

Incorporation of iodine in methane-derived authigenic carbonates: Implications for methane flux dynamics

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Iodine (I) exists as two inorganic species in seawater - iodate (IO_3^-) and iodide (I^-). Only the oxidized form (IO_3^-) is incorporated into carbonate minerals, enabling the utility of $I/(Ca+Mg)$ in carbonates as a paleo proxy to track the availability of dissolved oxygen in the water column. Continental margins are often characterized by sites with subsurface methane seepage towards the seafloor, leading to anaerobic oxidation of methane (AOM) in shallow sediments and subsequent bicarbonate production favoring precipitation of methane-derived authigenic carbonates (MDAC). These carbonates are a reliable geological recorder of seepage events. Redox reconstructions using trace and rare earth elements (REE) on MDAC have suggested variable redox conditions recorded in MDACs, including the presence of intermittent oxic conditions indicated by negative cerium (Ce) anomalies. However, in seep settings, enhanced AOM-induced alkalinity in the presence of organic matter is suggested as an alternative mechanism for generating a negative Ce anomaly. To better understand methane flux dynamics, we paired the $I/(Ca+Mg)$ paleo oxygen proxy with Ce and REE data on MDACs from globally distributed seep sites.

Our preliminary results from 22 samples identified $I/(Ca+Mg)$ ratios from 0.25 to 5.33 $\mu\text{mol/mol}$ in 70% of samples with a negative Ce anomaly. These findings suggest that changes in flux intensity and/or increased oxygen penetration in sediments would expose the MDAC to intermittent oxic conditions and subsequent incorporation of IO_3^- , reflected in high $I/(Ca+Mg)$ ratios and negative Ce anomalies. Higher $I/(Ca+Mg)$ ratios in samples from AC 645, a northern Gulf of Mexico seep site with negative Ce anomaly and biomarkers of aerobic methanotrophs, strongly support this inference. We also document aragonite has higher $I/(Ca+Mg)$ ratios than Mg-calcite. This could be due to the preferential precipitation of seep aragonites closer to the seafloor than seep calcites. Ongoing analysis will evaluate additional samples, including MDACs from the oxygen minimum zone, to further constrain $I/(Ca+Mg)$ systematics of seep carbonate records. Our study expands the utility of the $I/(Ca+Mg)$ proxy in