Relationship between water/rock ratio and conversion rate of the smectite to illite reaction

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The conversion of smectite to illite via a mixed-layer illite/smectite (I/S) is an important mineral reaction during sediment burial, very low-grade metamorphism and in hydrothermal alteration environments. Many experiments have been carried out to convert smectite to illite or I/S hydrothermally, but few studies considered the water content as a kinetic parameter for this conversion rate. This study aims to quantify the effect of water/rock ratio on the conversion rate of the smectite to illite reaction experimentally using natural smectite.

The smectite-to-illite conversion experiment was carried out on Na-saturated montmorillonite and 1 M KCl solution as a function of water/rock ratio at 325°C, 500 $\times 10^5$ Pa in cold-seal pressure vessels using gold capsules. The results show that the illitization extent and the conversion rate were dominantly controlled by the water/rock ratio in this experiment. A water/rock ratio of 0.2 to 2 (mass : mass) produced R0 I/S, whereas a water/rcok ratio of more than 3 produced R1 and R>1 I/S under the same conditions. The conversion rate of smectite-to-illite is linearly proportional to the logarithm of water/rock ratio. The experimental results were also used to modify the kinetic model of smectite-to-illite conversion proposed by Huang et al.(1993), to which the water/rock ratio factor has been added, that is, $dS/dt = -k \times [K^+] \times 1.1 \times (\ln(W/R)+1) \times S^2$. Where S = fraction of smectite layers in the I/S, t = time in seconds, k = the rate constant, $[K^+]$ = K^+ concentration in the molarity (M) in the solution.

References:

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Cu isotope compositions of Cu-sulfides from hydrothermal ore deposits

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Copper is a transition metal, which occurs widely as sulfide minerals and is commonly found in many hydrothermal ore deposits. The two stable isotopes, ^{63}Cu and ^{65}Cu, have natural abundances of 69.17% and 30.83%, respectively; and very subtle isotopic variations in the order of several per mil are observed in nature.

We conducted a reconnaissance study of Cu isotope compositions in Cu-sulfide minerals (chalcopyrite, tetrahedrite, chalcocite, azurite) from various types of hydrothermal sulfide deposits in China and Europe. Large Cu isotope fractionations are found in these deposits with δ^{65}Cu values extending from 3.42 to –3.77‰. In particular, Cu-sulfides from the Jinman low-temperature sandstone-hosted vein Cu deposit in Yunan province, South China show the lowest δ^{65}Cu values, whereas the Dongxiang sedimentary-hosted massive sulfide (SHMS-type) Cu-Pb-Zn deposit from Jiangxi province, Southeastern China displays the highest δ^{65}Cu values of up to 3.42‰. In the Dongxiang deposit, epigenetic chalcocites display a significant isotopic fractionation from the primary Cu-sulfide ores with low δ^{65}Cu values down to –1.26‰. Chalcopyrite from the Neves Corvo Sn-Cu polymetallic deposit (Portugal, Europe) shows small positive δ^{65}Cu variation from 0.02 to 0.25‰; similar δ^{65}Cu ranges are found in the Dongguashan Cu deposit from Anhui province, Southeastern China. The Hongtushan Archean VHMS-type Cu-Zn deposit from Liaoning province, Northeastern China displays higher δ^{65}Cu values of 0.69 to 1.06‰. These δ^{65}Cu values are rather similar to those reported for active modern seafloor hydrothermal massive sulfide vents such as those at 21°N EPR and Broken Spur. High-temperature magmatic-hydrothermal deposits such as the Dexing (Jiangxi, SE China) and Zijinshan (Fujian, SE China) porphyry Cu deposits show narrow δ^{65}Cu values of -0.60 to 0.42‰. A number of factors may account for Cu isotope fractionation in nature, including temperature, redox condition, biological activity, mineralogy, and the composition of source rocks to name but a few. Our results suggest that, in hydrothermal ore deposits, the dominant factors are probably temperature, source rock composition, and possibly microbial activity. It is suggested that transition metals such as Cu isotope compositions may hold great promises to provide new constraints for hydrothermal ore-forming processes and ore genesis.