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

**Stefan Claesson^{a*}, Elena V. Bibikova^b, Leonid Shumlyanskyy^{a,c}, Martin J. Whitehouse^a
& Kjell Billström^a**

^aSwedish Museum of Natural History, Box 50007, 10405 Stockholm, Sweden.

stefan.claesson@nrm.se, martin.whitehouse@nrm.se, kjell.billstrom@nrm.se.

^bVernadsky Institute of Geochemistry and Analytical Chemistry, R.A.S., Kosygina St. 19,
Moscow, 119991 Russia. bibikova@geokhi.ru.

^cM.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation, Palladina Ave.
34, 03680 Kyiv, Ukraine. shumlyanskyy@yahoo.com

*Corresponding author

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 ¹⁸O 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.

KEYWORDS

Eoarchean, zircon, O isotopes, Ukrainian Shield, U-Pb, Lu-Hf.

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 ($\delta^{18}\text{O}=5\text{-}7.5\text{‰}$) 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 $\delta^{18}\text{O}$ values of 8 to $>10\text{‰}$ are common (Valley et al., 2005). Such high $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$. 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 $\delta^{18}\text{O}$ 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 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 $\delta^{18}\text{O}$ values of 8-10 ‰ for zircon from a quartz-dominated rock with $^{207}\text{Pb}/^{206}\text{Pb}$ 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 $\delta^{18}\text{O}$ 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 Archaean and Palaeoproterozoic terranes which have been

amalgamated around Palaeoarchaeon cores at different times, both in the Archaean 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 Neoarchaeon (at ca. 2.7 to 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; Claesson et al., 2015; Shcherbak et al., 2005).

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; Claesson et al., 2015; Lesnaya, 1988; Lesnaya et al., 1995; Lobach-Zhuchenko et al., 2013; Lobach-Zhuchenko et al., 2014; Lobach-Zhuchenko et al., 2011). 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. 5m 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% SiO₂, 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 quartz 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 section. The petrography of the investigated samples, as identified from thin sections, is described below.

C10-U1, quartzose rock. This sample, which was collected ca. 1.5 m from the contact to the pyroxenite (Fig. 2A), has a fine-grained, granoblastic texture with 80% quartz, 15% plagioclase, 2% hypersthene, 2% biotite, 1% apatite, opaque minerals and zircon. The quartz grains are deformed and flattened with 'wavy' extinction. The grain size varies from 0.1 to ~1 mm. Crystal contacts are very irregular. Plagioclase (oligoclase) forms isometric grains up to 1-2 mm in size, which are undeformed and idiomorphic relative to quartz and hypersthene, and commonly form mono-mineral clusters up to 3-4 mm in size. Hypersthene occurs as rare fine (0.2-0.4 mm) anhedral grains which always occur in association with plagioclase. Biotite forms rare fine interstitial laths.

UR82/6, quartzose rock, was sampled next to C10-U1. It looks similar to C10-U1 in hand specimen, and was not investigated for its mineralogical composition in thin section.

C13-1, amphibolized garnet-bearing enderbite, was sampled at the SE end of profile (Fig. 2A). It is medium-grained with granoblastic texture, composed of ca. 40% plagioclase, 15% quartz, 15% hypersthene, 15% hornblende, 10% garnet, 4% opaque minerals, 1% apatite, and zircon. The rock is dominated by a mosaic aggregate of isometric, anhedral crystals that vary in size from 0.5 to 0.8 mm. Garnet occurs both as larger, up to 3-5 mm, porphyroblasts with idiomorphic outlines and inclusions of aggregates of other minerals, and as small euhedral grains.

C13-2, garnet-biotite gneiss, was sampled in a ca. 5 cm wide band surrounded by the quartzose rock represented by C10-U1 and UR82/6 (Fig. 2A, B). The texture is even-grained,

nemato- to granoblastic. The investigated thin section is not typical for the appearance of this rock in hand specimen, it is dominated by ca. 75% plagioclase and very low in garnet. Other minerals include ca. 15% biotite, 5% quartz, 1% opaque minerals, and zircon. The thin section is composed predominantly of an aggregate of fine (0.3-0.5 mm) isometric, hypidiomorphic and slightly deformed grains of plagioclase. Biotite occurs as numerous laths up to 0.2-0.3 mm in size that are irregularly oriented and displays strong pleochroism from weakly yellowish to bright reddish-brown. Quartz forms scanty grains that by shape resemble the plagioclase. Garnet is represented by up to 1 mm anhedral tabular crystals. Opaque minerals occur as fine (0.05-0.1 mm) isometric angular grains that are regularly distributed in the rocks and usually associated with biotite.

C13-3A, enderbitic garnet-rich gneiss and C13-3B, garnet-gneiss, were collected ca. 2 m NW from C13-1 (Fig. 2A). Samples C13-3A and 3B are two parts of the same specimen with different compositions. C13-3A was not investigated for its mineral composition. C13-3B is of medium grain size, even-grained, with granoblastic texture. It is dominated by ca. 70 % garnet, other minerals include ca. 15% quartz, 10% plagioclase, up to 5% opaque minerals, 1% biotite, and zircon. The garnet occurs as large, up to 2-4 mm, isometric and mostly idiomorphic pinkish grains. Some garnets contain in their central parts scanty fine inclusions of quartz and opaque mineral. In places garnet is replaced by biotite. The interstitial space between garnet crystals is filled by aggregates of fine grains of quartz and plagioclase. Quartz is heavily deformed, bent and fragmented, whereas plagioclase has preserved its hypidiomorphic shape and does not reveal any signs of deformation. Opaque minerals form fine (0.2-0.3 mm) isometric angular grains located primarily at garnet boundaries.

C13-4, amphibolized pyroxenite. This sample was collected a few m into the pyroxenite from the contact (Fig. 2A). It has an even-grained granoblastic texture dominated by up to 80% isometric hypidiomorphic crystals of orthopyroxene with an average grain size around

0.5 mm. Other minerals include ca. 15% hornblende, 2-3% spinel, 1% opaque minerals, serpentine, and occasional olivine. The interstitial space between orthopyroxene crystals is filled with fine anhedral grains of bright-green spinel and pale-green hornblende that apparently has developed after orthopyroxene. Besides interstitial hornblende grains, larger, up to 1 mm, isometric anhedral crystals of hornblende also occur. Spinel is commonly replaced by serpentine. One grain of olivine (up to 0.2-0.3 mm) was also noted in this thin section. This sample did not yield any zircon.

C13-5, amphibolized pyroxenite, contact zone. This sample was collected in the pyroxenite a few cm from the contact to quartzose rock (Fig. 2A). It was not investigated for mineral composition in thin section, but gave a small yield of zircon of variable appearances.

Zircon from the quartzose rock typically displays one or more CL-dark overgrowths on cores with variable internal textures. A minority of the cores are characterized by well-developed oscillatory zoning while other zircons display sector-like or more irregular zoning. Diffuse internal variations and relatively structure-less cores also occur. Some overgrowths are wider than the enclosed cores, while others are thinner and not fully developed around the whole cores. Zircon without well-developed core-overgrowth textures visible in their CL images also occur, and in some grains alteration textures are prominent in the rims. Under optical microscope the appearance of cores varies from somewhat turbid to transparent and structure-less. Some cores show traces of internal structures similar to those visible in CL, while the rims typically are more or less transparent and structure-less. CL images of several zircons with different internal textures are shown in Fig. 3. Optical photomicrographs and CL-images of six crystals with well-developed core-overgrowth textures and variously zoned cores, which have been analyzed in detail for O isotope compositions, are shown in Fig. 8. Zircon

from the other investigated samples also typically display variable and complex internal textures, including common overgrowths, but no cores with magmatic-style zoning.

3. METHODS AND RESULTS

Zircons from the quartzose rock, one garnet-biotite band enclosed in the quartzose rock, and surrounding lithologies in the profile described above (Fig. 2A), were analysed for their U-Pb, Hf and O isotopic compositions. We have also analysed OH/O ratios in selected zircon crystals from the quartzose rock, O isotopic compositions in zircon from enderbite sample 06-BG38, which has previously been analysed for U-Pb and Hf-isotopes (Claesson et al., 2015), and the O isotopic compositions of quartz separates from the quartzose rock and the enderbite.

High-spatial resolution U-Pb and O isotope analysis of zircon was performed at the SIMS facility Nordsim, Swedish Museum of Natural History, Stockholm. Several crystals were analysed in two or more locations, including both cores and rims. The spot size used for the U-Pb analysis was ca. 20x25 μm , and for $\delta^{18}\text{O}$ analysis ca. 10 μm . The internal O isotope profiles across cores and rims in six crystals were performed using a smaller spot size of ca. 4 μm . Analytical precision for 10 μm spots is 0.2‰, and for 4 μm spots 0.5‰ (1 SD).

Techniques for U-Pb and O analysis are described in Whitehouse and Kamber (2005) and Whitehouse and Nemchin (2009), respectively. Selected grains were analyzed for $^{16}\text{O}^1\text{H}$, which was measured concurrently with ^{16}O and ^{18}O in three Faraday cups. The sample was pumped in the airlock for >24 hours and the sample chamber liquid N_2 cold trap was used to reduce the background H_2O level. For these measurements, the detector used for $^{16}\text{O}^1\text{H}$ was operated at a nominal mass resolution of 6000 ($M/\Delta M$) in order to separate $^{16}\text{O}^1\text{H}$ from ^{17}O , the entrance slit was set to a narrower width (70 μm instead of 150 μm) to maximize the peak

flat at this resolution and the data acquisition period was slightly longer (96 s of instead of 64 s). $\delta^{18}\text{O}$ values are reported relative to SMOW. OH is reported as $\Delta\text{OH}/\text{O}_{\text{sample-standard}}$, defined as $^{16}\text{O}^1\text{H}/^{16}\text{O}$ relative to the drift corrected “background” $^{16}\text{O}^1\text{H}/^{16}\text{O}$ measured on the interspersed 91500 standard, which is assumed to have insignificant OH content. Temora 2, which also is assumed to have negligible OH, was analyzed as a monitor. Results from the U-Pb and O isotope analysis are given in Inline Supplementary Material Table S1.

Hafnium isotope analysis of zircon from the quartzose rock was performed at the Department of Geosciences, University of Oslo by LA-ICP-MC mass spectrometry. The diameter of analyzed spots is ca. 55 μm . The analytical technique followed that described in Elburg et al. (2013). The results are given along with corresponding U-Pb and O results in Table 1.

Oxygen analysis of bulk samples of separated quartz was done by laser fluorination at the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry RAS in Moscow. Sample size was ca. 1 mg and precision $\pm 0.1\%$. Three repeat runs of each sample gave within error the same results. Analytical techniques followed those described in Sharp (1990). The results are reported in Inline Supplementary Table S1.

Zircon cores from the quartzose rock yield Archean $^{207}\text{Pb}/^{206}\text{Pb}$ ages up to 3.8 Ga, while most of the rims yield ages of 2.7-2.8 Ga. Most of the U-Pb data is discordant, but several analyses are concordant at ca. 2.8 Ga and a few rims have concordant U-Pb ages of ca. 2.0 Ga. In addition, many cores are concordant or close to concordant, some clustering at 3.0-3.2 Ga, but mostly distributed along the concordia curve in the age interval 3.3 to 3.8 Ga (Fig. 4A). In spite of their concordancy or near-concordancy these dates do probably not all reflect real rock ages. Ancient Pb loss from Eoarchean zircon is inherently difficult to identify. This is because the curvature of the concordia curve varies with age, and for early Archean ages it

forms an almost straight, sub-horizontal (in conventional space) line. Ancient Pb loss from Eoarchean zircon therefore results in movement of individual data points along arrays which are sub-parallel to the concordia curve and in spite of the Pb loss, the points may remain concordant within analytical precision. In the present case a slight tendency towards reverse discordancy for some of the oldest dates (Fig. 4A) may also indicate some ancient radiogenic Pb mobility. Regardless of the precise interpretation of the oldest U-Pb ages, it is however safe to conclude that the zircon population from the Odesa quartz rock includes crystals which are up to ca. 3.8 Ga old, similar in age to the surrounding Odesa quarry enderbite.

The 2.7 to 2.8 Ga rims on zircon from the quartzose rock (Fig. 4A), and the majority of zircon in the garnet-biotite band as well as in the other samples from the investigated profile (Fig. 4B), formed during the period of granulite and high temperature amphibolite facies metamorphism which affected the Dniester-Bug region at that time. Superimposed Paleoproterozoic high grade metamorphism is reflected by 2.0 Ga zircon rims, crystallization of new zircon and a strong metamorphic overprint on the U-Pb system in older crystals. Both 2.7 to 2.8 Ga, and ca. 2.0 Ga zircon rims have previously been described from enderbite in the Odesa quarry (Claesson et al., 2015). U concentrations in most cores are 75-500 ppm, while the 2.7-2.8 Ga rims all have U concentrations higher than 500 ppm (Table1, Fig. 7A). Th/U ratios are >0.2 for most cores, while all rims have $\text{Th/U} \leq 0.2$.

Hf isotope compositions of cores and rims in zircon from the Odesa quartzose rock, back-calculated to $^{207}\text{Pb}/^{206}\text{Pb}$ ages derived from the same locations in the zircons, are shown in ϵ_{Hf} -time space in Fig. 5. The majority of analyses in cores form an array between 3.8 and 2.8 Ga with a slope corresponding to a Lu/Hf ratio close to zero, intersecting the evolution lines for CHUR and depleted mantle at ca. 3.5-3.8 Ga. Arrays with such slope, which is distinctly

different from that of evolving continental crust with a $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of ca. 0.015, may be produced by Pb loss. Some core analyses with $^{207}\text{Pb}/^{206}\text{Pb}$ ages less than 3.2 Ga, all in zircon from sample UR82/6, plot on the young side of this array. The analyses in rims form an array, also with a slope corresponding to a Lu/Hf ratio close to zero, ranging from 2.8 to 2.0 Ga and slightly displaced towards the young side compared to the main array for zircon cores.

The core analyses show no systematic correlation between U-Pb discordancy and Hf isotope signature, those with “oldest” signature include several which are >5% discordant while only one of the core spots on the young side of the main core array is >5% discordant (Fig. 5).

There is also no obvious correlation between CL texture and Hf isotope signature, as zircon with well-developed magmatic-style (e.g. Cavosie et al., 2004; Corfu et al., 2003) oscillatory zoning occurs not only in the main array but also among those with “younger” Hf isotope signatures (e.g. grain UR82/6-62, Fig. 3I).

$\delta^{18}\text{O}$ in analyzed zircon from the quartzose rock ranges, with two exceptions, between 7 and 10 ‰ and most analyzed spots have $\delta^{18}\text{O}$ above 8 ‰ (Fig. 6). High $\delta^{18}\text{O}$ is found in zircon with different internal textures, including cores with well-developed magmatic-style oscillatory zoning (Fig. 3). The $\delta^{18}\text{O}$ values do not show any correlation with U-Pb discordancy (Fig. 7B). There is also no systematic correlation between $\delta^{18}\text{O}$ and U concentration, although the lowest $\delta^{18}\text{O}$ is found predominantly in cores with <200 ppm U (Fig. 7C). To investigate the small-scale variation of $\delta^{18}\text{O}$ in cores and rims, O isotopic compositions were analyzed at very high spatial resolution (ca. 4 μm spots) along profiles in six grains which all yielded $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 3.3 Ga or more in their cores. In five of the profiles, $\delta^{18}\text{O}$ displays a scatter of ca. 2 ‰, between 8 and 10. This is not significantly larger than the analytical precision of 0.5 ‰ (1 σ), demonstrating limited internal variability. These

profiles do not reveal any systematic differences between cores and rims (Fig. 8A, B and D-F). Some variability in the cores of UR82/6-35 and C10-U1-7 is however indicated by single analyses of 10 μm spots which have yielded $\delta^{18}\text{O}$ values of 7.9 (Fig. 8A) and 7.2 (Fig. 8E) respectively. The profile in zircon UR82/6-52, in contrast, reveals a distinct difference in O isotope composition between core and rim (Fig. 8C). $\delta^{18}\text{O}$ in the five analyzed spots in this profile which are located in the rim varies between ca. 8 and 10 ‰, similar to other rims, while nine core analyses have $\delta^{18}\text{O}$ between ca. 5 and 7 ‰. A lower and variable $\delta^{18}\text{O}$ in the core of this crystal is confirmed by additional analyses with 10 μm spot size, distributed in the core and the rim. $\delta^{18}\text{O}$ in three core spots varies between 7 and 8 ‰, while one analysis in the core and four in the rim have higher $\delta^{18}\text{O}$ values of 9-10 ‰ (Fig. 8C). One more analyzed zircon with lower and variable $\delta^{18}\text{O}$ in its core, UR82/6-41 (Fig. 3C), was also analyzed in several additional locations with a 10 μm spot. $\delta^{18}\text{O}$ in the core of this crystal varies between 4 and 8 ‰ (n=7), while two analyses in the rim have $\delta^{18}\text{O}$ values of 8-9 ‰ which is similar to that in other rims.

$\delta^{18}\text{O}$ in zircon from the garnet-biotite band enclosed in the quartzose rock is also consistently high and similar to the quartzose rock zircon ($\delta^{18}\text{O}$ =8.7-9.1 ‰). Zircon from all other samples from the profile show lower values of <7 ‰, within the range for “normal” igneous Archean zircon and similar to $\delta^{18}\text{O}$ in the previously dated (Claesson et al., 2015) zircon from the Odesa quarry enderbite (Fig. 6).

In order to explore the possibility that O isotopes in analyzed zircon from the quartzose rock may have been reset by hydrothermal alteration, selected grains were also analyzed for $^{16}\text{O}^{1}\text{H}$ concentrations. This has recently been developed as a tool to monitor for changes to the $\delta^{18}\text{O}$ system due to water incorporation into the zircon crystal related to metamictization (e.g.

Pidgeon et al., 2013). Out of fifteen grains which were analyzed for $^{16}\text{O}^1\text{H}$, fourteen have $^{16}\text{O}^1\text{H}/^{16}\text{O}$ ratios which not are significantly higher than the ratio in zircon standards 91500 and Temora2 which were analyzed as references concurrently with the Odesa zircon. Indeed, most values are within the 2 standard deviation uncertainty on the 91500 measurements. One analysis, in zircon crystal UR82/6-45, shows an elevated $^{16}\text{O}^1\text{H}/^{16}\text{O}$. Post-analytical inspection showed that the analyzed spot in this crystal is located next to a crack which is visible under optical microscope. None of the other crystals shows any optically visible cracks or inclusions near the analyzed spots.

4. DISCUSSION

As shown by Valley et al. (2005), igneous zircon without signs of secondary alteration in Archean rocks generally have a restricted range of O isotopic compositions from mantle-like to slightly enriched in ^{18}O ($\delta^{18}\text{O}=5-7.5\text{‰}$). Occurrences of Archean zircon with higher $\delta^{18}\text{O}$ have been reported (e.g. Bowman et al., 2011; Ge et al., 2014; Kusiak et al., 2013; Moser et al., 2008; Wan et al., 2013), but the zircon in these studies is generally described as metamorphic or metamict. In the present study the data points for isotope analysis were selected to as far as possible avoid regions with signs of alteration or strong metamictization. Optically visible cracks or inclusions were avoided, and areas for analysis were preferentially located in CL-bright to intermediate parts of the crystals. Five analyses located in very CL-dark zircon regions (UR82/6-26b and 46b, C10-U1-8b, 21b and 39a) all have very high U concentrations of more than 1000 ppm. Several different methods have been applied to investigate alteration of individual zircon crystals, including OH/O ratios, laser Raman and IR spectroscopy, magnetism, solubility in HF, and the presence of non-formula elements such as Ca, Fe, and Al. The low $^{16}\text{O}^1\text{H}/^{16}\text{O}$ ratios measured in all but one of the zircons from the quartzose rock which were analyzed for OH in this study indicate that the bulk of the zircon

has not been greatly, if at all affected by alteration related to metamictization. The analysis in crystal UR82/6-45 which shows an elevated OH concentration next to a crack in the interior parts of crystal, on the other hand, demonstrates how the composition of zircon can be modified in the vicinity of fluid pathways. All in all, we conclude that the majority of crystals analyzed in this study do not appear to have been strongly affected by alteration.

Most analyzed zircon grains from the quartzose rock and the enclosed garnet-biotite band from the Odesa quarry reported here have $\delta^{18}\text{O}$ between 8 and 10 ‰. If the quartzose rock was originally a clastic sediment (Lobach-Zhuchenko et al., 2013; Lobach-Zhuchenko et al., 2014) and the O isotopic compositions of the zircon cores are primary, the sources for the detrital zircons must have been dominated by early Archean rocks with high $\delta^{18}\text{O}$ isotopic compositions, which appear to have been very uncommon in the Archaean. Provided the SiO_2 -rich composition reflects a primary quartz dominated mineralogy, it is likely to originally have been a mature sediment. It may then be speculated that that any primary minerals, including the zircon cores, are derived from an extensive source region and that the high $\delta^{18}\text{O}$ of the up to 3.8 Ga old zircon cores reflects an O isotope composition enriched in ^{18}O in a substantial segment of crust. It should also be pointed out that the surrounding enderbite, with $\delta^{18}\text{O} < 7$ ‰ in its zircon, cannot have been a source rock.

Regardless of its origin however, the setting of the quartzose rock and the enclosed garnet-biotite band in a localized zone, taken together with the high grade metamorphic conditions of the rock and the analytical results presented here, lend support to an alternative interpretation that these O isotope signatures may not be primary but instead represent secondary O isotope exchange in zircon. In the following sections we discuss preconditions, possible mechanisms and scenarios for such exchange.

4.1. Alteration of zircon

While it since long has been known that oxygen isotope ratios in metamict zircon may be altered (Bibikova et al., 1982), and that subsolidus metasomatic alteration (Hoskin, 2005; Nemchin et al., 2006) or dissolution-reprecipitation (Geisler et al., 2007) can involve O isotope exchange, it is generally accepted that the O isotopic composition in well crystallized, non-altered zircon not is modified by secondary chemical or thermal overprints affecting the host rock. This is supported by the occurrence of zircon with different isotopic compositions in cores and metamorphic overgrowths (Peck et al., 2003), and detailed microanalysis of the core-rim transition in metamorphic zircon has demonstrated an extremely low diffusivity of O (Bowman et al., 2011; Page et al., 2007; Valley, 2003). Experimental data on the diffusivity of O in zircon (Cherniak and Watson, 2003) do indicate that O diffusion is much enhanced by the presence of a fluid phase, and under certain conditions may be a geologically significant process, but no such example has been clearly documented in nature.

Metamictization of the zircon structure by accumulated damage from alpha-decay has been described by Murakami et al. (1991) as a three-stage process. Stage I is dominated by accumulation of isolated point defects. As long as the long-term ambient temperature stays above ca. 150-300°C these will anneal over time (Davis and Krogh, 2001; Moser et al., 2011; Pidgeon, 2014). Stage II is characterized by crystals with point defects and amorphous regions which gradually become more interconnected, while in Stage III most of the material is amorphous. For zircon which reaches Stage II the potential for O isotope exchange is significantly enhanced, though such zircon may subsequently be annealed by recrystallization during metamorphism (e.g. Pidgeon, 2014).

A standard method for characterization of the origin, evolution and alteration of zircon is the study of internal textures as revealed by CL and BSE imaging. Oscillatory zoning is a diagnostic feature of crystal growth in a magma (e.g. Cavosie et al., 2006), even though it has been observed in zircon from certain high-pressure metamorphic rocks (Corfu et al., 2003) no non-magmatic mechanism has been demonstrated to produce oscillatory zoning (Cavosie et al., 2004; Hoskin and Black, 2000). It may therefore be used to distinguish magmatic zircon from non-magmatic. Zoning in metamorphic, recrystallized or hydrothermal zircon, in contrast, is generally poorly-defined and irregular (Cavosie et al., 2004; Corfu et al., 2003). In granulite facies rocks zircon zoning in metamorphic zircon tends to be characterized by chaotic CL textures, and it is not uncommon to find whole zircon crystals or large domains of zircon that are more or less homogeneous when examined by common imaging techniques (e.g. Corfu et al., 2003).

4.2. $\delta^{18}\text{O}$ systematics of Odesa zircons

In the Odesa quarry profile (Fig. 2A), $\delta^{18}\text{O}$ in zircon from the quartzose rock with its enclosed garnet-biotite band is consistently higher than in the surrounding rocks, or in Archean rocks in general. The bulk aliquots of pure quartz separated from the quartzose rock and from enderbite sample 06-BG38 have yielded a $\delta^{18}\text{O}$ of 9.8 ‰ for the former, while $\delta^{18}\text{O}$ for quartz from the enderbite is 7.4 ‰. For zircon and quartz in isotopic equilibrium $\delta^{18}\text{O}$ is higher in quartz than in zircon, a difference which decreases with increasing temperatures. Depending on the detailed conditions, equilibrium temperatures of 500°C and 900°C can be estimated to correspond to $\delta^{18}\text{O}$ differences between quartz and zircon of ca. 4 and 2 ‰ respectively (Valley et al., 2003). The average difference between zircon and the bulk quartz separates presented here is smaller than that, ca. 1.5 ‰ for the enderbite and even less for the quartzose rock. However, in a metasedimentary rock, equilibrium conditions between minerals are

unexpected, and since quartz is relatively susceptible to O exchange during metamorphism, any pre-metamorphic equilibrium is unlikely to have been preserved during the high metamorphic reworking of the Odesa quarry rocks. The much higher closure temperature for O diffusion in zircon than in quartz also suggests that any isotopic equilibrium between these two minerals is unlikely to have been preserved during the retrograde phase of metamorphic reworking, in particular if this took place in the presence of a fluid phase. In summary, it is difficult to use the relation between $\delta^{18}\text{O}$ in quartz and zircon for any more detailed interpretation. The presented results do however indicate that the high $\delta^{18}\text{O}$ in zircon from the quartzose rock not is unique to the zircons, but reflects a different O isotope regime compared to that in surrounding rocks.

All rims and most cores in zircon from the quartzose rock, and all zircons from the garnet-biotite band, have similar high $\delta^{18}\text{O}$ compositions, and most crystals which have been subjected to multiple analyses do not show any systematic difference in $\delta^{18}\text{O}$ between the cores and rims. This indicates either that the cores and the younger rims have formed in similar high $\delta^{18}\text{O}$ environments, or that the primary $\delta^{18}\text{O}$ in the cores has been modified. If the O signature in the cores is secondary, the isotopic modification has approached or reached completion in most crystals. The two crystals UR82/6-52 and UR82/6-41 with lower and variable $\delta^{18}\text{O}$ values in the cores compared to the rims, the single spots in crystals UR82/6-35 and C10-U1 and other cores with lower $\delta^{18}\text{O}$ may then represent incipient or incomplete O isotopemodification. CL images of zircon cores from the quartzose rock show a wide variety of internal textures (Fig. 3), reflecting the polymetamorphic evolution of the rock and possibly also different primary sources for the zircon cores. We find no systematic correlation between texture and O isotope composition, cores with $\delta^{18}\text{O} > 8$ display magmatic-style oscillatory (e.g. Fig. 3F, K, T) and sector (Fig. 3A) zoning, as well as more irregular textures

(e.g. 3G, L, N). The few analyzed cores with lower $\delta^{18}\text{O}$ also display variable textures (e.g. Fig. 3C, I).

The degree of metamictization due to radiation damage is a function of U, Th concentration and time. For the quartzose rock zircon cores discussed here the Murakami radiation damage stage (Murakami et al., 1991; Pidgeon, 2014) at a given time for individual crystals is a direct function of the U concentration. Assuming a primary age of 3.8 Ga, at 2.7 Ga most of the cores were still in stage I while cores with 230-500 ppm U were in stage II and those few with >500 ppm U were in stage III (Table 1). The minority of zircons cores which have $\delta^{18}\text{O} < 8$ were predominantly in Stage I, but several other low-U zircon cores have $\delta^{18}\text{O} > 9$. We see no systematic correlation between estimated radiation damage at 2.7 Ga and O isotope composition (Fig. 7C). However, most natural zircon is heterogeneous and both the concentrations of U and Th and the structural damage caused by α -decay may vary on a smaller scale, for example between thin bands in oscillatory zoned crystals. It cannot be excluded that the spots sampled by the primary beam of the ion microprobe include sub- μm , U, Th-rich zones with strong radiation damage which may be petrographically unobservable (Hoskin and Black, 2000; Palenik et al., 2003).

Taken together, the relations described above lead us to suggest that the O isotope composition of zircon cores from the quartzose rock has been modified by a process which appears to have been independent of the crystallinity, or metamict state, of the zircon, has not erased primary magmatic-style zircon textures visible in CL, and has caused only limited disturbance of both the Hf isotope composition and the U-Pb system in zircon cores.

4.3. O diffusion as a potentially significant process in Odesa zircons

The observations and relations between different isotope systems in zircon from the Odesa quartzose rock summarized in the previous section are in accordance with the experimental results on diffusivity of O in zircon in the presence of a fluid phase by Cherniak and Watson (2003). While not in conflict with the evidence for preservation of O isotope signatures in high grade metamorphic zircon, these experimental results indicate that O exchange by diffusion may be an important process under hydrothermal conditions. As an example, at 700°C and in the presence of a fluid phase the O isotopic composition in the center of a 100 µm zircon crystal would be modified by diffusion in less than 1 Ma (Figure 16 in Cherniak and Watson, 2003). The diffusivity is strongly temperature dependent, at a more extreme metamorphic temperature of 900°C modification would take place in less than 10⁴ years while at 500°C the O composition would be retained for more than 10⁸ years (Cherniak and Watson, 2003). In an assessment of the potential of volume diffusion to modify isotopic compositions, the possible occurrence of sub-µm, U, Th-rich zones with strong radiation damage (Hoskin and Black, 2000; Palenik et al., 2003) should also be kept in mind. Such zones may reduce the actual volumes which need to be modified by volume diffusion compared to the nominal size of the textures observable by e.g. CL imaging.

Cherniak and Watson (2003) also demonstrate that the diffusivity in zircon is higher for O than for Pb, allowing for partial retention of the Pb isotopic memory in zircon crystals with potentially modified O isotopes, and that the diffusion rates of the middle REE, the predominant activators of CL in zircon, are considerably slower than for oxygen. This suggests that primary zonation patterns under certain conditions may also be preserved in zircon with modified O.

The experimental results by Cherniak and Watson (2003) have been challenged by several other studies based on investigations of natural zircon. Based on tests on unrecrystallized metamorphosed igneous zircons and metamorphic zircons, Bowman et al. (2011) concluded that fast diffusion of oxygen in zircon may, in nature, require the presence of a hydrous fluid rather than a threshold value of $f(\text{H}_2\text{O})$ as suggested by Cherniak and Watson (2003). If so, this does still not preclude fast diffusion under wet conditions as a geologically significant process but does constrain the possible environments in which it may take place. In the present case, any alteration of zircon cores in the Odesa quartzose rock under hydrothermal conditions must have preceded the formation of the zircon rims, which is interpreted to have taken place under fluid-absent high grade metamorphic conditions.

4.4 A possible scenario for evolution of zircon in the Odesa quartzose rock

One possible scenario which can accommodate the results presented for the quartzose rock and the enclosed garnet-biotite band from the Odesa quarry is that these rocks represent a zone which has been pervasively penetrated by high $\delta^{18}\text{O}$ fluids, either before or during the prograde stage of the ca. 2.7-2.8 Ga metamorphic episode that ultimately resulted in granulite facies conditions. Some support for a pre-3 Ga age of such a hypothetical hydrothermal event can be found in the Hf isotopic compositions of zircon cores. Cores with the oldest Hf crustal provenance ages, which constitute the lower right side margin of the main Hf array in Fig. 5, consistently have $^{207}\text{Pb}/^{206}\text{Pb}$ ages older than ca. 3.2 Ga, while the group of cores with younger Hf provenance ages than those defining the main array all have $^{207}\text{Pb}/^{206}\text{Pb}$ ages younger than that (Fig. 5). This may be interpreted to indicate exchange of Hf between zircon and ambient rock at about that time. Since a large fraction of the Hf in the rock, but almost no Lu resides in zircon, the $^{176}\text{Hf}/^{177}\text{Hf}$ in the rock outside zircon evolves towards higher values relatively rapidly, and Hf exchange with the ambient rock after a few hundreds of millions of

years may result in a substantial increase of the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio in zircon. A few zircon cores are also close to concordant at ca. 3.0-3.2 Ga (Fig. 4A).

During the 2.7-2.8 Ga metamorphic episode rims formed on older zircon crystals, and new zircon crystallized along with other minerals in narrow zones, which are today represented by the garnet-biotite bands. The higher U concentrations in the rims than in the cores indicate that these have not formed by solid state recrystallization of the cores but during at least partly open system conditions relative to the ambient quartz-dominated matrix. Solid state recrystallization would rather have resulted in CL-brighter rims with U-concentrations similar to, or lower than those in the cores. The rims may represent new zircon growth, or have formed by dissolution-reprecipitation in the presence of a fluid phase (Geisler et al., 2007). Their generally transparent, more or less structure-less appearance (Fig. 8) indicates that the rims have not formed during hydrothermal conditions (Grimes et al., 2009; Hoskin, 2005), and the CL images in Fig. 3 indicate that there was more than one episode of rim growth.

The quartzose rock may be a product of strong metasomatic alteration. The primary rock may have been similar to the ambient igneous rocks which now appear as enderbite, a metasedimentary rock, or some other primary lithology which has lost much of its major elements, and the zircon cores would then be remnants from the primary mineralogy. Once the secondary quartzose rock had formed, this lithology may have served as an impermeable matrix which shielded its constituent zircon from later disturbance(s) during subsequent metamorphic overprints, including ca. 2.0 Ga granulite facies metamorphism, thus preserving the U-Pb isotope record of its earliest history better than in other rocks from the investigated section.

4.5 Comparison with Hadean and other Eoarchaean zircon populations

While much of the results and discussion presented here for zircon cores from the Odesa quartzose rock may be relevant for the interpretation of early Archaean and Hadean zircon in general, a most noticeable difference is the CL-dark rims which surround all zircon cores from the quartzose rock and date to the c. 2.7-2.8 Ga metamorphic event. Any analogy with Hadean zircons, which do not have such rims, requires an explanation of this difference. One obvious explanation would be that the Hadean zircon population is detrital and largely extremely rounded, and that the rims were lost during rounding. It may also be noted that the scenario suggested in the previous section for evolution of the Odesa quartzose rock allows the O isotope composition of the zircon cores to have been modified before formation of the CL-dark rims.

5. CONCLUSIONS

Zircon from a strongly recrystallized, quartz dominated rock, which occurs in a high grade metamorphic, enderbite-dominated segment of the Dniester-Bug Domain, Ukrainian Shield, typically consist of cores overgrown by transparent, structure-less rims. The cores display a variety of internal textures, including magmatic-style oscillatory zonation, and yield U-Pb ages up to 3.8 Ga which are interpreted to reflect the primary crystallization age of at least some of these. Younger, concordant and close to concordant core ages down to ca. 3.0 Ga may also reflect primary crystallization ages, but may also be partly the result of ancient Pb loss. The rims, as well as zircon separated from adjacent rocks, give U-Pb ages of 2.6-2.8 and ca. 2.0 Ga which reflect previously identified episodes of high grade metamorphism. Hf isotope signatures indicate that the zircons are derived from crust with provenance ages of ca. 3.6-3.8 Ga. These Hf and U-Pb results are similar to those presented by Claesson et al. (2015)

for zircon from Dniester-Bug enderbite, but with the Hf and U-Pb systems in zircon cores more disturbed than in the enderbite zircon.

The majority of analyzed zircon from the quartzose rock have heavier O isotope compositions than are commonly found in Archaean igneous rocks, with $\delta^{18}\text{O}$ values of 8-10‰. O isotope compositions are similar in cores and rims. Zircon from a thin garnet-biotite dominated band enclosed in the quartzose rock also has similar heavy O isotopic compositions, while zircon from adjacent rocks representing surrounding lithologies have lower $\delta^{18}\text{O}$ <7‰ which is within the normal range for igneous zircon from Archean crust. If the quartzose rock was originally a clastic sediment and the O isotopic composition of the zircon cores is primary, the sources for the detrital zircons must have been dominated by early Archean rocks with high $\delta^{18}\text{O}$ isotopic compositions which appear to have been very uncommon in the Archaean. We suggest an alternative interpretation in which the O isotope signatures may not be primary, but instead represent secondary O isotope exchange under high grade metamorphic conditions in the presence of a fluid phase. The possible existence of zircon with preserved magmatic-style oscillatory zonation but modified O isotopic composition suggests that caution is required in the interpretation of O isotope data, especially for zircon from clastic metasedimentary rocks where the crystals occur out of their primary context.

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FIGURE CAPTIONS

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 Eoarchaeon 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 Fig 1B 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.

Fig. 2. Investigated section in the Odesa quarry. A) Schematic vertical section showing the wall in the Odesa quarry with locations of the quartzose rock and other investigated rocks in the section, from pyroxenite in the NW across the quartz-rich zone to garnet-bearing enderbite in the SE. The garnet-biotite bands, which occur together with the quartzose rock and typically are a few cm wide, are represented by two oversized bands. B) Photograph of the quartzose rock with garnet-biotite bands. One isoclinally folded band is shown in the center of the picture, and another can be seen in the upper left corner. For clarity, the contours of the bands have been filled in. The diameter of the coin is 2.9 cm.

Fig. 3. Cathodoluminescence (CL) photomicrographs of selected zircon crystals from the two quartzose rock samples C10-U1 and UR82/6, showing CL-dark rims on cores displaying various internal textures. The ca. 50 μm dark circular structures in the photomicrographs are laser ablation pits after Hf isotope analysis. Spots analyzed for U-Pb and O in these crystals are shown as large and small ellipses, respectively, with the exception for Fig. 3B, F, G, L, M, and N. U-Pb and O spots in these crystals in these panels are shown in Fig. 8, while the small ellipses on the CL images shown here mark the locations of spots analyzed for OH in these six crystals. As can be seen, several of the U-Pb and O analyzed spots were located in zircon which was consumed during subsequent laser ablation Hf analysis. A=UR82/6-34, B=UR82/6-35 (also shown in Fig. 8A), C=UR82/6-41, D=UR82/6-44, E=UR82/6-48,

F=UR82/6-49 (also shown in Fig. 8B), G=UR82/6-52 (also shown in 8C), H=UR82/6-58, I=UR82/6-62, K=UR82/6-63, L=UR82/6-65 (also shown in Fig. 8D), M=C10-U1-7 (also shown in Fig. 8E), N=C10-U1-8 (also shown in Fig. 8F), O=C10-U1-11, P=C10-U1-15, R=C10-U1-21, S=C10-U1-32, T=C10-U1-33, U=C10-U1-34. In most crystals, a very CL-dark inner rim and a lighter outer rim can be seen, in some crystals (e.g. 3D, H) separated by a CL-brighter zone, and a thin CL-bright outermost rim is seen in some crystals (e.g. 3M, N, T, U). Pronounced alteration textures are seen in some of the rims (e.g. outer rim in 3B and 3C, E, K, P), while others rims are more or less structure-less and apparently well-crystallized (e.g. inner rims in 3B and 3G, 3M, 3U). Some cores display oscillatory growth zoning (e.g. 3B, F, I, K, P, T) or sector zoning (3A), while others display more diffuse (e.g. 3C, L) or chaotic (e.g. 3D, G) zoning patterns.

Fig. 4. Concordia diagrams (Tera-Wasserburg space) showing U-Pb data for zircon separated from rocks in the investigated section, Odesa quarry. A) Zircon cores and rims from the two quartzose rock samples C10-U1 and UR82/6. B) Zircon from a garnet-biotite band (sample C13-2) and other analyzed samples in the section (C13-1, C13-3A and B, C13-5)

Fig. 5. ϵ_{Hf} -time diagram for the two quartzose rock samples C10-U1 and UR82/6, illustrating the evolution of analyzed zircon and their host rock, isotopic compositions of mantle sources and model crustal residence ages. Ages used for individual data points are the $^{207}\text{Pb}/^{206}\text{Pb}$ ages. Zircon cores and rims, and data points which are > and < 5% discordant are shown separately. The grey line shows the effect of Pb loss on 3.8 Ga old zircon, while the green band shows the evolution of 3.8 Ga old crust with a $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.015, which is intermediate between typical felsic and mafic crust with $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of ca. 0.010 and 0.020 respectively.

791

792 Fig. 6. $\delta^{18}\text{O} - {}^{207}\text{Pb}/{}^{206}\text{Pb}$ age diagram for zircon with <5% discordant U-Pb ages from the

793 Odesa quarry. In addition to samples from the section including the quartzose rock (Fig. 2A),

794 results for zircon from the previously dated, ca. 3.8 Ga old (Claesson et al., 2015) enderbite

795 sample 06-BG38 are also shown. The light blue field shows the range of $\delta^{18}\text{O}$ values in

796 unaltered zircon from igneous Archean and Proterozoic crustal rocks from Valley et al.

797 (2005).

798

799 Fig.7. Correlation diagrams for U-Pb and O data in zircon cores and rims from the quartzose

800 rock samples UR82/6 and C10-U1. A) U concentration - ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ age for samples with

801 <5% discordant age. U concentrations in the rims are generally higher than in the cores.

802 B) $\delta^{18}\text{O}$ – discordancy. $\delta^{18}\text{O}$ does not vary systematically with U-Pb discordancy.

803 C) $\delta^{18}\text{O}$ - U concentration. Most crystals with $\delta^{18}\text{O} < 8$ are relatively low in U, otherwise $\delta^{18}\text{O}$

804 does not vary systematically with U concentration.

805

806 Fig. 8. CL- and optical images, ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ ages and O isotopic compositions for zircon

807 crystals from the quartzose rock samples UR82/6 and C10-U1 displaying well-developed

808 core-rim textures and different zonation patterns in the cores. U-Pb analyzed spots are shown

809 as ca. 20x25 μm ellipses with dashed contours. O isotopic compositions have been analyzed

810 in ca. 10 μm spots, shown as ellipses with solid contours, and along profiles using a small, ca.

811 4 μm primary beam. Locations of small beam spots are shown as filled black or white circles,

812 and corresponding O isotopic compositions are shown in diagrams directly under the zircon

813 images. The ca. 50 μm dark circular structures in the photomicrographs are laser ablation pits

814 after Hf isotope analysis. A) Crystal UR82/6-35. The ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ ages in the core are 18%

815 and -3% discordant, and the age in the rim is concordant. B) Crystal UR82/-49. The $\delta^{18}\text{O}$

values in the small spot profile (Table 1) are shown from the right to the left in the diagram. The $^{207}\text{Pb}/^{206}\text{Pb}$ age is 13% discordant. C) Crystal UR82/6-52. The $^{207}\text{Pb}/^{206}\text{Pb}$ age is 2% discordant. D) Crystal UR82/6-65. The $^{207}\text{Pb}/^{206}\text{Pb}$ age in the core is 5% discordant. E) Crystal C10-U1-7. The $^{207}\text{Pb}/^{206}\text{Pb}$ ages in the core are 6 and -3% discordant. F) Crystal C10-U1-8. The $^{207}\text{Pb}/^{206}\text{Pb}$ ages in the core and in the rim are 2 and 5% discordant respectively.

Figures are in separate files

TABLE (for Inline Supplementary Material)

Table S1. U-Pb, Lu-Hf and O isotope data for analyzed zircon and quartz separates from the Odesa quarry.

Table S1 is in a separate file

Figure 1

Figure 2

Fig. 2
1.5 columns wide

200 μm

Figure 4

Fig. 4
2 columns wide

Figure 5

Fig. 5

Figure 6

Fig. 6
1.5 columns wide

1 column wide

Zircon from quartzose rock,
Odesa quarry

Figure 8

Fig. 8
1.5 columns wide

Supplementary material for on-line publication

[Click here to download Supplementary material for on-line publication: Claesson O in zircon Odesa Table S1 revised 151020](#)