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Can oxygen isotopes in magmatic zircon be modified by metamorphism? A case study from the Eoarchean Dniester-Bug Series, Ukrainian Shield

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ABSTRACT

Zircon occurs as a minor constituent in most differentiated magmatic rocks. Its robustness to later modification means that its isotopic and chemical composition generally records conditions prevailing when it formed, and the systematic changes in the oxygen isotope record of zircon through geological time have been used to trace the temporal evolution of crust–mantle interaction and intra-crustal recycling. Here we present U–Pb, Hf, and oxygen isotopic compositions for high grade metamorphic Archean rocks from the Dniester-Bug Series, western Ukrainian Shield. Zircon from a quartz-dominated rock is up to 3.8 Ga old, and enriched in ^{18}O compared to most previously reported values from Archean zircon. Similar values are recorded in zircon cores, which exhibit a variety of internal textures including magmatic-style oscillatory zonation, and rims. If this rock is metasedimentary and the isotope signatures in cores are primary, the zircon sources were characterized by heavier oxygen isotopic compositions than any known major area of Archean crust. Alternatively the O isotope compositions have been modified. We show that a large fraction of the analyzed zircon appear not to be modified by radiation damage, and speculate that O exchange may have taken place by diffusion during extreme metasomatic alteration of the host rock. The possibility that igneous-looking, apparently unaltered zircon may not preserve a primary oxygen isotope signature has implications for its use in the interpretation of crustal evolution, including early terrestrial geodynamics.

1. Introduction

The temporal and petrological information carried in zircon, its ability to preserve its chemical and isotopic composition during metamorphism and alteration, and its robustness during erosion and mechanical transport has made it the mineral of choice for crustal evolution studies. Well-preserved magmatic zircon has been shown generally to keep its primary oxygen isotopic composition during subsequent geological processes (Bowman et al., 2011; Page et al., 2007; Peck et al., 2003; Valley, 2003). Igneous zircon without signs of secondary alteration from Archean rocks generally show a restricted range of primitive to mildly elevated O isotopic compositions ($\delta^{18}O = 5–7.5‰$) compared to the value of ca. 5.3‰ in directly mantle-derived rocks, while a broader range to higher values is found in younger rocks. From the Proterozoic onwards, the range gradually increases, and from the mid-Proterozoic higher $\delta^{18}O$ values of 8 to >10‰ are common (Valley et al., 2005). Such high $\delta^{18}O$ values in zircon are taken as evidence that material which has been subject to O-isotope fractionation in the presence of water in supracrustal or near-surface low-temperature environments has been subsequently recycled to crustal depths where it melted to form a differentiated magma capable of crystallizing zircon with elevated $\delta^{18}O$. The temporal evolution of O isotopic compositions in igneous zircon has been interpreted to reflect changes in the composition of sediments, and the rate and style of recycling of surface-derived materials into magmas within the crust (Valley et al., 2005). In particular, elevated $\delta^{18}O$ in >4.0 Ga detrital zircon from the Jack Hills, Western Australia, has been used to infer the existence of cool oceans (Harrison, 2009; Mojzsis et al., 2001; Valley

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et al., 2002; Wilde et al., 2001), felsic crust and operation of plate recycling (Harrison, 2009; Harrison et al., 2008) during the Hadean period, for which there is no extant rock record.

We present U–Pb, Hf and O isotope data for zircon from polymetamorphic, granulite facies Archean rocks from the Dniester-Bug Series, western Ukrainian Shield, including $\delta^{18}O$ values of 8–10‰ for zircon from a quartz-dominated rock with $^{207}Pb/^{206}Pb$ ages up to 3.8 Ga and Hf isotope compositions indicating derivation from similarly aged crust. These zircons have varying internal textures, including magmatic-style oscillatory zonation patterns. We suggest that these O isotope signatures may not be primary but have been modified during metamorphism. The possible existence of magmatic-style zircon with modified $\delta^{18}O$ has implications for the use of O isotope signatures for the interpretation of crustal evolution and geodynamics.

2. Geological setting and samples

The Ukrainian Shield (Fig. 1A) is commonly divided into several blocks, or domains, separated by suture zones (e.g. Claesson et al., 2006). Tectonically the structure of the shield can be described as a collage of Archean and Palaeoproterozoic terranes which have been amalgamated around Palaeoarchean cores at different times, both in the Archean and in Palaeoproterozoic time (e.g. Glevassky and Glevasska, 2002; Kalyaev, 1976). Early Archean crust occurs in the Azov Domain in the east and in the Podolian Domain in the south-west. The oldest crust in the Podolian Domain includes the Dniester-Bug Series of supracrustal and associated basic and ultrabasic rocks, and widely occurring granitoid rocks dominated by enderbite–orthopyroxene bearing gneisses of mainly tonalitic composition. These have been metamorphosed in granulite and high temperature amphibolite facies, and eclogitic coronas on metabasic rocks formed at 900 °C and >6 kbar have been described (Dagelaysky, 1993, and references therein). The degree of deformation varies on both regional and local scale, commonly rocks are strongly deformed but low strain areas also occur. The Dniester-Bug region experienced high grade metamorphism in both Neoarchean (at ca. 2.7–2.8 Ga) and Palaeoproterozoic (at ca. 2.0 Ga) time. This was first demonstrated by Bibikova (1984) who dated clear transparent, roundish zircons separated from enderbite, which were interpreted to have formed during granulite facies metamorphism, to ca. 2.75 Ga while a younger generation of zircon from the same locality yielded ca. 1.9 Ga. The occurrence of both Neoarchean and Paleoproterozoic metamorphic zircon in rocks from the Dniester-Bug region has subsequently been confirmed by several studies (e.g. Claesson et al., 2006, 2015; Shcherbak et al., 2005).

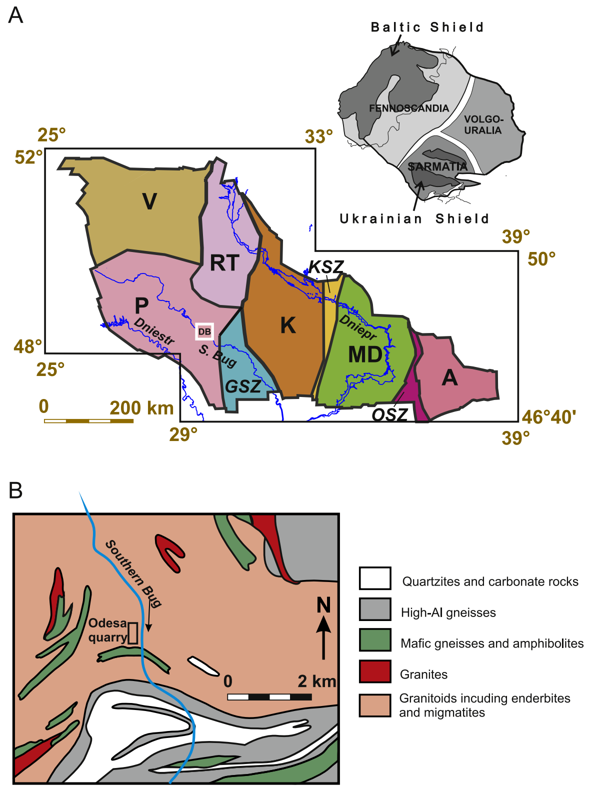

Fig. 1. Maps showing the outline of the Ukrainian Shield, the central parts of the Dniester-Bug region and the location of the Odesa quarry. (A) Outline of the Ukrainian Shield and its division into different domains, modified from a map by S. Bogdanova. The inset map shows the position of the shield in the East European Platform. The Podolian Domain (P) in the west and the Azov Domain (A) in the east both include Eoarchaean components. Other domains: V, Volyn; RT, Ros-Tykich; K, Kirovograd (Ingul); MD, Middle Dnieper. Suture zones: GSZ, Golovaniv; KSZ, Krivyy Rih; OSZ, Orekhiv-Pavlograd. For clarity, the white rectangle marked 'DB' in the Podolian Domain which denotes the area in the Dniester-Bug region shown in (B) is oversized. (B) Geological map of the middle Bug area, Dniester-Bug region. The black rectangle shows the location of the Odesa quarry. Based on a map from the 'PivnichUkrGeologiya' enterprise, with additions by V.-V. Nikolayevsky and simplifications by V.V. Balagansky.

Dniester-Bug Series rocks are exposed along the South Bug river, and in open pit rock quarries near the river (Fig. 1B). A key locality is the abandoned Odesa quarry, located on the southwestern side of the river, near the village of Zavallie, which has been investigated in detail for its structure and petrology, geochemical and isotopic compositions, and age (Claesson et al., 2006, 2015; Lesnaya, 1988; Lesnaya et al., 1995; Lobach-Zhuchenko et al., 2011, 2013, 2014). It is dominated by enderbitic gneisses and mafic rocks, with subordinate occurrences of siliceous gneisses and other lithologies. More massive ultramafic bodies also occur. The degree of deformation is highly variable and, while strongly deformed rocks predominate (Lobach-Zhuchenko et al., 2013), in places the enderbite is almost undeformed. U–Pb ages and Hf isotope compositions of zircon from the enderbite and Nd whole-rock data indicate that it is ca. 3.75 Ga old and was extracted from a source with chondritic to mildly depleted isotopic composition (Claesson et al., 2015). Most zircon U–Pb data for the enderbite is discordant, reflecting the strong polyphase metamorphic overprint. This is also reflected in internal zircon textures, with common overgrowths on cores of varying appearance (Claesson et al., 2015).

The target for the present study is a ca. 5 m wide, steeply dipping zone in the northern wall of the Odesa quarry where a quartz-dominated rock, first described by Lobach-Zhuchenko et al. (2013), is exposed along with other lithologies (section 2 in Fig. 2, Lobach-Zhuchenko et al., 2014). It occurs in a wider zone of garnet-bearing enderbites and other rocks (Lobach-Zhuchenko et al., 2013) and was interpreted by Lobach-Zhuchenko et al. (2014) as a quartzite of sedimentary origin. The quartz-dominated rock is bordered by a massive pyroxenite body on one side and by enderbite on the other (Fig. 2A). The composition varies from pure quartzitic with more than 90% SiO_2, hereafter referred to as quartzose rock, to varieties richer in garnet and biotite (Lobach-Zhuchenko et al., 2014), and it includes distinct cm- to dm-wide garnet–biotite dominated bands, hereafter referred to as garnet–biotite bands (Fig. 2B). We have investigated zircon from the quartzose rock (samples C10-U1 and UR82/6), a garnet–biotite band (sample C13-2), and from an enderbite representing the dominant lithology in the quarry (sample 06-BG38). Additionally, we have studied samples representing other lithologies surrounding the quartzose rock in a NW–SE section across the steeply dipping quartzose rock dominated zone, from pyroxenite in the NW to garnet-bearing enderbite in the SE (samples C13-1 and C13-3A to C13-5, Fig. 2A). Coordinates for the section are N48°13.935′, E029°59.295′, Enderbite sample 06-BG38 was collected in the Odesa quarry ca. 100 m to the SW from the