

Evaluating pore fluid Mg isotopic and elemental constraints on seawater Mg chemistry in the Cenozoic

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Interpreting Cenozoic climate and environment accurately using marine geochemical proxies requires high fidelity proxies that are resistant to diagenetic alteration over tens of millions of years. For mineral-based proxies that do not passively sample seawater, such as Mg/Ca and stable isotopic proxies, it is also necessary to place limits on the chemistry of seawater (i.e. the solution from which the minerals precipitate). The latter is predominantly true for Cenozoic proxies over time scales longer than elemental residence times (τ) in the ocean ($\tau_{Mg} \sim 10$ Ma; $\tau_{Ca} \sim 1$ Ma).

This study utilizes depositional reactive transport models of carbonate diagenesis to simulate measured pore fluid and solid Mg isotopic and elemental data from ODP Site 807A (ave. $CaCO_3 \sim 92$ wt%). The ultimate goal of the iterative modeling approach taken is to (1) evaluate the extent to which pore fluid chemistry can be used to elucidate the Mg chemistry of the Cenozoic ocean and (2) estimate the degree to which diagenesis alters the Mg isotope and Mg/Ca proxies. Previously published recrystallization rates, based on Ca and Sr isotopic and elemental data, constrain the models [1-2].

The Mg isotopic composition ($\delta^{26}Mg_{DSM3}$) of 807A pore fluids varies systematically from -0.79 to -0.25‰ between the shallowest (13.4 mbsf) and deepest (738 mbsf) fluids. There is notable structure in pore fluid $\delta^{26}Mg$ as a function of depth that is not well explained by diffusion, either of an initial seawater signal or between boundaries that reflect modern seawater (upper) and basement basaltic Mg (lower). Accordingly, reaction must be considered.

In the current study, endmember model scenarios are used to evaluate the applicability (and uncertainty) of pore fluid chemical data for constraining past seawater chemistry. The modeling assumes that carbonate recrystallization is the dominant reaction controlling the alteration of Mg pore fluid chemistry in the sedimentary column. The first endmember scenario generates seawater Mg concentration and $\delta^{26}Mg$ curves for a range of partition coefficients (K_{Mg}) assuming a constant value for the diagenetic fractionation factor. A second set of simulations assumes seawater Mg concentrations consistent with evaporite fluid inclusion data and constrains K_{Mg} and the Mg isotopic evolution of the ocean accordingly.

The model results are subsequently used to assess the potential for diagenetic alteration of bulk carbonate. Given low Mg concentrations, reactions rates on the order of $<2\%/Ma$, and an assumed equilibrium fractionation factor and partition coefficient that are different at depth than in the surface ocean, there is considerable leverage to change both the Mg isotopic composition and Mg/Ca of bulk carbonates over tens of millions of years.

[1] Fantle and DePaolo (2006) GCA, 70, 3883-3904.

[2] Fantle and DePaolo (2007), GCA, 71, 2524-2546.

Mineral-scale $^{87}Sr/^{86}Sr$ heterogeneities in the Elba Island intrusive complex: a consequence of prograde disequilibrium melting of the source

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Large $^{87}Sr/^{86}Sr$ variations are preserved at the mineral-scale within igneous units forming the late Miocene Elba Island intrusive complex (Italy), namely the San Martino granite porphyry laccolith (7.4 Ma), the Monte Capanne granite pluton and the Cotoncello felsic dyke (6.9 Ma). Decimetric K-feldspar megacrysts from the three units record a similar large core to rim decrease of $^{87}Sr/^{86}Sr_i$ ratios (from ≈ 0.719 to 0.715) while biotites included within feldspar cores, interpreted as an early crystallized magmatic phase formed from an early magma batch, have diverse initial Sr isotope ratios. Biotite inclusions from the pluton and the dyke have extremely high $^{87}Sr/^{86}Sr_i$ (≈ 0.733), while those in the porphyry record the lowest ratio in the intrusive system (≈ 0.712). It is noteworthy that reliable initial Sr isotope ratios for biotites included in the megacrysts have been determined as a consequence of the exceptional young emplacement age of the Elba Island intrusive complex.

The record of isotopic variations preserved at the mineral-scale in the different megacryst-bearing units of the Elba Island intrusive complex, reflects episodic recharge and mixing between crustally-derived magma batches having contrasting $^{87}Sr/^{86}Sr$ signatures. Intrusion of basaltic magmas in the crust causes high heating rates (>100 °C/Ma), preventing complete equilibration within rock-forming phases in the protolith prior to anatexis, as well as between the residuum and the melt during anatexis and magma segregation. Therefore, phases with $^{87}Rb/^{86}Sr$ ratios that are high (i.e. biotite), intermediate (i.e. muscovite) and low (i.e. hornblende and plagioclase) develop contrasting $^{87}Sr/^{86}Sr$ through time. Consequently, a range of isotopically distinct magma batches arise from disequilibrium melting of individual sources that are able to undergo melting through different reactions.

The increase in $^{87}Sr/^{86}Sr_i$ recorded by the San Martino system reflects mixing between magmas produced by the progression from muscovite- to biotite fluid absent melting within a metapelitic source. At higher temperatures, the progression from biotite to hornblende-dominated fluid absent melting within a layered, compositionally intermediate source generates the decrease in Sr isotope ratios recorded by the pluton-dyke magmatic system.