“Organic matter” in the Koshava tektite (or meteorite), NW Bulgaria – Raman and geochemical study

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The studied rock fragment (Yanev et al., 2015) is found in the Miocene gypsum bed of the Koshava mine. This is gray-black tabular boulder (60×80 cm, 20–30 cm thick) with fine layered structure. The compact layers, some mm thick, are built by irregular rosette-like aggregates of α-quartz and other minerals (94.45 wt%). Object of this study is the so called “organic matter” – amorphous brown-black mass (5.55 wt%), which fills the interstices. The fine layers, 5–10 μm thick, are partially or totally melted, consisting of chalcedony with tree-like, grille-like and others textures. Lenses up to 10 cm long and some cm thick are observed below the cover band; they are very heterogeneous and rich in organic matter. Two possible genetic hypotheses are pointed out: (i) tektite (Earth origin) or (ii) new, silica-carbonaceous type meteorite coming from a planet with Earth type crust e.g. Mars.

**Methods.** The Raman spectra are obtained in Max Plank Institute on a polished thin section with a single grating LabRAM HR (Jobin Yvon), using 532 nm laser excitation. The chemical composition of one wall-rock sample and another from the lenses was determined using Ultimate analysis (for C and H) and Dumas method (for the N) in the Institute of Organic Chemistry, BAS (analyst R. Todorova). The other elements were analysed on 10 points of the compact layers in a polished section with JEOL 733 Superprobe SEM and microprobe OPTEC System 5000 equipped with EDS (14 kV, 1 nA) of the Geological Institute, BAS. The trace element analyses of 7 spots of the quartz and 3 of the organic matter in the same sample were carried out using a WRX Excimer 193 nm laser-ablation system attached to a Perkin-Elmer ELAN DRC-e LA-ICP-MS in the same Institute. Spot diameter was 35 μm and laser frequency – 4 Hz. The NIST SRM 610 glass is used as external standard.

**Raman microspectrometry.** The obtained spectra (Fig. 1a) of the organic matter show 2 broad bands at 1390±4 (FWHM=125±4) and 1582±1 cm⁻¹ (FWHM=47.4±1.6 cm⁻¹) called D (“disordered”) and G (“graphite”) respectively (Bussemann et al., 2007; Charon et al., 2014). Their large width permits to attribute these bands to the disordered polyaromatic organic matter (kerogen-like). The same bands are observed in many meteorites (i.e. Lin et al., 2014, and others). The position of G band, very close to 1581 cm⁻¹ (graphite pick) and the width <50 cm⁻¹ indicate an onset of graphitization (presence of some graphitic domains). The same large bands are found also on the 4-, 5- or 6-angular forms presented on the Fig. 4 of Yanev et al. (2015). However, a graphite spectrum is found in the quartz rosettes characterized by very thin G pick (Fig. 1b).
Major and trace elements composition. The organic matter between the quartz rosettes consists of (wt%): C 69.94, H 13.6, N 7.53 with S 5.0, Si 0.26, Mg 0.2, Ca 1.1, Na 0.9, K 0.68, and Cl 0.9 determined by EMPA. The S content correlates positively with Ca (r=0.83) and Cl – with Na (r=0.63), indicating the presence of oldhamite and halite respectively (confirmed by XRD – Yanev et al., 2015).

In order to elucidate the origin of the Koshava rock fragments, the trace element abundance is compared with one terrestrial object (the coals) and meteorites. The studied organic matter (Fig. 2a) is very rich in many trace elements (in ppm): firstly in Ge (1110) and Mo (32.2) (highly coalphile elements, coal affinity index >5, Ketris, Yudovich, 2009), also in B (185), Zn (36), and W (12.7) (coalphile elements, affinity index 2–5). However, other coalphile (Pb) and moderately coalphile elements (Hf, Co, Ba, Sc, Nb, Ga, LREE) have concentrations lower than world brown coal values. Indeed some coal are enriched in Ge. On the other hand, Gellert et al. (2014) report high Ge and Zn amounts in the rocks of Gale crater of Mars also. The average coal P/C ratio is 7.1E−7, while in the organic matter of the studied sample is 1E−4, close to the ratio in the Martian Tissint meteorite – 4.2E−4 (Lin et al., 2014).

The REE distribution pattern is completely different from that of the brown coals (Fig. 2b) with a limited differentiation (La/Lu=0.37): depletion of the LREE and MREE, a little enrichment of HREE with a positive Sm anomaly. Only its negative Eu anomaly corresponds to those in the coals. This pattern of the organic matter of Koshava sample, except the anomalies, resembles to some of the pyroxene-olivine meteorites i.e. Tissint, EETA 79001A and others (Balta et al., 2015), indicating similar basic-ultrabasic environment of formation. The same is confirmed by the abundance of some moderately to highly compatible elements with respect to a spinel lherzolite (according to Pearce and Parkinson), such as Yb, V, Cr, and Ni, which in the studied organic matter have higher concentrations than those in the coal.

References


