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# Nanoscale distribution of Pb, Ti and Al in metamorphic zircon from the Eoarchean Dniester -Bouh Series, Ukrainian Shield

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Heterogeneous distribution of Pb in zircon was identified in ultra-high temperature (UHT) gneisses from the Napier Complex in East Antarctica by Kusiak et al. using secondary ion mass spectrometry [1] and metallic Pb nanospheres were discovered utilizing TEM [2]. Since then, several studies have documented Pb redistribution in zircon from rocks that did not experience UHT. Both metallic Pb nanospheres and Pb nanoclusters (as precursors to Pb nanospheres) were documented in Hadean and Eoarchean Jack Hills zircon from Western Australia [3]. A recent study [4] on experimentally heated zircon revealed that metallic Pb ($Pb^0$) nanospheres can coexist with Pb nanoinclusions containing Pb in different oxidation states, namely $Pb^{2+}$ and $Pb^{4+}$ (PbO, $Pb_2O_3$, $Pb_3O_4$ and $PbO_2$).

Here we document the most abundant known occurrence of Pb nanospheres present in >3.0 Ga cores and ca. 2.7 Ga rims of zircon grains from the Odesa quarry, Ukraine. Similar to previous studies, they are randomly distributed with sizes from <3 nm up to >10 nm. In >3 Ga zircon cores, they form aggregates up to 80 nm. These usually consist of minute (1-2 nm) Pb nanospheres coexisting with Ti clusters. The variability in size of the Pb nanospheres is evidence of the Ostwald ripening process, when fusion of tiny Pb clusters form these aggregates and, further, nanospheres. In ca. 2.7 Ga zircon rims, nanospheres are present, but they usually are in association with Si. No such aggregates were documented and no Ti, although Al is present. Additionally, veins containing Ca and Fe, with no Pb nanospheres, reveal evidence of fluid infiltration into the rims. The fact that Pb nanospheres are present in rims may be an indication of a later metamorphic event, most probably the ca. 2.0 Ga metamorphism known from this area. Absence of Ti in the rims resulted possibly from zircon recrystallization during this younger metamorphic event.

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[1] Kusiak et al. 2013, Geology 41, 291-294. [2] Kusiak et al. 2015, PNAS 112 (16) 4958-4963. [3] Kusiak et al. 2023, Sci. Rep. 13, 895. [4] Zieja et al. 2026, GCA 416, 154-167.