

## Pressure-induced chlorine isotope fractionation among chlorine-bearing minerals

XI LIU<sup>1</sup>, HAI-ZHEN WEI<sup>1\*</sup>, SHAO-YONG JIANG<sup>2</sup>,  
ANTHONY E. WILLIAMS-JONES<sup>3</sup>, JIAN-JUN LU<sup>1</sup>

<sup>1</sup>Department of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, PR China  
([haizhenwei@nju.edu.cn](mailto:haizhenwei@nju.edu.cn))

<sup>2</sup>Faculty of Earth Resources, China University of Geosciences, Wuhan 430074, PR China ([shyjiang@cug.edu.cn](mailto:shyjiang@cug.edu.cn))

<sup>3</sup>Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montreal, QC, Canada H3A 0E8 ([anthony.williams-jones@mcgill.ca](mailto:anthony.williams-jones@mcgill.ca))

Although it is believed that equilibrium fractionation of stable isotopes might not be significant at high temperature (Urey, 1947) [1], the recent theoretical predictions indicate that pressure-induced shifts in typical stable isotope compositions cannot be ignored. In order to quantify the extent of chlorine isotope fractionation among chlorine-bearing minerals and to evaluate the factors controlling chlorine isotope fractionation in terrestrial processes, the pressure effect of chlorine isotope fractionation for the major chlorine-bearing minerals (i.e., apatite-group minerals, muscovite, phlogopite, tremolite, marialite and metal halides) have been investigated by a density functional theory study.

At ambient P-T conditions, the reduced isotopic partition function ratio (i.e.,  $\beta$  factors) are strongly correlated with the metal-Cl bond length of the minerals, such that minerals in which chlorine is bonded to trivalent metals (e.g.,  $\text{Al}^{3+}$ ) with shorter metal-Cl bonds have higher  $\beta$ -factor than minerals in which the chlorine is bonded to monovalent metals (e.g.,  $\text{Na}^+$ ) with longer metal-Cl bonds. It is in an excellent agreement with the study by Schauble et al. (2003) [2]. As a result of a number of factors, including the adjacent atomic environment, the sites occupied by chlorine atoms in crystals, the Cl-metal coordination and the crystal density, the sensitivity of  $10^3 \ln \beta$  to pressure follows the sequence: halite > fluorochlorapatite > chlorapatite > marialite > hydroxyl-chlorapatite > tremolite > muscovite > phlogopite.

The pressure-induced chlorine isotope fractionation should be well concerned, which may explain the relatively larger variations of chlorine isotopic composition in high P-T processes.

[1] Urey H.C. (1947). The thermodynamic properties of isotopic substances. *J. Chem. Soc. (London)*, 562-581.

[2] Schauble E.A., Rossman G.R., Taylor H.P. (2003) Theoretical estimates of equilibrium chlorine-isotope fractionations. *Geochim. Cosmochim. Acta* 67, 3267-3281.