

Re/Os fractionation during generation and evolution of hydrocarbons

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Recent results [1] suggest that the Re-Os isotopic system can be used to date the emplacement of petroleum deposits. However, to fully exploit this potentially exciting new application of the Re-Os geochronometer, it is essential to identify the physical processes that fractionate the parent(Re)/daughter(Os) ratio in hydrocarbon systems. We are currently examining two processes that could potentially cause Re/Os fractionation: 1) fractional precipitation of the asphaltene component of petroleum; and 2) black shale maturation and hydrocarbon expulsion. To investigate the first process, we have separated the various asphaltene fractions according to their density and their molecular size. We find a rapid, linear decrease in Re concentration with decreasing asphaltene density. Natural precipitation of asphaltenes could thus provide a means of fractionating the Re/Os ratio in petroleum, if Os concentrations do not follow exactly the same distribution pattern observed for Re. To investigate the second process, we have performed artificial maturation experiments on the well-known Woodford shale source rock of the western United States. We find that Re and Os are both retained nearly completely by the experimental residue. This explains the earlier observation [2] that hydrocarbon maturation does not affect the depositional age determined by Re-Os analysis of black shale source rocks. On the other hand, the Re and Os concentrations of the extracted petroleum fluids are more than 150 times lower than those of the black shale residue. Thus mass balance considerations suggest that the Re/Os ratio of the extracted fluid could differ greatly from that of the black shale parent rock, despite the fact that the Re/Os ratio of the residue is essentially unchanged.

[1] Selby & Creaser (2005) *Science* **308**, 1293-1295.

[2] Creaser *et al.* (2002) *GCA* **66**, 3441-3452.

The partitioning of molybdenum between aqueous liquid and vapour at high temperatures and pressures

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In the study of porphyry Mo ore-forming systems, there is increasing debate over whether the fluid responsible for the dissolution and transport of Mo is a liquid, a vapour, or both. In order to help resolve this issue, it is necessary to have information on how Mo will tend to distribute between these two phases. With this in mind, we have conducted an experimental study designed to determine the partition coefficients of Mo between aqueous liquid and vapour at 300 to 370°C and saturated vapour pressure. The apparent distribution coefficient, $\log K_d$, increases with increasing temperature and pressure, but decreases with increasing Mo concentration of the liquid phase. For experiments conducted with a starting solution of 100 ppm Mo, vapour-phase Mo concentration exceeds that of the liquid at temperatures above about 360°C. The concentration of Mo in aqueous vapour at any given temperature is independent of the Mo concentration of the liquid, indicating that the dominant gaseous Mo species is $\text{MoO}_3 \cdot n\text{H}_2\text{O}$. Thermodynamic modeling indicates that bimolybdate (HMoO_4^-) is the dominant species in the liquid at the conditions considered, and thus the solubility of Mo in this phase was dependent on pH in our experiments. In order to determine the true partitioning of Mo between vapour and liquid, we calculated Henry's constants from the fugacity of $\text{MoO}_3 \cdot n\text{H}_2\text{O}$ and the molality of pH-independent molybdic acid (H_2MoO_4). These are 2.10, 21.05 and 116.09 bar kg mol^{-1} at 300, 325 and 350°C, respectively. Our results indicate that in the two-phase, aqueous liquid and vapour systems common to porphyry Mo ore-forming environments, both phases are likely to be important in the transport and deposition of Mo.