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# Elemental and Isotopic Tomography at Single-Atom-Scale in 4000 and 2400 Ma Zircons

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Atom probe tomography can determine the identity (mass-to-charge-state ratio=m/n) using time-of-flight spectroscopy and 3-D position of individual atoms in minerals such as zircon ($ZrSiO_4$). These data provide unique information for understanding the thermal history and mechanisms of mineral reaction and exchange, including radiation damage from decay of naturally occurring trace concentrations of U and Th. Nine needle-shaped specimens ~100nm in diameter at the apex were sampled from 2 zircons by FIB, Fig. 1a and b, and analyzed with a CAMECA local-electrode atom probe (LEAP) 4000X HR, as shown in Fig. 1c. With due care for complex isobaric interferences (molecules, multiple ionizations) and background correction, it is possible to individually identify up to $10^8$ atoms/needle (at 36% detection efficiency) by m/n (with mass resolution of ~ 1/1000@ m/n=16Da) and position (X-Y-Z coordinates on 0.2 nm-scale) [1].

The 3-D distribution of Pb and Y differ at the atomic scale in the 2 zircons [2]. Zircon #1 (4007 million years old (Ma), Jack Hills, W. Australia [3-5]) is homogeneous in Pb and Y, Fig. 1c. In contrast, incompatible elements, including Pb and Y, are concentrated in equant 5-10 nm dia. domains, spaced ~50 nm apart in zircon #2 (2438 Ma, Albion-Raft River-Grouse Creek mountains, Utah [6], Fig. 2. U is homogeneously distributed in both zircons. The analyzed domains suffered 4-8 x $10^{15}$ α-decay events/mg due to U and Th decay and yet both zircons yield >97% concordant U-Pb ages by SIMS, consistent with annealing of radiation damage during the life of the zircons. The $^{207}Pb/^{206}Pb$ ratios for these nm-scale domains, as measured by LEAP, average 0.17 for the 2400 Ma zircon #2 (3 needles). For the 4000 Ma zircon #1, the ratios average 0.43 (5 needles). These ratios are less precise (±40% 2σ) due to ultra-small sample size than, but in excellent agreement with, values measured by SIMS, i.e., 0.1684 and 0.4269, respectively. Thus Pb in both zircons is radiogenic. The Pb-Y-rich domains and lack of correlation with U in zircon #2 is best explained by diffusion of Pb and other incompatible elements (Y, rare earth elements (REE)) into 5-10 nm domains that were damaged by α-recoil and may have been metamict as the result of single U- or Th-decay chains. Diffusion distances of ~20 nm for these elements in crystalline zircon require temperatures above ~700°C for ~$10^7$ years [7]. This is consistent with the known history of zircon #2, as a xenocrystic 2438 Ma zircon included in a 29 Ma granodiorite phase of a long-lived, extension-related plutonic suite that experienced high-grade regional metamorphism. In contrast, the absence of enriched domains in zircon #1 suggests that this zircon did not experience similar high-grade metamorphism before or after it's deposition within the ~3000 Ma Jack Hills metaconglomerate [8].

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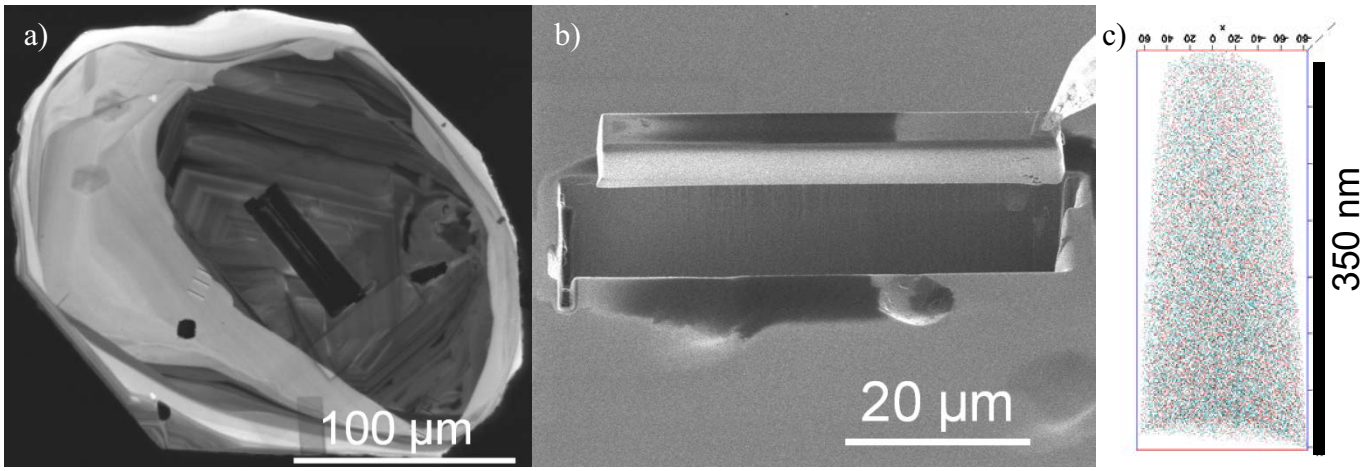


Figure 1. a) Cathodoluminescence image of the location of lift-out specimen (dark rectangle) seen on the polished section through the mid-section of zircon #1. Concentric banding results from mineral growth. b) Lift-out coupon in process, and c) an atom map from zircon #1 showing only Y in red and Pb in cyan. Note the uniformity of the Y and Pb distribution in this atom map with 4 x $10^7$ atoms.

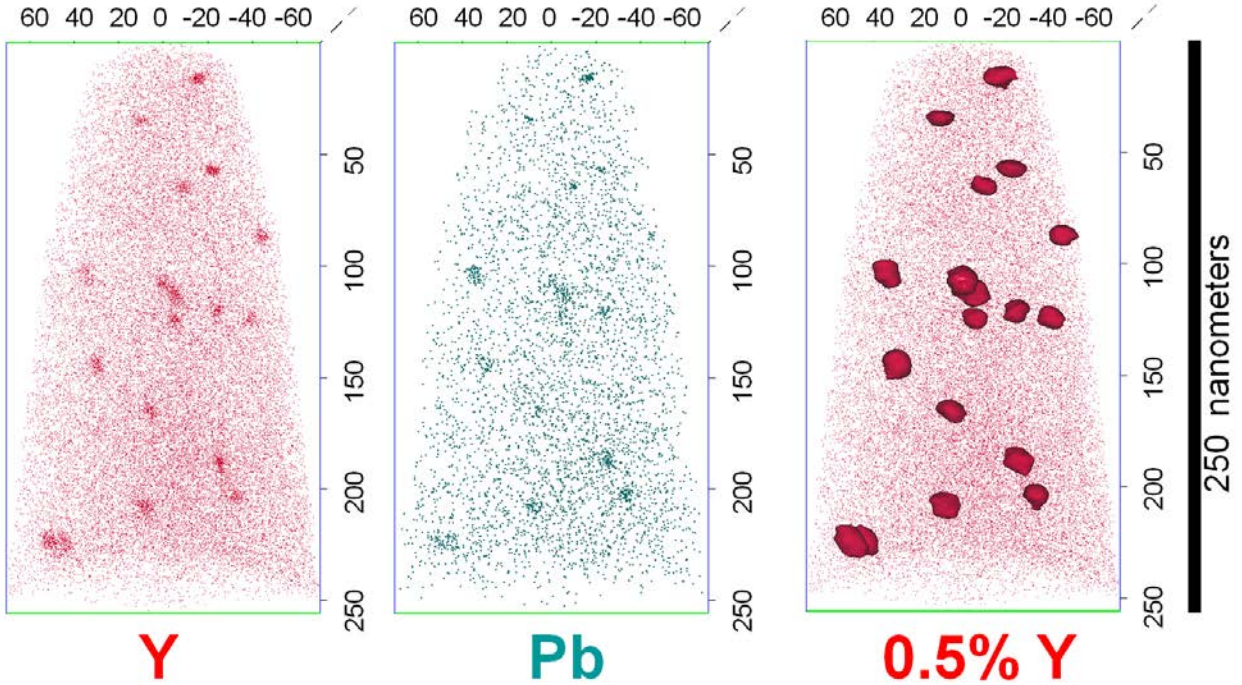


Figure 2. Atom maps (point clouds) from zircon #2 of Y and Pb on left of figure. Y atom map with an Y isoconcentration surface (at 0.5 atom % Y) on right of figure that reveals the equant domains that are randomly located in 3-D.