

Silicides and alloys from Koshava tektite (or meteorite), NW Bulgaria

Силициди и сплави в тектита (или метеорит) Кошава, СЗ България

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Koshava tektite/meteorite 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%) with interstitions occupied by amorphous brown-black mass (5.55 wt%), containing essentially C (ca. 70 wt%), H, N, S and some Si, Mg, Ca, Na, K, Cl (Yanev et al., this volume). The fine layers, 5–10 μ m thick, are partially or totally melted showing grille- or tree-like forms of glass drops replaced by chalcedony. Numerous very fine (<5 μ m) crystals of silicides (Fig. 1), mainly of Fe, also of Fe-Ni and Fe-Zn phases are observed in the “carbon” mass in both types of layers. Framboidal pyrite, some greigite, moissanite (determined by Vasil Arnaudov), calcite, barite and skeletal gypsum are presented in the “carbon” rich lenses of the rock fragment.

Methods. Polished sections were analyzed with JEOL 733 Superprobe SEM and microprobe OPTIC System 5000 equipped with EDS of the Geological Institute at BAS. The following Taylor’s standards are used: albite (s) for Na, corundum (s) for Al, periclase (s) for Mg, quartz (s) for Si, pyrite (n) for S, Kfs (n) for K, apatite (n) for Ca, rutile (s) for Ti, pyrolusite (n) for Mn, hematite (n) for Fe, and glass (s) for Ba. The results are influenced by the surrounded “carbon” mass due to the very small size of the analyzed crystals. X-ray study of wall-rock sample was performed with HR X’Pert diffractometer (Philips) in Max Planck Institute, equipped with a curved Ge monochromator in the primary beam and PANanalytical X’Celerator position sensitive detector, using Cu K α 1 radiation.

Fe silicides. Only 4 stable phases are known in the Fe-rich half of the Fe-Si phase diagram (Kubaschewski, 1982; Lacaze, Sundman, 1991 and others): ordered

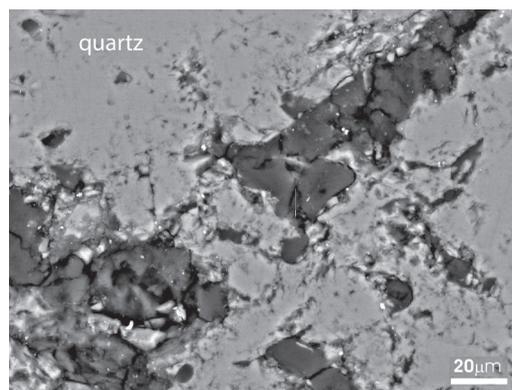


Fig. 1. BSE image of the “carbon” mass (black) with Fe silicide micronic crystals (white spots) between the quartz rosettes (grey)

bcc B_2 (or α_2) and DO_3 (or α_1), β (Fe_2Si), ϵ ($FeSi$), the last three melt congruently with eutectic points at 1200 and 1203 °C. These phases correspond to the following minerals, all found in the studied sample (Table 1): *gupeiite* Fe_3Si (corresponding to α_1), *hapkeite* Fe_2Si , and *naquite* $FeSi$ (or *fersilicite*). Only the hapkeite is proved by X-ray diffraction analysis (Zotov in: Yanev et al., 2015) having a cell parameter $a_0=2.818$ Å. Subsolidus phases exist in the Fe-Si system too: γFe and xifengite Fe_5Si_3 . The area between the pure Fe and α_2 phase (up to Si 19.5 at.%) is the field of the disordered bcc A_2 (or αFe) phase where we have analyzed many Fe_xSi alloys with Si content from 6.8 to 17 at.%, all containing also Ca up to 1.3% at.%. Fe silicides are common in meteorites, meteoritic craters, some of them are known also in fulgurites, metamorphic rocks, sediments (review of Hiltl et al., 2011; Muszer, 2014 and others) and in the residuals of spontaneous combustion of coal (Kruszewski et al., 2014).

Table 1. Microprobe analyzes of Fe silicides (at.%)

	Naquite		Hapkeite	Gupeite	Fe _x Si			
Si	45.87	40.12	35.50	24.53	16.54	12.70	9.87	6.81
Fe	51.98	58.59	64.10	74.85	82.98	86.38	89.61	92.62
Ca	1.30	0.68	0.40	0.62	0.36	0.49	0.50	–
K	0.25	0.20	–	–	0.07	0.16	0.02	0.20
S	0.60	0.41	–	–	0.05	0.27	–	0.37

Table 2. Microprobe analyzes of suessite, Fe-Zn phases and different alloys (at.%)

Elements	Suessite	Fe-Zn phases		Alloys				
		δ	Γ	Zn-Si	Ti-Fe-Si	Mg-Fe-Si		
Si	18.61	5.42	4.60	34.80	6.45	8.20	8.86	
Ti (Mn)	0.39	–	–	–	12.71	–	1.09 ^a	
Al	4.35	–	–	4.38	3.86	3.23	2.55	
Fe	55.03	13.47	71.57	0.78	73.64	70.29	74.59	
Mg	–	–	–	–	–	10.25	8.10	
Ca	3.99	0.59	0.64	0.97	0.04	1.81	1.62	
K	0.18	0.13	–	0.44	0.11	0.32	0.33	
Ni (Zn, Na)	17.45	80.39 ^b	23.19 ^b	58.64 ^b	3.19 ^c	5.90 ^c	2.86 ^c	

^aMn, ^bZn, ^cNa

Ti-Fe-Si and Mg-Fe-Si alloys with minor Al and Na (and Ca in the Mg-Fe-Si) were also found (Table 2).

Fe-Ni silicide. There is only one stable phase in this system (Ackerbauer et al., 2009) – τ (Fe₅Ni₃Si₂). It corresponds to the mineral *suessite* (Fe,Ni)₃Si, observed only in meteorites (www.MinDat.org), especially in the C-bearing ones (ureilites). It forms on the Fe-Ni-Si diagram a large field with varying Fe/Ni ratio between the gupeite (Fe₃Si) and Ni₃₁Si₁₂ phase. The equilibrium between these phases and the melt is peritectic at 1166 °C. Suessite with high amount of Ni, containing also Ca and Al was detected in the “carbon” mass (Table 2).

Fe-Zn phases. There are many phases in the Fe-Si-Zn system, all subsolidus, with varying compositions “suggesting that these are solution compounds with relatively wide homogeneity ranges” (Sha et al., 2010). It is not known any natural Fe-Zn phase, but we found (Table 2) the phases Γ (Fe₃Zn₇) and δ (FeZn₁₀), formed below 782 and 529 °C respectively. Their elevated Si content probably is due to the presence of FeSi or/and α Fe nanoparticles (Wang et al., 2005), the lasts having very high Si solubility.

We analyzed also an unknown Mg (11 at.%), Si (22), Y (25.7) and Cu (37) compound containing some quantities of Al (3) and Ba (1.3).

Discussion. Both genetic scenarios (tektite or meteorite) imply a fusion of the described rock fragment in the terrestrial atmosphere at a temperature exceeding 1700 °C and the formation of a glassy (SiO₂) crust. This crust preserved the vaporization of the “carbon” mass in the interior of the fragment. “Carbon” is only amorphized, forming “micro-furnaces” (dimension from tens to some hundreds of μ m) with fused quartz

“walls” (Fig. 1) where in extreme reducing conditions (probably at Fe-fayalite-quartz buffer) elemental Fe, Fe silicides and suessite crystallized. The subsolidus Fe-Zn phases are probably formed at decreasing of the temperature, after the fall of the rock fragment on the Earth surface. The primary Zn source is probably sphalerite, found in the quartz rosettes, but the Fe source is unknown (dispersed Fe ions in the “carbon” mass?).

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