Preliminary report on the experimental measurement of trace-element partitioning between zircon and hydrothermal metamorphic fluids at High/Ultra-High Pressure conditions

TIMOTHY J. PETERS[1,2] AND JOHN C. AYERS[1,2]

[1]Department of Earth and Environmental Science, Vanderbilt University, Nashville, TN, United States.
[2]Department of Civil and Environmental Engineering, Vanderbilt University, Nashville, TN, United States

Zircon (ZrSiO4) is one of the most important minerals available to study the geochemical and geodynamic evolution of the Earth. Recent developments in micron-scale *in situ* zircon geochemical and isotopic (U-Pb and Lu-Hf) analysis have caused an exponential growth in its use for understanding geodynamic processes during High and Ultra-high pressure (HP/UHP) metamorphism. Geochemical and textural evidence suggests that zircons in HP/UHP metamorphic terrains grew at sub-solidus conditions in the presence of a hydrous metamorphic fluid. However, to date no experimental studies have been performed to characterize the geochemical behavior of zircon in equilibrium with hydrous metamorphic fluids. Here we present preliminary experimental results aimed towards characterizing the trace-element partitioning behavior of zircon in hydrothermal fluids at High/Ultra-High Pressure (1.5 to 3.0 GPa) conditions.

An exploratory zircon growth experiment yielded D (zircon/fluid) increasing from light to heavy REE, typical of REE substitution favoring HREE incorporation in the Zr lattice site, and a D (Th)/D (U) ratio of ~2.5. Favorable partitioning of Y, Sc, Nb, Ta, and Hf into zircon is also observed. These measurements should aid in identifying zircons that have grown from a hydrothermal fluid and that can be used to date and characterize hydrothermal events and fluid compositions.

Time-resolved X-ray diffraction study of the *in situ* hydrothermal phase transformation from akaganéite to hematite

K.M. PETERSON[1]*, P.J. HEANEY[1] AND J.E. POST[3]

[1]Department of Geosciences, Pennsylvania State University, University Park, PA 16802, USA (*correspondence: kmp286@psu.edu)
[2]Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560-0119, USA (postj@si.edu)

Akaganéite nanoparticles commonly form when chlorine-rich fluids alter metallic Fe, and recently they have been discovered as a biogenic product. Although the precipitation of akaganéite (β-FeOOH) and its subsequent transformation to the stable phase hematite (α-Fe_2O_3) are well documented, the mechanism and the kinetics of this reaction are debated. The difficulty in characterizing the transformation can be attributed in part to the poorly crystalline nature of most natural akaganéite. Additionally, *in situ* analysis is challenged by the low precipitate yield in hydrothermal experiments within the Fe-Cl-H_2O system.

Here we present new observations from *in situ* heating experiments using time-resolved synchrotron X-ray diffraction (TR-XRD) conducted at the Advanced Photon Source (APS). Starting with ferric chloride solutions (0.45 M $FeCl_3$ + 0.01 M HCl), we have collected TR-XRD data of the hydrothermal precipitation of akaganéite and transformation to hematite. Design of a new heater and experimental protocol facilitated our collection of *in situ* data by precipitate sedimentation at the base of a sealed 0.7 mm quartz capillary. XRD data were collected every 30 seconds at temperatures ranging from 80-200°C. Rietveld refinements using the General Structure Analysis System (GSAS) allowed for quantitative measurements of reaction rates as a function of temperature. Moreover, we determined the dependence of unit cell parameters on temperature and particle size.

In our experiments, the akaganéite to hematite transformation was completed in 100, 20 and 4 minutes at temperatures of 150°C, 175°C and 200°C, respectively. Refined unit-cell parameters for each phase followed the same general trends at all temperatures. Lattice parameters of akaganéite did not significantly change throughout the reaction. The hematite *a* parameter decreased with increasing particle size, but the *c* parameter increased until all akaganéite had transformed, after which it decreased. Our results demonstrate that *in situ* structural and kinetic data of low-yield hydrothermal reactions can be successfully captured using our experimental design and TR-XRD.