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Alteration of ocean crust provides a strong temperature dependent feedback on the geological carbon cycle and is a primary driver of the Sr-isotopic composition of seawater

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A B S T R A C T

On geological timescales there is a temperature dependent feedback that means that increased degassing of CO_2 into the atmosphere leads to increased CO_2 drawdown into rocks stabilizing Earth's climate. It is widely considered that this thermostat largely comes from continental chemical weathering. An alternative, or additional, feedback comes from dissolution of seafloor basalt in low-temperature (tens of °C), off-axis, hydrothermal systems. Carbonate minerals precipitated in these systems provide strong evidence that increased bottom water temperature (traced by their O-isotopic compositions) leads to increased basalt dissolution (traced by their Sr-isotopic compositions). Inversion of a simple probabilistic model of fluid–rock interaction allows us to determine the apparent activation energy of rock dissolution in these systems. The high value we find ($92 \pm 7\ \mathrm{kJ\,mol^{-1}}$) indicates a strong temperature dependence of rock dissolution. Because deep-ocean temperature is sensitive to global climate, and the fluid temperature in the upper oceanic crust is strongly influenced by bottom water temperature, increased global temperature must lead to increased basalt dissolution. In turn, through the generation of alkalinity by rock dissolution, this leads to a negative feedback on planetary warming; i.e. off-axis, hydrothermal systems play an important role in the planetary thermostat. Changes in the extent of rock dissolution, due to changes in bottom water temperature, also lead to changes in the flux of unradiogenic Sr into the ocean. The decreased flux of unradiogenic Sr into the ocean due to the cooling of ocean bottom water over the last 35 Myr is sufficient to explain most of the increase in seawater $^{87}Sr/^{86}Sr$ over this time.

1. Introduction

The long-term carbon cycle is, to a first order, controlled by volcanic and metamorphic CO_2 degassing and the drawdown of CO_2 into carbonate minerals (Walker et al., 1981). The feedback processes that control the fine balance between degassing and drawdown are critical to maintaining a habitable planet (Berner and Caldeira, 1997) but are incompletely understood. The generally accepted mechanism for this planetary thermostat is that increased atmospheric CO_2 leads to increased surface temperature and precipitation and hence increased rates of CO_2 consumption via continental weathering (e.g., Walker et al., 1981; Berner et al., 1983; Berner, 2004 and references therein). This basic model has been developed to include many other factors such as: (i) changes in continental weatherability due to tectonic processes (e.g., Raymo and Ruddiman, 1992) and variations in vegetation (e.g., Pagani et al., 2009); and (ii) organic carbon cycling (e.g., France-Lanord and Derry, 1997). However, the basic premise of the model remains that continental chemical weathering is central to the long-term carbon cycle.

An alternative feedback mechanism that could control the long-term carbon cycle comes from the reaction of seawater with the oceanic crust in low-temperature, off-axis, hydrothermal systems (Francois and Walker, 1992; Brady and Gislason, 1997; Sleep and Zahnle, 2001; Gillis and Coogan, 2011; Coogan and Gillis, 2013). It has been argued that variations in deep-water pH are too small for changes in the deep ocean hydrogen ion concentration to provide a feedback on the long-term carbon cycle (Caldeira, 1995). However, variations in deep-water temperature (Brady and Gislason, 1997), perhaps combined with variations in seawater major element composition (Coogan and Gillis, 2013), provide viable feedback mechanisms. Off-axis hydrothermal systems circulate a volume of seawater equivalent to the entire ocean through the upper oceanic crust every few hundred thousand years (e.g., Johnson and Pruis, 2003). Fluid flows through the permeable upper crust (lavas) where it is heated by the cooling of the ocean lithosphere be-

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fore discharging back out of this aquifer into the ocean (e.g., Fisher and Becker, 2000). Reactions within the crust generate the alkalinity required for carbonate mineral precipitation (Coogan and Gillis, 2013). Because reaction rates are temperature sensitive, the extent of fluid–rock reaction within the crust is expected to depend on the temperature of the water entering the crust (i.e. ocean bottom water), providing a temperature-dependent feedback on CO_2 consumption (Brady and Gislason, 1997). This model is supported by the observation of higher CO_2 contents in altered late Mesozoic upper oceanic crust than late Cenozoic upper oceanic crust (Gillis and Coogan, 2011).

Carbonate minerals are found in the lava section of the crust where they occur in veins, filling pore spaces and replacing igneous phases (e.g., Staudigel et al., 1981; Alt and Teagle, 1999; Coggon et al., 2004; Gillis and Coogan, 2011; Rausch et al., 2013). Bulk-rock CO_2 contents are controlled by the abundance of secondary carbonates. These range from ∼0.5 to 4.0 wt% (Gillis and Coogan, 2011 and references therein) indicating a substantial C sink. Because deep seawater is not saturated with carbonate minerals, reactions in the crust are required to drive the precipitation of significant masses of carbonate minerals. It has been suggested that the carbonate mineral forming reactions involve Ca leaching from the rock charge balanced by Mg uptake into the rock (e.g., Berner, 2004). However, models of fluid–rock reaction show that neither leaching Ca from the crust charge balanced by exchange for Mg (i.e., without alkalinity generation), nor heating the hydrothermal fluid, can drive the precipitation of substantial amounts of carbonate. Instead carbonate mineral precipitation is largely driven by alkalinity generation (Spivack and Staudigel, 1994; Coogan and Gillis, 2013). The compositions of carbonate minerals thus provide information about the conditions within the crust during this alkalinity production.

Understanding past rates of chemical weathering of the continents, and paleo-hydrothermal chemical fluxes, is difficult. Perhaps the most widely used tracer of the relative rates of chemical dissolution of continental crust and mantle-derived (basaltic) material is the Sr-isotopic composition of seawater for which there is an exquisite paleo-record (e.g., Veizer et al., 1999). The simplest interpretation of variations in the Sr-isotopic composition of seawater is that an increase in $^{87}Sr/^{86}Sr$ indicates a relative increase in the flux of Sr from old continental material (high Rb/Sr). Conversely, a decrease in seawater $^{87}Sr/^{86}Sr$ indicates a relative increase in the flux of Sr from mantle-derived (or juvenile) material with low time-integrated Rb/Sr. The large increase in seawater $^{87}Sr/^{86}Sr$ over the last ∼35 Myr is widely considered to largely reflect an increased flux of radiogenic Sr from rivers draining the Himalaya which have been built over this time (e.g., Raymo and Ruddiman, 1992). The details of how this links to silicate weathering on the continents remains unclear in part because of uncertainty in the partitioning of the Sr-flux from silicate and metacarbonate material (e.g., Edmond, 1992; Bickle et al., 2001, 2005).

Here we use the compositions of carbonate minerals from the upper oceanic crust to investigate the conditions within the crust during the time interval in which they were forming. We use their O-isotopic compositions to determine the temperature of the fluid they grew from and their Sr-isotopic composition to determine the amount of basalt dissolved into this fluid. We develop a simple model of fluid–rock reaction in the crust that allows us to invert these data to determine the temperature sensitivity of fluid–rock reaction. We find a strong temperature dependence of rock dissolution suggesting an important role for off-axis hydrothermal systems in controlling Earth's thermostat; i.e., when bottom water temperatures increase basalt dissolution rates increase and the drawdown of CO_2 into the upper oceanic crust increases. Modelling the decreased flux of unradiogenic Sr from off-axis hydrothermal systems into the ocean due to bottom water cooling over the last ∼35 Myr shows that this is sufficient to explain most of the rise of seawater $^{87}Sr/^{86}Sr$ since this time.

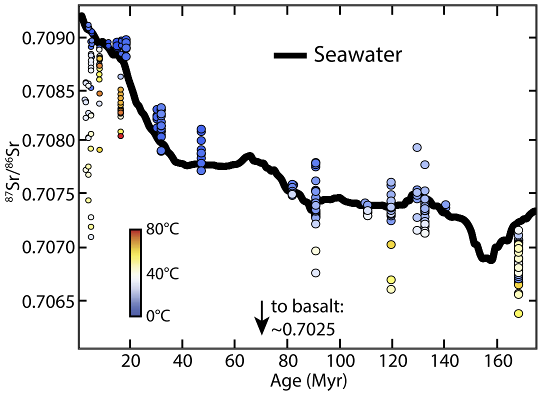

Fig. 1. Compilation of Sr-isotopic compositions of carbonates from the upper oceanic crust plotted as a function of the age of the crust they come from. Symbol colour reflects the temperature of carbonate precipitation using the carbonate O-isotope thermometer of Epstein et al. (1953) and the age dependence of the O-isotopic composition of seawater of Coggon et al. (2010). This is appropriate because the fluid $\delta^{18}O$ is little modified by fluid–rock reaction within the crust due to the high water-to-rock ratio (Anderson et al., 2013). The same fractionation factor was used for both aragonite and calcite because for many carbonate O- and Sr-isotope analyses the mineralogy is unknown, or mixed, and using the same fractionation factor only translates into a few degrees Celsius uncertainty. Note that higher carbonate precipitation temperatures are associated with lower $^{87}Sr/^{86}Sr$ due to larger amounts of basalt dissolution into the hydrothermal fluid. Larger symbols indicate those data used in the inversion while smaller symbols are data not used here due to coming from rapidly sedimented regions (see text for details). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Determining the temperature dependence of rock dissolution

2.1. A carbonate Sr- and O-isotope compilation

In order to empirically determine the temperature dependence of fluid–rock reaction within off-axis hydrothermal systems we need tracers of both the fluid temperature and the amount of basalt that dissolved into the fluid. Carbonate O-isotope thermometry provides an estimate of the temperature of fluid–rock reaction and carbonate Sr isotope data provide information about the proportion of seawater and rock derived Sr in the fluid. We use a global compilation of the O- and Sr-isotopic compositions of carbonate minerals from the upper oceanic crust (Fig. 1) to quantify the temperature dependence of fluid–rock reaction. This is based on the compilation of Gillis and Coogan (2011) supplemented with data from Rausch et al. (2013) and new data, largely from the Troodos ophiolite ($n = 28$; 10 of which are unpublished data provided by K.M. Gillis), but also from drill cores in modern crust ($n = 5$; Supplementary Table 1). This global dataset was filtered to exclude locations were the sedimentation rate was >20 m Myr^{-1} (compared to a global average of 3.5 m Myr^{-1}; Anderson et al., 2012) because at such anomalously high sedimentation rates reactions within the sediment pile are likely to invalidate our assumption (see below) that the hydrothermal system is recharged by pristine seawater. Instead, a portion of the fluid recharging the hydrothermal system likely comes through the sediment and may be modified by reactions within the sedimentary pile. Samples from crustal sections that were sedimented rapidly mainly come from two distinct sedimentary environments.

The first group of rapidly sedimented sites are located under the equatorial sediment bulge where high productivity in the water column leads to rapid deposition of carbonate-rich sediments (mainly DSDP/ODP Holes 504B, 896A and 1256D; in the latter site the sedimentation rate was >30 m Myr^{-1} initially although