

## Light is an active contributor to vital effect in coral skeleton proxies

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Biologists emphasize the Light Enhanced Calcification (LEC) for a long time, although the interaction between light and calcification in coral skeleton formation remains not understood.  $d^{18}\text{O}$ , Sr/Ca and Mg/Ca are regarded as temperature tracers. However, we have no information concerning potential light influence on proxies.

Symbiotic colonies of the coral *Acropora* sp. were cultured, under constant conditions, in a factorial design of three temperatures (21, 25 and 28°C) and two light intensities (200 and 400  $\mu\text{mol photon m}^{-2} \text{s}^{-1}$ ). Metabolic, growth and geochemical measurements ( $d^{18}\text{O}$ ,  $d^{13}\text{C}$ , Sr/Ca and Mg/Ca) were conducted on 6 colony sets representing each environmental (light temperature) condition. The experiment intended firstly to identify the separated influences of temperature and light on metabolism and calcification rates and secondly to compare them with corresponding skeletal  $d^{18}\text{O}$ ,  $d^{13}\text{C}$ , Sr/Ca and Mg/Ca variations.

Metabolic parameters responded as biologists could expect: photosynthesis increased with temperature, being always higher at high light. When colony was maintained at low light zooxanthellae (coral symbionts) density was higher at 25 and 28°C than under high light, illustrating the coral capability of shadow-adaptation. Calcification rate was also positively correlated to temperature, the quantity of deposited aragonite being always higher under high light. In opposite, surface expansion (equivalent to linear extension) did not show straightforward behavior. In addition, mean (for each data set) photosynthetic activity was related to mean calcification rate following logarithmic relationship.

Proxy responses showed huge scattering especially under high light and high temperature, exceeding by several °C the value calculated by using conventional calibrations, thus compromising the robustness of commonly admitted temperature tracers. The average assessed by the 6 values of  $d^{13}\text{C}$ , Sr/Ca and Mg/Ca measured on the 6 nubbins of each set were correlated to averaged calcification rates, following logarithmic relationship. Furthermore, they seemed to obey to the temperature-light synergy. In opposite, correlation between  $d^{18}\text{O}$  and calcification rate strongly depended on the light intensity, although  $d^{18}\text{O}$  seemed the most relevant temperature tracer. Examination of isotopic micro-measurements confirmed that isotopic fractionation could differ following light intensity. By considering individual values measured on each colony developed under high light, we underlined that photosynthetic activity, covering the total measured amplitude, was strongly related to symbiotic algae density, regardless temperature value, such as individual proxy values showed strong correlation with calcification rate according to light intensity, regardless temperature value. We deduced that in these conditions the high scattering that we observed could be due to the light effect, at least under high light.

No coral proxy is dependent on the sole temperature and no temperature calibration could be regarded as a universal law.

## Distribution of vanadium in a basaltic aquifer of Jeju Island, Korea: effects of geochemical reactions and hydrological mixing

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Hydrochemistry data (i.e., major cations and anions, and trace metals such as Fe, Mn, V, As, Mo and U) of 25 groundwater samples from the Gosan area at the southwestern part of Jeju volcanic island, South Korea, were examined to investigate physico-chemical factors controlling the spatio-temporal distribution of vanadium in a basaltic aquifer. The study area is comprised of a wide coastal agricultural land with hills with moderate slopes in the northeast. Groundwater sampling was conducted in May 2009 and October 2010. Groundwater in the study area usually contains high concentrations of V with an average of 12.2  $\mu\text{g/L}$  (max. 28.8  $\mu\text{g/L}$ ). Except for two samples that were influenced by seawater intrusion, as indicated by higher concentrations of Cl, Mg and  $\text{SO}_4$  and elevated  $\delta^{34}\text{S}$  values (14.5~18.9 ‰), groundwater in the study area is clustered into two major hydrochemical types: 1) a Mg-Cl- $\text{NO}_3$  type and 2) a Na- $\text{HCO}_3$  type. The latter type is characterized by higher pH values (8.2~8.9, avg 8.6), compared to water type 1 (pH: 6.9~8.3, avg 7.3). The concentrations of V are strongly correlated with pH ( $\gamma^2 = 0.89$ ) and are higher in the Na- $\text{HCO}_3$  type water. In addition, positive correlations were observed between pH and Cl-normalized concentrations of Na ( $\gamma^2 = 0.79$ ), K ( $\gamma^2 = 0.49$ ), and  $\text{HCO}_3$  ( $\gamma^2 = 0.64$ ). These observations indicate that water-rock interactions during southwestward regional groundwater flow in the basaltic aquifer largely control the observed hydrochemical changes and increasing V concentrations. However, V concentrations also tend to decrease in samples with higher concentrations of  $\text{NO}_3$  characteristic for Mg-Cl- $\text{NO}_3$  type waters. Examination of relationships between concentrations and  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values of nitrate in the study area revealed that nitrate is mainly derived from synthetic fertilizers (~3 to 4 ‰  $\delta^{15}\text{N}_{\text{NO}_3}$ ) applied to agricultural fields. During infiltration of rainwater into the aquifer, agricultural nitrate is locally attenuated by partial denitrification to low nitrate levels (~8 ‰  $\delta^{15}\text{N}_{\text{NO}_3}$ ). These observations suggest that there are two major paths of groundwater recharge in the study area: 1) regional flow accompanying water-rock interactions with V leaching from basalts, and 2) local flow dominated by direct infiltration of rainwater through agricultural land, accompanied by nitrate loading. We suggest that V concentrations of groundwater will decrease with increasing nitrate concentrations at times of increased local recharge.