Geological Applications of Atom Probe Tomography: New Information from Old Rocks

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Atom probe tomography (APT) makes it possible to study the compositional structure of geological materials at the nanoscale [1]. This type of information has not heretofore been available. We have applied APT to three terrestrial zircons of different ages that yields a picture that suggests that the early earth was cool and could have supported life processes as early as 4.3 Ga.

Zrc-1: 4.007 Ga; 01-13b-8-4, Jack Hills, W. Australia [2]: **Zrc-2:** 2.542 Ga core, 29 Ma rim; ARG-05-28-2, Grouse Creek Mts., Utah [3]: **Zrc-3:** 4.374 Ga core, 3.4 Ga rim; 01JH36-69, Jack Hills [1]

The 3-D distribution of Pb and Y differ at the atom-scale in the 3 zircons. Zrc-1 is homogeneous in Pb and Y (Fig. 1). In contrast, incompatible elements, including Pb and Y, are concentrated in sub-equant 5-10nm domains (up to 1 at.% Pb), spaced ~50 nm apart in Zrc-2 (Fig. 2) and Zrc-3 (Fig. 3). U is homogeneously distributed in all three zircons. The average ²⁰⁷Pb/²⁰⁶Pb ratios for these 100-nm-scale specimens, as measured by APT, are 0.17 for the 2.5 Ga Zrc-2, 0.43 for the 4.0 Ga Zrc-1, and 0.52 for the 4.4 Ga Zrc-3. The APT ratios are less precise ($\pm 5-10\% 2\sigma$) due to small sample size, but are in excellent agreement with values measured by SIMS, 0.168, 0.427, and 0.548 respectively. The average ²⁰⁷Pb/²⁰⁶Pb ratios within the 5-10 nm Pb-enriched domains are 0.17 in Zrc-2 (Fig. 4a) and 1.2 in Zrc-3. Thus Pb in the Pb-rich domains is radiogenic and unsupported. No Pb is detected outside the Pb-rich domains in Zrc-2 (Fig. 4b), while 207 Pb/ 206 Pb = 0.30 outside these domains in Zrc-3. These findings are best explained by diffusion of Pb and other incompatible elements (Y, REEs) 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 \sim 700°C for \sim 10⁶ yr. [4]. This is consistent with the known history of Zrc-2 and -3, which both have younger magmatic overgrowths attesting to reheating at 29 Ma in Zrc-2 and 3.4 Ga in Zrc-3. In contrast, the absence of enriched domains in Zrc-1 suggests that this zircon did not experience similar high-grade metamorphism before or after its deposition within the 3 Ga Jack Hills metaconglomerate. For all 3 zircons, SIMS measurements at 10-20-µm scale reintegrate nm-scale features and accurately determine the age of crystallization. Thus APT can provide unique constraints on otherwise cryptic thermal events; on Pb mobility and radiation damage; and for Archean zircons too small to be dated by SIMS, APT can determine ²⁰⁷Pb/²⁰⁶Pb ages.

References

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Figure 1. Atom map of Pb isotopes in 4.0 Ga Zrc-1.

Figure 2. a) Atom map of Y and Pb in 2.5 Ga Zrc-2. b) Isoconcentration surface for Y in Figure 2a. Figure 3. a) atom map of Pb and Y in 4.4 Ga Zrc- 3. b) close up atom map of Y clusters. c) atom map of single cluster showing Pb isotopes with Y.

Figure 4. Partial mass spectra from a) inside the clusters of Figure 2 and b) outside the clusters.