First zircon evidence of Hadean material in the Ukrainian Shield

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The oldest (ca. 3790 Ma) zircons in the Ukrainian Shield are known from igneous and metasedimentary rocks in the Dniester-Bouh and Azov domains. Recently, we have discovered even older, up to 3971 ± 4 Ma, captured zircons in metavolcanic rocks of the Hulyaipole Suite forming a synform in the central part of the Azov Domain. Previous U-Pb multigrain TIMS dating of zircons from metasandstone of the Hulyaipole Suite yielded an age of 2.9 ± 0.1 Ga for detrital and ca. 2.14 Ga for metamorphic zircons. We applied the LA-ICP-MS method for U-Pb dating and Hf isotope measurement in 36 zircon grains isolated from metatrachyandesite of the Hulyaipole Suite. The age of the oldest (>3575 Ma) zircons was further confirmed by SIMS dating. We distinguish two zircon populations: (1) 3085-2850 Ma, that have variable Hf isotope characteristics, with five grains having EHf from 6.2 to -0.5, and six grains from -7.5 to -21, indicating both significant mantle input and reworking of the older crust; (2) 3700-3360 Ma, which also have both juvenile Hf isotope characteristics (EHf up to 1.6), and strongly negative EHf values (down to -7.7 at 3705 Ma). In addition, the age of two grains exceeds 3800 Ma (3805 Ma with $\varepsilon Hf = -3.3$, and 3971 Ma with $\varepsilon Hf = -1.3$), and these represent the oldest zircons so far found in the Ukrainian Shield. Their Hf isotope characteristics also indicate the presence of Hadean material in the Azov Domain of the Ukrainian Shield. The minimum model age calculated at Lu/Hf = 0 for zircons with the lowermost ϵHf values in each of the age populations is ca. 4.1 Ga.