

Observations of some post-sourcing alteration factors on the metal signature of crude oils

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The influence of post-sourcing alteration effects on the metal composition of petroleum is presented from a number of case studies. Metals in oils from North Sea migration sequences on the Central Graben and Tampen Spur will be used to illustrate the influence of migration on metals. The effects of maturation, asphaltene precipitation, phase-controlled fractionation and biodegradation will be illustrated using case studies done on oils from the North Sea, China and the USA.

For example, metal data for the Tampen Spur migration sequence [1] is shown in Table 1. Maturity, rather than migration processes controls the metal contents of the Central Graben oils. The V/(V+Ni) ratio is a maturation and migration independent source facies indicator.

Sample	API	$\frac{V}{V+Ni}$	V	Ni	Co	Zn	$\frac{T_s}{T_m}$
Oil 1	40.7	0.889	820	102	2	110	5.0
Oil 2	38.4	0.918	8700	780	1	160	3.1
Oil 3a		0.888	15790	1993	4	547	2.8
Oil 3b	38.2	0.911	8876	867	4	294	2.8
Oil 3c	37.4	0.909	13535	1350	6	407	2.7
Oil 4	32.5	0.903	68180	7333	9	572	1.4
Oil 5	33.3	0.898	88970	10150	15	2930	1.4

Table 1: Metals in central Graben oils (ng/g oil).

Examples will be given of metals such as Zn, Pb and Au introduced to source rocks and their oils due to incorporation of minerals from nearby mineralized zones during formation of the source rock. Indications of possible incorporation of Fe into oils due to the action of Fe (III) reducing bacteria and of Co due to methanogenic bacteria will be presented.

[1] Larter, S.R *et al.* (1996), Benzocarbazole secondary migration tracers. *Nature* **383**, 593 – 597.

Characterization of secondary mineral formation on olivine by surface sensitive techniques

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The world faces a huge challenge to decrease carbon dioxide emission while maintaining reasonable growth. With a still increasing use of fossil fuels, a need is arising to develop methods for removing CO₂. A promising way to meet this challenge is to sequestering CO₂ as solid carbonate minerals.

The silicate mineral olivine, (Mg,Fe)₂SiO₄ reacts exothermally with carbon dioxide and forms other minerals, including carbonates. Unfortunately, the reaction rates are slow at standard temperature and atmospheric CO₂ pressure because olivine dissolution is slow, which makes mineral carbonation economically unfavourable. Changing the conditions, including pH, or using a catalyst can increase the reaction rate considerably.

An atomic force microscopy (AFM) study of a freshly fractured olivine (Fo₉₀) surface showed almost instantaneous mineral formation after rinsing the samples with Milli-Q water. After an hour, features grew, changed shape and distribution. Reaction favoured some sites on the fresh surface over others, indicating non-homogeneity either in composition or in crystal defects. Dissolution and a considerable increase in mineral precipitation were observed when olivine was heated for 4 hours at 160 °C in Milli-Q water, in an autoclave reactor. With higher CO₂ (P_{CO₂}=25 bars) and increased reaction time (15 hours), the green olivine surface turned red. X-ray powder diffraction (XRPD) could not identify the red precipitate, suggesting: 1) an amorphous phase, 2) too little material, or 3) the XRPD pattern of the red material was masked by an olivine peak. X-ray photoelectron spectroscopy (XPS) of the red precipitate showed a high proportion of iron and at least one additional oxygen binding environment. By comparing the XPS spectra for the red precipitate with iron oxide standards, the material was interpreted to be hematite (Fe₂O₃). New experiments to investigate the surface changes during exposure to higher pH solutions are underway.