

Paper Number: 5314

Geochronological implications of metallic Pb nanospheres in zircon exposed to high-grade metamorphism.

Kusiak, M.A.¹, Wirth R.², Wilde, S.A.³, Whitehouse M.J.⁴, Dunkley, D.J.^{1,3} and Lyon, I.⁵

¹Institute of Geological Sciences, Polish Academy of Sciences, Warsaw, Poland; monika.kusiak@twarda.pan.pl

²GeoForschungsZentrum, Potsdam, Germany

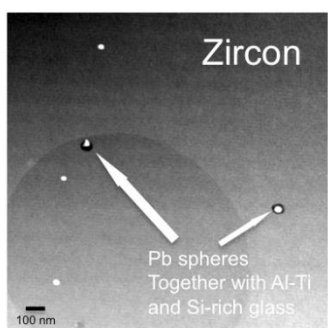
³Department of Applied Geology, Curtin University, Perth, Western Australia

⁴Swedish Museum of Natural History, Stockholm, Sweden

⁵SEAES; Material Sciences, University of Manchester, UK

Zircons from Neoproterozoic granulite and ultra-high temperature gneisses in the Napier Complex of East Antarctica preserve magmatic U-Pb ages greater than 3.8 Ga [1,2]. Early Secondary Ion Mass Spectrometry (SIMS) studies [3] identified isotopic disturbance of >3.4 Ga zircons, through reversely discordant age estimates (where $^{206}\text{Pb}/^{238}\text{U}$ ages are older than $^{207}\text{Pb}/^{206}\text{Pb}$ ages) and excessive within-run instability of Pb isotope counts during analysis. These results were confirmed by ion imaging studies that indicated within-grain separation and redistribution of radiogenic Pb from radiation-damaged zircon [4,5]. Isotopic mapping of ^{48}Ti , ^{89}Y , ^{180}Hf , ^{232}Th , ^{238}U , ^{204}Pb , ^{206}Pb and ^{207}Pb in sub-grain areas of zircon was done by SIMS using a CAMECA IMS 1280 at the Swedish Museum of Natural History in Stockholm, using both mono- and multi-collection modes. Maps of Pb and Ti isotopes revealed sub-2 μm patches of anomalously high concentration, with variably high $^{207}\text{Pb}/^{206}\text{Pb}$ values corresponding to apparent ages up to 4.1 Ga; there is no evidence of common Pb contamination as would be indicated by detectable ^{204}Pb . Inhomogeneous distribution of Pb in zircon affected by high-temperature metamorphism has also been detected in gneisses from India in a study combining ion imaging with ion tomography that revealed the likely tens of nanometer scale movement of the unsupported Pb [6], as well as in detrital zircon grains from the Jack Hills [7].

Using high-resolution scanning transmission electron microscopy (TEM) at the GeoForschungsZentrum in Potsdam, Germany, it was discovered, that these domains of anomalous Pb contain metallic lead nanospheres 5-35 nm in size [8] in a matrix of zircon (Fig. 1). The nanospheres occur in isolation (Fig. 1) and as multi-phase inclusions 20-80 nm across that also contain Ti and Al-rich phases and silica glass. These were interpreted as having formed as melt inclusions generated during annealing of radiation-



damaged zircon by high-temperature metamorphism [8]. The presence of Pb nanospheres in zircon from high-temperature gneisses goes some way in explaining anomalous isotopic age estimates that are sometimes obtained during SIMS analysis. Reverse discordance, including spuriously old $^{207}\text{Pb}/^{206}\text{Pb}$ age estimates, may result from the migration of radiogenic Pb within heat-annealed zircon, as well as from analytical effects induced by the non-simultaneous measurement of isotopes in zircon that contains Pb in nanospheres.

Figure 1: TEM image of zircon showing Pb nanospheres (white) in Si-rich glass together with Ti-Al-rich phases (dark areas around Pb nanospheres).

References:

- [1] Black L et al. (1986) *Contrib Mineral Petrol* 94: 427-437
- [2] Harley S and Black L (1997) *Antarctic Science* 9: 74-92
- [3] Williams I S et al. (1984) *Contrib Mineral Petrol* 88: 322-327
- [4] Kusiak M A et al. (2013) *American Journal of Sci* 313: 933-967
- [5] Kusiak M A et al. (2013) *Geology* 41: 291-294
- [6] Whitehouse M J et al. (2014) *Contrib Mineral Petrol* 168: 1042
- [7] Valley J W et al. (2014) *Nature Geoscience* 7: 219-223
- [8] Kusiak M A et al. (2015) *Proc National Academy Sci* 112: 4958-4963

