Lithium in Jack Hills Zircon: Evidence for extreme weathering of Earth's crust at 4300 Ma

T. USHIKUBO[1]*, N.T. KITA[1], A.J. CAVOSIE[2],
S.A. WILDE[3], R.L. RUDNICK[4] AND J.W. VALLEY[1]

[1]University of Wisconsin-Madison, Madison, WI 53706 USA (*correspondence: ushi@geology.wisc.edu)
[2]University of Puerto Rico, Mayagüez, Puerto Rico, 00681 USA
[3]Curtin University of Technology, Perth, WA 6102 Australia
[4]University of Maryland, College Park, MD 20742 USA

In situ Li analyses of early Archean detrital zircons from Jack Hills, Western Australia (4.3 to 3.4 Ga) by SIMS reveal that the Li abundances (typically 10 to 60 ppm) are over 1000 times higher than in zircons crystallized from mantle-derived magmas and in mantle-derived zircon megacrysts (typically <8 ppb). The Jack Hills zircons also have fractionated lithium isotope ratios (δ^7Li = -19 to +13 ‰), which are about five times more variable than those recorded in oceanic basalts (2-8 ‰) (e.g. [1]).

Multiple spot analyses and Li ion imaging of zircons from the Jack Hills and from granulite facies migmatites in the Adirondack Mountains reveal that Li concentration and δ^7Li correlate with CL zoning. Correlation of Li with REE, Y, and P suggests that Li substitutes via an interstitial mechanism and that Li^{+1} is important to charge balance $REEs^{+3}$ in the zircon structure. These results indicate that zircon preserves primary igneous Li compositions even if it has been subjected to prolonged high-grade metamorphism. Thus, Li composition can be used to characterize the origin of the host magma from which the zircons crystallized.

The high Li concentration, coupled with the extremely low δ^7Li observed in zircons as old as ~4300 Ma, suggests evolution in a magma contaminated by highly weathered crustal material (such as saprolite or laterite) [2, 3]. Thus, Li compositions of Jack Hills zircons strongly support the existence of chemically differentiated crust, sub-aerial weathering, and oceans as early as 4300 Ma.

[1] Tomascak (2004) *Rev. in Mineral. Geochem.* **55**, 153-195. [2] Kisakürek *et al.* (2004) *Chem. Geol.* **212**, 27-44. [3] Rudnick *et al.* (2004) *Chem. Geol.* **212**, 45-57.

Coffinite and ningyoite from the natural nuclear reactor at Bangombé, Gabon

S. UTSUNOMIYA[1], A.P. DEDITIUS[2], V. POINTEAU[2,3] AND
R.C. EWING[2]

[1]Department of Chemistry, Kyushu University, Fukuoka-Shi, 810-8560, Japan
[2]Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109-1005, USA
[3]CEA Saclay, DPC/SECR, F-91191 Gif-sur-Yvette Cedex, France

P-rich coffinite, $U(Si,P)O_4{\bullet}H_2O$, from the natural nuclear reactors in Bangombé, Gabon, is an important phase that incorporates percent levels of actinides and fission products. We have examined sample BAX03 (depth 12.2-12.3m) from Bangombé in order to understand micro- and nano-scale crystalo-chemical properties of P-coffinite.

Electron microprobe analysis (EMPA) was completed only on coffinite inclusions (~100 μm in size) in quartz to minimze the effect of alteration to U(VI)-phosphates and -sulfates. Based on the Si/P ratios three different chemical compositions; i) coffinite (<1.45 wt.% of P_2O_5) without uraninite inclusions, ii) P-coffinite, and iii) Si-ningyoite, $(U,Ca,Ce)_2(PO_4)_2{\bullet}1\text{-}2H_2O$. Phases ii) and iii) have inclusions of uraninite. The composition of coffinite i) is expressed to be $(U_{0.79}Ca_{0.05}REE+Y_{0.04})_{0.88}(Si_{1.03}P_{0.05})_{1.08}O_4$. The amount of $(Y+REE)_2O_3$ is <1.9 wt.%. Phosphorous substitutes for Si as evidenced by its negative correlation with Si (R^2=0.87) and positive correlation with Y+REE (R^2=0.6). The formula of P-coffinite (ii) is $(U_{0.71\text{-}0.88}Ca_{0.06\text{-}0.11}REE+Y_{0.07\text{-}0.18})_{0.92\text{-}1.08}(Si_{0.39\text{-}0.59}P_{0.28\text{-}0.4}S_{0.03\text{-}0.12})_{0.8\text{-}0.96}O_4$, and the P_2O_5 and $(REE+Y)_2O_3$ are as high as 9.3 wt.% and 8.64 wt.%, respectively. There is a positive correlation between Ca and P (R^2=0.62), but no correlation among P, Y+REE and Si. The chemical formula of Si-rich ningyoite is $(U_{1.43\text{-}1.73}REE+Y_{0.2\text{-}0.3}Ca_{0.18\text{-}0.23})_{1.88\text{-}2.3}(P_{0.7\text{-}0.8}Si_{0.6\text{-}0.8}S_{0.1\text{-}0.3}As_{0\text{-}0.1})_{1.32\text{-}1.64}O_4$. Silicon is positively correlated with P (R^2=0.7). The EMPA elemental maps reveal homogeneous distribution of P, Si, Nd, Y and U in P-coffinite and Si-ningyoite.

These results suggest that coffinite-(i) in Bangombé is not the alteration product of uraninite. But, P-coffinite and Si-ningyoite precipitated at the expense of uraninite under reducing conditons. The lack of correlation between P and Y+REE in P-coffinite and Si-ningyoite implies that these minerals may consist of nano-scale intergowths of coffinite and homogeneously distributed (Ca,U,Y,REE)-phosphates. This is supported by the elemental maps, as well as TEM results.