**MAGNETITE-BEARING BARRED OLIVINE COSMIC SPHERULES FROM THE NOVAYA ZEMLYA COLLECTION: SEM/TEM STUDY.** N. R. Khisina[1], D. D. Badyukov[1], R. Wirth[2], [1]Institute of Geochemistry and Analytical Chemistry of Russian Academy of Science, Kosygin st., 19, Moscow, Russia , khisina@geokhi.ru, [2]Helmholtz-Zentrum Potsdam, GFZ, Germany.

**Introduction:** Usually micrometeorites have many chemical and textural similarities with chondrites, especially with carbonaceous chondrites (i.e. CI, CM, CR) [e.g. 1, 2]. Cosmic spherules (CS) are formed by heating and melting of micrometeoroids on entering Earth atmosphere [3] and constitute an important fraction of the micrometeorites flux. Barred olivine (BO) CSs composed of parallel growth of olivine in a glassy mesostasis often with magnetite and are common among silicate CSs [4-6]. Here we present data on BO CSs from the Novaya Zemlya (NZ) micrometeorite collection 2006 and 2012. The aim of the work is to establish processes of BO spherules formation and some characteristics of their precursiors.

BO spherules abundance in the Novaya Zemlya collections is 40 % relatively of all CSs in 100 – 250 mm size fraction according to SEM observations of polished sections. For the study we chose 59 magnetite-bearing BO spherules with well-pronounced barred textures (Fig. 2). Bulk compositions of the spherules were obtained using WDS and partially EDS data for Si, Al, Fe, Mg, and Ca. BO spherule NZ6-IV-5-23 (Fig. 2) was studied with TEM. For the TEM study a thin films were prepared using a FIB technique.

**Results:** Bulk compositions of BO spherules from the Novaya Zemlya collection plotted on the Mg – Fe – Si diagram (Fig. 1) demonstrate the trend of compositions with solar atomic ratio Mg/Si≈1. Bulk NiO contents in BO spherules vary from 1.5 wt.% to below detection limit (<0.04 wt.%). The BO spherule NZ6-IV-5-23 examined with TEM is coarse-grained as compared to cryptocrystalline spherules[8] and consists of parallel rows of skeletal olivine bars up to 3 x 1 μm in width (Fig. 2), extended through the spherule; olivine bars are embedded in silica-rich pyroxene-feldspar glass and randomly decorated by single magnetite grains.

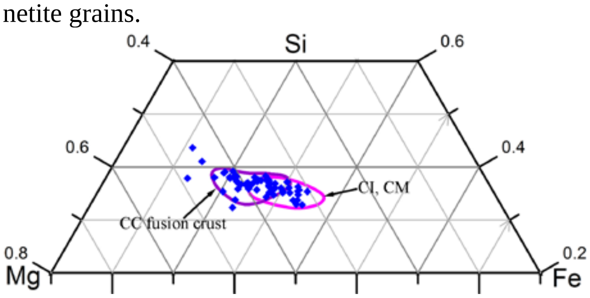


Fig. 1 Compositions of magnetite-bearting BO spherules (blue squares), CI and CM chondrites[7] and carbonaceous chondrite fusion crusts[11].

TEM images (Fig. 3) show that olivine crystals have orthogonal habitus with faces which are “scallop”-like when they are normal to direction of a given row and flat when they are parallel to a given row (Fig. 2). Olivine exhibits a sharp zonality from $Fo_{66}$ in the core to $Fo_{49}$ in the rim. Bulk NiO content in the center of olivine crystals is 1.7 wt.%. Ni correlates with Mg content in olivine crystals, and Ni enrichment in cores of olivine grains is documented by corresponding concentration profiles (Fig. 4). No Ni is detected either in magnetite or glass. Si-rich glass is homogeneous. Bulk chemical composition of the BO NZ6-IV-5-23 spherule together with chemical analyses data on olivine and glass are given in the Table.

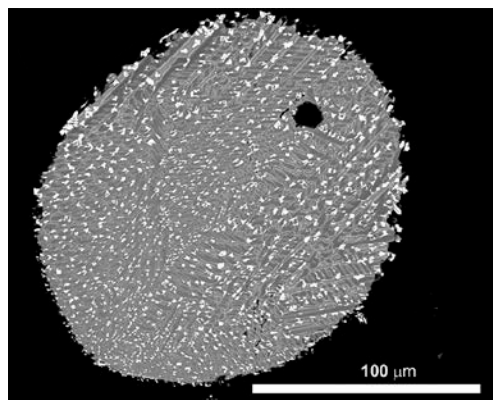


Fig.2 Backscattered electron image of BO spherule NZ6-IV-5-23.

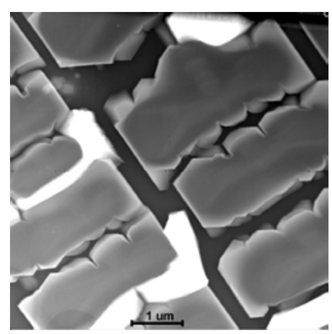


Fig.3 TEM image of inner microtexture of the spherule NZ6-IV-5-23. The micrtotexture is dominated by rows of olivine crystals (gray) in a homogeneous glass (dark grey). Magnetite (white) occupies interstitial spaces at the contacts with olivine crystals.

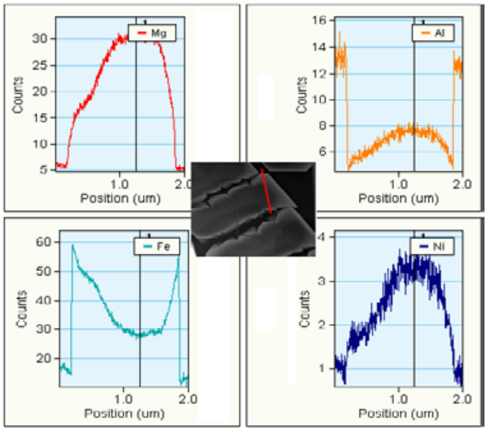


Fig. 4. Concentration profiles of Mg, Al, Fe, and Ni across olivine grain. A location of the profile is shown by a red line on the insertion.

**Discussion:** Coarse-grained texture and a sharp Fe-Mg zonality of olivine crystals in BO NZ6-IV-5-23 indicate relatively slow cooling rates of the precursor melt droplet and relatively long period of its solidification as compared to magnetite-free cryptocrystalline spherules [8]. Sharp Fe-Mg zonality and metastable (skeletal) shape of olivine crystals as well as inhibitted crystallization of pyroxene indicate that equilibrium crystallization was not achieved during solidification of melt droplets. Appearance of magnetite during the late stages of olivine crystallization indicates that solidification of the melt droplet took place at low altitudes under oxidation conditions of the Earth' atmosphere. This is in agreement with oxygen isotopic data [9,10] suggested interaction between atmospheric oxygen and BO spherules. TEM point chemical analyses data of olivine, magnetite and silicate glass in the NZ6-IV-5-23 (Table) led to the conclusion that NiO and $Fe_3O_4$ in the spherule have not been produced by oxidation of FeNi metal: $Fe^{3+}$ appeared during crystallization of olivine due to late oxidation of silicate melt, while NiO was present in silicate melt from the very beginning. During cooling of the melt droplet the $Fe^{2+}$ to $Fe^{3+}$ oxidation much probably occurred due to interacion between melt droplet and atmospheric oxygen, and magnetite crystallized from the $Fe^{3+}$-rich silicate melt at the late stage of olivine crystallization.

The bulk Fe-Mg-Si contents of the BO spherules are inside the fields of compositions of carbonaceous chondrites and carbonaceous chondrite ablation spherules[11] (Fig. 1). The same, NiO contents in BO spherules are between NiO values observed in olivines in carbonaceous chondrites (NiO < 1 wt.%) and in olivines from meteoritic ablation spherules (NiO > 2 wt.%) [5]. Therefore either carbonaceous chondrites or meteorite fusion crust could be suspected as chemical precursors of BO spherules, and the BO spherules could be referred to either cosmic or ablation spherules, correspondingly. This dilemma is discussed in the literature [5] although according the commonly adopted model [3] spherules as a whole are cosmic objects, namely melted micrometeorites. However each given micrometeorite is too small in size (up to several hundred micrometers) to represent a bulk chemistry of its coarse-grained precursor source, and spherules produced by melting of coarse-grained micrometeorites should exhibit therefore much wider diversity of bulk compositions with large deviations from the Mg/Si≈ 1 ratio as compared to bulk compositions of BO spherules, We assume that micrometeorites similar by chemistry to fine-grained matrix of carbonaceous chondrites (CI, CM, CR, Tagish Lake) can be precursors of BO; however, one may expect fusion crusts of other carbonaceous chondrite groups as precursors of BO too.

Table. TEM EDS analyses (wt.%) of an olivine crystal, a glass, and a bulk composition of spherule NZ6-IV-5-23. b .d. – below detection

| | Ol rim | Ol core | Glass | Bulk |
|---|---|---|---|---|
| MgO | 21.4 | 30.8 | 1.6 | 20.6 |
| $SiO_2$ | 34.2 | 34.7 | 45.2 | 33.3 |
| $Cr_2O_3$ | b.d. | 1.4 | b.d. | 0.5 |
| MnO | 0.5 | 0.3 | b.d. | 0.4 |
| FeO | 42.0 | 26.9 | 22.4 | 37.9 |
| NiO | b.d. | 1.75 | b.d. | 1.2 |
| $Al_2O_3$ | 1.6 | 4.2 | 18.9 | 2.9 |
| CaO | 0.2 | b.d. | 12.0 | 3.0 |

**Conclusions:** Bulk element chemistry, microstructure and mineralogy of BO spherules give evidence for a low-altitude oxidation occurred before a solidification of spherules due to interaction of melt droplets with atmospheric oxygen. $Fe^{3+}$ appeared during crystallization of olivine due to late oxidation of silicate melt, while NiO occurred in silicate melt from the very beginning. Therefore NiO and $Fe_3O_4$ in the BO have not been produced by oxidation of FeNi metal. Bulk compositional trend with Mg/Si ratio as 1 correlates with typical one for both fine-grained matrix and fusion crusts of carbonaceous chondrites.

**References:**

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