

OIL-SOURCE ROCK CORRELATIONS DETERMINED BY SULPHUR ISOTOPE GEOCHEMISTRY

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It is suggested that an oil-source rock genetic relationship should show as a similarity in sulphur isotopic compositions for total oil, source rock extract, kerogen and pyrite. Sulphur isotope analyses have been made of crude oils (asphaltenes, absorptive filtration fractions) and components of possible source rocks (extracted hydrocarbons, kerogens, pyrite and sulphate) from Kuwait (high-sulphur oils) and New Zealand (low-sulphur oils). In Kuwait, the crudes are isotopically very similar and suggest a single organic source. On the basis of the criteria: organic richness (EOM/TOC relationships); sulphur (and carbon) isotopic similarities of oils, extracts, pyrite and kerogen, samples from the Ratawi Formation (Raudhatain Oil Field) and the Minagish Formation (Burgan Oil Field) showed indications of source potential.

The sulphur isotopic compositions of New Zealand, low-sulphur crude oils cover a wide range. Oils from the Taranaki Basin have $\delta^{34}\text{S}$ values from +3 to +14 ‰; the lower values possibly representing plant assimilation of fresh water sulphate. Higher values, particularly those from the West Coast Basin (around +20 ‰) suggest closed ocean basin conditions (or fast sedimentation rate) whereas negative $\delta^{34}\text{S}$ values from East Coast Basin suggest open ocean (or low sedimentation rate) conditions. Shale samples analysed plot outside the corresponding oil range and cannot be considered as possible source rocks. However, coal samples from the Maui-4 well and Nelson outcrops show strong isotopic correlations with the Taranaki oils.

The results demonstrate the potential of stable isotope correlation methods in geochemical hydrocarbon exploration.

INTRODUCTION

The stable sulphur isotopic composition of organic matter is a subtle indicator for its source (Gaffney *et al.* 1980). Genetically related oils are characterised by a close similarity of $\delta^{34}\text{S}$ values (Thode, 1981). The amount of isotopic fractionation depends on environmental conditions, differing between marine and terrigenous environments as well as between open and closed systems (Smith and Batts, 1974; Krouse, 1977).

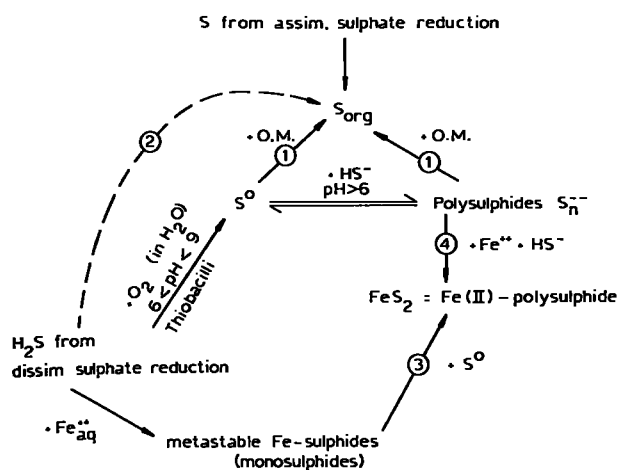
Sulphur isotopic compositions are not much affected by crude oil alteration processes, in particular, thermal maturation leads to no appreciable isotopic shifts except when oil maturation is occurring in high temperature reservoirs (Vredenburg and Cheney, 1971; Orr, 1974). There are no indications of a migration effect; for example, extensive vertical and horizontal migration has not changed the characteristic isotopic imprints of Middle East crude oils (Thode and Monster, 1970; Thode and Rees, 1970). Biodegradation and waterwashing only involve a preferential removal of non-sulphur components (Orr, 1978).

This paper seeks to examine the sedimentary sulphur cycle and isotopic fractionations therein. The predictions for isotopic distributions between oil and source rock components are examined using data in press from the low sulphur New Zealand oils and the high sulphur Kuwait crudes.

THE SEDIMENTARY SULPHUR CYCLE

Sulphur is an essential element for all plants, animals, and microorganisms, and is present in organic coordination (thiol-S) at concentrations <1% of the dry weight biomass (Siegel, 1975). Bacteria dominate the transformation of sulphur species in the biosphere, and the interactions C and S cycles of microbial communities under certain physico-chemical conditions produce stratified aquatic ecosystems (Bauld, 1986). In the underlying sediments, under anoxic and low redox conditions, inorganic and organic species of sulphur interact with each other as schematically indicated in Fig. 1. Plant-S from assimilative reduction of fresh-water sulphate and H₂S from dissimilative bacterial sulphate reduction act as S-sources for the geochemical cycle. The first process shows insignificant isotope fractionation, whereas the latter is accompanied by enrichment of ³⁴S in H₂S of up to 10 ‰ (Nielsen, 1979). The magnitude of this fractionation is dependent on the system being open or (partly) closed with respect to sulphate supply. Usually dissimilative sulphate reduction is the dominant S-source, but the assimilative pathway may be important in certain cases, e.g. for low-S lakes (Cook, 1981) or low-S coals (Hunt and Smith, 1985).

Sulphide is a very reactive ion, and is readily oxidised both chemically and biologically. Pyrite is produced from the transformation of (amorphous) iron monosulphides in the



Formation of S_{org}

① by assimilation of S⁰, possibly via polysulphide intermediates

② from H₂S via intermediate ester sulphate

Formation of pyrite

③ slow process leading to framboids

④ fast process leading to single crystals

Fig. 1: The sedimentary sulphur cycle.

presence of elemental S (Berner, 1970). To form framboidal pyrite greigite of spherical morphology is a pre-requisite (Sweeney and Kaplan, 1973). In the course of direct precipitation of non-framboidal pyrite from solution, however, acid-volatile monosulphides are not involved (Rickard, 1975). Whereas framboidal pyrite formation occurs on a time scale of years (Berner *et al.*, 1979), Howarth (1979) observed a very rapid formation of pyrite crystals within less than one day at pH = 5.

The ability of humic substances, protokerogen and kerogen to incorporate elemental S has been demonstrated by Prinzler

and Pape (1964), Martin and Hodgson (1973), DeRoo and Hodgson (1978), Dinur *et al.* (1980) and Idiz (1987). Polysulphide intermediates may play an important role in the process of S assimilation by organic matter (Aizenshtat *et al.*, 1981; Macqueen and Powell, 1983; Powell and Macqueen, 1984; Nriagu and Soon, 1985). On the other hand, Mango (1983) showed the ability of carbohydrates to assimilate S from H₂S gas, and Francois (1987) the possible formation of organic sulphur from H₂S via intermediate ester sulphate. The feasibility of the latter was demonstrated by Casagrande *et al.* (1979) using radioactive tracer techniques.

The role of elemental S as a very dynamic intermediate in the S-cycle is underlined by usually very low concentrations of a few ppm in marine sediments and crude oils (Goldhaber and Kaplan, 1974). It can be formed by the chemical or biological oxidation of H₂S in the presence or absence of O₂ (Krouse and McCready, 1979) with the aerobic chemolithotrophs among the colourless sulphur bacteria representing an intermediate case. The latter require the simultaneous presence of H₂S and O₂ established at the oxic-anoxic transition zone (oxycline) of the sediment (Bauld, 1986).

INTERMOLECULAR SULPHUR ISOTOPIC DISTRIBUTIONS

Within petroleum in general, the stable sulphur isotopes seem to be distributed between the various organic components in a characteristic manner as illustrated for selected samples in Fig. 2. The polarities of the fractions plotted increase from top to bottom: from light resins to heavy resins to asphaltenes. In the Waiotapu crude oil of terrestrial origin $\delta^{34}\text{S}$ decreases with increasing polarity and molecular weight of the fractions (Himer and Robinson, 1989); the opposite is the case for crudes of marine-brackish origin from the Molasse Basin (Southern Germany). Samples from the Burgan Oil Field (Kuwait), however, have the heavy resin

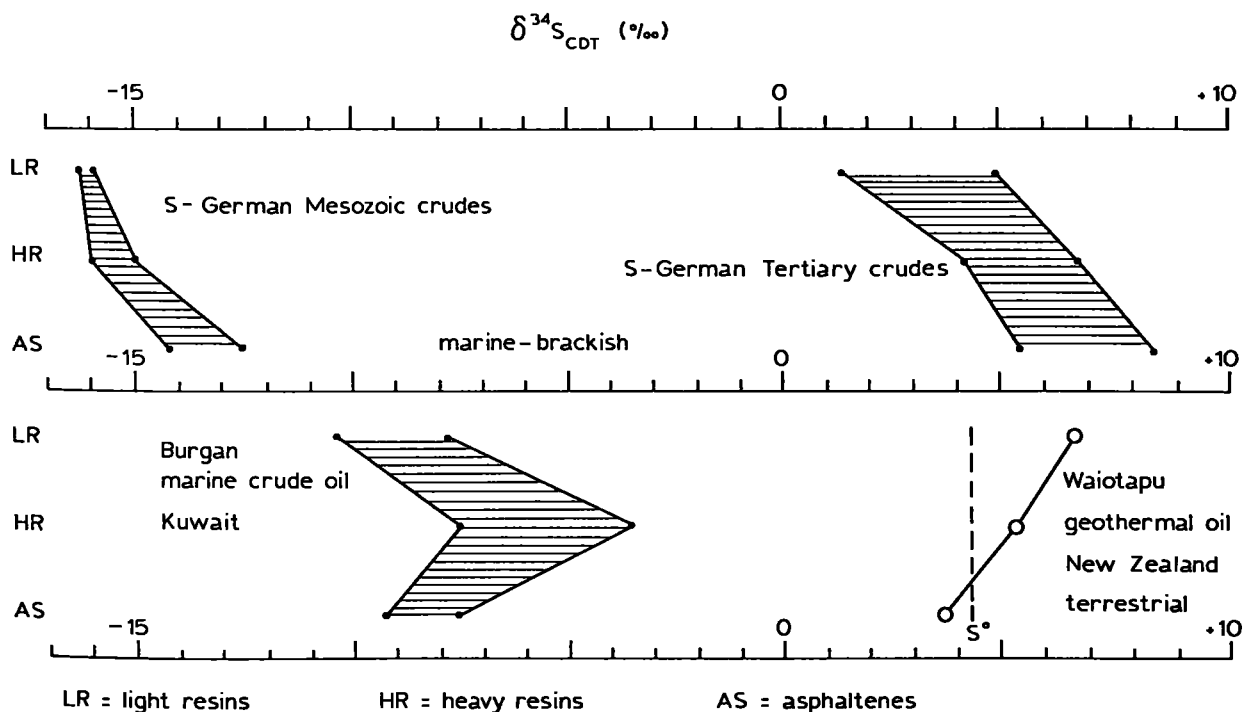


Fig. 2: Intermolecular sulphur isotopic distribution in selected crude oils.

fraction enriched in ^{34}S compared to the other two (Robinson *et al.*, in prep.). Bacterial degradation of crude oils apparently leads to isotopic homogenisation between the fractions (Monster, 1972; Orr, 1973).

The samples depicted in Fig. 2 have different geological histories and the presented empirical results demonstrate that the intermolecular S isotopic composition of petroleum must be affected by such factors as: the type of organic matter, the amount of S present, depositional environment, and the presence of bacteria. Thus, the intermolecular isotopic distribution may be a valuable fingerprinting parameter characterising one particular oil sample.

ISOTOPIC RELATION BETWEEN ORGANIC AND PYRITIC SULPHUR

Organic S and pyritic S are the stable end members in the sedimentary sulphur cycle (Fig. 1). Elemental S, as a dynamic intermediate in their production is present in negligible concentrations. Therefore both the organic and pyrite sulphur should have nearly identical $\delta^{34}\text{S}$ values. Since the sulphur is in the reduced form in both compounds, no significant isotopic fractionations would be expected if they are formed at the same time and by the same process from one sulphate source, and available iron and reactive organic matter are present in comparable amounts. Consequently, in the course of pyrolysis experiments isotopic differences between kerogen and bitumen sulphur rarely exceeded 7‰ (Idiz, 1987).

Similar $\delta^{34}\text{S}$ values for pyrite and organic matter have often been found in shale and coal samples (Hunt and Smith, 1985; Hackley and Anderson, 1986; Price and Shieh, 1986; Idiz, 1987). However, contrasting observations have been reported, too, mostly because some of the requirements mentioned above are not met, e.g. secondary sulphur from dissimilative sulphate reduction was added at a later stage. Furthermore, when mineralisation of S is severely limited by the availability of iron (Gibson, 1985), S-rich kerogens may be formed (Gransch and Posthuma, 1974) with isotopic compositions different from the mineralised S. According to the interpretation of data from Monterey shales (Idiz 1987) a limited supply of iron ions led to ^{32}S enrichment of 8 to 12‰ in the early formed pyrite compared to S subsequently incorporated in kerogen (Orr, 1986; Idiz, 1987). Because functional reaction sites in immature protokerogen compete together with available iron for the reduced sulphur, kinetic isotope effects are to be expected in cases when one of the two factors is dominating (Raiswell and Berne, 1985). Gautier (1986) observed a dependence of the pyritic $\delta^{34}\text{S}$ from the level of oxygenation of the depositional environment, but $\delta^{34}\text{S}$ values of coexisting organic S had not been determined.

APPLICATION TO CRUDE OIL-SOURCE ROCK CORRELATIONS

Location details and a short summary of the geological background are given by Hirner and Lyon (1989) for the New Zealand samples and Robinson *et al.* (in prep) for the Kuwait samples. Conditioning of the crude oils, separation of asphaltenes, isolation of oil fractions a to d by adsorptive filtration, and determination of elemental sulphur by XRS was performed according to techniques described by Hirner *et al.* (1984). Sulphur isotopic compositions were measured by the techniques given in Robinson and Kusakabe (1975).

Incorporation of sulphur in the crude oils

Sulphur isotopic type curves may represent effective parameters for characterising crude oils and source rocks extracts: In high-sulphur (2.1 to 4.2% S) marine Kuwait crudes ^{34}S is enriched in the heavy resin fraction 'd', in medium-S (0.23 to 0.91% S) marine-brackish Molasse crudes ^{34}S is enriched with increasing polarity of the fractions and in many low-sulphur (0.06 to 0.34% S) terrigenous New Zealand crudes ^{34}S is depleted with increasing polarity of the fractions.

Oil-oil-correlation

The distribution of the stable sulphur isotopes for the New Zealand oils are shown in Fig. 3. Crude oils from the Taranaki and West Coast Basins show positive $\delta^{34}\text{S}$ -values, whereas those from the East Coast Basin show negative ones.

A meaningful interpretation of stable sulphur isotope distributions must establish whether the investigated natural system is open or (partly) closed to the supply of sulphate (Chambers, 1982; Chanton, 1985). Because of its appreciable fractionation against the formation water-sulfate, the sulphur in E-coast oils must be derived by bacterial reduction of marine sulfate in an open ocean (or possibly low sedimentation) environment with an unlimited sulphate supply; these oils show the highest concentrations (up to 0.4 wt% S) of all New Zealand crudes (Gibbons and Fry, 1983). The $\delta^{34}\text{S}$ -values of West Coast Basin oils (Fig. 3a) point to complete reduction of the available marine sulphate (closed basin or possibly fast sedimentation rate conditions).

Moturoa Field and offshore Taranaki oils form subgroups within the oils of Taranaki Basin (Figs 3b, c). The sulphur in the Taranaki oils can be derived by bacterial reduction of marine sulfate. However, the sulphate reservoir must have been limited, leading to a significantly reduced isotopic discrimination (Chambers and Trudinger, 1979). Such conditions prevail under deposition in (partly) closed (lagoon?) basins or in areas with a correspondingly increased sedimentation rate.

Most of the crude oils investigated contain less than 0.1 wt% S, (for example, those of Moturoa Field). A significant portion of the sulphur in the latter oils could be primary sulphur derived from the original biomass (plants). Most of the rock samples contain <0.7 wt% organic sulphur and are typical of environments such as freshwater systems where the organic sulphur is possibly derived from plant assimilation of freshwater sulphate (Schiff and Hodson, 1973; Trudinger and Loughlin, 1981; Price and Shieh, 1986). Sulphur contents in land plants average approximately 1 wt%, and their isotopic values lie near to those of the source sulphate. For example, Cretaceous to Permian Australian coals show comparable low sulphur contents, and are characterised by freshwater conditions during deposition and maturation (Hunt and Smith, 1985). The isotopic composition of freshwater sulphate in relation to Australian coals is estimated by Smith *et al.*, (1982) to be $+4 \pm 3$ ‰ (Fig. 2).

The Kuwait crudes are of a very similar isotopic composition: $\delta^{34}\text{S}$ average -10.3 ± 3.4 ‰. Raudhatain oils seem to be slightly depleted in ^{34}S over Burgan ones, but the small number of samples analysed precludes any statistical treatment. Such uniformity in these Kuwait oils suggests derivation from one source only. However, Kuwait crudes are depleted in ^{34}S with respect to Tertiary and Cretaceous oils

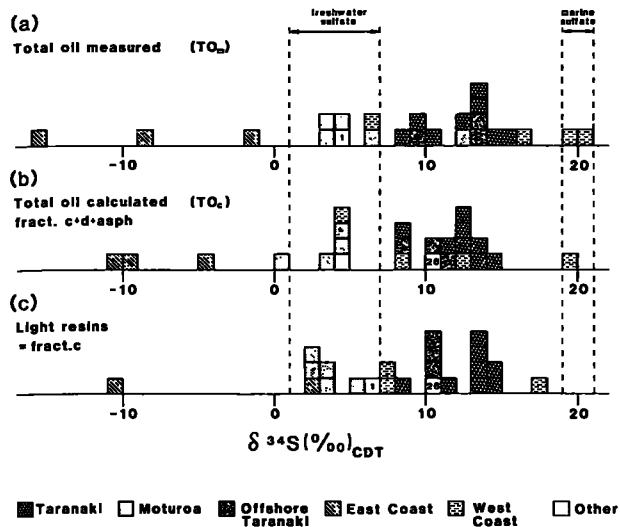


Fig. 3: The sulphur isotopic composition of New Zealand oils.

from Northern Iraq which show $-8.7\text{‰} < \delta^{34}\text{S}_{\text{CDT}} < -1.9\text{‰}$ (Thode and Monster, 1970).

Oil-extract correlation

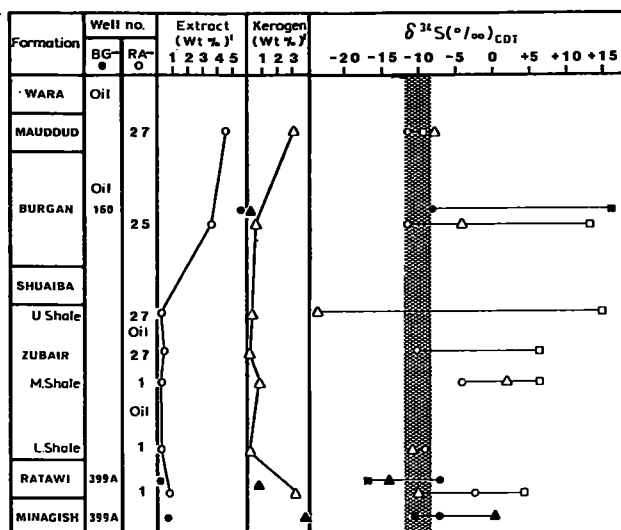
According to Tissot and Welte (1984) minimum TOC values of potential source rocks are 0.3 wt% for carbonates and 0.5 wt% for shales, and bitumen ratios (EOM/TOC) usually range between 0.02 and 0.2. Thus, the high extract yields (>3 wt%) of some Kuwait samples indicate the non-indigenous character of the extracted hydrocarbons, i.e. possible primary hydrocarbons have been diluted by higher amounts of hydrocarbons coming from outside and impregnating the rock sample. On the other hand it is very probable that Kuwait samples with TOC ≤ 0.4 wt% contain migrated or stained hydrocarbons only.

Obviously an isotopic correlation between crude oil and extract must be tested by other correlations, i.e. with pyrite and kerogen to distinguish impregnation effects from a true oil-source rock relationship.

Oil-source rock correlation

Assuming that the organic and pyritic sulphur have been formed at the same time and by the same process from one sulphate source, and available iron and reactive organic matter are present in comparable amounts, it is to be expected that the sulphur isotopic compositions of the total reservoir oil, source rock extract maltenes, total source rock extract, source rock extract asphaltenes, source rock kerogen, source rock pyrite should be similar. Within all organic fractions, the isotopic differences for genetically related oil-source rock pairs should be less than approximately 2 ‰ (Orr, 1986).

Indigenous source rock extracts and kerogens from Kuwait should show similar stable sulphur isotope ratios (Robinson et al., in prep), Formations and pairs showing good $\delta^{34}\text{S}$ correlation are from Mauddud, Zubair Lower Shale and Ratawi; and a poorer $\delta^{34}\text{S}$ correlation from the Minagish sample (Fig. 4). Mauddud, Minagish and Ratawi samples have sufficient kerogen to be considered potential source rocks, but not the Zubair Lower Shale sample. Only in Mauddud and Minagish samples are pyritic and organic sulphur of similar isotopic composition, probably indicating a common origin.



* G = Good oil/extract type curve fit † Related to 100wt % dried rocks
 Oil range ○ Extract △ Kerogen □ Pyrite

Fig. 4: Kuwait: sulphur isotopic composition of oils and possible source rock components.

For the New Zealand source rocks the best correlation between all phases includes samples from Maui-4 and some Nelson coals (Fig. 5). The pyrites in many samples including the Black Shale Castlepoint (Waipawa) and the West Coast coals are interpreted to have been precipitated during different events to those forming the organic sulphur. Shale samples show no significant correlations with the crude oils. Generally, Kapuni coals are not thermally mature and also the Pakawau samples are too immature to have produced oil. Only the deepest coal in Maui-4 is sufficiently mature to have sourced oil. It also gives a very good bio-marker correlation with the oil whereas shales did not (Collier, 1985).

CONCLUSIONS

Inorganic and organic forms of sulphur are linked to each other in the sedimentary sulphur cycle. Several relationships can be derived, which may be selectively used in solving practical problems of exploration and environmental geochemistry:

- Elemental S is incorporated in crude oils without significant isotopic fractionation.
- The incorporation of elemental S in organic components is a specific process, and is reflected by the intermolecular distribution of ^{32}S and ^{34}S in organic fractions.
- Sulphur isotopic crude oil/rock extract/rock kerogen correlation studies can be improved significantly by including mineral sulphur (pyrite).

In the New Zealand situation sulphur is incorporated in organic matter from different depositional environments with respect to bacterial reduction of sea water sulphate: East Coast Basin (open ocean or low sedimentation rate), Taranaki Basin (partly closed basin or medium sedimentation rate), and West Coast Basin (closed basin or rapid sedimentation). The sulphur of Moturoa oils (Taranaki Basin) may have been derived by plant assimilation of freshwater sulphate. New Zealand crude oils show no indications of systematic sulphur isotopic intermolecular ordering. This may be explained by their origin as a mixture of isotopically heterogeneous plant sulphur with isotopically systematic

cally-ordered, bacterially-reduced sulphate sulphur. In agreement with the results of a parallel carbon isotope study (Hirner and Lyon, 1989), rock samples from Maui-4 as well as some Nelson coals show strong isotopic correlations to Taranaki oils.

Kuwait crude oils from Burgan and Raudhatain fields are very uniform in their isotopic composition, thus forming one oil family probably derived from one source rock. This uniformity can be traced down to the intermolecular level, even for some rock extracts. Isotopic type curves for Kuwait crudes and extracts on the base of adsorptive filtration fractions are highly specific compared to South German and New Zealand oils. On the base of EOM/TOC relationships we interpret the excellent isotopic correlations of the Middle Cretaceous rocks to the crudes as impregnation effects by the reservoir oil, and argue for Lower Cretaceous source rocks (Ratawi/Minagish Fmn) strengthening the models presented by Dunnington (1967) and Ibrahim (1983).

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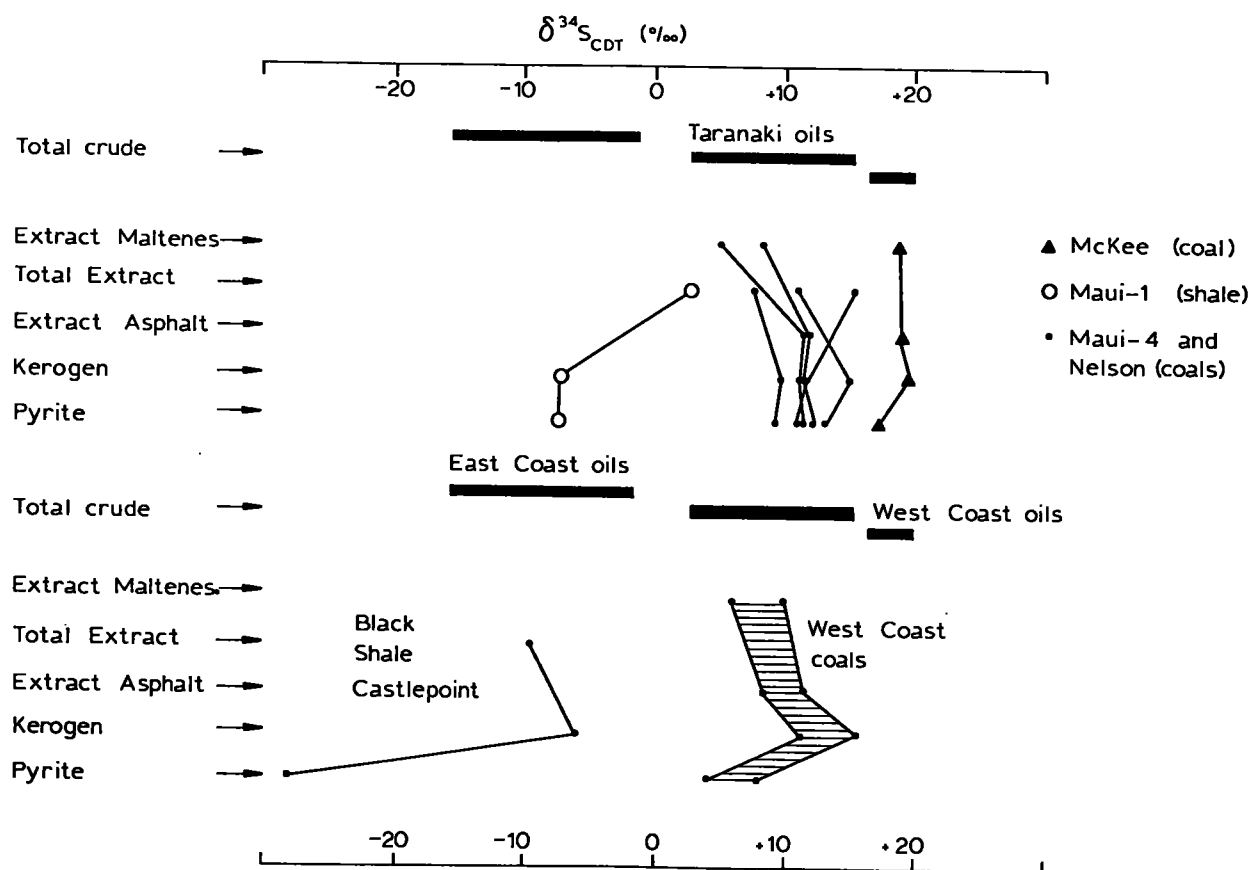


Fig. 5: New Zealand: sulphur isotopic composition of oils and possible source rock components.

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