Authigenic Silicate Minerals and the Magnesium Budget in the Oceans [and Discussion]

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Authigenic silicate minerals and the magnesium budget in the oceans

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The relative stabilities of authigenic Fe-rich and Mg-rich components in sheet silicates are considered for reactions of (*a*) clay minerals undergoing anoxic diagenesis; and (*b*) the montmorillonite phase formed by basalt–seawater interaction. For reaction (*a*) coexisting pyrite and a $Mg(OH)_2$ component of the silicate are close to equilibrium with $a_{Mg^{2+}}$ in pore fluids ($\Delta G = -0.29$ kcal/mol; -1.2 kJ/mol) and the excess Mg^{2+} present approximates to that added by diffusion from overlying seawater. Reaction (*b*) can be represented by a mixture of ferroan nontronite and talc components and the calculated temperature/stability relationship agrees with mineralogical zoning in the Reykjanes geothermal area. At $T = 523$ K the Mg-rich component is dominant and $a_{Mg^{2+}}$ is reduced to 1.7×10^{-5} (cf. 1.35×10^{-2} in seawater). Data from an experimental study at 473 K give the result $a_{\text{talc}} \approx 0.2$. Flux calculations give removal rates of Mg from the oceans of 0.06 × stream supply for reaction (*a*) and 0.6–1.7 × stream supply for reaction (*b*).

INTRODUCTION

Although quantitatively a minor component of marine sediments as compared with carbonate, opal, and detrital clay minerals, the authigenic silicate minerals are particularly important in that they provide a sink for the alkali and alkaline earth cations introduced to the oceans by stream supply. As such they have a central rôle in steady-state models of ocean geochemistry, and in equilibrium models of the oceans are required as controls on the concentrations of potassium, magnesium, silica, etc, in seawater.

Since the carbonate- and opal-free fraction of marine sediments is usually dominated by detrital silicate minerals it is clear that the identification of authigenic silicates may pose serious problems and in some cases it is possible only to infer their presence on the basis of the chemistry of sediment pore fluids. A clear analysis of the quantitative significance of authigenic silicates is also hindered by the lack of reliable thermodynamic data for these minerals and also by the need to consider the ranges of temperature and pressure encountered not only in the oceans themselves but also for seawater circulating through layer II of the ocean crust. In this paper two processes are discussed whereby authigenic silicate minerals remove magnesium from seawater. The term 'authigenic' is taken here to include not only material precipitating directly from seawater but also solid phases resulting from the interactions of seawater and detrital silicates.

THE OCEANIC MAGNESIUM BUDGET

In a recent review of the 'magnesium problem' Drever (1974) has emphasized the difficulties in balancing the river input of Mg with its removal in sediments, and the failure to identify a major sink for magnesium is a serious drawback to the steady-state model for the oceans.

The degree of this difficulty is evident from the following simple calculation. Dissolved magnesium is presently being added to the oceans by rivers at a rate of 1.33×10^{14} g a^{-1} (Garrels

& Mackenzie 1971). Since the area of all oceans is 361.1×10^6 km² it follows that if this stream flux of Mg is removed as an authigenic component which is spread uniformly over the sea-floor then the rate of removal of Mg is 3.68×10^{-5} g cm^{-2} a^{-1}. However, the accumulation rate of deep-sea clays is about 10^{-4} g cm^{-2} a^{-1} (according to Riley & Chester (1971) the rate of non-carbonate sedimentation in deep-sea areas is in the range 0.45–1.99 mm 10^{-3} a^{-1}) which means that the non-carbonate fraction of all pelagic sediments must consist of 40 % magnesium in order to balance stream supply! Alternatively, if the river input is incorporated uniformly into the sediment (rather than uniformly over the sea-floor) then since the supply rate of suspended matter by rivers is 183×10^{14} g a^{-1} (Garrels & Mackenzie 1971) it follows that the MgO content of marine sediments should be 1.1 % greater than river sediment or 2.0 % greater if Mg is concentrated only in the clay fraction. This is not supported by analytical data (Drever 1974).

TABLE 1. DREVER'S (1974) ESTIMATES OF Mg^{2+} REMOVAL FROM THE OCEANS

process	flux/(g a^{-1})	percentage of river flux
carbonate formation	7.5×10^{12}	6
ion exchange	9.7×10^{12}	8
glauconite formation	$< 3.9 \times 10^{12}$	< 3
Mg–Fe exchange	$< 29 \times 10^{12}$	< 24
burial of pore fluids	11×10^{12}	9
	$< 61 \times 10^{12}$	< 50

It is clear from these arguments that removal of Mg^{2+} ions by deep-sea sediments must be of trivial importance and that the optimum site for Mg removal from seawater by sediments is in near-shore regions with high rates of sediment accumulation. Table 1 summarizes Drever's (1974) estimates of Mg removal rates in the oceans. In this paper, only Mg–Fe exchange which occurs in rapidly-accumulating near-shore sediments and appears to be a likely candidate as a significant sink for magnesium, is discussed; secondly, Mg removal in the basalt–seawater system is considered.

MAGNESIUM REMOVAL DURING ANOXIC DIAGENESIS

In anoxic sediments where pyrite formation is actively occurring the redox potential is controlled by the couple $HS^- \rightleftharpoons S^\circ + H^+ + 2e$ (Berner 1963), and Drever (1971 *a*, *b*) has argued that the instability of ferric iron caused by the low E_h of such sediments results in the exchange of magnesium for iron in detrital clay minerals. The iron in octahedral sites of the silicate is reduced to Fe^{2+} ions, which migrate into the pore fluid to form pyrite and are replaced by Mg^{2+} ions from solution:

$$(Fe_2-\text{clay}) + 3\,Mg^{2+} \longrightarrow (Mg_3-\text{clay}) + \text{pyrite}. \qquad (1)$$

An alternative mechanism for this process (Sholkovitz 1973) suggests that Mg^{2+} ions are added to exchange sites in clay minerals previously blocked by precipitated ferric hydroxide which dissolves under reducing conditions:

$$Fe(OH)_3-\text{clay} + Mg^{2+} \longrightarrow (Mg-\text{clay}) + \text{pyrite}. \qquad (2)$$

Sholkovitz proposed this mechanism because the Drever mechanism influences pore-fluid alkalinity (see equation (3) below), while Sholkovitz was able to balance an alkalinity model for the anoxic sediments he studied without recourse to Mg–Fe exchange. An additional attraction of this mechanism is that the source of iron in pyrite formation, required by both equations (1) and (2), is usually iron-oxide coatings on clay particles which dissolve more easily than less accessible iron in the structure of clay minerals (Berner 1970). Bischoff, Clancy & Booth (1975) suggest that both mechanisms may describe the magnesium removal observed in the Santa Barbara Basin sediments studied earlier by Sholkovitz (1973) but Berner *et al.* (1970) could find no evidence of Mg removal in the reducing, organic-rich sediments they examined. Drever (1974) has concluded that 'anoxic, terrigenous, marine sediments do take up Mg^{2+}' and suggests that the absence of suitable clay minerals precludes Mg removal in anoxic sediments where this process has not been observed.

To test whether such reactions are predictable on thermodynamic grounds problems are encountered in estimating ΔG_f° values for the reactive clay components. For the Drever reaction, which can be written:

$$\begin{aligned}&2(\mathrm{Fe_2-clay}) + 6\mathrm{Mg^{2+}} + 8\mathrm{SO_4^{2-}} + 15\mathrm{CH_2O}\\ &\qquad\longrightarrow 2(\mathrm{Mg_3-clay}) + 4\mathrm{FeS_2}^+ + 15\mathrm{HCO_3^-} + 11\mathrm{H^+} + 2\mathrm{H_2O},\end{aligned} \tag{3}$$

the clay mineral transformation represented is the conversion of the nontronite component of a smectite to a saponite component, e.g. for the $\frac{1}{2}$ unit cell:

$$\mathrm{(X)_{0.33}Fe_2[Al_{0.33}Si_{3.67}]\,O_{10}(OH)_2} \longrightarrow \mathrm{(X)_{0.33}Mg_3[Al_{0.33}Si_{3.67}]\,O_{10}(OH)_2}. \tag{4}$$

In order to avoid the assignment of ΔG_f° values to clay minerals of unknown composition, free energies can be assigned to the reactive components rather than the complete clay minerals using the additive methods of Tardy & Garrels (1974) and Chen (1975). Thus, equation (4) becomes:

$$\mathrm{Fe_2O_{3(sil)}} + \mathrm{H_2O_{(sil)}} \longrightarrow \mathrm{Mg(OH)_{2(sil)}} + 2\mathrm{MgO_{(sil)}}, \tag{5}$$

where the subscript 'sil' refers to the oxides and hydroxides as components of the silicate. Since pyrite is present is anoxic sediments where the reactions given by equations (1) and (2) are thought to take place it can be assumed that sites are available for the addition of the saponite component of the silicate by either the Drever or Sholkovitz mechanism, and reactions written simply for the removal of Mg^{2+} ions from solution, e.g.:

$$3\mathrm{Mg^{2+}} + 4\mathrm{H_2O} = \mathrm{Mg(OH)_{2(sil)}} + 2\mathrm{MgO_{(sil)}} + 6\mathrm{H^+}, \tag{6}$$

or Mg^{2+} only can be removed as the hydroxide:

$$\mathrm{Mg^{2+}} + 2\mathrm{H_2O} = \mathrm{Mg(OH)_{2(sil)}} + 2\mathrm{H^+}, \tag{7}$$

$$\text{cf.: } \mathrm{Mg^{2+}} + 2\mathrm{H_2O} = \mathrm{Mg(OH)_{2(brucite)}} + 2\mathrm{H^+}. \tag{8}$$

Comparison of the thermodynamics of reactions (7) and (8) should be of interest since several workers have suggested that clay minerals can be upgraded to chlorite-like compositions by precipitation of 'brucite layers' in intersheet positions (see Drever (1974) and Elderfield (1976) for reviews of the literature). Alternatively, the uptake of Mg^{2+} only on exchange sites, as Sholkovitz suggests, can be considered:

$$\mathrm{Mg^{2+}} + \mathrm{H_2O} = \mathrm{MgO_{(EX)}} + 2\mathrm{H^+}. \tag{9}$$

Here the exchangeable cation is written as an oxide rather than as a cation since an equivalent of O^{2-} groups are added from the negative silicate framework in order to facilitate easy separation of the oxide and hydroxide components of the lattice (Tardy & Garrels 1974). For example, compare pyrophyllite and a fictive, dioctahedral tetrahedrally-substituted clay mineral with Mg^{2+} ions balancing the negative charge of the lattice:

$$Al_2Si_4O_{10}(OH)_2 \equiv Al_2O_3 . 4SiO_2 . H_2O \qquad (10)$$

$$Mg_{\frac{1}{2}x}Al_2[Si_{4-x}Al_x]\,O_{10}(OH)_2 \equiv \tfrac{1}{2}x(Mg^{2+}O^{2-})_{EX} . Al_2O_3 . (4-x)SiO_2 . \tfrac{1}{2}x\,Al_2O_3 . H_2O. \qquad (11)$$

Table 2. Mg^{2+} activities in equilibrium with oxide and hydroxide components of sheet silicates

reaction†	solid phase(s)	$\Delta G°$ kcal mol^{-1}	ΔG for seawater kcal mol^{-1}	$a_{Mg^{2+}}$ for $\Delta G = 0$‡
(8)	$Mg(OH)_2$ brucite	+22.78	+3.51	–
(7)	$Mg(OH)_2$ silicate	+18.98	$-0.29 + RT \ln a_{Mg(OH)_2}$	8.2×10^{-3}
(9)	MgO exchangeable	+6.09	$-13.2 + RT \ln a_{MgO}$	2.9×10^{-12}
(6)	$Mg(OH)_2 + 2MgO$ silicate silicate	+51.76	$-6.1 + 2RT \ln a_{MgO}$ $+ RT \ln a_{Mg(OH)_2}$	4.5×10^{-4}

† Refers to equation number in text.

‡ Maximum value, using $\gamma_{Mg^{2+}} = 0.26$ (Thompson 1966), $a_{Mg^{2+}} = 1.33 \times 10^{-2}$ for seawater, and $1.38–1.34 \times 10^{-2}$ for pore fluids of anoxic sediments (Sholkovitz 1973); ΔG°_f data from Tardy & Garrels (1974).

Table 3. Balance of excess Mg^{2+} in pore fluids of anoxic sediments by diffusion from overlying seawater

	excess magnesium			
reaction†	M pore fluid	mg cm^{-3} wet sediment	flux g cm^{-2} a^{-1}	diffusion coefficient required to balance flux/(cm^2 s^{-1})
(7)	1.99×10^{-2}	0.339	0.85×10^{-4}	4.9×10^{-7}
(9)	5.15×10^{-2}	0.876	2.21×10^{-4}	1.3×10^{-6}
(6)	4.96×10^{-2}	0.844	2.13×10^{-4}	1.2×10^{-6}

† Refers to equation number in text; calculation based on data in Sholkovitz (1973) and Bischoff *et al.* (1975).

Thermodynamic data for the reactions represented by equations (6) to (9) are given in table 2. While brucite has no stable coexistence with seawater there is a thermodynamic potential for reactions (6), (7) and (9) to proceed as written and a precipitated $Mg(OH)_2$ component of the silicate is close to equilibrium with seawater. Table 2 also lists the magnesium ion activities in equilibrium with the Mg component of the clay mineral. These show poor agreement with activities calculated from $m_{Mg^{2+}}$ in pore fluids of anoxic sediments, presumably due to the open system where Mg^{2+} removed by reactions (6), (7) and (9) is being replaced by diffusion of Mg^{2+} from overlying seawater. Table 3 lists the calculated flux of this 'excess magnesium' in pore fluids and (using a method similar to that of Bischoff *et al.* 1975) gives values of the diffusion coefficient of Mg^{2+} ions required to balance this flux of excess magnesium by diffusion from overlying seawater. The values of $D_{Mg^{2+}}$ ($0.49 - 1.3 \times 10^{-6}$ cm^2 s^{-1}) compare favourably with those in the literature (Manheim 1970; Tzur 1971; Lerman 1975).

Hence, Mg removal in anoxic sediments is predicted on thermodynamic grounds if equilibrium is considered between seawater and the reactive component of the smectite rather than between seawater and the smectite as a whole. If the latter are considered, then it is clear that the outcome of the calculation will depend on the specific clay–mineral formula adopted. However, the typical illite or montmorillonite in marine sediments can be represented by:

$$K_{b+c}\,(Al_{2-a-b}Fe_a^{III}\,Mg_b)\;[Si_{4-c}\,Al_c]\;O_{10}\,(OH)_2$$

and the thermodynamic stability of this mineral is given by:

$$\Delta G = \Delta G^{\circ} - RT\ln\,[K^+]^{b+c}\,[H_4SiO_4]^{4-c}\,[Mg^{2+}]^{b}\,[H^+]^{-(3b+c)}\ \text{kcal/mol}, \tag{12}$$

where
$$\Delta G^{\circ} = -0.765a + 22.77b + 8.29c - 22.9\ \text{kcal/mol}. \tag{13}$$

For seawater composition ($\log a_{K^+} = -2.208$, $\log a_{Mg^{2+}} = -1.87$, $\log a_{H_4SiO_4} = -4$, pH $= 8$), this becomes:

$$\Delta G = -0.765a - 4.4b - 5.066c - 1.076, \tag{14}$$

which is negative for any isomorphous substitution.

Magnesium removal in the basalt–seawater system

Recent geophysical and geochemical research has suggested that convective circulation of seawater through basaltic rocks in layer II of the oceanic crust takes place in the region of active ocean ridges (e.g. Lister 1972; Hart, 1973; Spooner & Fyfe, 1973; Dymond *et al.* 1973) and experimental simulations of this interaction (Hajash 1974; Knight 1974; Mottl, Corr & Holland 1974; Bischoff & Dickinson 1975; Williams 1975) indicates that significant chemical exchange takes place in this basalt–seawater system. Leaching of Fe, Mn, and heavy metals from basalt is observed which may account for the formation of ferromanganese deposits on ocean ridges. In addition, significant removal of magnesium from seawater is observed in agreement with the composition of modified seawater in the Reykjanes geothermal system of Iceland (Tomasson & Kristmannsdottir 1972). While such experimental studies are extremely useful in providing evidence for the addition and removal of components, they must be used with caution in the prediction of specific alteration minerals which act as sinks for certain elements, because of the difficulties in simulating equilibrium conditions in the laboratory. Nevertheless, they may be used as a guide to possible reactions in conjunction with calculated equilibrium conditions.

Early experimental work (Hawkings & Roy 1963) has shown that the product of hydrothermal alteration of basalt is a montmorillonite which does not form in the absence of magnesium. Hawkins & Roy noted that the Mg^{2+} ion plays a major kinetic rôle in montmorillonite formation. The only viable alternative as an octahedrally-coordinated cation in montmorillonite produced by basalt–seawater interaction is iron but at high temperatures the magnetite–haematite buffer will lower f_{O_2} and remove Fe as pyrite. It is unlikely that an Al-montmorillonite will form because an octahedrally-coordinated cation is required as a template for adsorption of silicic acid in the precipitation process and aluminium is likely to be present as $Al(OH)_4^-$ anions rather than Al^{3+} cations (figure 1). For this reason the forms of montmorillonite can be represented by the reaction:

$$Fe_2Si_4O_{10}(OH)_2 + 3Mg^{2+} = Mg_3Si_4O_{10}(OH)_2 + 3Fe^{2+} \tag{15}$$

showing a ferroan nontronite and a talc component of the silicate. The effect of temperature on this reaction is shown in figure 2 with the Mg-rich montmorillonite the predominant component at high temperatures and the Fe-rich component predominant at low temperatures. In fact, the low-temperature form is usually Fe^{3+} rather than Fe^{2+} since the oxygen buffer breaks down by addition of cold oxygenated seawater to the system (this is why the Fe-rich component is described as a nontronite rather than a minnesotaite). This sequence of mineralogies has certain similarities with the zoning of high-temperature alteration minerals at Reykjanes (table 4). Elsewhere the stability relationships for the Fe-rich component in equation (15) are considered, while the Mg-rich component is considered here.

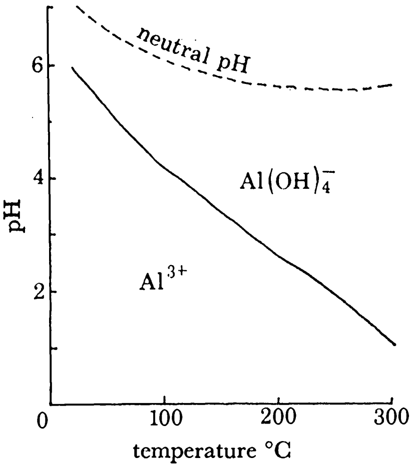

FIGURE 1. Aluminium speciation in hydrothermal systems. Data from Helgeson (1969).

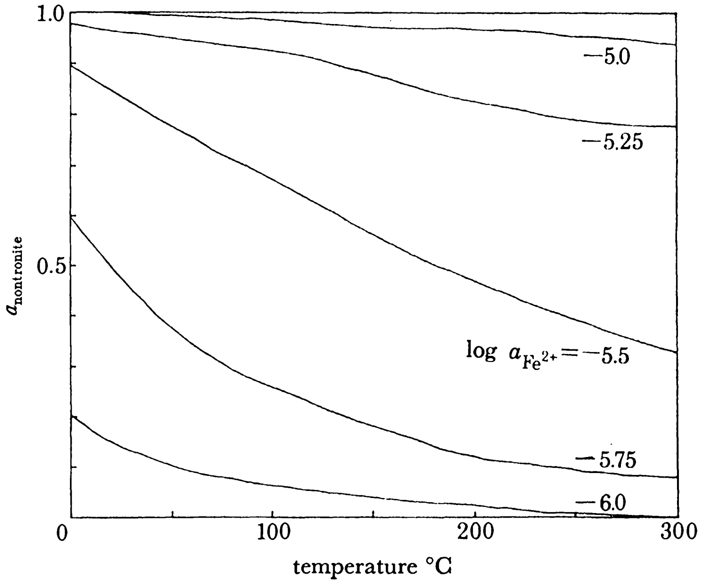

FIGURE 2. Stability of Fe, Mg-montmorillonite in hydrothermal systems. From Elderfield (unpublished data).

TABLE 4. MINERALOGICAL ZONING IN REYKJANES (ICELAND) GEOTHERMAL AREA

temperature/°C	mineral
< 100	dioct. montmorillonite
< 200	trioct. montmorillonite
200–230	random mixed layers
230–280	expanding 'chlorite'/normal chlorite

From Tomasson & Kristmannsdottir (1972).

If $a_{\mathrm{H_4SiO_4}}$ is controlled by quartz solubility (as at Reykjanes) then the removal of Mg^{2+} ions from seawater by a Mg-rich component of the montmorillonite alteration produce of basalt–seawater interaction is described by the reaction

$$\mathrm{Mg_3Si_4O_{10}(OH)_2 + 6H^+ = 3Mg^{2+} + 4SiO_2 + 4H_2O}, \tag{16}$$

and the equilibrium activity of magnesium ions is given by

$$-\log a_{\mathrm{Mg^{2+}}} = 2.01 + 2\,\mathrm{pH} - 4376/T - \tfrac{1}{3}\log a_{\mathrm{talc}}. \tag{17}$$

At 250 °C and low oxygen fugacity $a_{\mathrm{talc}} = 1$ can be assumed (figure 2) and at $\mathrm{pH} = 5.565$ (neutral), equation (17) gives the result $a_{\mathrm{Mg^{2+}}} = 1.69 \times 10^{-5}$. This is equivalent to 1.6 parts/10^6 Mg as compared with 1290 parts/10^6 Mg dissolved in normal seawater, and demonstrates the effectiveness of this reaction for removing magnesium from seawater. It is of interest further to apply equation (17) to real and simulated geothermal systems. Tomasson & Kristmannsdottir (1972) quote a Mg^{2+} concentration of 8 parts/10^6 at 190 °C in drill-hole 2 of the Reykjanes geothermal area. The drill-hole log shows both montmorillonite and 'chlorite' are present as alteration minerals and, for neutral pH, calculation predicts $a_{\mathrm{talc}} = 0.51$ in agreement with this mixture. In Bischoff & Dickinson's (1975) experimental study of basalt–seawater interaction a temporal decrease is seen in Mg^{2+} concentration from its seawater value to 30 parts/10^6 after 4752 h reaction, and the rate of Mg^{2+} decrease suggests that equilibrium was not yet attained. Application of equation (17) for $T = 473$, $\mathrm{pH} = 5.2$, gives a Mg^{2+} concentration of 62 parts/10^6 if $a_{\mathrm{talc}} = 1$. However, $a_{\mathrm{talc}} < 1$ is predicted at 200 °C (figure 2) and equation (17) gives the results $a_{\mathrm{talc}} = 0.48$ for 30 parts/10^6 Mg^{2+} and $a_{\mathrm{talc}} = 0.16$ for 10 parts/10^6 Mg^{2+}, which would seem to be the approximate equilibrium concentration for the experimental study. The montmorillonite observed by Bischoff & Dickson was a mixture of dioctahedral and trioctahedral smectites with a dominantly dioctahedral nature and a refractive index of 1.58, suggesting significant iron content.

Conclusion

The results described above demonstrate clearly the capacity of basalt–seawater interaction to remove magnesium from seawater. On the basis of chemical analyses of fresh and altered basalts Hart (1973) has suggested a rate of basalt alteration of 187×10^{14} g a^{-1}, which removes 0.82×10^{14} g Mg from seawater anually. Using a rock/water ratio of 1:10 Bischoff & Dickson (1975) observed a reduction of seawater Mg to 30 parts/10^6 which, as discussed earlier, appears to underestimate the magnitude of Mg removal. However, this value and Hart's estimate of basalt alteration give a Mg removal rate of 2.35×10^{14} g a^{-1}, which is 1.7 × stream supply as compared with Hart's estimate for Mg of 0.6 × stream supply. A recent estimate of Mg removal during anoxic diagenesis (Bischoff *et al.* 1975) is 8.5×10^{12} g a^{-1}, which is 0.06 × stream supply. Clearly the absolute value of Mg removal rate in the basalt–seawater system is subject to large error and caution must be exercised in applying a calculated flux which is based upon so few data. Nevertheless, it would seem that the basalt–seawater system provides a major sink for magnesium which is required for the steady state model of the oceans.

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Discussion

D. R. C. Kempe. (*British Museum* (*Natural History*), *Cromwell Road*, *London SW7 5BD*). Would Dr Elderfield like to comment on the final destination of the magnesium almost certainly released (along with iron, silicon, and aluminium) from the basalts during the development of the metasomatic garnets described in the previous paper? Magnesium is one of the elements lost freely during halmyrolysis, yet there is no appreciable amount of smectite, or any other mineral apart from garnet and calcite, in the micarb chalk. Further, could Dr Elderfield suggest any reason why the mineral that developed in the chalk should be garnet?

H. Elderfield. Apparently Mg has no unique fate during basalt–seawater interaction. As described in my paper, hydrothermal processes deduced from experiments or analogue situations are characterized by Mg uptake by basalt alteration products and one can predict that hot sea water emanating from ocean ridges will be found to be depleted in Mg. Furthermore, studies of the pore waters from DSDP sediments commonly show strong concentration gradients characteristic of a sink for seawater Mg. Alteration products have been shown to form at low temperatures and Mg released from basalts is removed as smectite. The absence of smectite at site 251 may be significant. A speculation is that the reaction producing garnets occurred at a sufficiently alkaline pH, caused by leaching of basaltic glass at near-zero convective water flow, to render authigenic smectite unstable and at a higher temperature than inferred from oxygen isotope studies where smectite is present. The iron released must, at least partially, be removed in the micarb chalk, whereas other elements may escape via pore waters, and must do so if alteration products have been sought but not found.