

Rates and Mechanisms of Thermochemical Sulphate Reduction in Ocean Ridge Hydrothermal Systems: Implications for Nutrient Supply to Ocean Ridge Communities

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There is no doubt that thermochemical sulphate reduction (TSR) takes place as part of the process of hydrothermal circulation of sea water through oceanic crust at the mid-ocean ridges. Evidence from epidosites shows quite clearly that iron and other chemical species are oxidised. These observations arise from chemical studies of rocks and ocean ridge fluids, and assume some measure of equilibrium. However, ocean ridge hydrothermal circulation is mechanically a dynamic process, in which diffuse downflow of sea water is focused into dynamic upflow at or closely adjacent to ridge crests, for example as black smokers. Thus, it is vital to determine whether the kinetics of TSR are sufficiently fast to permit this reaction to occur during fluid circulation, and then to establish the temperatures below which sulphate reduction does not take place because reaction kinetics are slow compared with those of fluid circulation. What, then, are the implications of this for the distribution of life along the mid-ocean ridges?

We have determined both the rates and mechanisms of TSR at 50 MPa and a range of temperatures using a combination of chemical and stable isotope data derived from laboratory experiments in homogenous reactions in which sulphate is reduced and an ionic organic species, e.g. acetate, is oxidised (Cross et al., 2000a, 2000b). TSR shows reaction kinetics that are first order with respect to sulphate and acetate and that are rapid on a human time scale (Table 1). Time series sulphur and oxygen isotopic data allow the mechanism of TSR to be determined with confidence. Sulphur isotopic determinations demonstrate that hydrogen sulphide is an essential catalyst in our experiments. TSR mechanisms involve initial hydrolysis of elemental sulphur forming sulphide and sulphate. Net sulphate reduction occurs via intermediates that include thiosulphate formed by the reaction between sulphide and sulphate. Equilibrium oxygen isotopic fractionation between sulphate and water (4.5‰, Mitzutani and Rafter, 1969) is attained during heating of experiments to run P and T. It is proposed that rapid exchange of oxygen occurs during formation and decomposition of the thio-sulphate intermediate.

The kinetic data in Table 1 correspond to a range in half-lives for sulphate, from hours at 350 C to months at 250 C. Residence times for seawater within black smoker systems are constrained by exit velocities (1 - 6 m/s; Cann & Strens, 1982; Cann et al., 1985), and are of the order of hours. At temperatures below a certain threshold, reaction kinetics are too slow to permit quantitative sulphate reduction to take place.

We are at the start of a programme designed through experiment and modelling to determine the following:

- 1) the temperature below which TSR fails to take place as seawater circulates through a mid-ocean ridge hydrothermal system
- 2) the identity of chemical species which are oxidised as sulphate is reduced
- 3) the nature of any catalyst involved in the reaction
- 4) the role of organic matter in the TSR reaction, with scenarios comparing Guaymas and the Mid-Atlantic Ridge
- 5) the consequences for nutrient supply to mid-ocean ridge biota.

An important aspect of this work is to establish whether or not interaction between black smoker fluids and sea water, in the presence of appropriate catalysts, can lead to the formation of amino acids or carboxylic acids.

Temperature		$10^3/T$	$\log k$	$t_{1/2} (\text{SO}_4^{2-})$ (days)
(°C)	(K)			
250	523	1.912	-5.740	264
260	533	1.876	-5.473	143
270	543	1.842	-5.217	79.3
275	548	1.825	-5.092	59.5
300	573	1.745	-4.501	15.2
325	598	1.672	-3.959	4.38
350	623	1.605	-3.460	1.39

Table 1: Sulphate half-lives experimentally determined for the rate of TSR.

- Cann JR & Strens R, *Nature*, **298**, 147-151, (1982)
Cann, JR, Strens, R. & Rice A, *Earth & Planetary Science Letters*, **76**, 123-134, (1988)
Cross MM, Manning DAC and Worden RH, *Geochimica et Cosmochimica Acta*, **submitted** (2000a).
Cross MM, Bottrell SH, Manning DAC and Worden RH, *Geochimica et Cosmochimica Acta*, **submitted** (2000b).
Mitzutani, Y and Rafter TA, *New Zealand Journal of Science*, **12**, 54-59, (1969)