

## Acid-base fractionation in the model Cl-bearing granite

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Existing experimental data indicate rather limited chlorine solubility in felsic melts [1]. On the other hand, melting temperature of the model haplogranite in presence of concentrated alkali halide solutions is significantly higher than in pure water, and, for a constant salt concentration increases with increasing pressure [2]. Taken together, these data show that any granite melts containing even small amount of dissolved Cl (of about  $n \cdot 10^{-1}$  wt.%) should liberate a very concentrated brine at the early, high-temperature stages of decompression/cooling induced crystallization. With continuing crystallization fluid in equilibrium with granite melt must evolve towards pure water. We have made melting experiments at 800°C and 2 kbar total pressure on the model granite composition Ab69Qtz31 in presence of aqueous NaCl solutions ranging in concentration from  $X_{\text{NaCl}} = 0.2-0.02$ . The experiments have shown that quench pH of the solution equilibrated with the melt depends strongly on the solution salinity: the quench pH of the most concentrated solution was about 9, while that of the least concentrated one—about 2. Acidic nature of the dilute salt solutions in equilibrium with granite melt was discovered some 40 years ago [3], whereas the very high pH values of the concentrated solutions are reported for the first time. The nature of the acid solutions is well understood as being due to hydrolysis reaction of the type:  $2\text{NaCl}(\text{fl}) + \text{H}_2\text{O}(\text{fl}) = \text{Na}_2\text{O}(\text{m}) + 2\text{HCl}(\text{fl})$  (1), where fl and m denote fluid and melt phase, correspondingly. The exact reason for the high quench pH observed in concentrated solutions remains as yet unknown, we suggest it results from dissolution of  $\text{Al}_2\text{O}_3$  in the course of schematic reaction:  $0.5\text{Al}_2\text{O}_3(\text{m}) + 3\text{NaCl}(\text{fl}) + 1.5\text{H}_2\text{O}(\text{fl}) = \text{AlCl}_3(\text{fl}) + 3\text{NaOH}(\text{fl})$ . In any event, the pH variations in alkali solutions liberated from an evolving granite melt must cause significant changes in the magmatic fluid transport properties in respect to various ore metals. This effect is demonstrated in the experiments on partitioning of W and Pb between the model melt and solutions of variable NaCl concentration.

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## Trace metal and Mo isotope systematics in petroleum fluids

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The presence of trace metals in oils has long been of interest for both their detrimental and beneficial effects during hydrocarbon exploration. For example, elevated levels of trace metals can cause problems during downstream refining processes due to catalyst poisoning. In contrast, the diagnostic potential of trace metals incorporated in fluids and host rocks has been successfully applied in various fingerprinting studies. The majority of work to date has focussed on the two most abundant metals found in oils, vanadium (V) and nickel (Ni), which have been used as tools in correlation and fingerprinting, and provide information on redox conditions during source rock deposition.

Here we focus on the molybdenum (Mo) isotope system, well known to display bi-polar redox chemistry [1], and thus providing a potentially valuable new tool to exploit in petroleum systems' studies. We have developed techniques for the determination of Mo isotopes in hydrocarbon (HC) fluids. Mo is extracted from its complex organic fluid matrix, through high pressure ashing, which renders the complete decomposition of the HC fluid, allowing the Mo to be purified via conventional ion-exchange methods [2]. Preliminary data from replicate samples suggest a precision of better than 0.1‰ in  $\delta^{98/95}\text{Mo}$ . We combine the Mo isotope data with more conventional elemental fingerprinting, as determined through isotope dilution HR-ICPMS analysis with a new multi-element spike. This method allows greater accuracy and precision than has been previously possible, both being better than 10%.

Samples display variably positive  $\delta^{98/95}\text{Mo}$  ratios, ranging from +0.4‰ to +1.7‰, within the range of sediments deposited under variably reducing conditions [3]. We will further explore the relationship between oil Mo isotope composition and its source rock, as well as biodegradation and maturation processes.

[1] Erikson, B.E. and Helz, G.R. (2000). *Geochim. Cosmochim. Acta* **64**, 1149–1158. [2] Archer, C. and Vance, D. (2009). *Nature Geosci.* **1**, 597–600. [3] Siebert C, *et al* (2006). *EPSL* **241**, 723–733