

Reconciling Experimentally Observed Sulphur Isotope Fractionation During Thermochemical Sulphate Reduction (TSR) with Field Data: A “Steady-State” Model of Isotopic Behaviour

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Published sulphur isotopic composition data for anhydrite from deeply buried petroleum reservoirs and the sulphides produced from it by Thermochemical Sulphate Reduction (TSR) indicate that there is no, or little, apparent fractionation in the sulphur isotopic compositions of the species (e.g. Orr, 1977). The similarity between the $\delta^{34}\text{S}$ values of anhydrite and associated sulphides has been used to confirm that anhydrite is the source of dissolved sulphate that undergoes TSR, forming H_2S that may precipitate as solid sulphides. However, experimental investigations of sulphur isotope systematics during TSR reveal that sulphur isotopes are fractionated by approximately 20 permil, depending upon reaction temperature, and that it is the residual sulphate that becomes enriched in ^{34}S (Cross et al., 2000b and references contained within).

TSR occurs in the aqueous phase, within reservoir formation water (Worden et al., 2000). It has been proposed that the experimental fractionation is not observed naturally because anhydrite dissolution rates are slower than the rate of TSR (Machel et al., 1995; Worden et al., 2000) or the rate of supply of dissolved sulphate to the site of chemical reaction is slow (Orr, 1977). Both explanations allow for bulk conversion of aqueous sulphate to sulphide, preventing fractionation of the sulphur isotopes. However, experimentally derived anhydrite dissolution rates are rapid (Cross et al., 1997) at temperatures considerably lower than those required for laboratory simulation of TSR (Cross et al., 2000a) and transport distances have been demonstrated to be short in the Khuff Formation, Offshore Abu Dhabi (Worden et al., 2000).

This contradiction may be explained by invoking a “steady-state” sulphur isotopic fractionation model. The model permits no net fractionation between sulphate and sulphide if either anhydrite dissolution or the transport of dissolved sulphate is the rate-determining step of the process. However, the model also allows zero fractionation of sulphur isotopes if anhydrite dissolution and transport of sulphate to the reaction site are both rapid compared to the kinetics of the TSR reaction, which appears to be a more realistic description.

The model assumes that the amount of solid, unreacted anhydrite remaining in the reservoir is always greatly in excess of the amount of dissolved sulphate and that the total amount of sulphur reduced is greater than the instantaneous reservoir of dissolved sulphate. It also assumes that the system is saturated with respect to anhydrite (or the rate of supply of dissolved sulphate to the site of reaction is lower than the rate of TSR, as discussed earlier).

There is no fractionation of sulphur isotopes during anhydrite dissolution, since the solid dissolves layer-by-layer rather than incongruently (Machel et al., 1995). Therefore, the aqueous sulphate will initially have the same $\delta^{34}\text{S}$ value as the solid anhydrite. The first sulphide produced by TSR expresses the experimentally determined fractionation (20 permil) and is therefore depleted in ^{34}S relative to the anhydrite. Preferential reduction of sulphate containing the lighter isotope causes enrichment of ^{34}S in the residual aqueous sulphate. Further anhydrite dissolution maintains sulphate saturation, but does not redress the preferential removal of ^{32}S . Therefore, the dissolved sulphate in the formation water will become enriched in ^{34}S relative to the solid anhydrite. If a constant sulphur isotopic fractionation of 20 permil between sulphate and sulphide is maintained and the aqueous sulphate becomes enriched in ^{34}S , then so must the sulphide.

As the $\delta^{34}\text{S}$ values of the sulphate and sulphide increase the $\delta^{34}\text{S}$ value of the sulphide will tend towards the $\delta^{34}\text{S}$ value of the parent anhydrite and the dissolved sulphate $\delta^{34}\text{S}$ value will become approximately 20 permil heavier than the parent anhydrite. At this stage, the $\delta^{34}\text{S}$ value of the sulphide formed is equivalent to that of the anhydrite that undergoes dissolution to replace the aqueous sulphate that has been reduced. A “steady-state”; phase of sulphur isotope fractionation during TSR reaction is established where the input of oxidised sulphur is balanced by the removal of reduced sulphur with the same $\delta^{34}\text{S}$ value. If the rate of anhydrite dissolution is rapid relative to TSR then sulphate saturation will be maintained and continuous sulphide formation will occur. This is consistent with the temporal variation in $\delta^{34}\text{S}$ values of hydrogen sulphide with increasing oil maturity that was observed by Orr (1977).

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