NANO- AND MICRO-GEOCHRONOLOGY IN HADEAN AND ARCHEAN ZIRCONS FROM EARTH AND THE MOON: ATOM-PROBE TOMOGRAPHY AND SIMS. J. W. Valley[1,2], T. B. Blum[1], D. A. Reinhard[3], A. J. Cavosie[1,2,4], T. Ushikubo[1,5], D. F. Lawrence[3], D. J. Larson[3], T. F. Kelly[3], M. J. Spicuzza[1], D. R. Snoeyenbos[6], A. Strickland[1], [1]WiscSIMS, Dept. of Geoscience, University of Wisconsin, Madison, WI 53706, USA (valley@geology.wisc.edu), [2]NASA Astrobiology Institute, Dept. of Geoscience, University of Wisconsin, Madison, WI 53706, USA, [3]CAMECA Instruments, Madison, WI 53711, USA, [4]Dept. of Applied Geology, Curtin University, Perth 6102, Australia , [5]Current address: Kochi Institute for Core Sample Research, JAMSTEC, Nankoku, Kochi 783-8502, Japan, [6]Dept. of Geosciences, University of Massachusetts, Amherst, MA 01003, USA.

Introduction: Atom-probe tomography (APT) and secondary ion mass spectrometry (SIMS) provide complementary *in situ* element and isotope data in minerals such as zircon. SIMS measures isotope ratios and trace elements from 1-20 μm spots with excellent accuracy and precision. APT identifies mass/charge and 3-dimensional position of individual atoms (±0.3 nm) in 100-nm-scale samples, volumes up to one million times smaller than SIMS. APT data provide unique information for understanding element and isotope distribution; crystallization and thermal history; and mechanisms of mineral reaction and exchange. Taken together, data from SIMS and APT document atom-scale isotope and trace element distribution leading to enhanced thermochronology of Hadean and Archean zircons.

Based on SEM imaging and SIMS analysis, 13 needle-shaped specimens ~100 nm in diameter were sampled from one Archean and three Hadean-age zircons by focused ion-beam milling and analyzed with APT. The 3-dimensional distribution of Pb and nominally incompatible elements (Y, REEs) differs at the atomic scale in each zircon. Zircon JH4.0 [1] (4.007 Ga, Jack Hills, W. Australia) and 15Q4 [2,3] (4.33 Ga, Apollo 15, Qz-monzodiorite) are not measurably heterogeneous in Pb, Y and REEs. In contrast, Pb, Y and REEs are clustered in sub-equant ~10-nm diameter domains, spaced 10-40 nm apart in zircons ARG2.5 [1] (2.542 Ga, Grouse Creek Mts., Utah) and JH4.4 [1,4] (4.374 Ga, Jack Hills). U and Th are not collocated with Pb in clusters and appear to be homogeneously distributed. The analyzed domains experienced 3 to 8 x 10^{15} α-decay events/mg due to U and Th decay and yet all zircons yield U-Pb ages by SIMS that are better than 94% concordant. The $^{207}Pb/^{206}Pb$ ratios for the 100-nm-scale specimens measured by APT average 0.17 for ARG2.5, 0.42 for the JH4.0 and 0.52 for JH4.4. These ratios are less precise (±10-18% 2σ) due to the ultra-small sample size, but in excellent agreement with values measured by SIMS (0.1684, 0.4269, and 0.5472, respectively) and the crystallization ages of the zircons. Thus Pb in these clusters is radiogenic, but is not spatially associated with its parent isotopes of U and Th. For the domain outside of clusters in JH4.4, the $^{207}Pb/^{206}Pb$ ratio is 0.3, consistent with the SIMS value of 0.2867 for the zircon overgrowth rim and an age of 3.4 Ga. In ARG2.5, all Pb is concentrated in clusters and there is no detectable Pb remaining outside of the clusters. The Pb-Y-REE-rich clusters and lack of correlation with U in ARG2.5 and JH4.4 are best explained by diffusion of Pb and other elements into ~10-nm amorphous domains formed by α-recoil. Diffusion distances of ~20 nm for these elements in crystalline zircon are consistent with heating at temperatures of 800°C for ~2 m.y. Such later reheating events are identified and dated by APT from $^{207}Pb/^{206}Pb$ model ages of clusters in JH4.4 and by the absence of detectable Pb outside of clusters in ARG2.5. SIMS dates for the zircon rims independently confirm reheating of ARG2.5 and JH4.4, which were xenocrysts in younger magmas when rims formed. The absence of enriched clusters in JH4.0 and 15Q4 shows that these zircons were not similarly reheated. Thus APT data provide thermochronologic information about crustal reworking even for zircons where no overgrowth is recognized.

This first combined nano- and micro-geochronology study of multiple zircons provides enhanced confidence in criteria for evaluating the fidelity of their geochemical records. Demonstration that Pb mobility occurred at sub-50-nm scale to form clusters shows that longer-distance Pb transport did not occur and that the much-larger 1-20-μm-scale volumes analyzed by SIMS were closed systems. The existence of 4.4 Ga zircons, the oldest known from Earth, is confirmed. Likewise, REE spectra and stable isotope ratios are supported as primary, reflecting magmatic compositions. Taken together, these data support models of a more-clement Early Earth than the name Hadean suggests. Differentiated crust existed by 4.4 Ga, just 100 m.y. after the formation of the Moon and Earth's core. The steam atmosphere cooled and precipitated as oceans before 4.3 Ga creating conditions habitable to life as much as 800 m.y. earlier than the oldest known microfossils.

References: [1] Valley J.W. et al. (2015) *Am. Mineral.,* in press. doi.org/10.2138/am-2014-5134. [2] Blum, T.B., et al. (2014) *Trans Am Geoph Un,* Abst V34A-06 [3] Valley J.W. et al. (2014) *Contrib. Min. Petrol, 167,* doi:10.1007/s00410-013-0956-4. [4] Valley J.W. et al. (2014) *Nature Geosci, 7*, 219-223.