DETAILED MINERALOGY AND TRACE ELEMENT CHEMISTRY OF DONINO IRON METEORITE: A PENTLANDITE AND HEAZLEWOODITE ISSUE. K. D. Litasov^{1,2}, A. Ishikawa³, and K. E. Kuper⁴, ¹Fersman Mineralogical Museum RAS, Moscow, 119071, Russia, ²Vereshchagin Institute for High Pressure Physics RAS, Troitsk, Moscow, 108840, Russia (litasov@hppi.troitsk.ru), ³Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo, 152-8550, Japan (akr@eps.sci.titech.ac.jp), ⁴Budker Institute of Nuclear Physics SB RAS, Novosibirsk, 630090, Russia (k.e.kuper@inp.nsk.su).

Introduction: Dronino is one of the famous iron meteorites found in Russia. The total weight of shower fragments exceeds 3 tons. It was classified as an ungrouped meteorite close to IVA irons. It contains about 10 wt.% of rounded sulfide inclusions up to a few mm in size, rare chromite, and Fe-bearing phosphate. Sulfide inclusions are often surrounded by Fe-oxide and hydroxide rims [1].

Previous investigations were related to the study of the fine structure and composition of metallic matrix [2-4] and trace element and crystallography of sulfide inclusions [5-6]. Specific crystallographic works on Dronino iron revealed new secondary hydroxide minerals chukanovite and droninoite [7-8].

Here, we present new mineralogical and trace element data, which allows us to confirm unusual nature of Dronino meteorite and provide new evidence for its origin and cooling history.

Methods: We studied several polished plates of the the Dronino meteorite 2–4 cm in size from a private collection. The microstructure and composition of minerals were studied on a Tescan MYRA 3 LMU SEM equipped with an EDX-Max-80 (Oxford Instruments) at 20 kV and 1.5 nA. The trace element composition was obtained using LA-ICP-MS on a Thermo Scientific Element XR instrument. The standards for most siderophile elements included alloy Ni-5 and metal of a homogenous sample of the Campo del Cielo meteorite [9]. The EBSD data were collected on a Hitachi S-3400 N scanning electron microscope equipped with an Oxford Instruments HKL detector with an accuracy of misorientations of 0.5–1.0 degrees.

Results: The sample sections contain abundant rounded and irregular shaped sulfide inclusions up to 7 mm in size. There are several types of sulfide inclusions: (a) homogenous, including those with minor reactionary rims with Ni-bearing taenite; (b) with abundant chromite inclusions (Fig.1a); (c) with reticulate microstructure formed by pentlandite network (Fig.1b-d). The last type is often surrounded by an oxidation rim (Fig.1b). We also observed unique and new feature for Dronino meteorite as coexisting sarcopside/graftonite (Fe_{2.8}Mn_{0.2})₃(P_{1.9}Si_{0.1}O₄)₂) and SiO₂ at the boundary between sulfide inclusion and metal (Fig.1d). The crystal structure of phosphate was confirmed by EBSD, however, we could not determine the SiO₂ structure and

tentatively described it as a glass. It is clear that SiO₂ is not a foreign phase or contamination. The SiO₂ glass is pure and contains only 0.5 wt.% FeO.

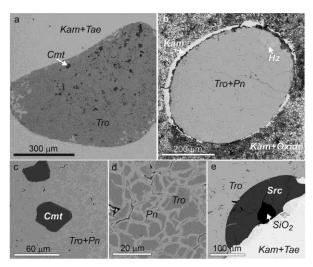


Fig. 1. BSE images of Dronino iron meteorite sample sections. (a) sulfide nodule with abundant chromite (Cmt) inclusions in kamacite (Kam) - taenite (Tae) matrix; (b) same, surrounded by oxidized rim; note kamacite rim on the sulfide nodule and tiny white heazlewoodite (Hz) in the troilite-pentlandite area; (c) enlarged zone of chromite inclusion in sulfide matrix; (d) reticulate microstructure of sulfide nodule formed by troilite (Tro) and pentlandite (Pn); (e) sarcopside (Src) with amorphous SiO₂ at the boundary of troilite nodule and metal.

The highest Ni content of Fe-Ni-metal is 60 wt.%, which is close to awaruite homogeneity range. Chromite is typical for iron meteorites and corresponds to $FeCr_2O_4$ with minor MnO (~0.7 wt.%) and V_2O_3 (~0.3 wt.%) contents.

Compositions of Ni-bearing sulfide (Table 1) vary inside the normal range of pentlandite in the low-temperature phase diagram (Fig.2) with deviations marked by high Co contents of some grains (up to 20.6 wt.%, Fig.3) and those corresponding to heazlewoodite (Hz) stoichiometry (Fig.2).

Trace element patterns of bulk Fe-Ni metal is very consistent with the previous data on Dronino meteorite (in mg/g, previous data from MetBull and [5] are in parentheses): P = 301 (447), Ti = 0.9, Cr = 34 (16-37),

 $\begin{array}{l} Mn=2.5\ (1.8),\ Co=0.64\ (0.56)\ wt.\%,\ Ni=9.98\ (9.8-10.0)\ wt.\%,\ Cu-35\ (32-37),\ Ga=0.48\ (0.56),\ As=3.8\ (3.5-7.2),\ Mo=3.34\ (4.08),\ Ru=2.79\ (2.64),\ Rh=0.68\ (0.72),\ Pd=2.44\ (2.29),\ Sb=0.61\ (0.67),\ W=0.44\ (0.38-0.48),\ Re=0.32\ (0.38),\ Os=2.11\ (2.01),\ Ir=1.71\ (1.57-1.68),\ Pt=2.99\ (2.82),\ and\ Au=0.5\ (0.28-0.68).\ The\ Ge\ content\ in\ Dronino\ metal\ from\ present\ study\ is\ low\ 0.76\ mg/g\ compared\ to\ <11\ mg/g\ in\ [5].\ The\ new\ data\ does\ not\ change\ definition\ of\ Dronino\ as\ ungrouped\ iron\ meteorite. \end{array}$

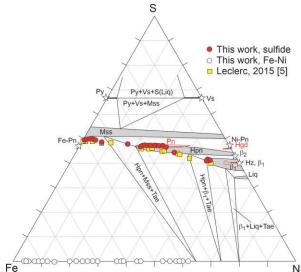


Fig. 2. Fe-Ni(+Co)-S plot showing composition of sulfide phases in Dronino iron meteorite. Schematic phase relations in the Fe-Ni-S system at 650 °C (black lines) and 500 °C (red lines) are shown [10]. Py – pyrite, Vs – vaesite, Mss – monosulfide solid solution, Hpn – High pentlandite, Pn – pentlandite, Hgd – high godlevskite, Hz – heazlewoodite, $β_1 - β_1$ -Ni₃S₂, Tae – taenite (γ-Fe,Ni), Liq – liquid.

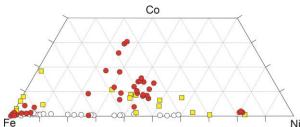


Fig. 3. Fe-Ni-Co relations in metal and sulfide phases from Dronino (see Fig.2 for legend).

Trace elements were analyzed only in unaltered homogenous Fe-sulfide (number of analyses is 8, in mg/g, the average previous data from [5] are in parentheses): P = 5.7 (8), Ti = 3.3 (5), Cr = 72 (12), Mn = 154-207 (18), Co = 24 (9), Ni = 320-740 (240), Cu = 84 (88-102), Zn = 23, Se = 2.4 (8), Mo = 2.5 (2.4), Ru

= 1.12, Te = 0.29, W = 0.17, and Pb = 0.9 (3.4). Low Se and Te contents are unusual for Fe-sulfide from iron meteorites.

Table 1. Examples of sulfide compositions from Dronino iron meteorite (wt.%).

Mineral	Hz	Pn	Pn	Pn
Fe	12.48	30.81	28.33	43.85
Co	1.31	5.03	20.56	6.38
Ni	57.98	30.34	17.58	15.42
S	27.48	33.16	33.42	33.44
Total	99.25	99.34	99.89	99.09

Discussion: Pentlandite coexisting with Fe-sulfides in meteorites is usually attributed to aqueous low-temperature terrestrial/cosmic alteration [11-12]. This interpretation is consistent with a clear correlation of reticulate structures and alteration rims in Dronino iron. However, the appearance of Fe-bearing Hz (or cubic β_1 -Ni₃S₂) and significant Co-enrichment of pentlandite are very unusual.

Experimental data show that Hz stabilizes at T < 550 °C and dissolves <3 at.% Fe [10]. The Ni₃S₂ phase in Dronino iron contains 10.3-10.8 at.% Fe and, thus, corresponds to β_1 -Ni₃S₂ formed at T > 600°C (Fig.2) or to the cryptocrystalline mixture of Hz and Fe-bearing sulfide. In the latter case it can correspond to low-T alteration.

Homogenous unaltered troilite and pyrrhotite contain < 0.08 wt.% Ni and < 24 mg/g Co. Thus, the Ni and Co source for Pn/Hz would be surrounding Fe-Ni metal. The Co enrichment likely requires higher a temperature than 100-150 °C of low-T aqueous metamorphism. We suggest that the appearance of Febearing Ni₃S₂ and Co-bearing pentlandite can be explained by a combination of high-T cosmic metamorphism on the parent body and subsequent low-T cosmic/terrestrial aqueous alteration along the weakened zones in Dronino meteorite.

References: [1] Grokhovsky V. I. et al. (2005) LPSC XXXVI, Abstract #1692. [2] Grokhovsky V. I. et al. (2005) Hyperfine Interact. 166, 671-677. [3] Oshtrakh M.I. et al. (2016) Hyperfine Interact. 237, 42. [4] Tempesta G. et al. (2018) Spectrochim. Acta B 144, 75–81. [5] Leclerc M. D. (2015) PhD thesis. Imperial Colledge London, 308 p. [6] Khontsova S. S. et al. (2019) AIP Conf. Proc. 2174, 020218. [7] Pekov I. V. et al. (2007) Eur. J. Mineral. 19, 891–898. [8] Chukanov N. V. et al. (2009) Geol. Ore Deposits 51, 767–773. [9] Litasov K. D. et al. (2019) Doklady Earth Sci. 485, 381–385. [10] Kitakaze A. et al. (2011) Can. Mineral. 49, 1687-1710. [11] Rubin A. E. (1997) MAPS, 32, 231-247. [12] Schrader D. L. et al. (2016) GCA 189, 359-376.