



Preliminary results for hydrogen isotope fractionation Experiments between Mg-Chlorite and molecular Hydrogen at low Temperatures and Pressures

T.C. Heijboer, T.W. Vennemann

Institute of Mineralogy and Geochemistry, University of Lausanne, CH-1015,
SwitzerlandTjerk.heijboer@unil.ch

Knowledge of the hydrogen isotope composition of hydrous minerals may place important constraints on fluid-rock interactions and the origin of fluids. However, equilibrium hydrogen isotopic fractionation factors between chlorite and water have not been calibrated at temperatures below 400°C. In this study exchange experiments were performed between natural aluminous Mg-chlorite ($\delta D = -44.5 \pm 2$ per mil) and molecular hydrogen ($\delta D = -293$ to -744 ± 2 per mil) using the same experimental methods, (A and B), and run conditions as Vennemann and O'Neil (1996). Run duration was varied between 1 week and 2 months. For Method A, an "infinite" reservoir of hydrogen (2000 mmol) was exchanged with small amounts of chlorite (5 mg). For Method B, an "infinite" reservoir of chlorite (0.5 gram) was exchanged with small amounts of hydrogen gas (20 mmol). In both methods the hydrogen isotopic composition of the "infinite" reservoir remained constant, while the other substance changed its hydrogen isotopic composition. δD values of chlorite were measured using analytical methods adapted after Sharp et al. (2001). Exchanged and un-exchanged hydrogen gas was measured using a ThermoFinnigan Mat 253 dual-inlet mass spectrometer directly from the experimental setup.

Experiments using chlorite with grain size between 45-125 micron at temperatures of 200, 250 and 300°C yielded $1000\ln(\alpha_{Chl-H_2})$ values of 673.7, 513 ± 3 , and 386, with fractions of exchange of 32, 49 and 55% and 64%. The $1000\ln(\alpha_{Chl-H_2})$ values at these temperatures correspond to $1000\ln(a_{chl-H_2O,g})$ values of 0, -66 and -73, and

-123, respectively. Three experiments using Method A at temperatures of 300, 350 and 400° C and with grain size <45 microns gave $1000\ln(\alpha_{chl-H_2O,g})$ values of -314, -218 and -204 and very small fractions of exchange (8, 5 and 10%) for run durations between three weeks and two months. These $1000\ln(\alpha_{chl-H_2})$ values correspond to un-realistically low $1000\ln(\alpha_{chl-H_2O,g})$ values of -195, -231 and -193.

The $1000\ln(\alpha_{chl-H_2O,g})$ values for Method B are 20-30 per mil higher at 200°C, are 20 to 30 per mil lower at 250°C and about 100 per mil lower than those estimated from measurements of natural samples (Kuroda et al., 1976; Marumo et al., 1980). A difference of 10 to 15 per mil between our experiments and the natural samples from (Kuroda et al., 1976; Marumo et al., 1980) may be explained by the pressure effect (Horita et al., 2002) as the samples from Kuroda et al., (1976); Marumo et al., (1980) were estimated to have formed at 0.25 to 0.5 kbar, however the larger differences that are observed may be related to hydrogen exchange on the surfaces of the chlorite grains.

Graham, C.M., Viglino, J.A. & Harmon, R.S., 1987. *Am. Miner.*, 72: 566-579.

Horita, J., Cole, D.R., Polyakov, V.B. & Driesner, T., 2002. *Geoch. et Cosmo. Acta*, 66(21): 3769-3788.

Kuroda, Y., Suzuoki, T., Matsuo, S. & Shirozu, H., 1976. *Contr. Min. and Petr.*, 57: 223-225.

Marumo, K., Nagasawa, K. and Kuroda, Y., 1980. *Earth Plan. Sci. Lett.*, 47: 255-262.

Sharp, Z.D., Atudorei, V. & Durakiewicz, T., 2001. *Chem. Geol.*, 178: 197-210.

Vennemann, T.W. & O'Neil, J.R., 1996. *Geoch. et Cosmo. Acta*, 60: 2437-2451.