Mg-, Ca-concentration and Sr-isotope evidence for lowtemperature flank flux as a significant contribution to the oceanic chemical mass balance

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Diffuse, relatively low-temperature hydrothermal fluxes on ridge flanks play a potentially significant role in the mass balance of a number of chemical components in seawater. For example, assuming a steady state ocean, oceanic mass balance models based on ₃He and on-axis mid-ocean ridge heat fluxes indicate an input deficiency of $16 \times 10_{12}$ mol/yr for Ca (on the same order of magnitude as the riverine flux), a sink for only 10-40% of estimated riverine Mg input, and flux of Sr that is 5 to 10 times too low to maintain a Sr isotope mass balance in the ocean (Palmer and Edmond, 1989; Mottl and Wheat, 1994; Elderfield and Schultz, 1996). The identification of these mass balance discrepancies provides indirect support for suggestions that the balance may be provided via the low-temperature, diffuse, off-axis hydrothermal flux.

We present Sr isotope and elemental composition of pore fluids collected from an advective hydrothermal system on the flank (1-4 Ma crust) of the Juan de Fuca ridge. The data show a strong signature of basaltic Sr input into and Mg removal from seawater associated with these low-temperature systems. Additionally, depth-concentration profiles of the 'conservative' elements Ca and Mg through the water column above the East Pacific Rise show mid-depth anomalies in (salinity normalized) concentrations. This may also be interpreted as qualitative support for a significant off-axis sink for Mg and input for Ca.

Sr isotope and major element profiles of sediment pore waters were measured for six cores taken during the Flank Flux cruise in 1990 (Wheat and Mottl, 1994). The cores were taken from two areas approximately 40 and 110 km east of the ridge axis, with estimated basement temperatures of 40°C and 70-90°C, respectively. Mg and Ca ocean water profiles to a depth of 2600 m (approximately 50m above the ridge crest) were measured by TIMS isotope dilution, with analytical precision of 0.04% and 0.09% (1 sigma), respectively. At this precision, Mg and Ca do not show conservative behaviour.

In all pore-water profiles from the Juan de Fuca flank, $_{87}Sr/_{86}Sr$ ratios decrease in a regular fashion (Fig. 1) from seawater values (0.70918) to values as unradiogenic as 0.70720. This is accompanied by a decrease in Mg concentration and Mg/Sr ratio to as low as 2.39 mmole/kg and 0.02, respectively.

Assuming that the hydrothermal endmember of low-temperature systems extrapolates to zero Mg (Mottl and Wheat, 1994), we calculate endmember ${}_{87}$ Sr/ ${}_{86}$ Sr ratios of 0.70716 to 0.70740. This identifies a potentially large source of unradiogenic Sr input into the oceans that was not detected in a previous study of ridge flank pore fluids (Hess *et al.*, 1991).

Following Sr isotope mass balance calculations of previous workers (Palmer and Edmond, 1989;



FIG. 1. Sr isotope profile of pore-water through a 5 m core on the Juan de Fuca flank.

Elderfield and Schultz, 1996), using estimates of heat flow partitioning between on- and off-axis fluxes (Mottl and Wheat, 1994), and taking our new data as representative of flank fluxes, we find that lowtemperature fluids provide an excess of unradiogenic Sr over that required to explain the observed Sr isotope rate of change in seawater (0.00008/Ma). For example, taking nominal values for riverine and high-temperature fluxes, the isotopic balance could be satisfied if only approximately 50% of the off-axis flux had characteristics we observed on the Juan de Fuca flank.

There are several possibilities to explain the mass balance discrepancy. It is possible that the Sr-isotope/ heat signature we infer from the Juan de Fuca fluids is not simply extrapolated to fluids of other temperatures. For example, cooler fluids may not have the same proportional isotopic offset per degree from seawater composition as the 40-90°C fluids. Cooler fluids from older crust may contribute substantially less Sr flux than predicted from the heat:Sr relation established from the Juan de Fuca fluids. It is also likely that fluid composition is quite heterogeneous, depending on local geometry and fracture system of the crust. As our sample suite effectively represents a single datum, it provides no constraint on the variability that may be inherent in the Sr:heat properties of off-axis systems. It is unlikely that the measured isotopic values are the consequence of sampling an unradiogenic, nonbasaltic isotopic reservoir. The sediments cored at these sites are derived from the western margin of North America, and have Sr isotope compositions higher than seawater. The crust is no older than 4 Ma, so remobilization of Sr from calcite precipitated from old seawater will not provide an important perturbation in isotopic composition.

The influence of the off-axis flux may also be reflected in concentration profile anomalies of Ca and Mg at mid-depths (> 1000m deep) above the East Pacific rise. Mg is depleted by up to 1% from surface water values, and Ca shows a profile inversely correlated with Mg (Fig. 2).

The depletion of Mg and enrichment of Ca is qualitatively consistent with the effect expected of hydrothermal fluxes. This is further supported by the strong correlation of the Ca profile and ₃He anomalies, which are typically ascribed to a high-temperature hydrothermal source. However, using ₃He:heat, Mg:heat and Ca:heat properties observed at high-temperature axial vents does not provide fluxes consistent the observed profiles. For example, the ³He gradient implies a decrease in Mg in the water column that is only 6–16% of the measured



FIG. 2. Vertical profiles of Mg and Ca concentrations in seawater above the East Pacific Rise (at $45^{\circ}N$ $179^{\circ}E$), normalized to salinity = 35. The deepest sample is approximately 50m above the ridge axis.

anomaly. If $_3$ He is primarily vented on-axis, then it would severely underestimate elemental fluxes that have a significant off-axis component (Elderfield and Schultz, 1996).

Large errors still exist in any mass balance calculation, primarily because of uncertainties in riverine input and the characterization of off-axis heat and chemical fluxes. Data from pore fluids above low temperature hydrothermal systems are at least qualitatively consistent with the hypothesis that, off-axis diffuse flow is an important component of the Sr isotope and Mg-Ca mass balance, and these new data begin to constrain the compositions of this low-temperature endmember.

References

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