix. Despite the energetic penalties of EPS production, biofilm formation capability likely evolved on early Earth because of several proposed crucial cell survival functions. The potential toxicity of mineral surfaces towards cells in promoting biofilm formation, however, has not been fully appreciated.

We examined here the effects of nanoparticulate oxides (amorphous $SiO_2$, anatase $\beta$-$TiO_2$, and $\gamma$-$Al_2O_3$) on EPS- and biofilm-producing wild-type strains and their isogenic knock-out mutants which are defective in EPS-producing ability. In particular, we used the Gram-negative wild-type *Pseudomonas aeruginosa* PAO1 and its EPS knock-out mutant $\Delta^{-}$*psl*, and the Gram-positive wild-type *Bacillus subtilis* NCIB3610 and its EPS-knock-out mutant *yhxB*Δ.  Results showed that (a) cell viability was lower in the presence of each oxide relative to its oxide-free control, (b) toxicity was mineral-specific, and could be related to surface charge and particle size, (c) toxic minerals could induce EPS production, (d) the amount of EPS generated in the presence of oxides was related to relative toxicity of the minerals, and (e) Gram-positive cells were less susceptible to mineral toxicity than Gram-negative cells. Taken together, these results indicated a previously unrecognized role for microbial extracellular polymeric substances (EPS) in shielding bacterial cells against the toxic effects of mineral surfaces.

The function of EPS proposed here is distinct from the previously proposed roles. It is likely that EPS played multiple functions, including our hypothesized role of protecting against mineral toxicity. Furthermore, not all minerals are toxic or benign, and toxicity depends on surface chemistry and particle size. Our results provide insight to the potential impact of nanoparticulate mineral surfaces in promoting increased complexity of cell surfaces, including EPS and biofilm formation, on early Earth.