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# **Eoarchean Zircons in the Napier Complex, East Antarctica**

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# 1. INTRODUCTION

There is not much evidence as to the nature of the Earth's earliest crust. The available information has been gleaned mostly from the studies of the oldest crystals of mineral zircon (ZrSiO<sub>4</sub>), either detrital grains (e.g. Wilde et al. 2001) or from oldest known igneous rocks, such as the Acasta orthogneiss in the Slave Province of Canada with an age of 4.03 Ga (e.g. Bowring and Williams 1999; Iizuka et al. 2006). One of areas, where Eoarchean rocks ( 4.0– 3.6 Ga) occur and protoliths that include some of the oldest crust on Earth occur, is the Napier Complex of Enderby and Kemp Lands in East Antarctica, including Tula Mountains of Enderby Land (e.g. Black et al. 1986; Kusiak et al. 2013a,b; Król et al. 2020) and Aker Peaks in Kemp Land (Belyatsky et al. 2011; Kusiak et al. 2021). The Napier Complex is an Archean craton composed mostly of high-temperature gneisses and granulites. The craton was metamorphosed at least twice, et ca. 2.8 Ga and ca. 2.5 Ga under granulite to ultrahigh-temperature (UHT) granulite condition (e.g. Kelly and Harley 2005; Harley et al. 2019). The UHT metamorphism had temperature as high as >1100 °C (e.g. Hokada et al. 2004), making these some of the highest temperature metamorphic rocks found in the Earth's crust.

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#### 2. RESULTS

Here we present zircon results from three cases: 1) presence of Pb nanospheres in grains from Gage Ridge, 2) Lu-Hf data from Aker Peaks, and 3) oxygen results.

## **Metallic Pb nanospheres**

Already the first publication documenting U-Pb geochronology of these rocks discussed the issue of the reversely discordant data recognized during in-situ analysis (Williams et al. 1984). Ion imaging of analysed zircon grains revealed zonation of Y and Ti characteristic for magmatic grains. However, distribution of <sup>206</sup>Pb and <sup>48</sup>Ti (Fig. 1) does not correspond to either magmatic zonation or crystal imperfections. Some of these patches yield <sup>207</sup>Pb/<sup>206</sup>Pb ages of >4 Ga, mostly reversely discordant. Other areas document data with ages younger than the magmatic crystal-lization age. Reversely discordant data are result of ancient Pb mobilization being independent of the oxygen isotope, REE content and metamictization of zircon (Kusiak et al. 2023).

It has been documented by Transmission Electron Microscopy (TEM), that in some of the ancient grains >3.4 Ga metallic lead nanospheres of 5 -30 nm in size occur. These nanospheres are randomly distributed, they occur either as droplets or in polyphase inclusions up to 80 nm across and contain amorphous Si-rich phase, together with unidentified Ti and Al-bearing phases (Fig. 2). Where inclusions contain multiple phases, Pb occurs as single or multiple nanospheres without crystal facets. No hydrous Pb phase(s) or voids large enough to penetrate the focused ion beam (FIB) foils were documented.



Fig. 1. Zircon grain n3850-47: (A) CL image, black box representing area covered in B) and C); (B) SII image of <sup>206</sup>Pb; (C) SII image of <sup>48</sup>Ti; (D) Raman spectroscopy image with marked zones of different crystallinity: zone 1 (moderately radiation damaged area), zone 2 (amorphous area), zone 3 (glassy area with retained zircon composition); (E) Electron diffraction pattern (EBSP) obtained from a crystalline component (zone 1) of the same grain. Modified after Kusiak et al. (2017).



Fig. 2: (A) High-angle annular dark-field (HAADF) TEM image of zircon from Gage Ridge with Pb nanospheres, and (B) the EDX spectrum of zircon rich in Pb and the silicate matrix enriched in Ti-Al (Cu peak comes from Cu grid under the FIB foil); (C) enlarged area with metal Pb (white), Al+Th-rich phase (grey) and Si-rich phase (dark grey); (D) clarification sketch of image (C). Modified after Kusiak et al. (2015).

## Lu-Hf isotopes

Aker Peaks in Kemp Land is 200 km east from the Tula Mountains of Enderby Land. Zircon grains from trondhjemitic and mafic gneisses were analysed by secondary ion mass spectrometry (SIMS) and yield concordant U-Pb dates between 3.86 Ga and 3.70 Ga. This age can be attributed to magmatic and possibly to metamorphic activity (Kusiak et al. 2021).



Fig. 3: (A) <sup>176</sup>Hf/<sup>177</sup>Hf versus <sup>207</sup>Pb/<sup>206</sup>Pb age subdividing data by sample and by SHRIMP upper intercept age group for the trondhjemitic gneiss; (B) Comparison between the Aker Peaks zircon data (Kusiak et al. 2021) with that reported for zircons of Napier Complex gneisses from Mount Sones and Gage Ridge by (H&B) Hiess and Bennett (2016) and (G) Guitreau et al. (2019). Modified after Kusiak et al. (2021).

Concurrent analysis of  ${}^{207}$ Pb/ ${}^{206}$ Pb ratios and Lu-Hf isotopes in the trondjemitic sample by laser ablation ICPMS provided initial  $\epsilon$ Hf(t) estimates for this age range that are slightly sub-chodritic (values 0 to -2; Fig. 3). This can be attributed to the incorporation of older crust into the magmatic protoliths of the gneisses although there is no requirement that these crustal sources would be older than Eoarchean.

#### Oxygen data

The question as to whether there was emergent land in the Eoarchean (4.0–3.6 Ga) is fundamental not only for understanding Earth's evolution but also for life itself. Magmatic rocks with isotopically light oxygen can indicate interaction of magmas or their sources with surface water (e.g. meteoric water). Consequently, the presence of such rocks in the geological record of the early Earth can provide an indicator for the emergence of land. Zircon from two Eoarchean orthogneisses in the Tula Mountains, Napier Complex, East Antarctica, show such light isotopic signatures. A ca. 3.75 Ga trondhjemitic gneiss and a ca. 3.55 Ga dioritic gneiss, both with high Y-HREE-Nb-Ta that can be ascribed to the melting of shallow sources at < 1.0 GPa, contain zircon with exceptionally low  $\delta^{18}$ O values of 1.0–2.7‰ (normalized to Vienna Standard Mean Ocean Water; Król et al. 2024). The lowest  $\delta^{18}$ O value in zircon previously reported from Paleoarchean orthogneisses is 3.7‰ at 3.56 Ga (Fig. 4).



Fig. 4: Compilation of  $\delta^{18}$ O versus age for magmatic and detrital zircon throughout Earth history. The data points are plotted at their respective crystallization ages determined by U–Pb geochronology. Zircon  $\delta^{18}$ O data from sample 78,285,013 represent granitic gneiss from Gage Ridge, Tula Mountains (Kusiak et al. 2013a). The upper dashed line indicates the evolution of "maximum"  $_{\delta^{18}}$ O in zircon through geological history (Valley et al. 2003). The mantle zircon  $\delta^{18}$ O range represented by grey band is from Valley et al. (1998). NAC — North Atlantic Craton; SCC — South China Craton. Modified after Król et al. (2024).

#### 3. SUMMARY

**Pb nanospheres in zircon**: Documenting the micro-composition and mineralogy of Eoarchean zircon and Pb-enriched domains is essential for understanding the processes of Pb redistribution in zircon and its effect on geochronology.

**Lu-Hf in zircon**: The scatter in the U-Pb dataset is attributed to isotopic disturbance of Pb during the UHT metamorphism at 2.5 Ga. If data are not corrected, results can lead to overestimation of model crust formation ages, a critical problem in the search for evidence of Hadean crust in Eoarchean rocks and for estimation of timing and rate of ancient continental growth.

**Oxygen in zircon**: We show that although the generation of such isotopically light signatures can be achieved through mixing with seawater during a hydrothermal event, the proportion of oxygen from seawater would have to be exceptionally high. In contrast, only a small and more realistic proportion of water with much lighter  $\delta^{18}$ O, such as that characteristic of meteoric water would be required. These new results, therefore, are consistent with the presence of shallow magmatic or hydrothermal systems involving meteoric water at 3.73 Ga, providing the earliest known evidence for the emergence of land on Earth.

#### References

- Belyatsky, B.V., N.V. Rodionov, A.V. Antonov, and S.A. Sergeev (2011), The 3.98–3.63 Ga zircons as indicators of major processes operating in the ancient continental crust of the east Antarctic shield (Enderby Land), *Dokl. Earth. Sci.* **438**, 770–774, DOI: 10.1134/S1028334X11060031.
- Black, L.P., J.W. Sheraton, and P.R. James (1986), Late Archean granites of the Napier Complex, Enderby Land, Antarctica: A comparison of Rb-Sr, Sm-Nd and U-Pb isotopic systematics in a complex terrain, *Precambrian Res.* **32**, 4, 343–368, DOI: 10.1016/0301-9268(86)90036-7.
- Bowring, S.A., and I.S. Williams (1999), Priscoan (4.00–4.03 Ga) orthogneisses from northwestern Canada, *Contrib. Mineral. Petrol.* **134**, 3–16, DOI: 10.1007/s004100050465.
- Guitreau, M., M. Boyet, J.-L. Paquette, A. Gannoun, Z. Konc, M. Benbakkar, K. Suchorski, and J.-M. Hénot (2019), Hadean protocrust reworking at the origin of the Archean Napier Complex (Antarctica), *Geochem. Perspect. Lett.* **12**, 7–11, DOI: 10.7185/geochemlet.1927.
- Harley, S.L., N.M. Kelly, and M.A. Kusiak (2019), Chapter 35 Ancient Antarctica: The Archean of the East Antarctic Shield. In: M.J. Van Kranendonk, V.C. Bennett, and J.E. Hoffmann (eds.), *Earth's Oldest Rocks*, 2nd ed., Elsevier, 865–897, DOI: 10.1016/B978-0-444-63901-1.00035-6.
- Hiess, J., and V.C. Bennett (2016), Chondritic Lu/Hf in the early crust–mantle system as recorded by zircon populations from the oldest Eoarchean rocks of Yilgarn Craton, West Australia and Enderby Land, Antarctica, *Chem. Geol.* **427**, 125–143, DOI: 10.1016/j.chemgeo.2016.02.011.
- Hokada, T., K. Misawa, K. Yokoyama, K. Shiraishi, and A. Yamaguchi (2004), SHRIMP and electron microprobe chronology of UHT metamorphism in the Napier Complex, East Antarctica: implications for zircon growth at >1,000 °C, *Contrib. Mineral. Petrol.* **147**, 1–20, DOI: 10.1007/ s00410-003-0550-2.
- Iizuka, T., K. Horie, T. Komiya, S. Maruyama, T. Hirata, H. Hidaka, and B.F. Windley (2006), 4.2 Ga zircon xenocryst in an Acasta gneiss from northwestern Canada: Evidence for early continental crust, *Geology* 34, 4, 245–248, DOI: 10.1130/G22124.1.
- Kelly, N.M., and S.L. Harley (2005), An integrated microtextural and chemical approach to zircon geochronology: refining the Archaean history of the Napier Complex, east Antarctica, *Contrib. Mineral. Petrol.* **149**, 57–84, DOI: 10.1007/s00410-004-0635-6.
- Król, P., M.A. Kusiak, D.J. Dunkley, S.A. Wilde, K. Yi, S. Lee, and I. Kocjan (2020), Diversity of Archean crust in the eastern Tula Mountains, Napier Complex, East Antarctica, *Gondwana Res.* 82, 151–170, DOI: 10.1016/j.gr.2019.12.014.
- Król, P., M.A. Kusiak, M.J. Whitehouse, D.J. Dunkley, and S.A. Wilde (2024), Eoarchean low δ<sup>18</sup>O zircon indicates emergent land at 3.73 Ga, *Precambrian Res.* 408, 107416, DOI: 10.1016/j.precamres.2024.107416.

- Kusiak, M.A., M.J. Whitehouse, S.A. Wilde, D.J. Dunkley, M. Menneken, A.A. Nemchin, and C. Clark (2013a), Changes in zircon chemistry during Archean UHT metamorphism in the Napier Complex, Antarctica, Am. J. Sci. 313, 9, 933–967, DOI: 10.2475/09.2013.05.
- Kusiak, M.A., M.J. Whitehouse, S.A. Wilde, A.A. Nemchin, and C. Clark (2013b), Mobilization of radiogenic Pb in zircon revealed by ion imaging: Implications for early Earth geochronology, *Geology* **41**, 3, 291–294, DOI: 10.1130/G33920.1.
- Kusiak, M.A., D.J. Dunkley, R. Wirth, M.J. Whitehouse, S.A. Wilde, and K. Marquardt (2015), Metallic lead nanospheres discovered in ancient zircons, *Proc. Natl. Acad. Sci. U.S.A.* **112**, 16, 4958– 4963, DOI: 10.1073/pnas.1415264112.
- Kusiak, M.A., S.A. Wilde, R. Wirth, M.J. Whitehouse, D.J. Dunkley, I. Lyon, S.M. Reddy, A. Berry, and M. de Jonge (2017), Detecting micro- and nanoscale variations in element mobility in high-grade metamorphic rocks: implication for precise U-Pb dating of zircon. In: D.E. Moser, F. Corfu, J.R. Darling, S.M. Reddy, and K. Tait (eds.), *Microstructural Geochronology: Planetary Records Down to Atom Scale*, Geophysical Monograph Series, John Wiley & Sons, Inc., American Geophysical Union, 279–292, DOI: 10.1002/9781119227250.ch13.
- Kusiak, M.A., D.J. Dunkley, S.A. Wilde, M.J. Whitehouse, and A.I.S. Kemp (2021), Eoarchean crust in East Antarctica: Extension from Enderby Land into Kemp Land, *Gondwana Res.* 93, 227– 241, DOI: 10.1016/j.gr.2020.12.031.
- Kusiak, M.A., R. Wirth, S.A. Wilde, and R.T. Pidgeon (2023), Metallic lead (Pb) nanospheres discovered in Hadean and Eoarchean zircon crystals at Jack Hills, *Sci. Rep. UK* **13**, 895, DOI: 10.1038/s41598-023-27843-6.
- Valley, J.W., P.D. Kinny, D.J. Schulze, and M.J. Spicuzza (1998), Zircon megacrysts from kimberlite: oxygen isotope variability among mantle melts, *Contrib. Miner. Petrol.* 133, 1–11, DOI: 10.1007/s004100050432.
- Valley, J.W., I.N. Bindeman, and W.H. Peck (2003), Empirical calibration of oxygen isotope fractionation in zircon, *Geochim. Cosmochim. Acta* 67, 17, 3257–3266, DOI: 10.1016/S0016-7037(03)00090-5.
- Wilde, S.A., J.W. Valley, W.H. Peck, and C.M. Graham (2001), Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago, *Nature* **409**, 175–178, DOI: 10.1038/35051550.
- Williams, I.S., W. Compston,, L.P. Black, T.R. Ireland, and J.J. Foster (1984), Unsupported radiogenic Pb in zircon: a cause of anomalously high Pb-Pb, U-Pb and Th-Pb ages, *Contrib. Mineral. Petrol.* 88, 322–327, DOI: 10.1007/BF00376756.

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