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CRYSTAL CHEMISTRY OF ZIRCON CRYSTALS FROM TWO FELSIC DYKES OF THE MALOYANISOL DYKE SWARM (AZOV REGION, UKRAINE): EVIDENCE OF A COMPLEX EMPLACEMENT HISTORY?

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Zircon crystals from two felsic dykes belonging to the Maloyanisol dyke swarm (Eastern Azov region, Ukraine) were investigated by EMPA, XRD, FTIR and LA-ICP-MS methods. The analytical results reveal the characteristic features of the crystal chemistry and structure of zircons from both dykes, and show heterogeneity of zircon populations. The identified variations in chemical composition and local amorphization explain the different U-Pb ages of studied zircons and reflect the complex history of magma evolution during the formation of the Maloyanisol dyke swarm.

Introduction. The Maloyanisol dyke swarm extends in the NW direction for some 40 km from the city of Mariupol. Majrity of the dykes are presented by ultramafic to mafic lamprophyres and dolerites; felsic dykes are less common. The latter are the youngest, as they cut through mafic and lamprophyric dykes. Previous results of the U-Pb isotope dating of zircons from two macroscopically very similar fine-grained trachyrhyolite dykes do not give a clear certainty about their age but show definite difference between them. For the dyke AZ12, the concordia age is 1729 ± 16 Ma, whereas data on the dyke AZ16 are reversely discordant with only one concordant result. The $^{206}Pb/^{238}U$ weighted average age is 1751 ± 15 Ma, whereas the $^{207}Pb/^{235}U$ average age is 1724 ± 12 Ma.

We conducted a comprehensive mineralogical study of zircons from both dykes to understand (1) the crystallochemical reasons for these discrepancies and (2) the relationship between the crystallization history of zircons and the evolution of their parent melts.

Samples & Methods. Zircon crystals were taken from two trachyrhyolite dykes represented by porphyritic rocks with phenocrysts of quartz and microcline. Rocks are made of (vol. %) K-Na feldspar – 55-60, quartz – 30-35, biotite – 2-3, magnetite – 1-3; accessory minerals are muscovite, zircon, fluorite, titanite, rutile, apatite, monazite, allanite, pyrite and ilmenite.

Four to six zircon crystals from each dyke were used for EMPA, LA-ICP-MS and FTIR spectroscopic analyses. For X-ray diffraction analysis, 1 g of zircon powder was prepared from the corresponding monofractions.

Micro-XRD measurements were carried out using the Rigaku SmartLab X-ray diffractometer system equipped with a high-flux 9kW rotating Cu anode and 2D-detector. *EMPA* was performed using a JEOL Hyperprobe JXA-8530F equipped with a thermal field emission gun and five spectrometers. *LA-ICP* mass spectrometry measurements were done with Aglient 8900 ICP-QQQ system connected with Teledyne Analyte Excite. Polarized *FTIR* spectra of single crystals were obtained in the range of 1000–6000 cm^{-1} on Bruker IFS-66 (Berlin) and Nicolet 6700 (Kyiv) instruments equipped with IR microscopes. All preparation work and measurements, except of the use of Nicolet 6700, were carried out at TU Berlin.

Results & Discussion. Zircon from sample AZ12 is represented by transparent colorless prismatic crystals about 0.1×0.25 mm in size with poorly developed pyramidal terminations. BSE and CL images show faint zoning with no inherited cores (Fig. 1). Zircons from sample AZ16 form larger (0.2-0.3 mm) prismatic to short-prismatic crystals with rarely developed pyramidal faces. CL imaging displays fine oscillatory magmatic zonation.

On BSE images zircons from AZ-12 look mostly homogeneous with rare zoning and many amoebas-like inclusions filled in with heterogeneous porous partly crystallized material of captured magma. KFS, quartz, albite, drops of Fe-enriched glass and small crystals of Fe-Ti oxide were detected there using EDX.

Oscillatory zoning is clearly visible in AZ16 zircons, and porous metamict areas are present in the cores of some crystals (Fig. 1). Three types of inclusions were found in this sample: (1) larger amoeba-like inclusions containing quartz in a two-phase (Si-Al-Fe and F-C-REE) glassy matrix, indicating liquation in a Fe- and REE-enriched silicate melt; 2) smaller oval "drops" of porous material, similar in composition to Na-K feldspar (Na:K:Ca≈7:2:0.3) with small (<1 μm) apatite grains; and (3) oval KFS inclusions. The latter were found in a crystal with a metamict porous core. We consider the first two types as evidence of the high temperature of the magma and its rapid cooling.

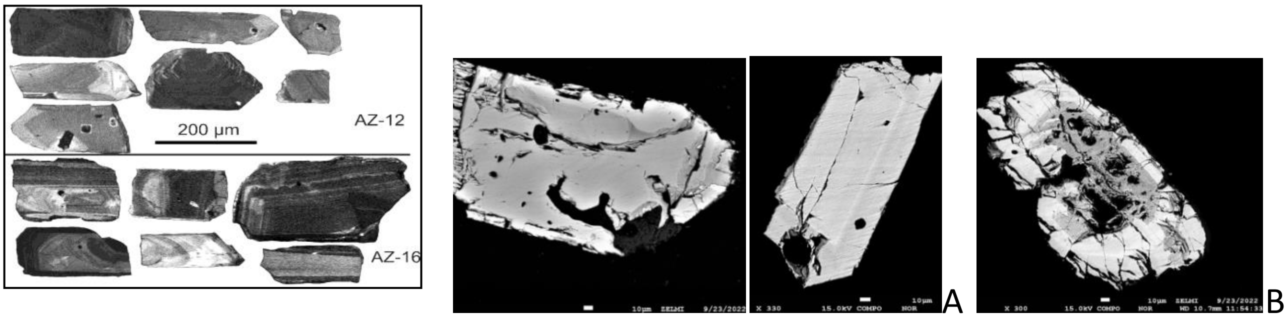

Figure 1. CL images (left) and BSE micrographs (right) of zircons from trachyrhyolite dykes. A – AZ12, B – AZ16.

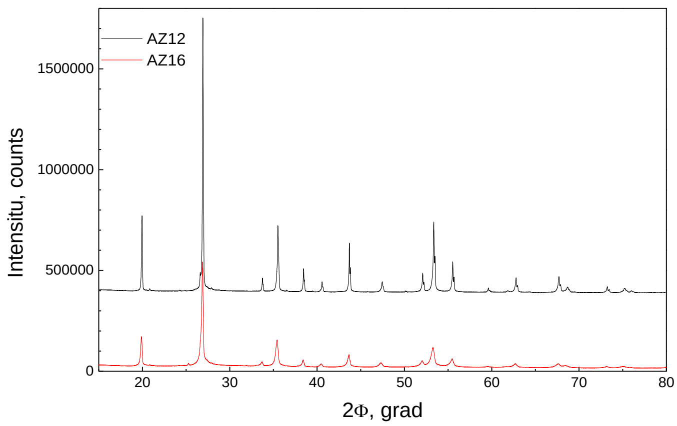

Figure 2. Diffractograms of the two zircons.

XRD data reveal definite differences in the crystal structures of zircons from the two dykes. The diffractograms show a strong decrease in peaks' intensity along with an increase of their width and shift to lower 2θ in AZ16 comparing to AZ12 (Fig. 2). All these features are consistent with significant amorphization of AZ16 zircons, whereas in the sample AZ12 zircon structure is much better preserved.

Using the obtained crystal cell parameters (Table) and published data [1], we roughly estimated the total radiation dosages obtained by the zircons studied as $0{,}09 \cdot 10^{16}$ α/mg and $0{,}170 \cdot 10^{16}$ α/mg for AZ12 and AZ16, respectively.

IR spectroscopy methods were used to assess the structural types and content of OHn defects in zircon crystals, as well as the degree of their metamictization.

Table. Unit cell parameters of the studied zircons

AZ12		AZ16	
a	6.617	***a***	6.627
c	5.997	***c***	6.026
V	262.586	V	264.613

The broadening of the second overtone bands of Si–O vibrations in 1300–2100 cm^{-1} region (Fig. 3) and poor resolution of these complex envelopes indicates decrease of crystallinity. The better differentiation of the narrow bands in the spectra of zircons from AZ12 indicates a higher degree of their crystallinity comparing to significantly metamict zircons from AZ16. This conclusion is confirmed by the cell parameters data (Table) and the received radiation doses, calculated for zircons from these dykes.

In the 3000–3800 cm^{-1} spectral range the broad, intense absorption bands, occasionally with superimposed weaker narrow polarized peaks at 3600–3700 cm^{-1} (O-H stretching vibrations of the bonds in H_2O and OH groups, respectively; Fig. 3), as well as the band ~ 1600 cm^{-1} (H_2O bend vibrations) are observed. These bands indicate presence of structurally bound H_2O molecules, probably, water of inclusions, and in smaller quantities – OH groups in the zircon structure. Such assignment is confirmed by the weak two-phonon absorption bands of both water molecules (~5200 cm^{-1}) and OH groups (~4420 cm^{-1}) [1, 2] that are fixed in spectra of many crystals from dyke AZ16. The water content is rather variable, especially in different grains from dyke AZ16. More metamict crystals have a higher content of OH_n defects.

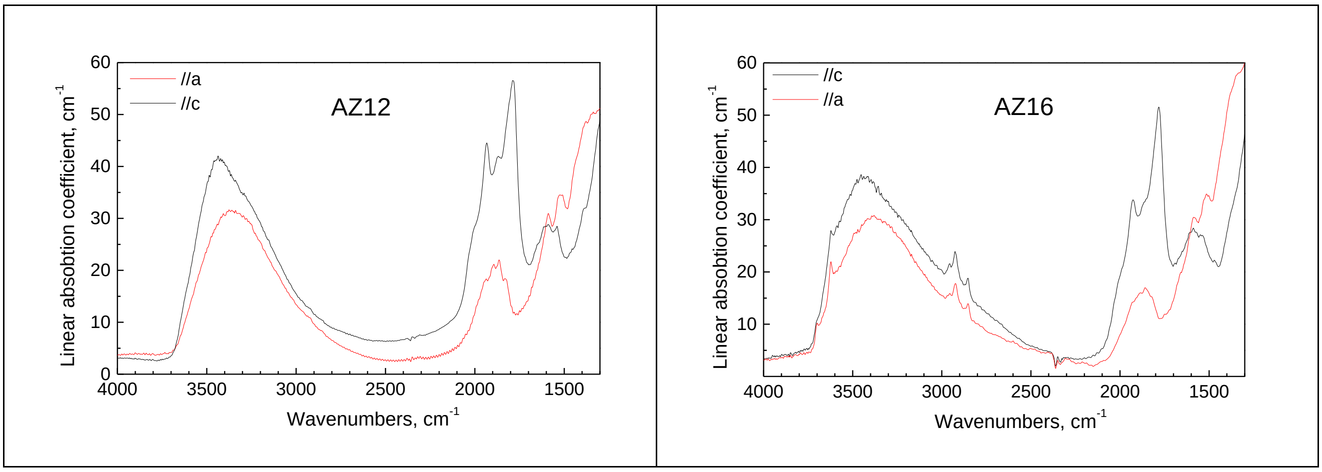

Figure 3. IR spectra of different zircon crystals from dykes AZ12 (left) and AZ16 (right) in 4000 – 1300 cm^{-1} range in polarized light.

EMPA data show clear differences in the chemical composition of zircons from different dykes, as well as between their crystalline and amorphous parts. Zircons from AZ16 contain less Zr and significantly more Hf, Y, and Nb compared to zircons from

AZ12. The metamict cores of AZ16 crystals are strongly depleted in Zr and Si and enriched in Y, Ca, F, and Fe. Hafnium, unlike Zr, shows a slight tendency to accumulate in altered cores (Fig. 4, 5), its concentration is moderate in AZ12 (0.77-0.95 wt.%) and high in AZ16, ranging from 1.33 up to 2.2 wt.%. , which corresponds to the felsic composition of the dykes. Yttrium concentrations are highly variable, especially in AZ16, and show a general correlation with Hf (Fig. 4).

Most of the studied grains from sample AZ12 contain moderate amounts of Th and U (60-200 ppm), while in AZ16 Th reaches 400 ppm and U - 700 ppm (Fig. 5). Due to the clear correlation between these elements, the Th/U ratio in both samples varies slightly - from 0.8 to 1.1.

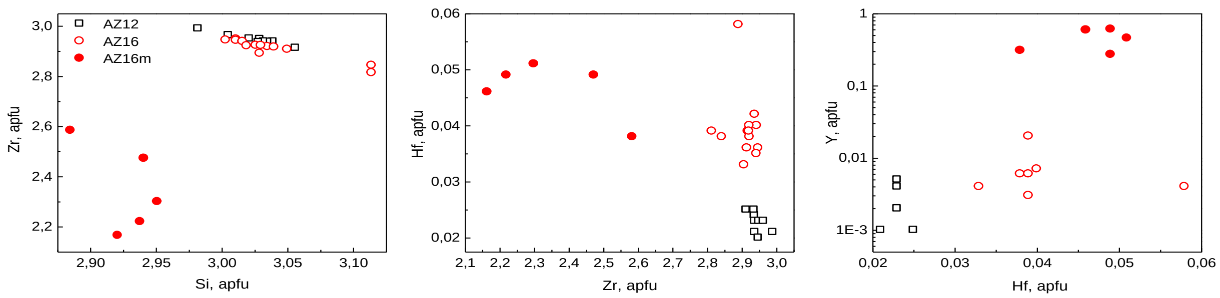

Figure 4. Variations of selected cations in zircons from the dykes AZ12 and AZ16. EMPA data.

Niobium is positively correlated with Ta, forming an continuous sequence of points in Figure 5. Higher concentrations (up to Ta 2-33 ppm, Nb 16-240 ppm) and greater variability are observed in AZ16 zircons.

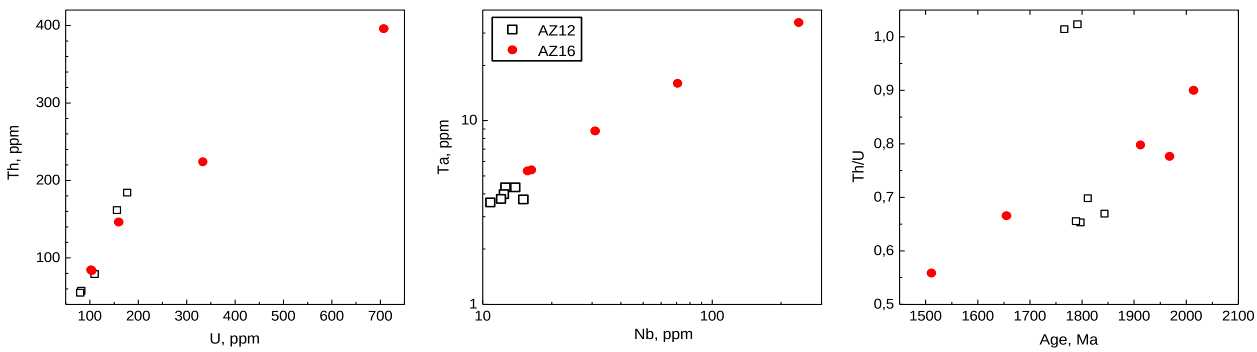

Figure 5. Correlations between U and Th, Nb and Ta, and between Th/U ratio and U-Pb age of zircons studied? According to LA-ICP-MS data.

Zircons from both dykes have typical of igneous rocks chondrite-normalized patterns, with a gradual increase from light towards heavy REE (Fig. 6), that resemble slightly altered zircons from Azov deposit [3]. Intensities of Ce and Eu anomalies differ in two samples and even in different crystals from the same sample (Fig. 5). These differences in REE contents are consistent with Th/U ratio and U-Pb age measured in different crystals (Fig. 4).

Combining all results and excluding amorphous and recrystallized areas, we can assume at least two generations of zircon in the AZ16 dyke: the older, 1900-2000 Ma with very pronounced Ce and Eu anomalies, and much younger, 1510-1660 Ma, characterized by less differentiated REE distribution and lower Th, Nb and Ta concentrations. Anomalously young age of the latter can be caused by the loss of radiogenic Pb in altered areas during resorption-precipitation cycles.

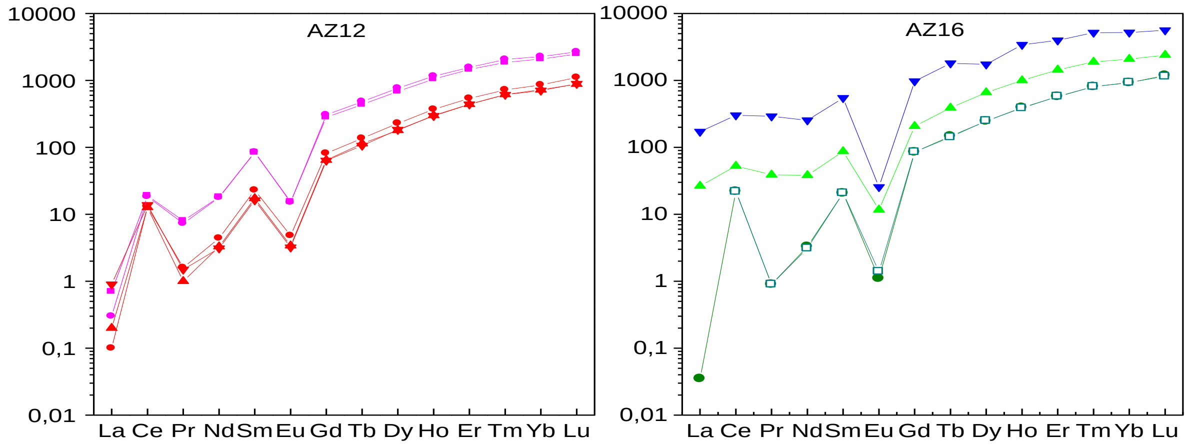

Figure 6. Chondrite-normalized REE patterns in zircons from the dykes studied.

Conclusions

Zircons from two macroscopically similar felsic dykes of Maloyanisol dyke swarm reveal clear differences in their crystallinity, water abundance, main and trace elements compositions, as well as in inclusions and U-Pb age.

Metamictization is characteristic for some crystals from sample AZ16. It follows by loss of Zr and enrichment in nonformula elements, mostly Ca, Y, F, Al, REE.

Strong variations in REE, Nb, Hf, Th contents in different crystals of zircons from the AZ16 dyke and different types of melt inclusions may be caused by capture of the zircons from host rocks and continuous crystallization during injection of new portions of melt from co-genetic magma batches during the melt uplift.

References

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