



# Diffusive cation fluxes in deep-sea sediments and insight into the global geochemical cycles of calcium, magnesium, sodium and potassium



Xiaole Sun<sup>a,\*</sup>, John Higgins<sup>b</sup>, Alexandra V. Turchyn<sup>a</sup>

<sup>a</sup> Department of Earth Sciences, University of Cambridge, CB2 3EQ Cambridge, UK

<sup>b</sup> Department of Geosciences, Princeton University, Princeton, NJ 08544, USA

## ARTICLE INFO

### Article history:

Received 20 April 2014

Received in revised form 3 October 2015

Accepted 21 December 2015

Available online 23 December 2015

### Keywords:

Biogeochemical cycles

Diagenesis in marine sediments

Cation fluxes within marine sediments

## ABSTRACT

The biogeochemical cycles of the ocean's major cations – calcium, magnesium, sodium and potassium – are linked to the ocean's alkalinity budget through terrestrial weathering and the subsequent formation and burial of calcium carbonate in the ocean. Chemical reactions within ocean sediments play a critical role in the biogeochemical cycles of the major cations, as indicated by geochemical gradients (both positive and negative) in the concentrations of these cations within the pore-fluid system (i.e. fluid trapped between sediment particles). Here we review the biogeochemical cycles of calcium, magnesium, and sodium, and provide new estimates of the diffusive fluxes of these cations within marine sediments to explore the importance of these sedimentary processes. We quantify these fluxes by compiling a global database of pore fluids from the various Ocean Drilling Programs (Deep Sea Drilling Program – DSDP, Ocean Drilling Program – ODP, International Ocean Drilling Program – IODP), comprising nearly 700 locations, which allows a wider geographic coverage and therefore better integrated flux estimates than previous work has allowed. The myriad of seafloor chemical reactions that may influence the concentrations of the major cations in pore fluids include authigenic carbonate precipitation, carbonate dissolution, clay mineral formation, and ion exchange; as previous work has shown, we confirm that these integrated fluxes are globally significant. Because the DSDP/ODP/IODP cores begin sampling one meter below the sediment–water interface, additional studies of the processes within the top meter are needed to accurately calculate total cation fluxes across the sediment–water interface. Delineating the various processes that control the major cation chemistry of seawater over geologic time scales remains critical for understanding the operation of the CO<sub>2</sub> silicate-weathering thermostat on geologic timescales.

© 2015 Elsevier B.V. All rights reserved.

## Contents

1. Introduction . . . . .	65
2. The biogeochemical cycles of calcium, magnesium, sodium and potassium . . . . .	66
2.1. Calcium . . . . .	66
2.2. Magnesium . . . . .	66
2.3. Sodium . . . . .	66
2.4. Potassium . . . . .	67
3. Quantification of the cation flux within marine sediments. . . . .	68
4. Assessing the influence of other processes in marine sediments – fluid flow and long-term changes in the chemical composition of seawater. . . . .	70
5. The flux of calcium, magnesium, sodium and potassium within marine sediments. . . . .	71
6. Discussion . . . . .	73
6.1. Carbonate dissolution/precipitation. . . . .	73
6.2. Clay authigenesis or 'reverse weathering'. . . . .	75
6.3. Ion exchange. . . . .	75
7. Summary. . . . .	75
Acknowledgments . . . . .	76
Appendix A. List of the studied sites and the calculated fluxes of calcium, magnesium, sodium and potassium . . . . .	76
References. . . . .	76

\* Corresponding author at: Baltic Sea Centre, Stockholm University, SE - 10691, Stockholm, Sweden.  
E-mail address: [xiaole.sun@su.se](mailto:xiaole.sun@su.se) (X. Sun).

## 1. Introduction

Silicate weathering plays a key role in the global carbon cycle by delivering alkalinity, in the form of cations, to the ocean (Walker et al., 1981; Berner et al., 1983; Meybeck, 2003; Maher and Chamberlain, 2014; Torres et al., 2014). However, of the four major cations in the ocean – calcium, magnesium, sodium, and potassium – only the removal of calcium (in calcium carbonate) is associated with a significant sink of ocean alkalinity (Milliman, 1993; Milliman and Droxler, 1996). The fact that the sink for ocean alkalinity is nearly entirely calcium while the source of alkalinity comprises all four major cations requires that there must be processes that exchange calcium for magnesium, sodium and potassium or independently consume alkalinity in order to maintain the charge balance (Berner and Berner, 2012). These processes link the biogeochemical cycles of the non-calcium cations (e.g. magnesium, sodium, and potassium) to the global alkalinity balance and the silicate weathering-thermostat over geologic timescales (Walker et al., 1981).

The primary sources of calcium, magnesium, sodium, and potassium to the ocean are from water–rock interactions either on the continents (terrestrial weathering and subsequent riverine input – Berner et al., 1983; Meybeck, 1987, 2003; Berner and Berner, 2012) or in the seafloor (low- and high-temperature hydrothermal alteration of oceanic crust – Edmond et al., 1979; Von Damm, 1990; Mottl and Wheat, 1994; Elderfield and Schultz, 1996; Wheat and Mottl, 2004). The primary sinks for cations from the ocean are the formation and deposition of minerals in marine sediments or within the oceanic crust. Historically, the fluxes within the global biogeochemical cycles were quantified by measurements of cation concentrations and water fluxes in rivers and hydrothermal systems and the chemical composition (and sedimentation rates) of marine sediments (Garrels and Mackenzie, 1971; Berner and Berner, 2012). This approach, however, is not without problems. For example, measurements of river chemistry today capture a ‘snapshot’ of modern river fluxes, which may or may not represent true geochemical fluxes over glacial–interglacial, or million-year, or multi-million year timescales (e.g. Vance et al., 2009). In addition, it is difficult at times to discriminate between authigenic and detrital minerals (especially clays) in marine sediments (Mackenzie and Garrels, 1966; Kastner, 1999; Michalopoulos and Aller, 2004). Therefore, modern measurements of input and output fluxes need not – and most likely do not – reflect a system at, or near, steady-state.

In addition, other processes occurring over the Earth’s surface environment remain poorly quantified. The relative concentrations of various elements in high-temperature hydrothermal systems and water fluxes are reasonably well constrained because black smoker-type fluids have been well sampled and there are robust estimates of the amount of heat, and therefore water, carried by these systems (Von Damm, 1990; Elderfield and Schultz, 1996). However, a large fraction of the seafloor heat flux is carried by lower-temperature fluids on ridge flanks and these fluxes are poorly constrained due to fewer sampled sites of altered oceanic crust and an incomplete understanding of the hydrology and geochemistry on ridge flanks (Rudnicki et al., 2001; Wheat et al., 2003; Wheat and Mottl, 2004; Wheat and Fisher, 2008; Anderson et al., 2014).

The objective of this review is to explore another process on the Earth’s surface environment that plays a role in the biogeochemical cycle of the major cations: diffusive fluxes of cations within marine sediments due to mineral precipitation and dissolution in the subsurface. If all of the minerals and sediment particles falling on the sediment–water interface were ultimately buried, the elemental composition of the sediments at the sediment–water interface would be a fair reflection on what is removed from the Earth’s surface environment. However, below the sediment–water interface exists a highly dynamic environment, which alters the chemical makeup of the sedimentary pile (e.g. Froelich et al., 1979; Calvert and Pedersen, 1993; Borowski et al., 1996; Van Cappellen and Wang, 1996; Archer and Maier-Reimer,

2002; Burdige et al., 2010; Arndt et al., 2013; Meister et al., 2013). Subseafloor processes such as microbial oxidation of organic carbon, carbonate dissolution and reprecipitation and sedimentary ion exchange on clay minerals have received growing attention in the past decades (e.g. Berner et al., 1970; Ben-YaaKov, 1973; Froelich et al., 1979; Berner, 1980; Milliman, 1993; Morse and Arvidson, 2002; D’Hondt et al., 2004; Zeebe, 2007; Burdige et al., 2010; Schrag et al., 2013; Jones et al., 2014). Global quantification for some of these processes remains enigmatic, however, and some processes such as authigenic clay formation and ion exchange in deep-sea sediments particularly remain poorly quantified.

We can interrogate the chemical reactions involving the major cations through numerical modeling of pore fluid profiles within marine sediments (e.g. Boudreau, 2003; Burdige and Gieskes, 1983; Rabouille and Gaillard, 1991; Holland, 1978; Dhakar and Burdige, 1996; Soetaert et al., 1996; Wang and Van Cappellen, 1996; Meister et al., 2013). Pore fluids are the fluids trapped in the pore space between sediment particles (Bates and Jackson, 1984). Due to reactions in the sediment pile, the chemical composition of the pore fluids often evolves away from the chemical composition of seawater (e.g. Fig. 1). How much the pore-fluid composition evolves depends on 1) the rate of chemical reactions occurring within marine sediments; 2) fluid transport by diffusion or advection within the pore fluids; 3) the initial chemical composition of seawater (e.g. Jørgensen, 2002; Morse and Mackenzie, 1990; Burdige, 2006). Once the effects of advection of fluids and changes in seawater chemistry have been considered, it is possible to resolve and then quantify the rate of chemical reactions within the subseafloor sedimentary pile, which may turn marine sediments into an additional source to or a sink from the ocean for some elements (Broecker, 1971; McDuff and Morel, 1980; Sillén, 1967). Quantification of these processes requires the concentration gradient of the element of interest within the pore fluids, which defines the net direction and magnitude of the flux. Similar fluxes for an element can be obtained with either small changes in pore fluid concentration over shorter length-scales or large changes in concentration in pore fluid over longer length-scales.

Processes occurring within the uppermost meter of sediments – here called the boundary layer – are particularly important for understanding the interaction of these sedimentary diffusive fluxes with the overlying ocean. For example, seminal work by Sayles (1979), focusing on the top meter of sediment from cores throughout the Atlantic Ocean, found a globally significant upward fluxes of calcium and sodium from this ‘boundary layer’ into the overlying ocean and large downward fluxes of magnesium and potassium from the ocean throughout the boundary layer into deeper sediments. More recently, studies of chemical reactions in this boundary layer have demonstrated rapid changes in near-surface pore fluid chemistry, at times only centimeters below the sediment–water interface. The chemical environment from above the sediment–water interface to immediately below can change dramatically, driving large ion exchange across this surface (e.g. Hales and Emerson, 1996; Aller et al., 2004; Jahnke and Jahnke, 2004; Burdige et al., 2010). These detailed studies are often from one or two locations, and are therefore difficult to extrapolate to fluxes to and from the global ocean, therefore, estimates of the global cation flux from the boundary layer across the sediment–water interface remains poorly constrained.

This review focuses on the diffusive flux of cations within deeper sediments, below this reactive near-surface meter of sediments. This deeper flux is easier to resolve and globally extrapolate, because over the past decades the increasing coverage of the ocean floor through the various International Ocean Drilling Programs (DSDP/ODP/IODP) have included measurements of concentrations of various elements within sedimentary pore fluids, although measurements start one meter below the sediment–water interface. Measurements of these concentration gradients, along with knowledge of sedimentation rates and porosity allow us to better quantify different chemical reactions occurring deeper within ocean sediments. Because of the timescales

Download English Version:

<https://daneshyari.com/en/article/4718122>

Download Persian Version:

<https://daneshyari.com/article/4718122>

[Daneshyari.com](https://daneshyari.com)