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Authors
Antonelli, Michael A
Pester, Nicholas J
Brown, Shaun T
et al.

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Title: Effect of Paleoseawater Composition on Hydrothermal Exchange in Mid-Ocean Ridges

Authors: Michael A. Antonelli[a,1], Nicholas J. Pester[b], Shaun T. Brown[a,b], Donald J. DePaolo[a,b]

Affiliations: [a]Department of Earth and Planetary Science, University of California - Berkeley, Berkeley, CA 94720, USA. [b] Lawrence Berkeley National Laboratory, 1 Cyclotron Rd, Berkeley, CA 94720, USA.

[1]Corresponding author. E-mail address: Mantonelli@berkeley.edu (M.A. Antonelli).

Abstract:

Variations in the Mg, Ca, Sr, and SO_4 concentrations of paleoseawater can affect the chemical exchange between seawater and oceanic basalt in hydrothermal systems at mid-ocean ridges (MOR). We present a model for evaluating the nature and magnitude of these previously unappreciated effects, using available estimates of paleoseawater composition over Phanerozoic time as inputs and $^{87}Sr/^{86}Sr$ of ophiolite epidosites and epidote-quartz veins as constraints. The results suggest that modern hydrothermal fluids are not typical due to low Ca and Sr relative to Mg and SO_4 in modern seawater. At other times during the last 500 Myr, particularly during the Cretaceous and Ordovician, hydrothermal fluids had more seawater-derived Sr and Ca, a prediction that is supported by Sr isotope data. The predicted $^{87}Sr/^{86}Sr$ of vent fluids varies cyclically in concert with ocean chemistry, with some values much higher than the modern value of ~0.7037. The seawater chemistry effects can be expressed in terms of the transfer efficiency of basaltic Ca and Sr to seawater in hydrothermal systems, which varies by a factor of ~1.6 over the Phanerozoic, with minima when seawater Mg and SO_4 are low. This effect provides a modest negative feedback on seawater composition and $^{87}Sr/^{86}Sr$ changes. For the mid-Cretaceous, the low $^{87}Sr/^{86}Sr$ of seawater requires either exceptionally large amounts of low-temperature exchange with oceanic crust or that the weathering flux of continentally-derived Sr was especially small. The model also has implications for MOR hydrothermal systems in the Precambrian, when low seawater SO_4 could help explain low seawater $^{87}Sr/^{86}Sr$.

Significance Statement:

Circulation of seawater through mid-ocean ridges results in large-scale chemical transfer between the solid Earth and oceans. Driven by magmatic heat, seawater undergoes hydrothermal reactions that affect the concentrations of Mg, Ca, SO_4, and Sr in the oceans over millions of years. Changes in the composition of seawater during the past 500 million years may have previously unrecognized effects on the composition of hydrothermal fluids flowing back into the oceans through time. This work presents a model suggesting that Ca, and Sr exchange in particular, may have been much different in the geologic past, which has important implications for the interpretation of Sr isotope records in paleoseawater and ancient oceanic crust.

Main Text: \body

Mid-ocean ridge (MOR) hydrothermal circulation, fuelled by persistent heat from shallow magma reservoirs, is a key component in the long-term regulation of global climate and ocean chemistry (1). Hydrothermal fluids that emerge from these systems, at temperatures up to ~400 $^\circ$C, are chemically distinct from seawater due to reactions with newly forming oceanic crust. Relative to seawater, fluids emanating from modern MOR hydrothermal systems are enriched in Ca and transition metals, have lower pH and Eh, and have little to no Mg and $SO_{4\,(2–5)}$.

Hydrothermal circulation at MOR is dominated by two important chemical reactions: the removal of seawater SO_4 through mineral precipitation with seawater Ca, and the removal of seawater Mg through precipitation of hydroxy-silicate minerals (3, 6, 7). Seawater SO_4 is primarily lost through the formation of anhydrite ($CaSO_4$) early during hydrothermal circulation, as anhydrite precipitation occurs by simply heating seawater >130 $^\circ$C (8). There can also be minor losses of SO_4 through thermochemical sulfate reduction (9, 10) and bacterial processes.

Seawater Mg is lost from hydrothermal fluids at both low and high temperatures, by exchange of seawater Mg for basaltic Ca through the transformation of primary igneous minerals to alteration phases such as montmorillonite and chlorite (3). This Mg:Ca exchange process is accompanied by the generation of acidity and the release of basaltic Ca (and Sr) into the hydrothermal fluids (7, 11).

The overall chemical and isotopic exchange in modern MOR hydrothermal systems is partly determined by the peculiarities of modern seawater, which has relatively high dissolved [Mg] (53 mmol/kg) and [SO_4] (28 mmol/kg) (brackets indicate concentration), and relatively low dissolved [Ca] (10 mmol/kg) and [Sr] (91 µmol/kg). At various times in the geologic past these proportions (53:10:28:91) were much different (Fig. 1). The origins of these variations are not well understood (12), but their existence has substantial consequences for the evolution of fluids during hydrothermal circulation.

Paleoseawater chemical variations

The record of seawater [Mg], [Ca], and [SO_4] through the Phanerozoic is largely derived from fluid-inclusion measurements in marine halite (12–14) (Fig. 1), but is corroborated in general terms by other observations. During the Cretaceous and Devonian periods, seawater apparently

had substantially lower [Mg] and [SO₄], and higher [Ca] relative to modern seawater. In the late Permian and Cambrian, seawater compositions were more similar to modern. Support for such historical variability in seawater composition comes from: i) the alternating dominance of aragonite *vs.* calcite as the primary biogenic carbonate mineral (12), ii) Mg/Ca ratios in hydrothermal veins (15), iii) δ^{44}Ca variations in evaporite deposits (16), iv) sulfur isotope models (17, 18), and v) Mg/Ca ratios in calcifying marine organisms (19).

Estimates for paleoseawater [Sr] are not as well developed and not all consistent. Most evidence from altered ophiolite assemblages and the fossil record indicate elevated [Sr] in seawater during times of elevated [Ca] (20–22), with fairly small overall changes to the seawater Sr/Ca ratio. However, lower than modern Sr/Ca ratios for the period between 30-180 Ma have also been proposed based on analyses of carbonate veins in altered oceanic crust (23). For the purpose of evaluating our model we have constructed a notional Phanerozoic seawater [Sr] curve (Fig. 1) based on combining the Sr/Ca record from invertebrates (20) and benthic foraminifera (24) with the record for seawater [Ca] (adopting the assumptions of previous authors), but compare this with results using constant modern seawater [Sr] which approximates the results of lower Sr/Ca estimates (23).

Hydrothermal charge-balance model

Hydrothermal flow through mid-ocean ridge systems is complicated in several ways. Some fluids enter the oceanic crust close to the ridge, where they are rapidly heated as they percolate downwards and are then vented back to the ocean quickly (3). Other fluids enter the crust much farther from the ridge, have a longer and slower transit through the system, and may or may not be heated to the high temperatures characterizing the axial portions of the system. Although it is difficult to account for the complexity in a simple model, certain material and charge balance constraints are likely to be met by the dissolved ions in the fluids.

Our approach is to use knowledge of modern systems to establish a model that we then apply to ancient systems. Modern high-T hydrothermal fluids that vent back to the ocean have zero [Mg], elevated [Ca], zero [SO₄], and slightly elevated [Sr] that is largely, but not completely, derived from basalt based on ^{87}Sr/^{86}Sr evidence (3–5, 25–27). Analyses of modern high-T vent fluids suggest that the overall change in fluid chemistry, especially for the three major ions Mg, Ca, and SO₄, can be constrained by charge balance. The positively charged seawater Mg^{2+} and Ca^{2+}, and

negatively charged SO_4^{2-} ions are removed from the fluids, yet the seawater proportions (53:10:28) are such that there is a total positive charge excess per kilogram of fluid equal to $[Mg^{2+}]_{sw} + [Ca^{2+}]_{sw} - [SO_4^{2-}]_{sw}$. As end-member hydrothermal fluids have zero [Mg], charge balance is maintained through the net release of Ca^{2+} from basalt. According to this model, the final average Ca concentration in venting hydrothermal fluids (~35 mmol/kg) can be calculated from the initial seawater concentrations as:

$$[Ca]_{hyd} = [Mg]_{sw} + [Ca]_{sw} - [SO_4]_{sw}$$

[1]

Where $[Ca]_{hyd}$ is the Ca concentration in high-T hydrothermal fluids, and $[Mg]_{sw}$, $[Ca]_{sw}$, and $[SO_4]_{sw}$ are the magnesium, calcium, and sulfate concentrations in seawater, respectively. More rigorous reaction-path modeling, which includes other cations (such as Na, K, Fe) and processes such as albitization and the formation of actinolite (SI Appendix, SI Text, Fig. S1), corroborates this charge balance equation.

The hydrothermal Ca is a combination of seawater Ca plus Ca released from basalt. The minimum amount of Ca released from basalt must be equal to $[Ca]_{hyd}$ - $[Ca]_{sw}$. However, there is evidence that in lower temperature parts of the hydrothermal circulation system, virtually all of the seawater Ca is removed through precipitation of anhydrite ($CaSO_4$) (25), so that virtually all of the Ca in the venting fluids is derived from basalt. This inference is strongly supported by the observation that ~80% of the Sr in end-member vent fluids is also derived from basalt (3–5, 26, 27). The key aspects of our model relate to the sources of hydrothermal Ca and Sr which, based on equation [1], should have been substantially different in the geologic past due to differences in the proportions of dissolved Ca, Mg and SO_4 relative to the modern system. Since ultimately we wish to relate the changes in hydrothermal geochemistry to changes in Sr isotopes, it is important to correctly model the behavior of Sr relative to Ca.

Our model for fluid evolution in MOR systems, which is meant to describe the global average MOR hydrothermal fluid evolution, can be expressed in four steps (SI Appendix, Fig. S2):

1. As seawater flows into fractures in warm basalt and is heated above 130°C, $CaSO_4$ (anhydrite) precipitates, removing essentially all of the original dissolved seawater Ca or SO_4, depending on which is present in larger concentration, and a fraction of the dissolved seawater Sr that depends on the amount of Ca removed.

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2. With continued heating and flow, but still at moderate temperature, basalt releases Ca along with Sr in exchange for Mg until any remaining seawater SO_4 is precipitated as $CaSO_4$. In this secondary phase of anhydrite formation, which applies only when $[SO_4]_{sw}$ > $[Ca]_{sw}$, the anhydrite incorporates Sr from both seawater and basalt. The Mg released from basalt is continually returned to the solid phase as secondary hydroxylated Mg minerals. (In real systems there is overlap between steps 1 and 2.)
3. At high-T (>250°C) Ca and Mg continue to be released from basalt, but all of the Mg is returned to the solid phase as secondary hydroxylated Mg minerals; the most prominent being chlorite, whereas the released Ca and accompanying Sr mostly accumulate in the fluid.
4. With continued heating, additional Ca and Sr from the fluids exchanges with Ca and Sr in the basalts with no change in total fluid concentration of either element (we subsequently refer to this as high-T Ca, Sr exchange).

This model allows us to make predictions about how differences in seawater composition in the geologic past will be manifest as changes in the extent of Ca, Mg, SO_4, and Sr exchange between seawater and oceanic crust, ultimately evidenced by changes in the $^{87}Sr/^{86}Sr$ of hydrothermal vent fluids. The test of the model comes from measured values of $^{87}Sr/^{86}Sr$ in high temperature vein epidote samples from ophiolites (28–34).

In Fig. 2 we illustrate the model described above, where modern seawater ([Mg]:[Ca]:[SO$_4$] of 53:10:28 mmol/kg) leads to vent fluid with $[Ca]_{hyd}$ = 35 mmol/kg and zero [Mg], which is approximately the same as for average modern vent fluids and for reaction path simulations (SI Appendix, SI Text, Fig S1a,c). For paleoseawater with a Cretaceous composition (30:30:10), only 1/3 of $[Ca]_{sw}$ can be removed through anhydrite precipitation in step-1 (because $[Ca]_{sw}$ > $[SO_4]_{sw}$), step-2 does not occur, and the fluids emerge with $[Ca]_{hyd}$ = 50 mmol/kg, some 20 mmol/kg of which is inherited from the incoming seawater (Figs. 2, SI Appendix, Fig. S1b). In our model, the oceanic crust is a source for Ca at all values of seawater [Ca], [Mg] and $[SO_4]^*$.

Strontium isotope evolution in hydrothermal fluids

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*It has also been proposed that [Ca] vs. [Mg] data for paleoseawater produce a pattern that points towards basalt as a sink for seawater Ca when it is present at levels greater than ~20 mmol/kg, and as a source for Ca at lower levels (62). However, a chemical mechanism for this idea has not been proposed, and replacement of seawater Mg by basaltic Ca appears to be thermodynamically favorable at all temperatures (SI Appendix, SI Text, Fig. S1).

To estimate the $^{87}Sr/^{86}Sr$ of hydrothermal fluids, we extend the charge-balance model assuming that Sr passively follows Ca during anhydrite precipitation, basalt dissolution, and chlorite/epidote precipitation. During anhydrite precipitation (Step 1), seawater Sr is assumed to be removed in anhydrite with a Sr/Ca ratio of 0.003 (R_{Anh}). For modern seawater, this is a simplification roughly equivalent to removing 99% of seawater Ca as anhydrite with a Sr/Ca distribution coefficient of 0.1 [the average equilibrium experimental value (35)]. The predicted anhydrite Sr/Ca agrees with data from modern seafloor anhydrite deposits (36, 37). When $[Ca]_{sw}$ < $[SO_4]_{sw}$, such as in the modern oceans, there is further anhydrite precipitation until sulfate is fully removed (Step 2). This second phase of anhydrite precipitation occurs as Ca is released from the basalts. It is assumed that basaltic Sr is released with basaltic Ca in proportion to the bulk basalt concentrations (2) (R_{bslt} = basalt Sr/Ca = 0.002) and incorporated into anhydrite using the ratio R_{Anh}, as illustrated in SI Appendix (Fig. S3). The continued release of basaltic Ca during Step 3 is also accompanied by a proportional release of basaltic Sr using the ratio R_{bslt}.

Model steps 1-3 arrive at the correct $[Sr]_{hyd}$ for average modern vent fluids (~110 µmol/kg, where $[Sr]_{sw}$ = 91 µmol/kg, SI Appendix, Fig. S4), but produce a value of $^{87}Sr/^{86}Sr$ that is slightly higher than the observed average value of ~0.7037 (26). We infer that this mismatch indicates that there is further high-T Ca, Sr exchange between hydrothermal fluid and basalt (Step 4). This "exchange" occurs as a result of continued dissolution of Mg, Ca, Sr-bearing primary minerals and precipitation of secondary minerals that also contain these elements; it is assumed to leave the fluid [Ca] and [Sr] unchanged (and [Mg] = 0), but results in a further shift of fluid $^{87}Sr/^{86}Sr$ toward basalt values. Assuming Sr and Ca are exchanged in the proportion R_{bslt}, a fraction of about 0.1 (denoted θ_{exch}, SI Appendix, SI Text) of the total Ca in modern hydrothermal vent fluids (~35 mmol/kg), must exchange with basalt in order to produce the low $^{87}Sr/^{86}Sr$ of average modern vent fluids (0.7037). Exchange processes are documented by several lines of evidence, at low temperature in the $^{87}Sr/^{86}Sr$ of basalt-hosted carbonate veins and anhydrite deposits, and at high temperature in the isotopic compositions of altered ophiolite assemblages (11, 38). For simplicity, in the model we assume that the exchange happens after all of the Mg has been removed from the fluid.

The model Sr concentration of hydrothermal vent fluids can be expressed as:

$$[Sr]_{hyd}=[Sr]_{sw}-[Sr]_{anh}+[Sr]_{bslt} \qquad [2]$$

Where $[Sr]_{sw}$ is the strontium concentration of seawater, $[Sr]_{anh}$ is the strontium lost during anhydrite precipitation, and $[Sr]_{bslt}$ is the strontium gained from the basalts. The isotopic composition of Sr is calculated by mixing the seawater Sr remaining after anhydrite precipitation with the Sr released from basalt during Ca-Mg exchange, according to:

$$\left(\frac{87_{Sr}}{86_{Sr}}\right)_{hyd}=\frac{[Sr]_{hyd,sw}}{[Sr]_{hyd}}\left(\frac{87_{Sr}}{86_{Sr}}\right)_{sw}+\frac{[Sr]_{hyd,bslt}}{[Sr]_{hyd}}¿ \qquad [3]$$

Where $[Sr]_{hyd,sw}$, $[Sr]_{hyd,bslt}$, and $[Sr]_{hyd}$ are the seawater Sr, basaltic Sr, and total Sr concentrations in the output hydrothermal fluids, respectively; $(^{87}Sr/^{86}Sr)_{sw}$ is the strontium isotope ratio of seawater, and $(^{87}Sr/^{86}Sr)_{Bslt}$ is the strontium isotope ratio of basalt (assumed = 0.7025).

The use of an average $^{87}Sr/^{86}Sr$ of modern vent fluids (= 0.7037) to calibrate our model could be questioned based on the observation that $^{87}Sr/^{86}Sr$ is somewhat variable between ridges and is loosely correlated with spreading rates (26). Although there is variability, the data as reported yield a mean and standard deviation for different ridges of 0.7037 ± 0.0004, which is not so large as to invalidate use of the average. Causes of $^{87}Sr/^{86}Sr$ variability are most simply related to variability in Ca concentrations. The average [Ca] of modern hydrothermal vents represents a combination of fluids that have undergone full titration of seawater Mg, and then approached equilibrium with basalt at different temperatures (SI Appendix, SI Text, Fig. S1). At lower temperatures albitization increases [Ca] (in exchange for seawater Na), and at higher temperatures amphibole formation lowers [Ca] (replaced mostly by basaltic Na and Fe). Along with differences in temperature, variability in fluid residence times also affects reaction extent, and may help explain low-temperature vents with fully titrated [Mg] and high $^{87}Sr/^{86}Sr$ (39, 40). Since Sr follows Ca exchange and the replacement of seawater Mg by basaltic Ca is thermodynamically favorable at all temperatures, a charge-balance model is a logical approach to integrating variable fluid histories (SI Appendix, SI Text, Fig. S2). When applying the model to other times in the geologic past, it is straightforward to account for possible variations in global

spreading rate using the correlation of (26), but global rates are unlikely to have varied by more than about 20% relative to modern (41), which would correspond to an increase in average $^{87}Sr/^{86}Sr$ of only about 0.0002.

We relate the Ca-Mg-SO$_4$ chemistry of hydrothermal systems to Sr isotopes because the Sr isotopic record of high-T hydrothermal precipitates is the primary test of our model, and has direct implications for the interpretation of paleoseawater $^{87}Sr/^{86}Sr$. To most simply replicate modern systems, and in accordance with our reaction-path simulations (SI Appendix, SI Text) and with natural and experimental observations (6–8, 38), anhydrite precipitation is separated into two phases (SI Appendix, Fig. S2). Anhydrite-1 is derived entirely from seawater, whereas anhydrite-2 includes variable proportions of basaltic calcium and strontium (as observed in modern ocean drill cores). Therefore equation [2] can be expanded to:

$$[Sr]_{hyd} = [Sr]_{sw} - [Sr]_{anh1} - [Sr]_{anh2,sw} + [Sr]_{bslt1} + [Sr]_{bslt2} \qquad [4]$$

Where $[Sr]_{anh1}$ is the seawater Sr lost during the first phase of anhydrite precipitation, $[Sr]_{anh2,sw}$ is the seawater Sr lost to anhydrite-2, $[Sr]_{bslt1}$ is the basaltic Sr remaining in the fluid after formation of anhydrite-2, and $[Sr]_{bslt2}$ is the basaltic Sr gained during the final exchange of seawater Mg for basaltic Ca. The final Ca,Sr exchange required to explain the isotope data (θ_{exch}, SI Appendix, SI Text) does not affect any concentrations within the hydrothermal fluids, and is not explicitly denoted in equation [4]. The [Sr] in the fluids and minerals discussed is only a minor component, and thus has been ignored in terms of its effects on charge-balance.

To calculate hydrothermal fluid $^{87}Sr/^{86}Sr$ for Phanerozoic paleoseawater, we replace the terms in mixing equation [3] with those from our charge-balance equations (defined in SI Appendix, SI Text) in order to arrive at our final model. It is important to note that a four-isotope approach (42) is not necessary for our purposes, as we use only the seawater record as input values. When accounting for the different sinks and sources for seawater and basaltic Sr during hydrothermal circulation, including high-T exchange (model step 4), we arrive at:

$$\left(\frac{^{87}Sr}{^{86}Sr}\right)_{hyd} = \frac{[Sr]_{sw} - [Sr]_{anh1} - [Sr]_{anh2,SW} - [Sr]_{exch,sw}}{[Sr]_{hyd}} \left(\frac{^{87}Sr}{^{86}Sr}\right)_{sw} + \frac{[Sr]_{bslt1} + [Sr]_{bslt\,2} - [Sr]_{exch,bslt} + [Sr]_{exch}}{[Sr]_{hyd}}$$

[5]

Where $[Sr]_{exch,sw}$ and $[Sr]_{exch,bslt}$ are the amounts of seawater and basaltic strontium within the hydrothermal fluids that are exchanged with the basalt during step 4, respectively (SI Appendix, SI Text), and their sum is $[Sr]_{exch}$. Our final charge-balance model for average high-T hydrothermal $^{87}Sr/^{86}Sr$ over the Phanerozoic takes into account the gains and losses in Sr during anhydrite precipitation, basalt dissolution, and exchange of Sr between hydrothermal fluids and basalt; all of which are calibrated to modern hydrothermal vent fluid compositions.

Variability in hydrothermal $^{87}Sr/^{86}Sr$ over the Phanerozoic

Applying the model to paleoseawater requires the record of seawater [Mg], [Ca], [SO$_4$], and [Sr] (Fig. 1), and the record of paleoseawater $^{87}Sr/^{86}Sr$ (Fig. 3) derived from measurements of marine carbonate (43). The result is a calculated curve representing the predicted $^{87}Sr/^{86}Sr$ of average *high-temperature* MOR hydrothermal fluids through time, where the past ~150 Ma are generally better constrained than the rest due to availability of published data (Fig. 3). Using the seawater Sr concentration history from Fig. 1, the model-predicted values of $^{87}Sr/^{86}Sr$ for hydrothermal fluids vary over a large range from about 0.7030, which is lower than modern vent fluids, to about 0.7075, which is much higher than modern vent fluids. The corresponding fraction of recycled seawater Sr in venting hydrothermal fluid varies from about 20% to 80% during the Phanerozoic, and is maximized during periods of high seawater [Ca] and [Sr] and low seawater [Mg] and [SO$_4$]. The relationship between the fraction of recycled seawater Sr and the vent fluid $^{87}Sr/^{86}Sr$ is not simple because the seawater $^{87}Sr/^{86}Sr$ is also changing with time.

The relatively few available strontium isotope data from ophiolite epidosite and epidote-quartz veins are plotted in Figure 3 for comparison, based on the inference that they best record high-T MOR-type hydrothermal fluids through time. Epidote forms at temperatures greater than ~300°C, and is likely to precipitate from fully evolved vent fluids. Furthermore, epidosites and epidote-quartz veins in particular are thought to form preferentially along concentrated flow-

paths where water/rock ratios are high (29, 44–46) and are thus likely to be the best records of high-T fluids through time. Epidosites and epidote-quartz veins from the two youngest oceanic crustal sections [Pito Deep and Site 504B (33, 47)] have $^{87}Sr/^{86}Sr$ values that are close to typical average modern vent fluids, reinforcing the hypothesis that they record vent fluid chemistry in older rocks.

The available epidosite/epidote-quartz Sr isotope data (Fig. 3) are broadly consistent with the model. For the Cretaceous period, the Sr isotopes in epidosites and epidote-quartz veins from Troodos and Oman indicate that the model predicts the correct sense of change, but yields an amplitude that is too large. For other periods there are few ophiolite data, and the seawater concentration estimates for Sr are less reliable, but the model generally corroborates high observed $^{87}Sr/^{86}Sr$ in Ordovician epidotes when using the seawater [Sr] curve from Figure 1. The curves shown in Figure 3 are mostly illustrative of how the seawater chemical changes shown would translate into changes in $^{87}Sr/^{86}Sr$ of hydrothermal fluid dissolved Sr. The fact that the observed variations in ophiolite $^{87}Sr/^{86}Sr$ are not as extreme as predicted by the model could indicate that the Ca, Mg, SO_4, and Sr variations in paleoseawater were not as extreme as shown in Figure 1.

Lower estimates of Cretaceous seawater Sr/Ca (23), as roughly approximated by the constant seawater [Sr] calculations (Fig. 3), yield predicted hydrothermal $^{87}Sr/^{86}Sr$ somewhat too low relative to the available data. Our conclusion is that the model captures essential aspects of the exchange at mid-ocean ridges and the available data, but requires more data to be sufficiently refined for accurate predictions of paleo-hydrothermal behavior. In particular, it is important to accurately model the behavior of Sr relative to Ca, something that can be done only crudely with currently available experimental and field data (35–37).

Another potential issue concerns the role of carbonate in the hydrothermal systems. There is evidence for elevated amounts of carbonate precipitation in oceanic crust at certain times in the geologic past (48, 49). In the modern ocean, the amount of dissolved carbonate in seawater (~2 mmol/kg as opposed to 28 mmol/kg SO_4), which would precipitate in an analogous manner to sulfate as fluids are heated, serves as only a small sink for seawater Ca and Mg. If dissolved inorganic carbon were present in the oceans at higher concentration in the geologic past, it could

potentially affect the charge balance. However, estimates suggest that total dissolved carbon in the oceans has not changed significantly over the past 70 million years (50).

Hydrothermal Ca and Sr fluxes through time

Our model provides an approach for estimating the effects of seawater chemistry on chemical exchange between seawater and oceanic crust in the *high temperature* parts of MOR circulation systems. The removal of Mg and SO_4 from seawater in our model is not different from previous studies [(12) and references therein]; at all times these components are fully removed from the circulating seawater at and near MOR's. Overall, our modeling indicates that seafloor hydrothermal systems respond to changes in the chemical composition of seawater, but this is unlikely to be a major cause of seawater chemical variations.

The model generates estimates of seawater and basaltic [Ca] and [Sr] in hydrothermal vent fluids. The total amount of Ca and Sr transferred from basalt to the oceans is the product of these concentrations and the total amount of fluid flowing through MOR hydrothermal systems globally. Calculated values for the relative fluxes of high-T hydrothermal [Ca] and [Sr] derived from basalt (per unit expelled hydrothermal fluid) vary by a factor of ~1.6 throughout the Phanerozoic, with a notable low in the Cretaceous (Fig. 4a). The transfer of Sr and Ca from basalt to the oceans (Fig. 4a) is less efficient during periods when seawater [Mg] and [SO_4] are low compared to [Ca] and [Sr]. This behavior serves as a small negative feedback on seawater [Ca] and [Sr] (Fig. 4b), and also has implications for $^{87}Sr/^{86}Sr$ and ^{40}Ca in seawater throughout Earth history (51).

Over the Phanerozoic, the model shows a gradual decrease in the efficiency of Sr and Ca transfer from basalts with decreasing age, as a result of generally decreasing seawater [Mg]/[SO_4] towards the present day. This Phanerozoic trend is reversed in the Late Cenozoic, and is also punctuated by a relatively short pulse during the Permian, when seawater compositions were similar to modern.

An interesting aspect of our results is that while Cretaceous seawater $^{87}Sr/^{86}Sr$ was relatively low (Fig. 3), our model suggests that MOR hydrothermal systems were less efficient at transferring Sr from oceanic crust to seawater (Fig. 4a). Possibly counterbalancing this effect is the amount of global hydrothermal fluid flux, which some have inferred was higher than modern in the

Cretaceous (52, 53) as a consequence of globally higher seafloor generation rates Our results therefore suggest that either low temperature exchange of Sr between basalt and seawater (including weathering of ocean-island basalts) was responsible for a large fraction of the overall basalt-seawater exchange (42, 48, 54), or conversely, that there was an exceptionally small continental weathering flux of radiogenic Sr during the Cretaceous. Supporting the prior interpretation are records of low-temperature hydrothermal crust alteration (48), which suggest that higher water temperatures increased the magnitude of low-temperature basalt-seawater exchange. Such small temperature differences (~10 C), however, would have little effect on our results for high-T fluids.

Seawater SO_4 levels alone can affect the transfer of basaltic Sr to the oceans because basaltic Sr can be captured in anhydrite. If decoupled from oscillations in seawater [Mg] and [Ca] (such as those that occur during the Phanerozoic), low seawater $[SO_4]$ leads to an increase in basaltic Sr delivery to the oceans per unit of hydrothermal fluid. This result may be important for understanding hydrothermal circulation during the Archean and Proterozoic, when seawater $[SO_4]$ may have been especially low (12, 55, 56). Neoproterozoic $^{87}Sr/^{86}Sr$ values, for example, are generally lower than for the Phanerozoic (57), which could be partially explained by contemporaneously low levels of seawater $[SO_4]$. Sulfate could also affect the exchange of radiogenic ^{40}Ca between seawater and the oceanic crust [53].

The fate of seawater sulfate in oceanic crust, however, is poorly constrained (58, 59); anhydrite is likely to be a sink for oceanic sulfate, despite its retrograde solubility, but it is uncertain how much of it is fixed into the crust versus dissolved back into the oceans prior to subduction. Sulfur isotope studies demonstrate that seawater sulfate has been incorporated into the mantle throughout geologic time [e.g. (60, 61)] and models indicate that only ~20-35% of the modern sulfur burial flux is in the form of pyrite (59), which suggests that the remaining sulfur sink is initially in the form of sulfate or sulfur intermediates, but this estimate can vary significantly based on the amount of recycled evaporite material in rivers (58). Although we have not attempted to create a global model for seawater [Ca] and [Sr] through time, differences in low-temperature fluxes and retrograde outputs from altered oceanic crust [e.g. (42, 48)], along with potential differences in reaction rates caused by paleoseawater variability, would be important to consider [a dual-porosity model is presented in the SI Text to explore the effects of reaction rate

differences on hydrothermal exchange (SI Appendix, SI Text, Fig. S5)]. On the other hand, if our calculations, relating to high temperature hydrothermal fluids, were to represent the average exchange of Sr between oceanic basalt and the oceans, it would require re-evaluation of the relationship between the seawater $^{87}Sr/^{86}Sr$ curve and continental weathering fluxes.

Author contributions: S.T.B. and D.J.D. conceived idea for study; M.A.A. and N.J.P. developed Sr-isotope and charge-balance models with input from D.J.D. and S.T.B.; N.J.P. performed reaction-path simulations; D.J.D. and M.A.A. developed dual-porosity model; M.A.A., D.J.D., and N.J.P. wrote the paper.

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<u>Figure Captions 1-4</u>

Fig. 1. Compilation of data for seawater [Mg], [Ca], [SO$_4$], and [Sr] estimates over the Phanerozoic. Data for [Mg] (light blue squares and rectangles), [Ca] (dark blue triangles), and [SO$_4$] (grey diamonds), are in mmol/kg and derive from fluid inclusions in marine halite (13, 14). Large light blue rectangles are [Mg] estimates based on measured Ca/SO$_4$. Rough seawater [Sr] estimates (in μmol/kg, dashed red line) were calculated from the [Ca] estimates, based on consistent binned Sr/Ca measurements in low-Mg biological calcite over the Phanerozoic from various studies (20, 24), but are subject to uncertainties. Lower estimates of seawater Sr/Ca (23) lead to approx. modern Sr concentrations from 30-180 Ma. Geologic eras and periods of calcite and aragonite seas are demarcated at the top of the graph.

Fig. 2. Schematic representation of hydrothermal budgets for Mg, Ca, and SO$_4$. The numbers in blue are concentrations in mmol/kg for [Mg]:[Ca]:[SO$_4$] based on the charge balance calculations presented below and formalized in equation [1]. Numbers in brackets reflect mmol/kg of SO$_4$ lost from seawater to anhydrite-1 (Anh$_1$), and anhydrite-2 (Anh$_2$), and mmol/kg of Mg lost from seawater to chlorite and other silicates (Chl).

Fig. 3. Calculated hydrothermal strontium compositions through time, based on equation [5], varying input seawater [Mg], [Ca], [SO$_4$], [Sr], and ^{87}Sr/^{86}Sr composition. [Mg], [Ca], [SO$_4$], and [Sr] data are the same as for Fig. 1. Black line is seawater ^{87}Sr/^{86}Sr composition through time (43), red line is the calculated ^{87}Sr/^{86}Sr of output hydrothermal fluid. Dotted red line is model result for hydrothermal ^{87}Sr/^{86}Sr using constant modern seawater [Sr], which is approx. consistent with lower estimates of Sr/Ca for ~30-180 Ma (23). Grey diamonds are ^{87}Sr/^{86}Sr data from epidosites and epidote-quartz veins from ophiolites and oceanic drill-cores (28–34). Several of the late Cambrian epidosite samples plotting highest above our model predictions have δ^{18}O values indicative of metamorphic resetting (28).

Fig. 4a,b. Calculated basaltic [Ca] and [Sr] in hydrothermal fluids through time, based on equation [5], varying input seawater [Mg], [Ca], [SO$_4$], and [Sr] (Fig. 1). a) basaltic [Ca] (dark blue) and basaltic [Sr] (red) within hydrothermal fluids through time, and b) in hydrothermal fluids relative to seawater [Ca] and [Sr]. Dotted red lines are model results using constant modern seawater [Sr].