

## Tomography at Single-Atom Scale of $^{207}\text{Pb}$ and $^{206}\text{Pb}$ in a 4374 Ma Zircon

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Local-Electrode Atom Probe (LEAP) tomography can identify and determine the position ( $\pm 0.2\text{nm}$ ) of individual atoms in minerals. These data allow 3-D observations at an unprecedented scale, including new insights on thermal history, radiation damage and element mobility in zircon. "Needles" were milled by FIB ( $\sim 150\text{nm}$  dia.  $\times \sim 1\mu\text{m}$ ) and analysed by LEAP from the 4374 Ma core of a zircon from the Jack Hills, WA that has a 3400 Ma magmatic rim. In 3-D, Pb & YREE are co-localized and concentrated in  $\sim 5\text{nm}$  clusters, spaced  $\sim 20\text{-}50\text{nm}$  apart. The  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios (7/6) by LEAP average:  $1.23 \pm 0.11$  inside clusters,  $0.32 \pm 0.10$  outside clusters, and  $0.52 \pm 0.08$  for the full volume of 2 needles ( $0.04\mu\text{m}^3$ ,  $6 \times 10^8$  ions detected). Significant  $^{204}\text{Pb}$  is not detected. U appears homogeneously distributed. Thus Pb in clusters is radiogenic and unsupported by U. LEAP data for other zircons (Valley *et al.* 2012 AGU) suggest that Pb & YREE were concentrated in clusters by diffusion into nanodomains of  $\alpha$ -recoil damage. Diffusion distances of  $\sim 20\text{nm}$  for these elements in crystalline zircon require temperatures  $> 700^\circ\text{C}$ . In the 4374 Ma zircon, 7/6 by SIMS is 0.5476 in the core and 0.2912 in the rim (3400 Ma) in agreement with LEAP. A model age for LEAP 7/6 = 1.23 in clusters would be older than Earth; however, diffusion during magmatic heating at 3400 Ma (rim age) could produce unsupported Pb clusters with  $(7/6)_{3400\text{Ma}}$  of 1.20. Thus, LEAP uniquely explains closed system behavior at the 20- $\mu\text{m}$ -scale of SIMS while documenting Pb mobility at nm-scale. These results refute challenges (based on Pb mobility) to the accuracy of SIMS analyses of age for zircons with similar history and confirm the existence of a population of  $\sim 4.4$  Ga zircons from the early Earth.

## Rhenium-osmium dating of Mississippi-Valley-Type ore deposits: The Robb Lake Pb-Zn deposit, British Columbia

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Mississippi-Valley-Type (MVT) ore deposits are formed by fluid flow in sedimentary basins and comprise a large portion of global Pb-Zn resources. Dating the formation of MVT deposits has been attempted by dating their host rocks (Sm-Nd, U-Pb), paleomagnetic measurements or Rb-Sr dating of sphalerite, but all of these methods and results remain inconclusive and controversial to some degree. Pyrite as a major phase in MVT deposits can be dated directly using the long-lived Re-Os isotope system, which has been established to date sulfide formation.

The Robb Lake Pb-Zn deposit in northeastern B.C. is hosted by Silurian-Devonian platform carbonates, and forms part of a sequence of MVT deposits in the northern Rocky Mountains. The timing of its formation is still subject to controversy as two groups of ages are commonly cited. On the one hand, sulfide-forming fluid flow is considered to be associated with the Late Devonian - Early Carboniferous Antler orogeny, based on Rb-Sr studies, fluid inclusion composition, stable isotope data, and ages from other western Canadian MVT deposits along the Presqu'ile Barrier (Pine Point, NWT, [1]). On the other hand, Laramide ( $\sim 65$  Ma) ages have been suggested based on numerical modeling of regional fluid flow and paleomagnetism [2].

The Re-Os systematics of pyrite from Robb Lake are quite complex with substantial Re-Os being contained in both the pyrite and the associated dolomite breccia. Leaching of the dolomite using HCl allows for a more reliable age to be calculated from pyrite. A Re-Os isochron for this leached pyrite yields an age of  $331 \pm 40$  (MSWD = 151). Identifying and removing data points that likely still have dolomite contamination produces an age of  $351 \pm 35$  (MSWD = 18). The Re-Os data, although complex, confirm a Carboniferous age for sulfide formation associated with the Antler Orogeny.

[1] Nelson *et al.* (2002) *Econ Geol* 97, 1013-1036. [2] Symons *et al.* (1993) *Can J Earth Sci* 30, 1028-1036