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## Records of Neogene seawater chemistry and diagenesis in deep-sea carbonate sediments and pore fluids

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### ABSTRACT

Deep-sea pore fluids are potential archives of ancient seawater chemistry. However, the primary signal recorded in pore fluids is often overprinted by diagenetic processes. Recent studies have suggested that depth profiles of Mg concentration in deep-sea carbonate pore fluids are best explained by a rapid rise in seawater Mg over the last 10–20 Myr. To explore this possibility we measured the Mg isotopic composition of pore fluids and carbonate sediments from Ocean Drilling Program (ODP) site 807. Whereas the concentration of Mg in the pore fluid declines with depth, the isotopic composition of Mg in the pore fluid increases from  $-0.78\text{‰}$  near the sediment–water interface to  $-0.15\text{‰}$  at 778 mbsf. The Mg isotopic composition of the sediment, with few important exceptions, does not change with depth and has an average  $\delta^{26}\text{Mg}$  value of  $-4.72\text{‰}$ . We reproduce the observed changes in sediment and pore-fluid Mg isotope values using a numerical model that incorporates Mg, Ca and Sr cycling and satisfies existing pore-fluid Ca isotope and Sr data. Our model shows that the observed trends in magnesium concentrations and isotopes are best explained as a combination of two processes: a secular rise in the seawater Mg over the Neogene and the recrystallization of low-Mg biogenic carbonate to a higher-Mg diagenetic calcite. These results indicate that burial recrystallization will add Mg to pelagic carbonate sediments, leading to an overestimation of paleo-temperatures from measured Mg/Ca ratios. The Mg isotopic composition of foraminiferal calcite appears to be only slightly altered by recrystallization making it possible to reconstruct the Mg isotopic composition of seawater through time.

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### 1. Introduction

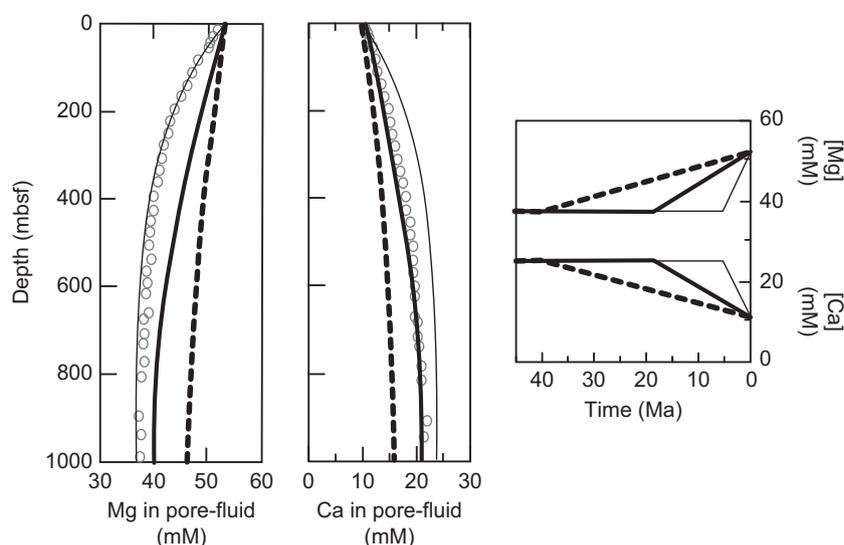
Deep-sea sediment pore fluids retain a ‘memory’ of past changes in seawater chemistry attenuated by diffusion and modified by chemical reactions within the sediment column and underlying crust. The pore-fluid diffusion approach has been successfully applied to reconstruct changes in the  $\delta^{18}\text{O}$  and chlorinity of seawater during the Last Glacial Maximum (Adkins and Schrag, 2001; Schrag et al., 1996) and has also been proposed for changes in the major element chemistry of seawater on much longer timescales (Fantle and DePaolo, 2006; Fig. 1). In the case of changes in  $\delta^{18}\text{O}$  and chlorinity of seawater, reactions within the sediment column can be largely neglected and the pore fluid profile can be related to the changes in the upper boundary condition (i.e. the change in bottom-water  $\delta^{18}\text{O}$  and chlorinity). This is not the case for pore-fluid reconstructions of changes in the major element chemistry of seawater over geologic timescales

as most of the elements of interest (e.g. Mg, Ca,  $\text{SO}_4$ ) are significantly (and perhaps irretrievably) altered in the pore-fluid by chemical reactions within the sediment column and in the underlying crust. Recent work by Fantle and DePaolo (2006) argued that in thick, rapidly accumulating carbonate sediments, changes in the Mg content of the pore-fluid associated with chemical reactions (calcite recrystallization) are small. As a result, observed pore fluid profiles at these sites may reflect secular changes in the Mg content of seawater over the Neogene. However, this result is sensitive to the partitioning of Mg into recrystallized calcite, a variable which is poorly constrained in deep-sea sediments. The partitioning of Mg into recrystallized calcite also has implications for understanding the effects of diagenesis on Mg/Ca ratios in foraminiferal calcite, a widely used paleo-temperature proxy (Anand et al., 2003; Katz et al., 2010; Lea et al., 1999) which is known to be affected by dissolution (Brown and Elderfield, 1996; Dekens et al., 2002; Regenberg et al., 2006).

We have previously demonstrated that the isotopic composition of Mg in marine pore fluids can be used to identify sources and sinks of Mg in the sediment column and underlying crust (Higgins and Schrag, 2010). In this study, we try to tease apart the

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**Fig. 1.** Mg and Ca pore-fluid profiles at site 807A resulting from changes in the upper boundary condition (seawater concentration) assuming a non-reactive sediment column and no flux at the lower boundary. Data from Kroenke et al., (1991; ○). See text for details of the numerical model.

relative contributions of carbonate recrystallization and changes in Neogene seawater Mg to pore-fluid Mg profiles by providing new constraints on the partition coefficient of Mg in recrystallized calcite. We do this by measuring the magnesium isotopic composition ( $\delta^{26}\text{Mg}$ ) of the pore-fluid and sediments from ODP site 807 on the Ontong Java Plateau (Kroenke et al., 1991). We simulate these profiles, together with previously published data for Sr and Ca using a time-dependent diffusion–reaction model of recrystallization in the sediment–pore fluid system. The model fits yield an internally consistent value for the partition coefficient of Mg in recrystallized calcite and changes in the Mg content of seawater over the Neogene. We explore the sensitivity of the model to different values of the distribution coefficients of Mg, Mg isotope fractionation factors associated with recrystallization, and the diffusivity of ions in sediment pore fluids. We discuss our results in the context of paleo-proxies based on the Mg content of biogenic calcite and Neogene seawater chemistry.

## 2. Methods

### 2.1. Sample location and description

Site 807 is located on the Ontong Java Plateau at 2803 m water depth. Pore fluids at site 807 are characterized by declining Mg concentrations, from 52.3 millimolar at 4.45 m below seafloor (mbsf) to 38.9 mM at 778.9 mbsf. Ca concentrations increase with depth, from 10.6 mM at 4.45 mbsf to 21.2 mM at 778.9 mbsf, as do Sr concentrations, which rise rapidly, from 130  $\mu\text{M}$  to 927  $\mu\text{M}$ , in the upper  $\sim 200$  m of the sediment column and plateau and/or slightly decline thereafter. The sediment is composed almost entirely of biogenic carbonate (86.9–98.9 wt%; largely coccoliths and foraminifera) and characterized by sedimentation rates averaging 2–3 cm/kyr over the studied interval (0–997 mbsf). A transition from ooze to chalk occurs at 293 mbsf, and from chalk to limestone at 1098 mbsf. Relative contributions of coccoliths and foraminifera to the carbonate budget at site 807 are not known precisely, but nearby sediments of Holocene age suggest  $\sim 50/50$  (Broecker and Clark, 2009). Measured Mg/Ca and Sr/Ca ratios of the carbonate sediment exhibit some scatter with depth, ranging from 2.0 to 4.8 mmol/mol and 1.0 to 1.8 mmol/mol, respectively (Delaney and Linn, 1993). Measured Mg/Ca ratios of the bulk sediment are consistent with typical Mg/Ca

ratios in foraminifera from the Ontong Java Plateau (Dekens et al., 2002; Lea et al., 2000) but must to some degree reflect mixing between high-Mg/Ca (1–4 mmol/mol Mg/Ca) foraminifera and low-Mg/Ca (0.2–0.3 mmol/mol Mg/Ca) coccolith sediment (Stoll et al., 2001).

### 2.2. Analytical measurements of Mg isotopes

Magnesium isotope measurements of the ODP pore fluids from site 807 followed the analytical protocols developed by Higgins and Schrag (2010; see Section S1 in the Supplementary Information). Measurements of Mg isotope ratios were conducted on a GV Isoprobe P multi-collector (MC-) ICP-MS in the Laboratory of Cosmochemistry at Harvard University and on a Thermo Scientific Neptune MC-ICP-MS at the Woods Hole Oceanographic Institute. See Section S1 in the Supplementary Information for further details.

Magnesium isotope ratios are reported using delta notation

$$\delta^{25,26}\text{Mg} = \left( \frac{\left( \frac{^{25,26}\text{Mg}}{^{24}\text{Mg}} \right)_{\text{SAM}}}{\left( \frac{^{25,26}\text{Mg}}{^{24}\text{Mg}} \right)_{\text{STD}}} - 1 \right) \times 100$$

where  $\left( \frac{^{25,26}\text{Mg}}{^{24}\text{Mg}} \right)_{\text{STD}}$  is the measured  $^{26}\text{Mg}/^{24}\text{Mg}$  ratio of the DSM-3 Mg standard (Galy et al., 2001, 2003). Repeat measurements of the Cambridge-1 Mg standard on the GV-Isoprobe P yielded  $\delta^{25}\text{Mg}$  and  $\delta^{26}\text{Mg}$  values of  $-1.34 \pm 0.14\text{‰}$  and  $-2.62 \pm 0.26\text{‰}$  ( $2\sigma_{\text{sd-external}}$ ;  $n=215$ ) relative to DSM-3. On the Thermo Neptune, Cambridge-1 Mg standard yielded  $\delta^{25}\text{Mg}$  and  $\delta^{26}\text{Mg}$  values of  $-1.34 \pm 0.06\text{‰}$  and  $-2.59 \pm 0.12\text{‰}$  ( $2\sigma_{\text{sd-external}}$ ;  $n=46$ ). Both measured values are indistinguishable from published values ( $\delta^{25}\text{Mg} = -1.33 \pm 0.07\text{‰}$ ;  $\delta^{26}\text{Mg} = -2.58 \pm 0.14\text{‰}$  (Galy et al., 2003)). A total of six samples (two carbonates and four pore fluids), measured on both the GV Isoprobe P and the Thermo Neptune MC-ICP-MS, were found to have the same  $\delta^{25}\text{Mg}$  and  $\delta^{26}\text{Mg}$  values to within 0.08‰ ( $1\sigma_{\text{sd}}$ ). Plotted in three-isotope space ( $\delta^{25}\text{Mg}$  vs.  $\delta^{26}\text{Mg}$ ) all measured samples fall on a line with a slope of  $0.5206 \pm 0.0062$  ( $R^2=0.9988$ ), consistent with mass-dependent fractionation of Mg isotopes.

### 3. Numerical model of the sediment pore-fluid system

Reconstructing changes in the magnesium content of seawater over the Neogene from deep-sea pore fluids in carbonate

sediments is possible only if the effects of both transport and calcite recrystallization on the magnesium pore-fluid profile can be accurately quantified. To do this we developed a numerical model of the sediment column at site 807 that tracks Mg, Ca, and Sr in both the pore-fluid and sediment. Our modeling approach can be separated into two parts. First, we use pore fluid Sr and Ca isotope profiles to determine rates of carbonate recrystallization following previous studies (Fantle and DePaolo, 2006, 2007; Richter and DePaolo, 1987). Second, we apply these recrystallization rates to magnesium in the pore fluid and sediment and use the magnesium isotope profiles of both the sediment and pore fluid to determine the partition coefficient for magnesium into recrystallized calcite. The distribution coefficient determines how much (if any) of the pore fluid magnesium profile is due to recrystallization. The residual is then modeled as a change in the upper boundary condition of the model—the magnesium content of seawater over the Neogene.

Our model is based on a 1-D diffusion–advection–reaction equation used by many authors (Berner, 1980; Fantle and DePaolo, 2006; Richter and DePaolo, 1987; Schrag et al., 1992)

$$\phi(z) \cdot \frac{\partial ({}^nX)}{\partial t} = \frac{\partial}{\partial z} \left( \phi(z) \cdot D_{nX} \cdot \frac{\partial ({}^nX)}{\partial z} \right) - \frac{\partial}{\partial z} \left( \phi(z) \cdot \omega(z) \cdot {}^nX(z) \right) - \phi(z) \cdot F_{pX(z)} \quad (1)$$

where  ${}^nX$  is the concentration of isotope  $n$  of element  $X$  (e.g.  ${}^{24}\text{Mg}$ ,  ${}^{25}\text{Mg}$ , or  ${}^{26}\text{Mg}$ ) in  $\text{mol kg}^{-1}$  pore-fluid,  $z$  is depth below the sediment–water interface,  $D_{nX}$  is the depth-dependent bulk sediment diffusion coefficient ( $\text{m}^2 \text{yr}^{-1}$ ) for element  $X$ ,  $\phi$  is the depth-dependent but time-invariant porosity,  $\omega$  is an advective velocity ( $\text{m yr}^{-1}$ ), and  $F_{nX(z)}$  is the recrystallization reaction for element  $X$  ( $\text{mol X kg sed}^{-1} \text{yr}^{-1}$ ). We define  $F_{pX(z)}$  following Richter and DePaolo (1987):

$$F_{pX(z)} = R(z) \cdot M(z) \cdot ({}_s^nX - \alpha_{X-\text{calcite}} \cdot K_X \cdot {}^nX) \quad (2)$$

where  $R(z)$ , is the depth/age dependent rate constant for recrystallization ( $\text{yr}^{-1}$ ),  $M(z)$  is the local solid to fluid mass ratio,  ${}_s^nX$  is the concentration of isotope  $n$  of element  $X$  in  $\text{mol kg}^{-1}$  sediment,  ${}_f^nX$  is the concentration of isotope  $n$  of element  $X$  in  $\text{mol kg}^{-1}$  pore-fluid,  $\alpha_{X-\text{calcite}}$  is the isotopic fractionation factor for element  $X$  relative to the low mass (e.g.  ${}^{24}\text{Mg}$ ,  ${}^{40}\text{Ca}$ ), and  $K_X$  is the distribution coefficient for element  $X$  between fluid and solid.  $K_X$  is related to the distribution coefficient for the element  $X$  to Ca ratio ( $K_{X/\text{Ca}}$ ) by  $K_X = (\text{Ca}_s/\text{Ca}_f) \cdot K_{X/\text{Ca}}$  where  $K_{X/\text{Ca}} = (\text{X}/\text{Ca})_s/(\text{X}/\text{Ca})_f$ . To calculate pore fluid Ca profiles we assume mass balance for calcite recrystallization such that  $M_{\text{Ca}} + M_{\text{Mg}} + M_{\text{Sr}} = 1$ , where  $M$  is the mol fraction of that element in the newly recrystallized calcite. In addition we assume that recrystallization results is associated with no net calcite precipitation or dissolution (see Section 4.2). We initially assume that the chemistry of the re-crystallizing biogenic carbonate is identical to the bulk sediment but explore the possibility of selective recrystallization the different sediment components (foraminifera and coccolithophores) given their very different Mg/Ca ratios and  $\delta^{26}\text{Mg}$  values.  $R(z)$  is parameterized following Richter and DePaolo (1987):  $R(z) = \lambda + \beta \cdot e^{-\gamma/z}$  where  $\lambda$ ,  $\beta$ , and  $\gamma$  are coefficients for the rate of recrystallization as a function of depth.

We model the deposition of a sediment column and the chemical cycling of its pore fluid using boxes of unconsolidated sediment, deposited at rates determined by the age and thickness of the sediment column, and compacted according to the observed porosity/depth relation (Richter and DePaolo, 1987, 1988; Schrag et al., 1992). The modeled sediment column at site 807 is made up of 142 boxes, 10.7 m thick (initially), deposited over 45 Myr. Initial conditions for the pore fluid are acquired from the concentration and isotopic composition of seawater at the time of sediment deposition. Boundary conditions for the model

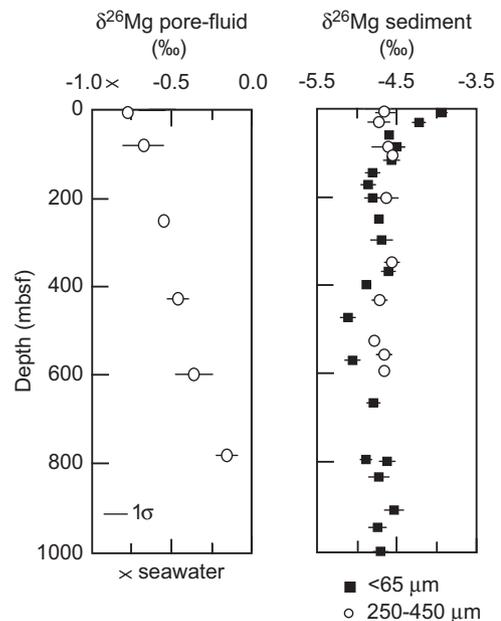
are the concentration and isotopic composition of Mg, Ca, and Sr in seawater through time (upper) and finite-flux of Mg and Ca across the lower boundary based on the observation of small but discernable gradients in Mg and Ca in deep pore fluids. We include fluid flow from compaction but neglect any externally-driven flow in light of previous work on nearby DSDP site 289 by Richter (1996) which found no evidence of external flow based on a coupled diagenetic model of Sr and  $\text{SO}_4$ . For additional details on the numerical model see Section S2 in the Supplemental Information.

The principle variables in the model are (1) the rate of sediment recrystallization ( $R(z)$ ); (2) distribution coefficients for Mg and Sr between pore-fluid and calcite ( $K_{\text{Mg}/\text{Ca}}, K_{\text{Sr}/\text{Ca}}$ ); (3) fractionation factors for Mg and Ca isotopes associated with recrystallization; (4) the lower boundary condition. Our approach is to find the set of values for these variables which satisfies the observations from the pore fluid and sediment. Our modeling yields an internally consistent set of values for the distribution coefficients for Mg and Sr in recrystallized calcite, isotopic fractionation factors for Mg and Ca associated with recrystallization, and secular change in the Mg content of seawater over the Neogene. Many of the unknowns, for example the rate of sediment recrystallization, distribution coefficients for Sr, and Ca isotope fractionation factors, have been explored in previous studies (Fantle and DePaolo, 2006, 2007; Richter and DePaolo, 1987). Our favored distribution coefficients of Mg in calcite and associated Mg isotopic fractionation factors are determined iteratively based on the model fit to the concentration and isotope depth profiles of Mg, Ca, and Sr.

## 4. Results

### 4.1. Magnesium isotopes in pore fluids and carbonate sediments

Magnesium isotope data for pore fluids and sediments from site 807 are shown in Fig. 2 and listed in Table 1. Measured  $\delta^{26}\text{Mg}$  values in the pore fluid systematically increase with depth from



**Fig. 2.** Measured  $\delta^{26}\text{Mg}$  values of the pore fluid ( $\circ$ ),  $<65 \mu\text{m}$  sediment size fraction ( $\blacksquare$ ), and  $250\text{--}450 \mu\text{m}$  sediment size fraction ( $\circ$ ). Error bars are  $1\sigma$  uncertainties on repeat analyses of a single separated sample or full sample replicates on different MC-ICP-MS's. See Table 1.

**Table 1**

List of samples analyzed for Mg isotopes ( $\delta^{25}\text{Mg}$  and  $\delta^{26}\text{Mg}$ ). Measured samples include pore-fluids ( $n=6$ ), the  $< 65 \mu\text{m}$  size fraction of the carbonate sediment ( $n=21$ ), and the  $250\text{--}450 \mu\text{m}$  size fraction of the carbonate sediment ( $n=10$ ). Errors are  $1\sigma$  uncertainties from multiple measurements of a single sample or the external reproducibility of replicate samples.

Sample	Type	Depth (mbsf)	$\delta^{25}\text{Mg}$ (‰)	$1\sigma$	$\delta^{26}\text{Mg}$ (‰)	$1\sigma$
807A-1H	Porefluid <sup>a,b</sup>	4.45	-0.41	0.02	-0.78	0.02
807A-9H	"a	79.85	-0.36	0.10	-0.68	0.13
807A-27H	"a,b	250.85	-0.25	0.05	-0.55	0.01
807A-45X	"a	425.7	-0.28	0.04	-0.46	0.07
807A-63X	"a,b	596.1	-0.19	0.05	-0.36	0.12
807A-82X	"a,b	778.9	-0.12	0.02	-0.15	0.07
807A-2H	< 65 $\mu\text{m}$ sed. <sup>a</sup>	7.65	-2.01	0.08	-3.92	0.08
807A-4H	"a	29.6	-2.18	0.10	-4.23	0.09
807A-7H	"a	58.15	-2.39	0.09	-4.60	0.13
807A-10H	"a	85.15	-2.37	0.09	-4.49	0.09
807A-13H	"a	115.16	-2.37	0.06	-4.56	0.11
807A-16H	"a	143.66	-2.52	0.06	-4.81	0.10
807A-19H	"a	170.65	-2.49	0.11	-4.86	0.10
807A-22H	"a	200.65	-2.47	0.07	-4.81	0.11
807A-27H	"a	248.15	-2.47	0.04	-4.73	0.06
807A-32X	"a	294.45	-2.47	0.10	-4.68	0.15
807A-39X	"a	366.15	-2.41	0.08	-4.61	0.09
807A-42X	"a,b	395.46	-2.58	0.07	-4.88	0.04
807A-50X	"a	469.65	-2.67	0.06	-5.12	0.10
807A-60X	"a	565.85	-2.66	0.03	-5.06	0.10
807A-70X	"a	662.65	-2.54	0.07	-4.80	0.09
807A-84X	"a	794.15	-2.42	0.05	-4.63	0.10
807C-2R	"a	790.13	-2.56	0.05	-4.89	0.08
807C-6R	"a	829.98	-2.41	0.10	-4.72	0.14
807C-17R	"a	904.16	-2.37	0.09	-4.54	0.13
807C-24R	"a	943.89	-2.53	0.07	-4.74	0.11
807C-30R	"a	997.77	-2.42	0.11	-4.70	0.11
807A-2H	250–450 $\mu\text{m}$ sed. <sup>a,b</sup>	7.65	-2.47	0.03	-4.65	0.06
807A-4H	"a	29.6	-2.48	0.13	-4.72	0.15
807A-10H	"a	85.15	-2.43	0.09	-4.61	0.21
807A-12H	"a	103.5	-2.43	0.02	-4.56	0.04
807A-22H	"a	200.65	-2.38	0.08	-4.63	0.15
807A-37X	"a	345.15	-2.37	0.07	-4.57	0.10
807A-46X	"b	431.8	-2.48	0.03	-4.72	0.10
807A-55X	"b	518.4	-2.49	0.04	-4.79	0.04
807A-59X	"b	554.0	-2.44	0.09	-4.67	0.10
807A-62X	"b	585.9	-2.45	0.03	-4.66	0.05

<sup>a</sup> Indicates samples measured on a GV Isoprobe P MC-ICP-MS.

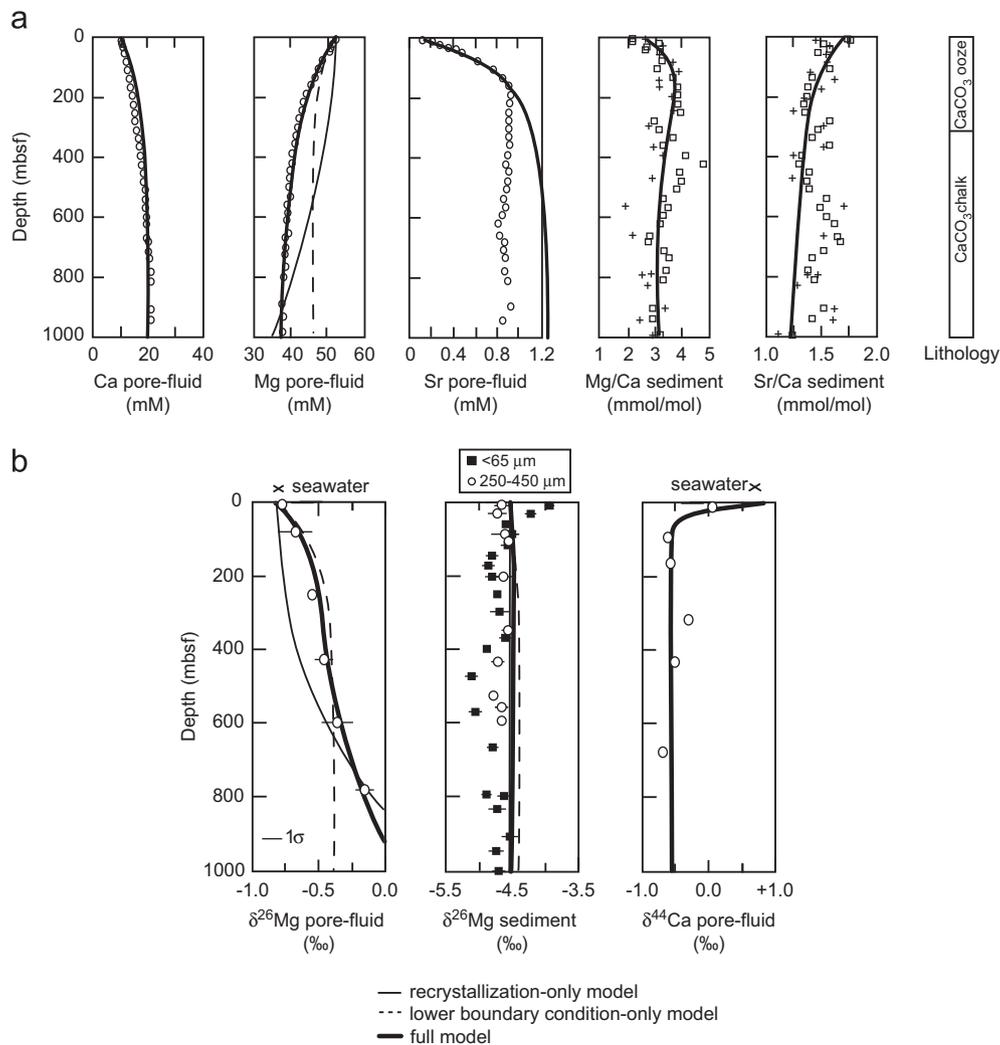
<sup>b</sup> Indicates samples measured on a Thermo Neptune MC-ICP-MS. (See text and Supplementary Information for further details.)

–0.78‰ at 4.45 m to –0.15‰ at 778.9 m. Measured  $\delta^{26}\text{Mg}$  values in the  $< 65 \mu\text{m}$  size fraction of the carbonate sediment decline with depth, from a value of –3.92‰ at 7.65 mbsf to –4.70‰ at 997 mbsf ( $n=21$ ). It is tempting to attribute the enriched  $\delta^{26}\text{Mg}$  values in the youngest two samples of the  $< 65 \mu\text{m}$  size fraction to simple mixing between foraminiferal and coccolith calcite, the latter of which is characterized by  $\delta^{26}\text{Mg}$  values of  $\sim -2\text{‰}$  (Müller et al., 2011; Ra et al., 2010). However, measured Mg/Ca ratios of these samples do not lie on a mixing line between coccolith and foraminiferal calcite (Fig. S1). Measured  $\delta^{26}\text{Mg}$  values of the 250–450  $\mu\text{m}$  size fraction are more or less invariant throughout the core, averaging  $-4.67 \pm 0.07\text{‰}$  ( $1\sigma$ ;  $n=10$ ). These  $\delta^{26}\text{Mg}$  values are indistinguishable from average  $\delta^{26}\text{Mg}$  value of –4.71‰ measured by Pogge von Strandmann (2008) for seven different species of foraminifera from sediment core-tops.

#### 4.2. Numerical model of Mg, Ca, and Sr in the pore-fluids and sediments at site 807

The objective of the modeling was to find the set of variables that produces a good fit to concentration and isotopic profiles of Mg, Ca, and Sr in the pore-fluid and sediment at site 807. Fig. 3 shows our preferred model fit, with values of key variables given

in Table 2 and Fig. 4. Recrystallization rates inferred from the model fit to pore-fluid Sr concentrations and Ca isotopes indicate that 45% of the bulk sediment at site 807 is exchanged with the pore fluid over 44 Myr, in line with previous estimates (Fantle and DePaolo, 2006). About 60% of this exchange occurs within the first 5 million years. The depth-dependence of recrystallization is similar to that found by Fantle and DePaolo (2006), though we do not use the Sr isotopic composition of the sediment and pore fluid to calibrate our deep recrystallization rates. The modeled Sr distribution coefficient ( $K_{\text{Sr/Ca}}$ ) is 0.016 and similar to the values of  $K_{\text{Sr}}$  used by Richter and DePaolo (1987) and Fantle and DePaolo (2006) when multiplied by  $[\text{Ca}]_{\text{solid}}/[\text{Ca}]_{\text{fluid}}$ . Modeled pore-fluid Sr concentrations depart from observations below  $\sim 200$  mbsf, which we attribute to celestite ( $\text{SrSO}_4$ ) precipitation. Solubility calculations indicate that celestite is supersaturated between 100 and 500 mbsf at site 807 (Fantle and DePaolo, 2006) and similar asymptotic Sr profiles have been directly linked to celestite precipitation in deep-sea carbonate sediments elsewhere (Baker and Bloomer, 1988; Richter, 1996). Although no celestite has been reported from site 807, calculations of the mass of celestite required to produce similar Sr concentration profiles at other ODP and DSDP pelagic carbonate sites is only 0.02–0.03 wt% (Richter, 1996). Recrystallization leads to Sr loss from the sediments, as indicated by the decline in modeled Sr/Ca ratios (Fig. 3). We note that the predicted



**Fig. 3.** (a) Ca, Mg, and Sr in the pore-fluid and sediments from site 807A. Data from Kroenke et al. (1991;  $\circ$ ), Delaney and Linn (1993;  $\square$ ), and this study ( $+$ ). Thick black (—) line is our preferred model of Ca, Mg, and Sr in the pore-fluid and sediments from site 807. Thin black (—) and dashed (---) lines represent model runs where we considered only the lower boundary condition or recrystallization in the sediment column (i.e. no secular change in seawater chemistry). Key variables for the model fit are listed in Table 2. (b) Preferred model fit to  $\delta^{26}\text{Mg}$  values in the pore-fluid and sediments and  $\delta^{44}\text{Ca}$  values of the pore-fluid. Seawater values indicated by ( $\times$ ). Pore-fluid Ca isotope data from Fantle and DePaolo (2007). Thick black (—) line is our preferred model of Ca, Mg, and Sr in the pore-fluid and sediments from site 807. Thin black (—) and dashed (---) lines represent model runs where we considered only the lower boundary condition or recrystallization in the sediment column (i.e. no secular change in seawater chemistry). Key variables for the model fit are listed in Table 2.

decline in Sr/Ca is not obvious in the sediment data. Sr/Ca in the bulk sediment likely reflects variations in the relative abundance of coccolith (high Sr/Ca) and foraminiferal (low Sr/Ca) calcite in addition to the effects of recrystallization.

At site 807, the pore-fluid profiles of Mg concentrations and isotopes in the upper  $\sim 400$  m of the sediment column are largely determined by the choice of  $K_{\text{Mg}/\text{Ca}}$  and isotopic fractionation factors ( $\alpha_{26/24\text{-calcite}}$ ) whereas the Mg concentration and isotope profiles below 400 m are determined largely by our choice of a lower boundary condition and associated isotopic fractionation factors (Fig. 3). Pore-fluid profiles of Mg concentrations and isotopes at site 807 cannot be reproduced in our model without including the effects of both recrystallization within the sediment column and exchange of Mg across the lower boundary. The value of  $K_{\text{Mg}/\text{Ca}}$  in our preferred modeled fit is 0.0024 (Fig. 3; Table 2). This value of  $K_{\text{Mg}/\text{Ca}}$  is consistent with a Mg/Ca ratio in recrystallized calcite of  $\sim 12$  mmol/mol in near-surface sediments, a factor of 4 higher than the unaltered bulk sediment at site 807. Thus recrystallization at site 807 appears to be associated with a

net transfer of Mg from pore-fluid to sediment. Uptake of Mg into recrystallized carbonates accounts for  $\sim 30\%$  of the observed decline in pore-fluid Mg concentrations with depth and increases the Mg/Ca of the sediment by 35% from 0 to 180 mbsf (Fig. 3). Because the Mg/Ca of the recrystallized calcite depends on the Mg/Ca of the pore-fluid, lower seawater Mg/Ca in the past leads to a smaller increase in sediment Mg/Ca during recrystallization. This explains why the modeled Mg/Ca peaks at  $\sim 180$  mbsf and then declines with increasing depth/age. We note the general agreement between modeled and measured Mg/Ca ratios in the bulk sediment but again recognize that, given their very different Mg contents, changes in the relative abundance of coccolith and foraminiferal calcite likely play an important role in determining variability in bulk sediment Mg/Ca. As only  $\sim 30\%$  of the decline in pore-fluid Mg can be explained by recrystallization, the remaining 70% must then be attributed to an increase in the Mg content of seawater over the Neogene. The secular change in seawater Mg required by the model where  $K_{\text{Mg}/\text{Ca}}=0.0024$  is shown in Fig. 4. The Mg isotope fractionation factor for calcite recrystallization in our favored model is 0.9963. Changes in the

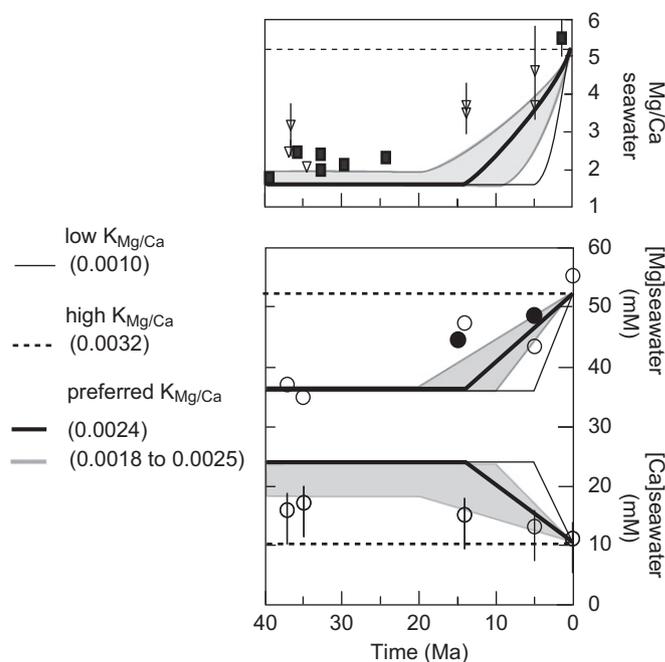
**Table 2**

Key model variables for preferred, low- $K_{Mg/Ca}$ , and high- $K_{Mg/Ca}$ , and coccolith recrystallization model runs. Those variables not listed under the low- $K_{Mg/Ca}$ , high- $K_{Mg/Ca}$ , or coccolith model runs remain the same as the preferred model fit. See text for further details.

Model	Variable	Value
Preferred	<i>Re-crystallization</i>	
	$\lambda$ ( $\text{Myr}^{-1}$ )	0.001
	$\beta$ ( $\text{Myr}^{-1}$ )	0.09
	$\gamma$ (m)	140
	$R_{LB}$ ( $\text{Myr}^{-1}$ )	1.25
	<i>Boundary conditions</i>	
	$[\text{Mg}]_{\text{sed-init}}$ (molal)	0.028
	$[\text{Sr}]_{\text{sed-init}}$ (molal)	0.0165
	$\delta^{26}\text{Mg}_{\text{sed-init}}$	-4.50‰
	$\delta^{26}\text{Mg}_{\text{seawater}}$	-0.82‰
	<i>Distribution coefficients</i>	
	$K_{\text{Sr}/\text{Ca}}$	0.016
	$K_{\text{Mg}/\text{Ca}}$	0.0024
	$K_{\text{Mg}/\text{Ca-LB}}$	0.0017
<i>Fractionation factors</i>		
$\alpha_{44/40\text{-calcite}}$	1.000	
$\alpha_{26/24\text{-calcite}}$	0.9963	
$\alpha_{26/24\text{-LB}}$	0.9950	
Low $K_{Mg/Ca}$	$K_{Mg/Ca}$	0.0010
	$\alpha_{26/24\text{-calcite}}$	0.9920
High $K_{Mg/Ca}$	$K_{Mg/Ca}$	0.0032
	$\alpha_{26/24\text{-calcite}}$	0.9975
Coccolith (45% of bulk)	$[\text{Mg}]_{\text{coccolith}}$ (molal)	0.0023
	$[\text{Mg}]_{\text{foraminifera}}$ (molal)	0.042
	$\delta^{26}\text{Mg}_{\text{coccolith}}$	-2.50‰
	$\delta^{26}\text{Mg}_{\text{foraminifera}}$	-4.65‰
	$K_{\text{Mg}/\text{Ca-coccolith}}$	0.0012
	$K_{\text{Mg}/\text{Ca-coccolith-LB}}$	0.00045
	$\alpha_{26/24\text{-calcite}}$	0.99525
$\alpha_{26/24\text{-LB}}$	0.99450	

modeled  $\delta^{26}\text{Mg}$  values of the bulk carbonate are small—an increase of  $< 0.1\%$  in near surface sediments (0–260 mbsf) and a very slight  $\leq 0.1\%$  decline with depth thereafter.

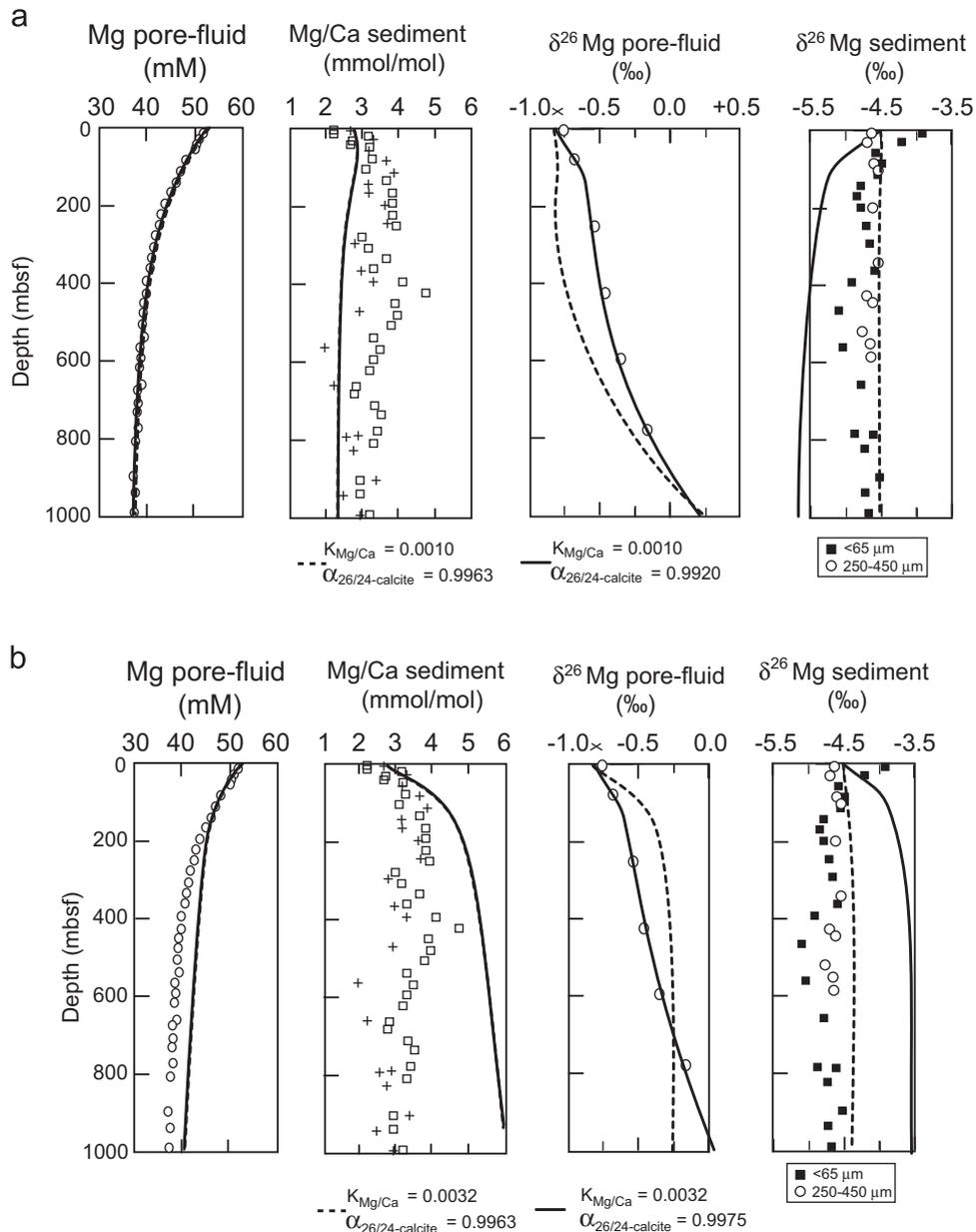
Mg concentration and isotope profiles deep in the sediment column at site 807 exhibit very different behavior. Mg concentrations are constant or decrease slightly whereas  $\delta^{26}\text{Mg}$  values of the pore fluid continue to increase (Fig. 3a and b). One possible explanation for these profiles is recrystallization associated with the conversion of chalk to limestone, which occurs between 1100 and 1200 mbsf at site 807 (Kroenke et al., 1991). We model the conversion of chalk to limestone as recrystallization at the lower boundary, with the recrystallization rate and associated Mg isotopic fractionation factor determined by the fit to the pore-fluid data. Because the slope of the pore-fluid Mg concentration profile near 1000 mbsf is almost zero, the recrystallization associated with the chalk–limestone conversion must be nearly isochemical, consistent with a low  $K_{Mg/Ca}$  value of 0.0017. In contrast, large Mg isotopic fractionation factors ( $\alpha_{26/24\text{-calcite}}=0.9950$ ) are required at the lower boundary to explain the increase in the Mg isotopic composition of the pore-fluid. The rate of sediment recrystallization at the lower boundary inferred from the model is difficult to accurately quantify due to large changes in sediment porosity (0.45–0.10 between 1000 and 1200 mbsf) and uncertainties in how much of the underlying sediment is involved. We estimate rates of recrystallization for the conversion of chalk to limestone of  $\sim 6\%$  per million years for the 200-m thick column of sediment between 1100 and 1300 mbsf. Pervasive recrystallization associated with the chalk–limestone conversion is supported by a large increase in the abundance of nonbiogenic carbonate in smear slides ( $> 50$  wt% below 1098 mbsf).



**Fig. 4.** Secular changes in seawater Mg and Ca associated with different values of  $K_{Mg/Ca}$ . The preferred model is indicated by the thick black lines and corresponds to a rise in seawater Mg and decline in Ca over the last 15 Myr. The shaded area represents the range of model solutions that yield reasonable fits to the data. The low- $K_{Mg/Ca}$  (0.0010) model is represented by the thin black line whereas the high- $K_{Mg/Ca}$  (0.0032) model is represented by the dotted black line. See Table 2 for key variables. Reconstructions of Mg and Ca in seawater from fluid inclusions in halite measured by Horita et al., (2002;  $\circ$ ), Zimmermann (2000;  $\bullet$ ). Reconstructions of seawater Mg/Ca ratios are taken from the fluid inclusion data ( $\Delta$ ), and measured Mg/Ca ratios of calcium carbonate veins in hydrothermally altered oceanic crust (Coggon et al., 2010;  $\blacksquare$ ).

Sensitivity tests of our modeled best guess to different values of  $K_{Mg/Ca}$  and Mg isotope fractionation factors show how well the history of seawater Mg is constrained by our model (Fig. 5a and b). For  $K_{Mg/Ca}$ , we first examined two endmember values of 0.0010 and 0.0032. When  $K_{Mg/Ca}=0.0010$ , a value similar to the foraminiferal partition coefficient (Lea et al., 1999), Mg contents increase slightly ( $\sim 15\%$ ) in the upper 60 m of the sediment column, followed by a  $\sim 15\%$  decline in Mg/Ca to 1000 mbsf (Fig. 5a). As a result, virtually all the decline in pore-fluid Mg concentrations with depth must be attributed to a secular increase in seawater Mg over the Neogene (Fig. 4). The required increase in seawater Mg is large (15 mM Mg) and extremely rapid ( $\sim 5$  Myr). Modeled  $\delta^{26}\text{Mg}$  values of the pore fluid are shifted to lower values by up to  $\sim 0.3\%$  compared to our preferred model (Fig. 5a). Modeled  $\delta^{26}\text{Mg}$  values of the bulk sediment do not change. A much lower Mg isotope fractionation factor for recrystallization within the sediment column of 0.9920 improves the model fit to the  $\delta^{26}\text{Mg}$  values of the pore-fluid (Fig. 5a); however, this lowers the modeled  $\delta^{26}\text{Mg}$  values of the sediment by  $> 1\%$ . In addition, such a large fractionation factor for Mg isotopes ( $\sim 8\%$ ) seems unlikely.

When  $K_{Mg/Ca}=0.0032$ , a value  $\sim 3$ -fold higher than foraminiferal partition coefficient, all the decline in Mg concentrations in shallow pore-fluids is attributed to uptake during recrystallization. This scenario is analogous to assuming that Mg and Ca in seawater have remained constant. The high value of  $K_{Mg/Ca}$  results in a  $> 2$ -fold increase in the Mg/Ca ratio of bulk carbonate sediments, from 2.8 to 6.15 mmol/mol (Fig. 5b). Modeled  $\delta^{26}\text{Mg}$  values of the sediment change slightly compared to our preferred model. However, modeled  $\delta^{26}\text{Mg}$  values in shallow pore fluids are shifted towards heavier values by up to  $0.3\%$ . A smaller Mg isotope fractionation factor of 0.9975 improves the model fit

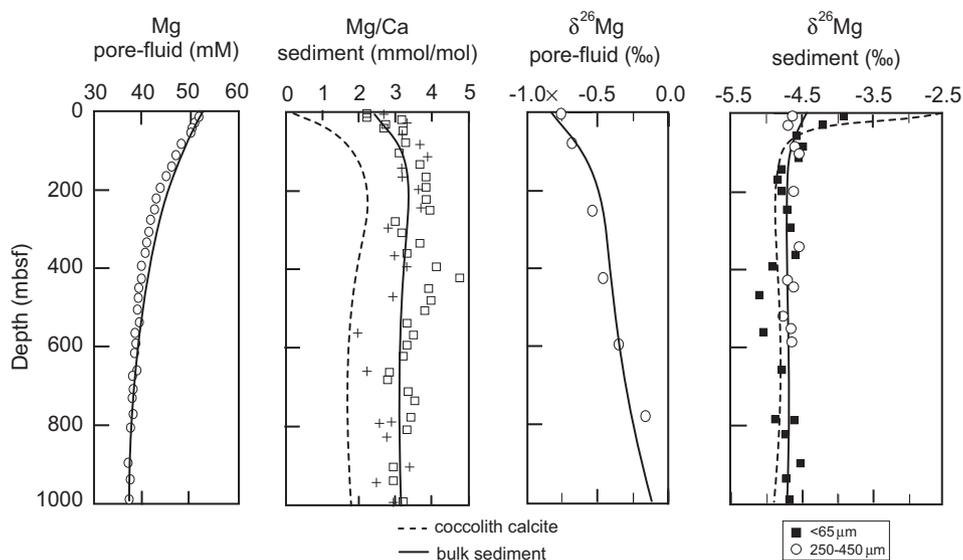


**Fig. 5.** (a) Sensitivity tests for the low- $K_{\text{Mg}/\text{Ca}}$  (0.0010) model. The dotted black line represents all variables same as our preferred model except for  $K_{\text{Mg}/\text{Ca}}$  and the history of seawater Mg and Ca (solid line in Fig. 4). Solid black line reflects low- $K_{\text{Mg}/\text{Ca}}$  model where  $\alpha_{26/24\text{-calcite}}$  is re-tuned to yield a good fit to the pore-fluid Mg isotope profile. Although this tuning improves the fit to the pore-fluid data, it requires extreme values of  $\alpha_{26/24\text{-calcite}}$  (0.992) and results in a large negative shift in the  $\delta^{26}\text{Mg}$  values of the bulk sediment. (b) Sensitivity tests for the high- $K_{\text{Mg}/\text{Ca}}$  (0.0032) model. The dotted black (---) line represents all variables same as our preferred model except for  $K_{\text{Mg}}$  and the history of seawater Mg and Ca (dotted line in Fig. 4). Solid black (—) line reflects high- $K_{\text{Mg}}$  scenario where  $\alpha_{26/24\text{-calcite}}$  is re-tuned to yield a good fit to the pore-fluid Mg isotope profile. Although this tuning improves the fit to the pore-fluid data, it results in a large positive shift in the  $\delta^{26}\text{Mg}$  values of the bulk sediment. Note the misfit in modeled Mg concentrations in the pore-fluid below  $\sim 200$  m. Improving the model fit to the pore-fluid Mg profile would require changing our parameterization of recrystallization or allowing  $K_{\text{Mg}/\text{Ca}}$  to increase with depth. Both these adjustments will tend to increase modeled  $\delta^{26}\text{Mg}$  values of the pore-fluid, worsening the model fit to the data.

to the  $\delta^{26}\text{Mg}$  values of the pore-fluid; however, this increases the modeled  $\delta^{26}\text{Mg}$  values of the sediment by up to 0.8‰ (Fig. 5b). Such a dramatic shift in the  $\delta^{26}\text{Mg}$  values of the sediment is not supported by the data. Further sensitivity test indicates that values of  $K_{\text{Mg}/\text{Ca}}$  ranging from 0.0018 to 0.0025 are consistent with the pore-fluid and sediment concentration and isotopic profiles (Fig. S4). This range in  $K_{\text{Mg}/\text{Ca}}$  values all require a large increase in the Mg content of seawater over the Neogene, but indicate that the precise timing of the change is somewhat uncertain. In summary, the model is sensitive to  $K_{\text{Mg}/\text{Ca}}$ . Values of 0.0032 (no upper boundary change) and 0.0010 ( $< 5$  Myr upper boundary change) are hard to reconcile with measured Mg concentrations and isotopes in the pore fluid and sediment.

Values of  $K_{\text{Mg}/\text{Ca}}$  that yield reasonable model fits to the data range from 0.0018 to 0.0025 and require a large ( $> 10$  mmol) and rapid (10–20 Myr) increase in seawater Mg over the Neogene.

We also examined the sensitivity of the model to recrystallization of different fractions of the bulk carbonate sediment. In particular, we explored the possibility that the recrystallizing carbonate was composed entirely of coccolith calcite. Coccolith calcite makes up  $\sim 50\%$  of the bulk sediment mass and yet it accounts for only  $\sim 5\%$  of the bulk carbonate Mg, owing to its very low Mg content (0.2–0.3 mmol Mg/mol Ca; (Stoll et al., 2001)) compared to foraminifera (1–5 mmol Mg/mol Ca; (Dekens et al., 2002; Lea et al., 2000)). The  $\delta^{26}\text{Mg}$  value of coccolith calcite is also distinct at  $\sim -2\%$  compared to a  $\delta^{26}\text{Mg}$  value of  $\sim -4.65\%$



**Fig. 6.** Model results assuming the recrystallizing carbonate is composed entirely of coccoliths. The dotted black (---) line represents the coccolith fraction. Solid black (—) line reflects the bulk sediment (coccoliths+foraminifera). Measured  $\delta^{26}\text{Mg}$  values of the  $<65\ \mu\text{m}$  sediment size fraction ( $\square$ ), and  $250\text{--}450\ \mu\text{m}$  sediment size fraction ( $\circ$ ). Measurements of the  $<65\ \mu\text{m}$  size fraction are expected to fall between the coccolith and bulk compositions. See Table 2 for model variables.

for foraminifera (Chang et al., 2004; Pogge von Strandmann, 2008; Ra et al., 2010). Model results and associated variables for selective recrystallization of coccolith calcite are shown in Fig. 6 and Table 2. Changes in the Mg content of seawater over the Neogene are similar to those obtained for our preferred model of bulk sediment recrystallization.  $K_{\text{Mg}/\text{Ca}}$  values are significantly lower at 0.0012 and 0.00045 for the sediment column and the lower boundary, respectively. The lower values of  $K_{\text{Mg}/\text{Ca}}$  are a consequence of the very low Mg content of the recrystallizing coccolith calcite. The required Mg isotopic fractionation factors are larger, at 0.99525 and 0.9945, for the sediment column and lower boundary, respectively. The Mg content of the coccolith fraction of the sediment increases by 10-fold but the total increase in bulk Mg content is similar to the case of bulk recrystallization ( $\sim 37\%$ ; Fig. 6). The modeled  $\delta^{26}\text{Mg}$  values of the coccolith fraction of the sediment decline precipitously from an initial value of  $-2.5\text{‰}$  to  $-4.9\text{‰}$  within 250 m of the seafloor. When considered in the context of our data, we find that recrystallization of coccolith calcite (with some contribution from the breakdown of foraminiferal calcite) can account for the decline in  $\delta^{26}\text{Mg}$  values observed in the youngest samples of the  $<65\ \mu\text{m}$  size fraction.

## 5. Discussion

Our results show that the Mg, Ca, and Sr concentrations and isotopes in deep-sea pelagic carbonate sediments and pore fluids are best explained by the combined effects of recrystallization and a large increase in the Mg content of seawater over the last 10–20 Myr. Our model fits for site 807 yield new estimates of the distribution coefficient for Mg during calcite recrystallization, quantifies the effect of recrystallization on the Mg isotopic composition of the sediment and pore fluid, and provides an independent constraint on the history of seawater Mg and Ca over the Neogene. In this section, we compare our results to previous studies and discuss the implications of our work for understanding the effects of burial recrystallization on Mg-based paleoproxies, the potential of pore fluids as records of seawater chemistry, and pore-fluid Mg and Ca profiles more generally.

### 5.1. Distribution coefficients for Mg during recrystallization

Distribution coefficients for Mg ( $K_{\text{Mg}/\text{Ca}}$ ) during calcite precipitation have been determined experimentally in the lab and range from 0.012 to 0.040 (Huang and Fairchild, 2001; Mucci and Morse, 1983; Oomori et al., 1987). These values are all much higher ( $4\times$  to  $>20\times$ ) than the  $K_{\text{Mg}/\text{Ca}}$  values in our preferred model fits. As has been shown for Sr (Lorens, 1981), experimentally determined values depend strongly on precipitation rate and are likely much too high given that the experimental precipitation rates are many orders of magnitude higher than the rates observed in deep-sea sediments (Baker et al., 1982). By comparison, the values of  $K_{\text{Sr}/\text{Ca}}$  determined experimentally at similar precipitation rates (Huang and Fairchild, 2001; Lorens, 1981; Mucci and Morse, 1983) are typically a factor of 5–10 higher than those determined by previous modeling studies for deep-sea pore-fluids (Richter and DePaolo, 1987), a similar factor to what we surmise for  $K_{\text{Mg}/\text{Ca}}$ . We note that previous work by Fantle and DePaolo (2006) on Mg in the pore fluid at site 807 used three values for  $K_{\text{Mg}}$  values: 0.4, 0.6 and 0.84, corresponding to  $K_{\text{Mg}/\text{Ca}}$  values of 0.00044, 0.00066, and 0.00093. All three values are lower than the  $K_{\text{Mg}/\text{Ca}}$  values inferred from our preferred models of the bulk sediment.

### 5.2. Implications for Neogene major element seawater chemistry

Obtaining a good model fit to the Mg pore-fluid and sediment concentration and isotopic profiles requires large increase in the Mg content of seawater over the Neogene. Without this change, the modeled uptake of Mg by the sediments is much larger than can be accounted for by observations of sediment Mg/Ca and Mg isotopes (Fig. 5b). The changes in seawater Mg required by our model are consistent with independent geochemical observations from fluid inclusions in halite (Horita et al., 2002; Lowenstein et al., 2001; Zimmermann, 2000; Fig. 3c). Fantle and DePaolo (2006) first recognized the potential role of secular variations in seawater chemistry on pore-fluid Mg profiles at site 807. Our reconstruction of seawater Mg over the Neogene is in agreement with the work of Fantle and DePaolo (2006) although we predict that the rise in Mg occurred over a longer time period

(~10–20 Myr compared to < 10 Myr in Fantle and DePaolo, 2006). The difference between our result and that of Fantle and DePaolo (2006) is directly related to the value of  $K_{Mg/Ca}$ . The values of  $K_{Mg/Ca}$  used by Fantle and DePaolo (2006) require that all the changes in Mg in the pore fluid (and then some) are due to a secular increase in Mg in seawater. A more modest change in seawater Mg implies smaller corrections for Neogene foraminiferal Mg/Ca records (Medina-Elizalde et al., 2008).

The relative abundance of Ca in sediment as compared to pore fluid ( $Ca_{sed}/Ca_{pw} > 1000$ ) and rapid rates of recrystallization mean that pore-fluid Ca concentrations at site 807 will reflect changes in calcite solubility and any net precipitation or dissolution within the sediment column (Fantle and DePaolo, 2006, 2007). The expectation is that there should not be any information on the history of Ca concentrations in seawater in deep-sea pore-fluid profiles. We suggest that in fact the Ca pore-fluid profile at site 807 does reflect changes in the Ca concentration in seawater for three reasons. First, the deep ocean is maintained at calcite saturation by the dissolution of carbonate minerals in the water column or very shallow sediments (within upper few cm). Thus the Ca concentration in very shallow pore-fluids is at equilibrium with respect to calcite. This is true regardless of the concentration of Ca in seawater. Second, calcite solubility increases by only ~10% at site 807 due to the effects of pressure and temperature. This change is too small to explain the 2-fold increase in pore-fluid Ca concentrations with depth. Third, estimates of the amount of net calcite precipitation/dissolution occurring within the sediment column from pore-fluid profiles of alkalinity and  $SO_4$  are insufficient to explain the observed increase in Ca concentrations with depth. Between 0 and 350 m, pore-water  $SO_4$  declines by ~6 mmol. As discussed above, this decline is likely due to minor amounts of sulfate reduction and thus should be associated with a 12 Eq increase in pore fluid alkalinity (two units of alkalinity for one unit of  $SO_4$  reduced neglecting  $NH_4^+$ ). The observed increase in pore-fluid alkalinity over the same depth interval is only ~3 mEq. The missing 9 mEq would have to have been consumed by calcite precipitation, the only other quantitatively important lever on pore-fluid alkalinity in carbonate sediments. The effect of this precipitation would be to lower pore-fluid Ca by 4.5 mmol in the upper 350 m of the sediment column. Considering the pore-fluid alkalinity profile below 350 m, the observed decline (~3 mEq) may also be due to net calcite precipitation, although alteration of the underlying basalt may also play a role. Alternatively, if the decline in pore fluid  $SO_4$  is due to a boundary condition change (unlikely given the large increase in the S isotopic composition of pore fluid  $SO_4$  mentioned above), changes in alkalinity should largely reflect calcite dissolution/precipitation. As pore fluid alkalinity varies by only 4 mmol predicted changes in pore fluid Ca are small.

In summary, changes in calcite solubility and net precipitation/dissolution appear to have a relatively small effect on pore-fluid Ca concentrations at site 807 and cannot explain a 2-fold increase in Ca with depth. As a result, we conclude that a large component of the increase in pore-fluid Ca at site 807 is due to the preservation of a primary seawater signal. This surprising and perhaps counterintuitive result occurs because (1) Ca is at equilibrium with respect to calcite at or near the sediment-water interface, regardless of the concentration of Ca in seawater; (2) the fluxes of Ca into and out of the pore-fluid during diagenesis at site 807 are almost perfectly balanced. This explains why our model (which does not include changes in solubility or net precipitation/dissolution) produces a good fit to the pore-fluid Ca profile when we assume Neogene history of Ca in seawater that approximately mirrors the change in Mg. Better constraints on the rate and distribution of net calcite precipitation/dissolution within the sediment column could improve this fit.

The concentrations of seawater Ca inferred from pore-fluid profiles at site 807 are higher than the values calculated from Cenozoic fluid inclusions (Fig. 4). Some of this discrepancy could be due to uncertainties in the fluid inclusion data as seawater Ca is reconstructed from measurements of  $SO_4$  in the fluid inclusion using assumptions about the degree of gypsum saturation in the ocean (Horita et al., 2002) or from an overestimation of the Ca change in our model due to the minor involvement of other ions (e.g. Na,  $SO_4$ ). The large a rapid change in seawater Ca inferred from our model of pore-fluid profiles at site 807 has obvious implications for the magnitude of the increase in seawater Mg/Ca (Fig. 4). Because Mg declines while Ca increases, the Mg/Ca of seawater undergoes a dramatic increase from the Miocene to the present, from values 1.5–2 to the modern value of ~5. This change is similar to that proposed by Coggon et al. (2010) based on observations of Mg/Ca ratios in basalt-hosted calcium carbonate veins but somewhat larger than that favored by Broecker and Yu (2011) based on Mg/Ca ratios in foraminifera.

### 5.3. Implications for Mg/Ca in re-crystallized carbonates

Although there is still uncertainty as to the exact value of  $K_{Mg/Ca}$  (e.g. the range listed in Table 2), all preferred  $K_{Mg/Ca}$  values indicate that recrystallization is a net sink of Mg from the pore fluid and should lead to an increase in the Mg content of the carbonate sediment. This result contrasts with previous work by Fantle and DePaolo (2006) who argued that recrystallization is a net source of Mg to the pore fluid (i.e. that Mg is lost from the carbonate during recrystallization). Our results  $K_{Mg/Ca}$  are consistent with observations by Sexton et al. (2006) who, on the basis of SEM,  $\delta^{18}O$ , and Mg/Ca analyses of re-crystallized foraminiferal tests, argued for an increase in the Mg content during recrystallization associated with the recrystallized calcite containing a few mol% Mg. Our work suggests that paleo-temperatures derived from measuring Mg/Ca ratios in recrystallized foraminifera could have a warm temperature bias. For example, the modeled increase in bulk sediment Mg content in the upper 180 m (0–6 Myr) at site 807 is ~35%, corresponding to an artificial warming of ~3.5 °C.

### 5.4. Implications for Mg isotopes in re-crystallized carbonates

Given the large amount of Mg that is exchanged between pore-fluid and sediment during recrystallization, it is clear that the Mg isotopic composition of the sediment will be sensitive to diagenesis. Surprisingly, measured  $\delta^{26}Mg$  values of the sediment are relatively invariant, with the exception of the youngest samples from the < 65  $\mu m$  size fraction. Explaining these observations requires a large Mg isotope fractionation factor associated with recrystallization. The Mg isotopic fractionation factors ( $\alpha_{26/24-calcite}$ ) determined by our preferred model of the pore-fluid and sediment  $\delta^{26}Mg$  values are 0.9963–0.9950; much larger than have been previously observed for Mg in most inorganic and biogenic carbonates (Buhl et al., 2007; Galy et al., 2002; Higgins and Schrag, 2010; Hippler et al., 2009; Immenhauser et al., 2010; Müller et al., 2011) but of similar magnitude to what is seen in foraminifera (Chang et al., 2004; Pogge von Strandmann, 2008; Wombacher et al., 2011).  $\alpha_{26/24-calcite}$  values of 0.9979–0.9975 are observed in experimental studies of Mg isotopes in inorganic calcites (Galy et al., 2002; Immenhauser et al., 2010). Similar values are found to be associated with the precipitation of dolomite in organic-rich marine sediments (Higgins and Schrag, 2010), although much larger values (~0.995) have been proposed for equilibrium fractionation factors for Mg in calcite based on theoretical calculations (Rustad et al., 2010; Schauble, 2011). Could kinetics explain the difference between experimentally determined Mg isotope fractionation factors and theoretical

models? Studies of Ca isotopes during precipitation have demonstrated a strong but complicated rate dependence with values approaching 1 at very slow precipitation rates (DePaolo, 2011; Fantle and DePaolo, 2007; Tang et al., 2008). We note that unlike Ca, the magnitude of the Mg isotope fractionation factor appears to increase at the slow precipitation rates characteristic of diagenesis in deep-sea sediments. Immenhauser et al. (2010) found evidence for rate-dependent Mg isotope fractionation during calcite precipitation consistent with that proposed here, although overall they observe much smaller ( $\alpha_{26/24\text{-calcite}}$ ) values (0.9977–0.9984).

Finally, because recrystallization is most intense in young sediments and the residence time of Mg in seawater is long (~15 Myr), the  $\delta^{26}\text{Mg}$  of the re-crystallized carbonate should, all else being equal and with some smoothing, record variations in the  $\delta^{26}\text{Mg}$  of the overlying seawater. Although recrystallization must be taken into account, the Mg isotopic composition of pelagic carbonates may still prove to be a reliable record of the  $\delta^{26}\text{Mg}$  of seawater.

### 5.5. Implications for pore fluid profiles of Mg, Ca, and Sr in deep-sea carbonate sediments

Pore-fluid profiles of Mg and Ca like those seen at site 807 are frequently observed in deep-sea sediments (Elderfield et al., 1982; Gieskes, 1975; McDuff and Gieskes, 1976). In some cases, Mg declines and Ca increases almost linearly to the underlying oceanic crust. These profiles are attributed to low-temperature alteration of basalt (Gieskes and Lawrence, 1981; Perry et al., 1976). In other cases, such as site 807, the Mg profile is concave down within the sediment column. Although the concavity of the Mg profile could conceivably be due to reaction at the lower boundary plus upward (basement to sediment) fluid flow, this is not the case at site 807 as the pore-fluid profile of K is approximately linear. Although the linearity in the K profile is suggestive of a small amount of upward fluid flow (see Mg profile for lower boundary condition only in Figure 3a), if both Mg and K profiles were due to basalt alteration/clay authigenesis, we would expect similar curvature in their pore-fluid profiles. As a result, the ~1:1 exchange of Mg for Ca at site 807, although very similar to what is observed for low temperature basalt alteration, appears to be driven by the recrystallization of a low-Mg calcite to a somewhat higher Mg calcite and changes in the abundance of Mg and Ca in seawater over the Neogene. Mg isotopes provide a powerful tool for distinguishing between basalt alteration and recrystallization as Mg isotopes are fractionated in opposite senses during the precipitation of clays and carbonate minerals in marine sediments (Higgins and Schrag, 2010; see Supplemental Information for details).

## 6. Conclusions

Pore-fluid profiles of Mg, Ca, and Sr in deep-sea carbonate sediments can be explained to a first order by the recrystallization of biogenic carbonate and changes in the Mg content of seawater over the Neogene. Mg isotopic measurements of the pore fluid and sediment, when combined with a model of sediment and pore-fluid Sr and Ca, provide new estimates of the partition coefficient for Mg in recrystallized calcite and refine reconstructions of seawater Mg over the Neogene. Our results favor a relatively large and rapid rise in seawater Mg over the Neogene (15 mmol Mg over the last 10–20 Myr) and are broadly consistent with previous studies (Fantle and DePaolo, 2006) and independent reconstructions from fluid inclusions (Horita et al., 2002; Lowenstein et al., 2001) and basalt-hosted carbonate veins

(Coggon et al., 2010). Our results also imply that recrystallization increases the Mg content of pelagic calcite. If the bulk recrystallization rate and partition coefficients apply to individual foraminiferal tests, measured Mg/Ca ratios samples older than a few million years will be elevated due to diagenetic recrystallization, leading to an overestimate of calculated paleo-temperatures. It is likely that the actual bias is smaller than this as individual foraminifera tests are selected for analysis based on the quality of preservation, and are also subjected to cleaning methods that may remove some secondary carbonate. Finally, this study provides new constraints on the behavior of Mg isotopes in carbonates during recrystallization, with  $\delta^{26}\text{Mg}$  values of foraminiferal calcite shifting by at most a few tenths of per mil. This suggests that foraminiferal calcite may preserve a record of the Mg isotopic composition of seawater through time. Curiously, records of the  $\delta^{26}\text{Mg}$  of seawater inferred from foraminifera measured at site 807 show little change over the Neogene in spite of the dramatic rise in seawater Mg.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.epsl.2012.08.030>.

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