

SHOCK-PRODUCED SIDERITE IN IIE IRON METEORITE ELGA. N. R. Khisina¹, A. Burmistrov¹, and R. Wirth², ¹Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences, Kosygin st., 19, Moscow, Russia, e-mail khisina@gmail.com, ²Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, 4.3, Telegrafenberg, 14473 Potsdam, Germany

Introduction. Meteorite Elga relates to differentiated IIE irons which are considered to have formed by impact-induced metal-silicate melting and mixing [1-7]. Elga is composed of a FeNi matrix with rounded silicate inclusions usually connected by silicate veins or cracks. Unlike many IIE irons Elga exhibits well pronounced shock metamorphism documented by numerous melt pockets inside silicate inclusions and the rims developed both around the silicate inclusions and along the veins connected them. The rims are either single-layered consisting of schreibersite or double-layered consisting of schreibersite plus oxide. Hematite-trevorite-siderite assemblage in oxide layers of rims was identified with EMPA and Raman spectroscopy [8] and siderite composition was estimated as $\text{Fe}_{0.96}\text{Ni}_{0.04}\text{CO}_3$. The melt pockets often contain fragments of a breccia (Fig.1) transferred by shock wave from the silicate-metal boundary. Previous FIB/TEM and microRaman spectroscopic study of a schreibersite+ oxide breccia clast from the melt pocket in one of silicate inclusions [8, 9] revealed rounded precipitates of FeCO_3 siderite in the schreibersite matrix. Siderite in irons is commonly considered as formed by terrestrial alteration [10]. Here we report an extraterrestrial origin of siderite in Elga.

Results. Inclusions of siderite in schreibersite matrix look like either small precipitates of ellipsoidal shape uniformly distributed within the schreibersite, or large irregular rounded “islands” (Fig. 2).

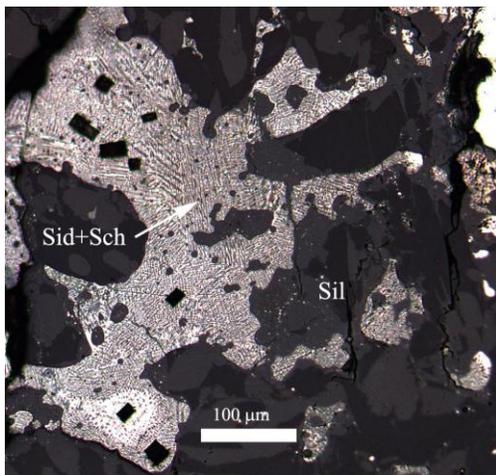


Fig. 1. The siderite-bearing schreibersite+oxide breccia clast.

Siderite is identified from the EDS TEM analysis and TEM X-ray mapping. TEM images show abundant small and irregular shaped particles in siderite that are different in contrast from the siderite matrix. They are brighter than siderite in BF images, and inversely darker in HAADF images. The microstructure of the breccia clast is consistent with carbonate-phosphide liquid immiscibility in Fe-Ni-P-O-C melt [8].

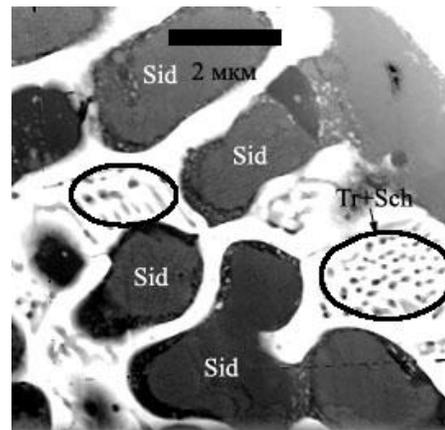


Fig.2. Microstructure of the breccia clast. Large grey inclusions are siderite, white matrix is schreibersite. TEM image. The trevorite+ schreibersite areas are bounded by rings.

EELS spectra with C-K edge, O-K edge and Fe $L_{2,3}$ were collected from a large siderite inclusion (Fig. 3). Peaks at 310 eV, 533 eV and 539 eV are attributed to siderite [11]; the σ^* peak at ≈ 290.5 eV closely relates to σ^* peak of siderite at 290.2 eV [11], although it is broadened toward the higher energy region (Fig. 3). However, the EEL spectra of siderite in Elga are different from normal siderite. (i) Fe $L_{2,3}$ spectra of the Elga sample show peaks at 711 eV and 724.5 eV attributed to Fe^{3+} [12] instead of peaks at 709 eV and 722 eV of Fe^{2+} in siderite [12]. (ii) The siderite peak at 544 eV is absent. (iii) The peaks observed at 287.5 eV and 529 eV cannot be assigned to siderite at all. We found that the EELS spectra of siderite from Elga are very similar to that of siderite recovered from high P - high T experiments [13]. From SAED data, a quite good agreement is found between d -spacings observed for Elga siderite and those given for recovered high-pressure siderite (HPS) phase [13].

Discussion. High pressure structure of carbonates $\text{Me}^{2+}_3(\text{C}_3\text{O}_9)$ has been predicted by Oganov et al. [14] as based on $(\text{C}_3\text{O}_9)^{9-}$ rings of three corner-sharing

$(\text{CO}_4)^{3-}$ tetrahedra. Quenchable $(\text{Mg,Fe}^{3+}_x)_{3-0.5x}(\text{CO}_4)_3$ HPS was produced experimentally at high pressures and high temperatures [13].

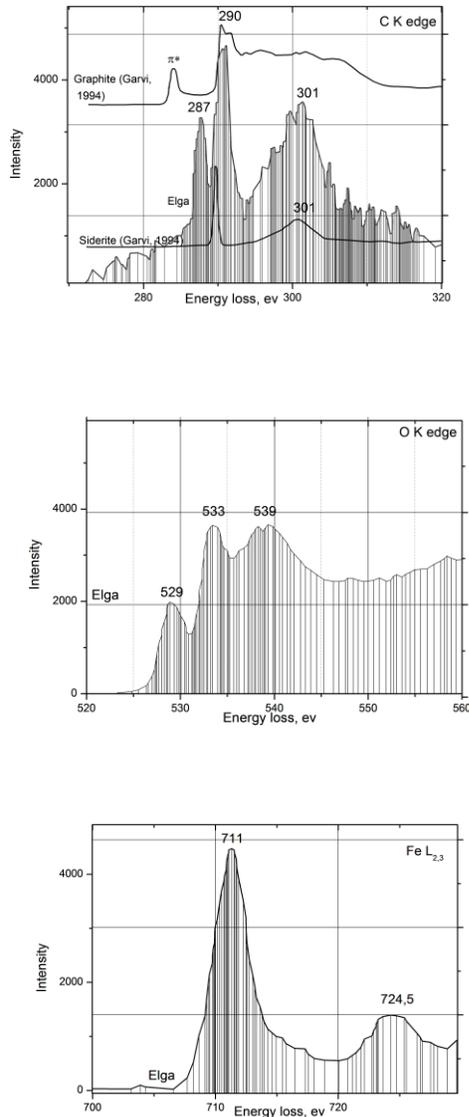


Fig.3. C K-edge, O K-edge and $\text{Fe}_{2,3}$ EELS spectra of siderite in the breccia clast.

The presence of Fe^{3+} iron in the HPS was concluded from $\text{Fe L}_{2,3}$ EELS spectra collected from recovered sample, and the broadening of the C-K edge peak at 290.5 was explained by a presence of $(\text{C}_3\text{O}_9)^{6-}$ rings in the HPS structure [13]. The peak at 287.4 eV was assigned to $1s \rightarrow \pi^*$ electron transition in molecular CO , and the reaction $4\text{FeO} + 5\text{CO}_2 = \text{Fe}_4(\text{CO}_4)_3 + 2\text{CO}$ was suggested for the assemblage produced in the experiment [13]. Instead of CO we assign the peak at 287.5 eV in Elga sample to C-O-C O-bridging functional

groups formed by corner-sharing CO_4 tetrahedra in HPS structure. The reasons are the following: (i) Not gas nanobubbles but nanosized solid flakes of low specific weight occur in the Elga siderite; (ii) EEL spectra of C-O-C epoxy functional groups show the $1s-\pi^*$ peak at about 287.5 eV; the same peak observed in C K-edge spectra of graphene oxide structure was assigned to O-bridging bond [15]. Peak at about 529 eV can be related to iron vacancy in HPS; the same peak in O K-edge spectrum from graphene oxide was referred to O-in-vacancies in graphene oxide structure [15]. Thus the EEL spectra from carbon-rich regions in *Sch-Ox* fragment (Fig. 2) confirm the high-pressure siderite $\text{Fe}^{3+}_2\text{v}_1(\text{C}_3\text{O}_9)$ in the breccia clast in Elga (v is a vacancy). Both EELS and SAED data on the Elga siderite are in good agreement with the data given for recovered HPS phase [13]. We suggest reaction $\text{Fe}_2\text{O}_3 + 3\text{CO}_2 = \text{Fe}^{3+}_2\text{v}_1(\text{C}_3\text{O}_9)$ for shock-induced HPS formed in Elga. The CO_2 involved in shock-induced reactions to form HPS could have been brought to the Elga parent body either by impactor or, more probably, trapped by silicate target from the atmosphere during impact. The latter scenario seems reasonable because during shock wave propagation through the rock, cracks and fissures within the rock can trap components of the atmosphere. If so, then Mars can be a potential candidate for a parent body of Elga.

Conclusion. The results demonstrate the first finding of natural high-pressure Fe^{3+} -siderite phase (HPS). The HPS has a stoichiometry as $\text{Fe}^{3+}_2\text{v}_1(\text{C}_3\text{O}_9)$ and occurs in shocked zones of meteorite Elga. The source of CO_2 in Elga needs to be debated.

References: [1]^oBogard D. D. et al. (2000) *GCA*, 64, 2133-2154. [2]^oMcDermott K. H. et al. (2016) *GCA*, 173, 97-113. [3]^oOlsen E. et al. (1994). *Meteoritics* 29, 200-213. [4]^oRuzicka A. et al. (1999) *GCA*, 63, 2123-2143. [5]^oRuzicka A. (2014) *Chem. Erde*, 74, 3-48. [6]^oSnyder G. A. et al. (2001) *Earth Planet. Sci. Lett.*, 186, 311-324. [7]^oTakeda H. et al. (2003) *GCA*, 67, 2269-2287. [8]^oKhisina N. R. et al. (2017) *Geochemistry International*, 4, 1. [9]^oTepliyakova S. N. et al. (2012) *Zapiski of Russian Mineralogical Society*, 141(2), 42-52. (in Russian). [10]^oRubin A. E. (1997) *MPS*, 32, 231-247. [11]^oGarvie L. A. J. et al. (1994) *Am. Mineral.*, 79, 411-425. [12] Isambert A. et al. (2003). *J. Geophys. Res.*, 108, B6, 2283. [13]^oBoulard E. et al. (2011) *PNAS*, 108, 5184-5187. [14]^oOganov A. et al. (2008) *LPSL*, 273, 38-71 [15]^oD'Angelo D. et al., (2015) *Carbon*, 93, 1034-1041.