Reversible functional group interconversion in organic hydrothermal reactions: The central role of ketones

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Studies of reactions of organic compounds under hydrothermal conditions suggest complex, often reversible, pathways that link functional groups of increasing oxidation state from alkanes all the way to carboxylic acids [1]. Ketones represent a critical functional group in this reaction chain, since oxidation to carboxylic acid requires the only carbon-carbon bond cleavage reaction in the pathway.

Here we describe the results obtained for experimental studies of a model ketone, dibenzylketone (DBK) under aqueous hydrothermal conditions (72h, 300°C and ~70MPa). We used a cold-seal vessel with gold capsules containing DBK, water and both the presence and the absence of minerals. We are interested in how minerals control the major products and reaction pathways for ketones, either reduction towards an alkane or oxidation towards a carboxylic acid. We also seek relative kinetic information for the various functional group interconversions, to determine rate-limiting steps along the pathways. This work will provide mechanistic information that reveals how minerals affect the reactions.

The observed reaction products for DBK depend upon the nature of the added mineral. In the absence of minerals, DBK yields products from both carbon-carbon bond cleavage reactions ('forward' to the carboxylic acid) and also products corresponding to deoxygenation and reduction to the corresponding alkane 1, 3-diphenylpropane ('backwards' to the alkane). In the presence of pyrrhotite (FeS), the reaction follows mainly the backwards reduction pathway (alcohol to an alkene and then to the alkane). Each intermediate structure in this sequence is clearly identified. The slowest reaction in the sequence is reduction of the ketone and the fastest is dehydration of the alcohol. In the presence of hematite (Fe_2O_3), mainly carbon-carbon bond cleavage products are observed. The bond-cleavage products are the same as those identified as arising from benzyl radicals formed via homolytic bond fragmentation. These results show how oxidation states of minerals can influence organic reaction pathways and products.

[1] Seewald (2003) *Nature* **426**, 327–333.

Whole rock geochemical, Nd-Pb-Sr isotopic characteristics and Re-Os ages for molybdenite of the Shangguisi granite porphyry in East Qinling

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The Shanggusi molybdenum-bearing granite porphyry located in the eastern part of all the known molybdenum deposits in east Qinling. The rocks are highly silicious, have high contents of alkalis, low abundances of Fe_2O_3, FeO, MgO, CaO, MnO, TiO_2 and P_2O_5. All of these granites are weakly peraluminous with A/CNK of 0.98–1.03, and with A/NK of 1.01–1.08. The REE patterns are characterized by enriched LREE and slightly flattened HREE with negative Eu anomalies (Eu/Eu*=0.33–0.56). The average 10, 000×Ga/Al ratios are 3.8–4.8 with an average value of 4.22, which is a little higher than the global average of 3.75 for A-type granites [1]. The Shanggusi granites belong to the A_1 type [2]. Five Re-Os model ages of the disseminated molybdenites range from 122.5 (±2.1)Ma to 124.8 (±1.8)Ma with weighted averaged age of 123.6Ma (MSWD=0.45), and isochron age of 123.4±2.4Ma (MSWD=1.07). Most of the samples with $(^{87}Sr/^{86}Sr)i<0.703$ (0.684–0.703), and only two samples with reasonably $(^{87}Sr/^{86}Sr)i$ ratios: 0.7156 and 0.7077. εNd (t)=-8.9–-9.7. $(^{206}Pb/^{204}Pb)t=16.70–18.43$, $(^{207}Pb/^{204}Pb)t=15.39–15.48$, $(^{208}Pb/^{204}Pb)t=37.65–37.94$.

The Shanggusi porphyry molybdenum deposit is the second stage of the Yanshanian ore-forming processes (135~110Ma). The ore-forming time correspond with the peak lithospheric thining stage of east China. The diagenesis and mineralization, generated by the lithospheric delamination mechanism induced by the intro-plate orogenic processes [3], is one marker for the orogeny belt begin to enter into the extensional tectonic environment.

[1] Whalen *et al.* (1987) *Contrib. Mineral. Petrol* **95**, 407–419. [2] Eby (1992) *Geology* **20**, 641–644. [3] Zhang *et al.* (1996) *Science in China (Series D)* **26**, 193–200 (in Chinese)