First-principles investigations of equilibrium calcium isotope fractionation between clinopyroxene and orthopyroxene

C.-Q. FENG [1], T. QIN [1], S.-C. HUANG [2], Z.-Q. WU [1] AND F. HUANG [1]

[1]School of Earth and Space Sciences, University of Science and Technology of China, Hefei, Anhui 230026, China (fcq007@mail.ustc.edu.cn,tian91@mail.ustc.edu.cn,wuzq10@ustc.edu.cn,fhuang@ustc.edu.cn)

[2]Department of Earth and Planet Sciences, Harvard University, 20 Oxford St., Cambridge, MA 02138, USA (huang17@fas.harvard.edu)

Equilibrium calcium isotope fractionations between clinopyroxene and orthopyroxene, the two major Ca-bearing minerals in the upper mantle, are calculated with density functional perturbation theory (DFPT). The results suggest that orthopyroxene has higher $^{44}Ca/^{40}Ca$ ratios than clinopyroxene due to smaller coordination numbers (CN) of Ca in orthopyroxene than that in clinopyroxene (6 vs. 8). We further find that Ca concentration of orthopyroxene significantly influences $\Delta^{44/40}Ca_{opx\text{-}cpx}$ especially when Ca/Mg in orthopyroxene is below 1:15. Our results successfully explain the observations of variable Ca isotopic fractionation between coexisting orthopyroxene and clinopyroxene from Kilbourne Hole and San Carlos mantle peridotites, i.e., $\Delta^{44/40}Ca_{opx\text{-}cpx}$ increasing from 0.36‰ to 0.75‰ with $[CaO]_{opx}$ decreasing from 1.03wt.% to 0.75wt.% (Huang *et al*, 2010). This reveals that crystalline environment such as the average Ca-O bond length parameter may be controlled by Ca content in orthopyroxene when Ca is a minor element. Our calculations also suggest that, although $\delta^{44}Ca$ of orthopyroxene may increase dramatically with decreasing CaO content, the average Ca isotope composition of the upper mantle is relatively constant because $[CaO]_{cpx}$ is much higher than $[CaO]_{opx}$. Furthermore, if Ca content and Ca isotope compositions of clinopyroxene and othorpyroxene are known, Ca isotopic fractionation between clinopyroxene and orthopyroxene can be used as a potential two-pyroxene Ca isotope thermometry.

[1] Huang S. *et al* (2010), *EPSL* **292**: 337-344.

Evaluating the sulfur cycles in the early Cambrian ocean: An example from the Yanjiahe Formation, Yangtze Gorges area, South China

LIAN-JUN FENG[1]

[1] Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China, (feng.lian.jun@gmail.com)

The Yanjiahe Formation represents the earliest beginning of the Cambrian period in the Yangtze Gorges area, South China. In this study, we first report the sulfur isotope compositions of chromium-reducible sulfur ($\delta^{34}S_{CRS}$) and carbonate-associated sulfate ($\delta^{34}S_{CAS}$) from the Yanjiahe Formation. The difference between $\delta^{34}S_{CAS}$ and $\delta^{34}S_{CRS}$ from the Yanjiahe Formation is similar to that from the other basins worldwide (less than 30 per mil), reinforcing low marine sulfate concentrations across the Ediacaran-Cambrian boundary and into the Cambrian [1].

The Yanjiahe Formation has large-magnitude $\delta^{34}S_{CRS}$ ratios, ranging from 3.3 to 26.1 per mil, similar to the other basins worldwide. However, the sulfur isotope record in pyrite from the upper part (orgnic-rich limestone) shows more positive ratios than that from the lower part (oganic-lean dolomite), probably reflecting local influences.

[1] Loyd, S.J., *et al Earth and Planetary Science Letters,* 2012. **339**: p. 79-94.

www.minersoc.org
DOI:10.1180/minmag.2013.077.5.6