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Effects of Ca-enrichment on authigenic carbonate formation at cold vent sites off Costa Rica: a numerical model approach

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THE Costa Rican forearc is characterized by active fluid venting related to mud diapirism and volcanism. The geochemical compositions of fluids obtained from dewatering sites indicate that mineral precipitation or dehydration is the major driver of fluid mobilization and upward migration. The peculiar situation at the latter sites is that Ca concentrations in the upward migrating fluids are well above seawater levels. In turn, these Ca-enriched fluids could offer a potential reason for widespread carbonate caps on top of the mounds. Here, a reactive-transport numerical model is applied to investigate the main biogeochemical processes at cold vents off Costa Rica (Fig. 1). It is used to determine the vent-driven $CaCO_3$ (calcium carbonate for solid phase) precipitation, quantification of methane turnover and Anaerobic Oxidation of Methane (AOM) at five different stations with varying Ca concentrations (Table 1). We also analysed the control parameters such as Ca concentrations and saturation state affecting $CaCO_3$ precipitation rates. Fluids from two of the five sites (Culebra Fault, and Mudpie) are enriched in Ca. In contrast, fluids at the other two sites (Mound 11 and Quepos Slide) have relatively small amounts of Ca.

At the active-vent location of Mound 11, ~98% of the CH_4 is released into the bottom waters due to the high advection rates (200 cm y^{-1}). The smaller CH_4 turnover by AOM at Mound 11 also

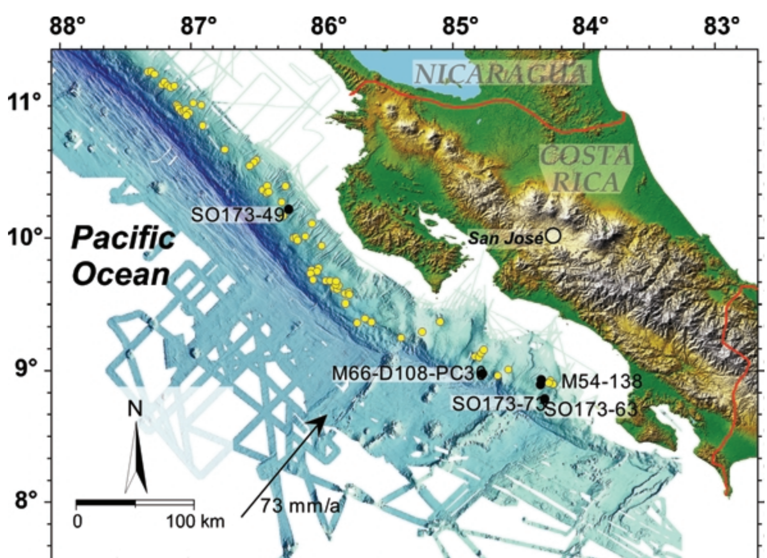

FIG. 1. Location of the study area and sampling vent sites (M54-138, SO173-73, SO173-63, M66/D78-PC30 and SO173-49) off Costa Rica.

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TABLE 1. Summary of the parameter values used as boundary values for modelling. BW indicates concentrations of dissolved species at the upper boundary of the model column, whereas BS is the concentrations of dissolved species at the bottom of the sediment column.

	M54-138	SO173-73	SO173-63	M66-PC30	SO173-49	
Pore-water boundary values						
BW O_2/BS O_2	0	0	0	0	0	mM
BW NO_3/BS NO_3	0	0	0	0	0	mM
BW Cl/BS Cl	551/210	555/324	522/321	551/381	550/291	mM
BW SO_4/BS SO_4	28.19/0	28.32/0	28.19/0.1	26.93/0.37	28.77/0	mM
BW Ca/BS Ca	0/9.16	0/8.08	0/4.11	0/31.10	0/22.43	mM
BW CH_4/BS CH_4	0/68	0/68	0/68	0/68	0/68	mM
BW total PO_4/ BS total PO_4	$4.06/3.25 \times 10^{-3}$	$3.45/3.45 \times 10^{-3}$	$3.49/19.92 \times 10^{-3}$	$1.87/2.87 \times 10^{-3}$	$6.10/1.36 \times 10^{-3}$	mM
BW total NH_4/ BS total NH_4	$3.70/1744 \times 10^{-3}$	$7.94/2905 \times 10^{-3}$	$105.83/2565 \times 10^{-3}$	$218/3578 \times 10^{-3}$	$0/6557 \times 10^{-3}$	mM
BW H_2S/BS H_2S	0/0	0/0	0/0	0/0	0/0	mM
BW HS/BS HS	0/0	0/0	0/0	0/0	0/0	mM
Solid species boundary values						
$CaCO_3$	4.24	4.24	4.24	4.24	4.24	wt.%

causes reduced alkalinity production and as a result retards the formation of authigenic carbonates. In comparison, moderate flow rates (0.1–40 cm y^{-1}) at Culebra Fault, Quepos Slide and Mudpie lead to reduced CH_4 output (Fig. 2). The greater efficiency of AOM and Ca fluxes here increases the $CaCO_3$ precipitation rates, thus larger Ca fluxes from below induce more

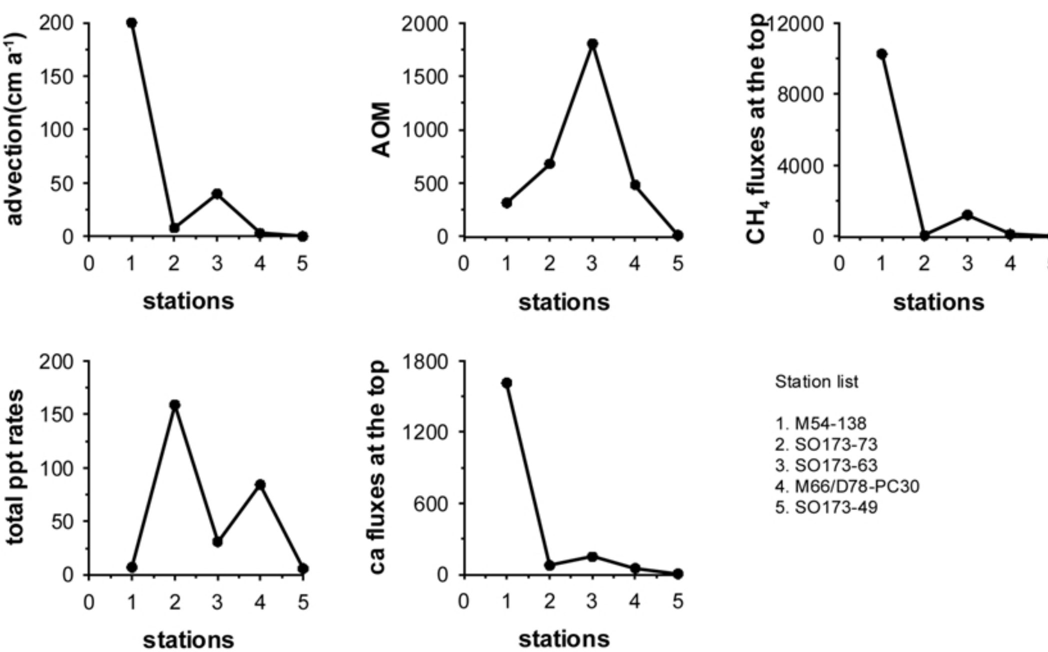

FIG. 2. Summary of advection (cm y^{-1}), turnover and $CaCO_3$ precipitation rates (μmol cm^{-2} y^{-1}) at simulated stations.

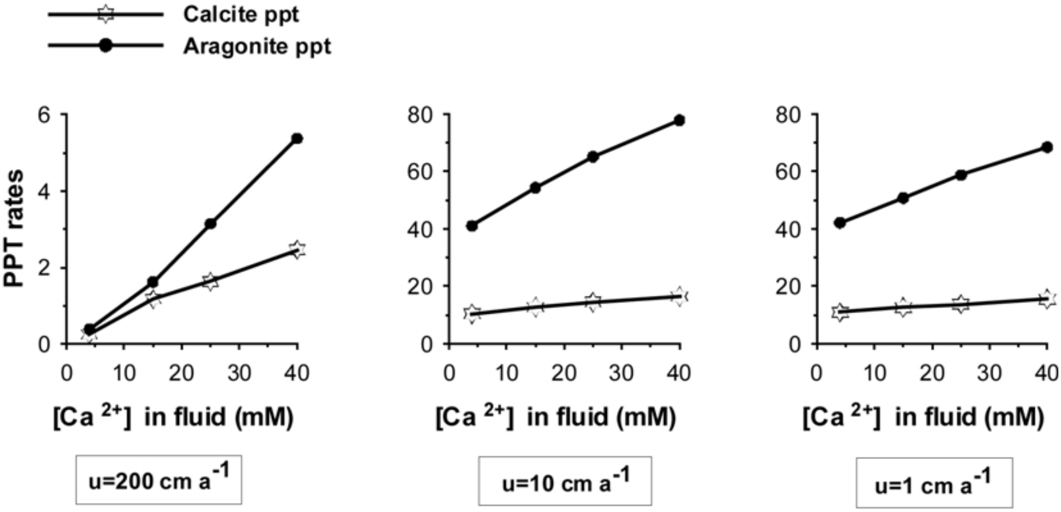

FIG. 3. Diagrams showing how the precipitation rates of calcite and aragonite (μmol cm^{-2} y^{-1}) respond to variations of Ca concentrations in the ascending fluids.

precipitation of $CaCO_3$. Simulations with varying fluid-flow rate and increased Ca concentrations in the ascending fluid demonstrate that the impact of Ca-enrichment from fluid venting on carbonate precipitation rate is significant (Fig. 3). This effect is more pronounced at smaller advection rates. The saturation state of upward migrating fluids is a sensitive parameter affecting the $CaCO_3$ precipitation in surface sediments, particularly at large advection rates.