Secular change in $\delta^{34}S$ value of early palaeozoic kerogens from the Tarim Basin relative to marine sulphates

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Ten mature to over-mature kerogen samples from the Tarim Basin, NW China, after pyrite was removed using $CrCl_2$+HCl solution [1], were measured for $\delta^{34}S$ values. Five of the samples were analyzed for organic sulphur contents. The results show that organic sulphur in four samples among the five comprises 91 to 98% of total sulphur. The other kerogen has sulphur ~72% from organic sulphur, however, suggesting that significant pyrite sulphur has contributed to the $\delta^{34}S$ measurement value (-2.95‰) (Fig. 1).

Mudstone and shale with TOC from 1.7 to 2.0% in the Cambrian have kerogen $\delta^{34}S$ values ranging from +13.8 to +19.4‰ (n=3). The values are about +15 to +20‰ lighter than contemporary seawater sulphates [2]. Micrite and mudstone from the Lower Ordovician and from the bottom of Middle Ordovician, are +6.7 and +8.7‰, respectively. The lowest $\delta^{34}S$ values, from -15.3 to +6.8‰ (n=5), were measured from the Middle - Upper Ordovician marlstone and muddy micrite with TOC from 0.6 to 4.4%. The kerogen $\delta^{34}S$ values gradually decrease from the Cambrian, early Ordovician to late Ordovician, which is consistent with the secular change of seawater $\delta^{34}S$ values during the period with the difference of about 18‰ [2] (Fig. 1). This changing trend is the first finding.

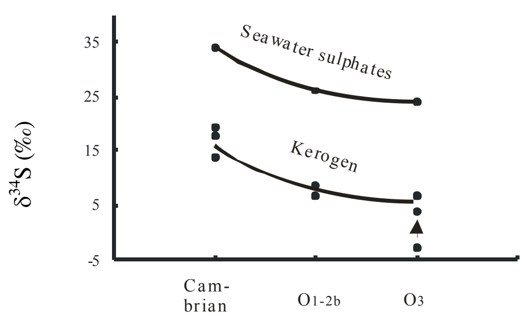

Figure 1: Diagram showing that changing trend of kerogen $\delta^{34}S$ values parallels to seawater sulphates (note: $O_{1\text{-}2b}$ represents Lower and bottom of Middle Ordovician).

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Occurrence and characteristics of fatty acids interaction with clay minerals of surface sediments from the East China Sea

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To obtain information on occurrence and protection pathway of fatty acids in clay minerals, we conducted mineral and GCMS analysis of less than 2μm particle-size fractions from two muddy surface sediments, the East China Sea, by sequential treatments including soxhlet extraction, saponification and acid hydrolysis. Every treatment allowed for the release of acid moieties occurring in each sample. XRD results show that the diffraction peak (d_{001}) of smectite of clays is 14.25nm, while after saponification and acid hydrolysis are 13.30nm and 12.3nm respectively, suggesting the occurrence and combined location of fatty acids with clay minerals have a distinct diversity. So it can be concluded that there are three interaction modes of fatty acids with clay minerals: free fatty acids obtained by soxhlet extraction is in micropores of clays, "OH^-" labile fatty acids obtained by saponification is on interlamination edge of smectite and clay surface, and "H^+" labile fatty acids obtained by acid hydrolysis occur in interlamination of smectite.

GCMS analysis shows that fatty acids of three moieties are different in quantity, composition and distribution. Percentage of unsaturated fatty acids are highest in free acids, followed by "H^+" labile acids and "OH^-" labile acids, while the reverse is true for normal saturated fatty acids. Also, percentage of branched acids and dicarboxylic are highest in "OH^-" labile acids, and $i+a_{15:0}/n_{15:0}$ and $i_{17:0}/n_{17:0}$ ratio are also highest in the same acid moiety. These results indicate "OH^-" labile acids are subjected to strong degradation by bacteria and "H^+" labile acids are degraded weakly and relatively stable. Due to free acids are in micropores of clay minerals, they could be influenced by organic matter input greatly. Fatty acids characteristics are related nearly with acids occurrence, which results in different degradation degree of three acids fractions and their preservation process. Thus, processing methods are deserved to be considered carefully in fatty acids degradation research.

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