

# Sulphur transport and sulphur isotope fractionations in ocean floor hydrothermal systems

M.J. Bickle  
J.C. Alt  
D.A.H. Teagle

Dept. Earth Sciences, University of Cambridge, CB2 3EQ, UK.  
Dept. Geological Sciences, 1006 C.C. Little Building, University  
of Michigan, Ann Arbor, MI 48109-1063, USA.

The behaviour of sulphur is one of the more problematic aspects of chemical transport by high temperature hydrothermal circulation in the oceanic crust. Seawater sulphate is either deposited as anhydrite in the ocean crust when seawater is heated to about 150°C or reduced by reaction with FeO in basalt to be converted to H<sub>2</sub>S or precipitated as pyrite. There is no good evidence for a deep layer of anhydrite in the oceanic crust and Sleep (1991) postulated that any anhydrite deposited was redissolved and returned to the oceans by unsteady flow systems. However the oceanic crust is significantly oxidised (Alt *et al.*, 1994) and fluids vented from black smokers are more oxidised than fluids in equilibrium with basalts (Seyfried and Ding, 1993). Sulphate is the main oxidising agent in seawater. Seawater sulphur is isotopically heavier than basaltic sulphur and reduction of seawater sulphate to sulphide would leave an elevated  $\delta^{34}\text{S}$  signature in the altered basalt. Small elevations in  $\delta^{34}\text{S}$  are noted in both the oceanic crust (Alt *et al.*, 1994) and ophiolites (Alt, 1994). Here we evaluate the relationship between amount of oxidation and

change in  $\delta^{34}\text{S}$  for simple models of fluid-rock interaction in which both the amount of sulphate reduction and sulphur isotope exchange are kinetically limited.

Oxidation in the oceanic crust is modelled with the presumption that reduction of SO<sub>4</sub> is stoichiometrically related to oxidation of FeO to Fe<sub>2</sub>O<sub>4</sub> and that the reaction is controlled by a linear kinetic law proportional to the fraction of FeO remaining in the rock. Reaction progress is calculated after Lichtner (1988) and the rate of reaction to the rate of transport may be described by the dimensionless Damköhler Number ( $N_{Dr}$ ).  $\delta^{34}\text{S}$  isotopic compositions are calculated numerically, using the reaction progress from the analytical solution with sulphur isotope exchange between fluid and solid sulphur species also related by linear kinetics ( $N_{Di}$ ). The models simulate infiltration of seawater into the oceanic crust by calculating the oxidation and mean  $\delta^{34}\text{S}$  profile in a rock column infiltrated by fluid with 28 mmolar sulphate,  $\delta^{34}\text{S} = 21$ , and with the rock initially containing 87.5 moles.m<sup>-3</sup> of sulphide and sufficient FeO to reduce 492.5 moles.m<sup>-3</sup> of

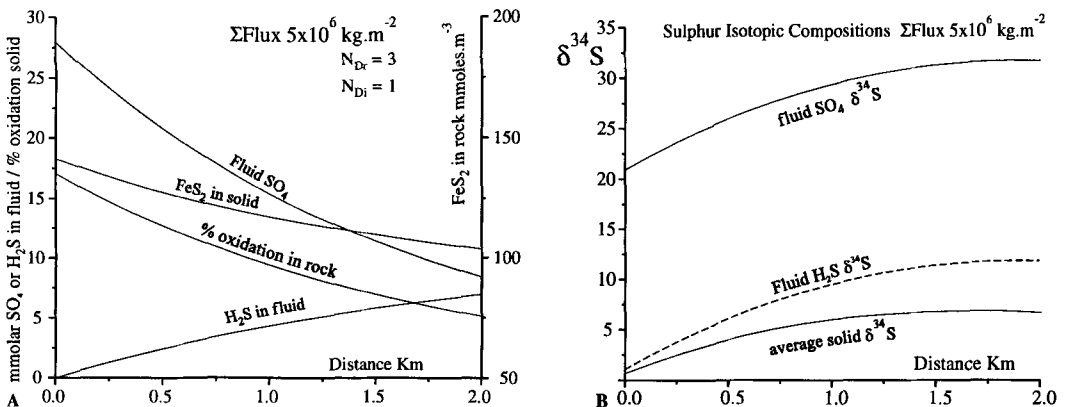


FIG. 1. Models with a time-integrated flux of  $5 \times 10^6 \text{ kg.m}^{-2}$   $N_{Dr} = 3$  and  $N_{Di} = 1$ . (a) Sulphate, sulphide concentrations in fluid and % oxidation of rock (left-hand axis) and sulphide concentration in rock (right hand axis). Note that most SO<sub>4</sub> is reduced. (b) Sulphur isotopic composition of SO<sub>4</sub> in fluid, H<sub>2</sub>S in fluid and average isotopic composition of rock.

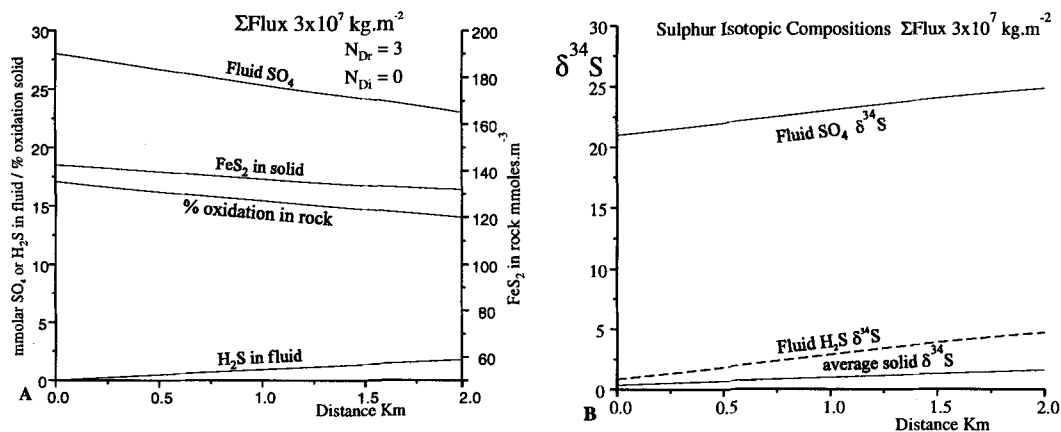


FIG. 2. Models with a time-integrated flux of  $3 \times 10^7 \text{ kg.m}^{-2}$   $N_{\text{Dr}} = 3$  and  $N_{\text{Di}} = 0$ . (a) shows concentrations and (b) sulphur isotopic compositions as in Fig. 1.

sulphate to  $\text{FeS}_2$  by oxidation of the iron to  $\text{Fe}_3\text{O}_4$ . The concentration of  $\text{H}_2\text{S}$  in the fluid phase is approximated by a linear increase from 0 to 10 mmolar at the point at which  $\text{SO}_4$  is exhausted. Sulphate-sulphide isotopic fractionation is taken as 20‰ appropriate to  $\sim 300^\circ\text{C}$ .

Figs. 1 and 2 illustrate solutions scaled for alteration over 2 km path lengths with 1) a time-integrated flux of  $5 \times 10^6 \text{ kg.m}^{-2}$ , from thermal model estimates of the seafloor high- $T$  flux (Sleep, 1991), and 2) a flux of  $3 \times 10^7 \text{ kg.m}^{-2}$ , as indicated by oceanic mass balance calculations (Palmer and Edmond, 1989) and Sr-isotope modelling for the Troodos ophiolite (Bickle and Teagle, 1992). The velocity with which the oxidation reaction is advected in oceanic crust is  $\sim 0.06$  so that a time-integrated flux of  $5 \times 10^6 \text{ kg.m}^{-2}$  would transport an oxidation front  $\sim 3$  km, comparable to the fluid path length in oceanic crust. Fig. 1 shows that most  $\text{SO}_4$  in the fluid phase is reduced, an average of 9% of FeO is oxidised to  $\text{Fe}_2\text{O}_3$  and  $\delta^{34}\text{S}$  of the sulphide is increased to an average of  $\sim +5\%$   $\delta^{34}\text{S}$  ‰. In this model limited fluid-solid sulphur isotopic exchange has been assumed which elevates the rock  $\delta^{34}\text{S}$  and reduces fluid  $\delta^{34}\text{S}$ . The amount of oxidation is at the low end and the  $\delta^{34}\text{S}$  values at the high end of the ranges exhibited by rocks from hole 504B (Alt *et al.*, 1994). Predicted fluid  $\delta^{34}\text{S}$  values of  $\sim +10\%$  are high compared with the observed range of black smoker fluids (+0.9 to +5.5‰). A higher time-integrated fluid flux (Fig. 2) reduces only a small fraction of  $\text{SO}_4$  in the fluid and oxidises  $\sim 15\%$  FeO. The vent fluids remain significantly oxidised as expected with an oxidation transport distance of  $\sim 18$  km. The amount of oxidation and the predicted sulphide  $\delta^{34}\text{S}$  values

( $\sim 5\%$  for sulphide deposits and  $\sim 2.2\%$  for average rock in the recharge path) are comparable to those observed on Troodos (Alt, 1994). Adoption of more complex models in which fluid-solid exchange characteristics and sulphur isotopic fractionations vary in time and space modify these parameters but does not invalidate the relationship between sulphur isotopic compositions and the extent of oxidation.

The results indicate that sulphate reduction may cause oxidation of the seafloor and the observed elevation of  $\delta^{34}\text{S}$  above basaltic values. Models with the lower time-integrated flux estimate of  $5 \times 10^6 \text{ kg.m}^{-2}$  are also consistent with the observation that  $\text{H}_2\text{S}$  predominates in black smoker fluids. If the higher time-integrated flux estimates characterise seafloor hydrothermal alteration, such as those appropriate to oceanic Sr-isotope budgets or Sr-isotopic alteration on Troodos, then high temperature hydrothermal vents would return a significant fraction of isotopically heavy sulphate to the oceans.

## References

- Alt, J.C. (1994) *Geochim. Cosmochim. Acta*.
- Alt, J.C., E. Zuleger and J. Erzinger (1994) *Proc. ODP, Sci. Results*, 137/140.
- Bickle, M.J. and D.A.H. Teagle (1992) *Earth Planet. Sci. Lett.*, **113**, 219–37.
- Lichtner, P.C. (1988) *Geochim. Cosmochim. Acta*, **52**, 143–65.
- Palmer, M. and J.M. Edmond (1989) *Earth Planet. Sci. Lett.*, **92**, 11–26.
- Seyfried, W.E. and K. Ding (1993) *Geochim. Cosmochim. Acta*, **57**, 1905–17.
- Sleep, N.H. (1991) *J. Geophys. Res.*, **96**, 2375–387.