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Oxygen isotope composition of quartz from the Koshava tektite, NW Bulgaria

Изотопен състав на кислорода в кварца на тектита Кошава, СЗ България

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Introduction

Koshava tektite is found at the depth of 290 m in the Miocene gypsum bed of the mine of the same name (Yanev et al., 2015). This is a gray-black tabular boulder, 60×80 cm and 20–30 cm thick, with fine layered structure. The compact layers, several mm thick, are built by irregular rosette-like aggregates (size up to 1 mm) of α-quartz (94.45 wt%). The size of the single crystals is up to 0.5×0.25 mm. Very often a "grille" of micronic chalcedony droplets can be observed in the rosette center. A set of planar deformation features (PDF) within some quartz crystal are found. The interstitions are occupied by amorphous brown-black mass (5.55 wt%), containing essentially C (~70 wt%), H, N, S and some Si, Mg, Ca, Na, K, and Cl. This mass is attribute to the disordered polyaromatic organic matter (kerogen-like) according to its FTIR patterns (Zotov in: Yanev et al., 2016a). The fine layers, 5–10 μm thick, are partially or totally melted showing grille- or tree-like forms of glass drops replaced by chalcedony. Here the organic matter is presented as worm-like forms. Numerous very fine (<5 μm) crystals of native Fe, silicides, mainly of Fe (hapkeite is proved by RDA and EMPA), also of Fe-Ni (suessite is proved by EMPA), Fe-Zn phases, alloys (Yanev et al., 2016b) and single sphalerite are observed in the organic matter in both types of layers. The surface of the block is covered by mm thick crust with regmaglypts, actually replaced by quartz microcrystals with graphite. Highly porous lenses (10–12 x 1–2 cm) built essentially of organic matter are found under the crust. They host zonal, probably glassy globules (from 20 x 20 μm to 280 x 170 μm in size) with pure SiO_2 peripheries, inner zones containing varying proportions of SiO_2 and C. Framboidal pyrite, some greigite, moissanite, calcite, barite, oldhamite(?) and skeletal gypsum are presented in these lenses.

Two hypotheses for this rock fragment with such composition and features (PDF, strong melting phenomena, regmaglypts, presence of pyrogenic minerals and alloys) found inside the uniform gypsum layer without other sediments were proposed (Yanev et al., 2015): (1) tektite, unusually large in size, or (2) Miocene stone meteorite of new, silica-carbonaceous type. To clarify its provenance, terrestrial or extraterrestrial, the triple oxygen isotope study of the quartz was performed.

Sample preparation and isotope analysis

Oxygen isotope analysis was performed by laser fluorination technique (Sharp, 1990). The BrF_5 was used as the reagent to extract oxygen from the quartz according to reaction: $SiO_2 + BrF_5 = SiF_4 + O_2 + BrF_5$.

The analyzed sample comes from the solid part of the rock fragment. Because the organic matter that surrounded the quartz rosette can react with the bromine pentafluoride the chemical treatment of the sample was performed. The crushed sample was boiled at the concentrated H_2O_2 during 12 h. After the boiling it was leaved at the hydrogen peroxide about 48 h. This treatment allowed obtaining near clear sample with the transparent quartz grains without organic matter. Four portions from this sample, each measured ~1–1.5 mg were used for fluorination.

These samples were heated by 30 W infrared (CO_2) laser (New Wave Research, USA) at the BrF_5 atmosphere. Oxygen obtained was purified using the cryogenic traps before the mass-spectrometric measurements. The measurements were carried out relatively well-calibrated reference gas O_2 at the dual inlet manner with the mass-spectrometer DELTA plus (Thermo, Germany). The calibration of δ-values at the V-SMOW scale was performed by the measurements of NBS 28 quartz, UWG-2 garnet and San Carlos olivine (Valley et al., 1995). The accuracy of $\delta^{18}O$ and $\delta^{17}O$ values determinations was better than ±0.1‰.

Results and discussion

The isotope data are presented at the Table 1 and at the $\delta^{18}O$ vs. $\delta^{17}O$ diagram (Fig. 1). Oxygen isotope composition of quartz studied can have the terrestrial origin because all data points are grouped near the TFL (Terrestrial Fractionation Line, Sharp et al., 2018). The studied sample plots on the $\delta'^{18}O$ vs. $\Delta'^{17}O$ diagram (Fig. 2) on the field of sedimentary quartz. It is interesting that the $\delta^{18}O$ and $\delta^{17}O$ values of quartz from the Koshava tektite are very high: the $\delta^{18}O$ value varies from 28.27‰ to 29.16‰ and the $\delta^{17}O$ value – from 14.73‰ to 15.18‰. This "scatter" values can be inherited from the sediment substrate during the impact event. However, it is possible that the sharp temperature gradient during the impact could lead to this heterogeneity. Such compositions can be suit of kinetic isotope fractionation during the partial degassing of the sediment substrate during the impact event. For example, during the partial dehydration of some terrestrial and meteorite minerals, both $\delta^{18}O$ and $\delta^{17}O$ values of silicate rests are increase with the extent of the dehydration increase (Clayton, Mayeda, 2009). The data measured are slightly below than TFL.

Table 1. Oxygen isotope composition of quartz from the Koshava tektite

$\delta^{18}O$‰	$\delta^{17}O$‰	R (17/18)
29.16	15.18	0.521
28.66	14.98	0.523
28.27	14.73	0.521
28.28	14.81	0.524

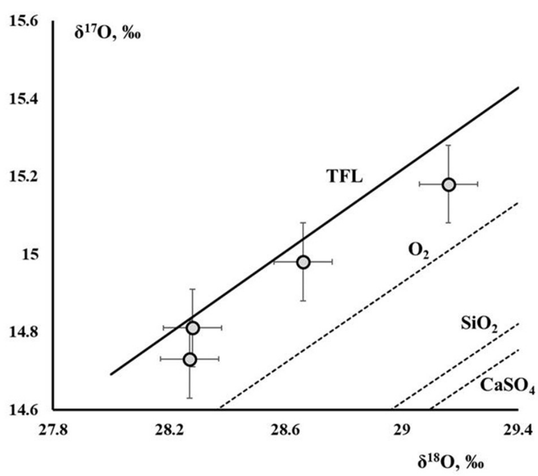

Fig. 1. Oxygen isotope composition of quartz from the Koshava tektite. The Terrestrial Fractionation Line (TFL) is drawing according to equation $\delta^{17}O=0.5266*\delta^{18}O-0.054$ (Sharp et al., 2018). The dashed lines were calculated according to equation of mass-dependent kinetic isotope fractionation (Young et al., 2002) during evaporation of O_2, SiO_2 and $CaSO_4$.

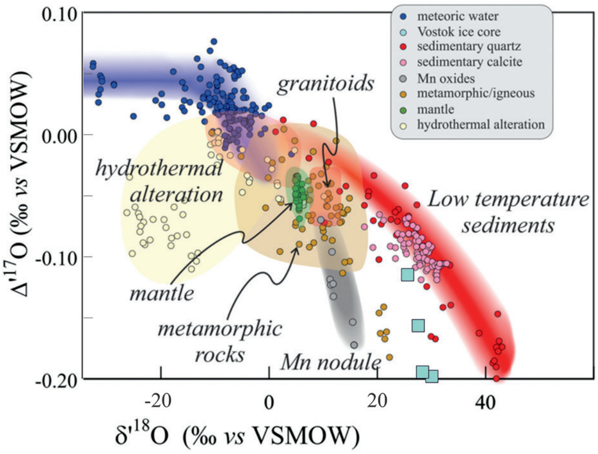

Fig. 2. $\delta'^{18}O$ vs. $\Delta'^{17}O$ diagram with characteristic fields of different terrestrial materials (according to Scharp et al., 2018) and place of the studied quartz samples of Koshava tektite (the blues squares)

According the calculation of mass-dependent kinetic isotope fractionation (Young et al., 2002) during evaporation of SiO_2, O_2 and $CaSO_4$ the data points should be moved in this direction.

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