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NANOMETER-SIZED MINERAL GRAINS AND THEIR GENETIC TYPES IN METEORITES

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Abstract: Three genetically different types of nanometer-sized mineral grains in meteorites can be distinguished based on literature and original data: (a) primitive condensates, (b) metamorphic grains, and (c) weathering products. The first of these groups were formed by condensation in a gas-dust nebula in either a presolar or solar environment. Metamorphic grains were formed as a result of thermal, shock or aqueous metamorphism on the meteorite parent bodies. The third type can clearly be characterized as terrestrial weathering products, which are generally found in meteorite finds and are rare or absent within meteorites recovered shortly after having fallen. Nanometric components are found predominantly within the fine-grained silicate material of primitive meteorites. It is suggested that enhanced accretional properties of nanometer-sized grains could be responsible for the primary accretion of condensed nanoglobules within a protoplanetary nebula.

The nature of nanometer-sized inclusions of native W and native Ag originally discovered in the Krymka chondrite is preliminarely discussed.

Key words: meteorite, mineral, genetic type, nanometer-sized grain, origin.

The search for and study of the precursors of primary mineral dust formed within the protoplanetary nebula is important if we hope to decipher the nature of the building materials of the solar system planetesimals and planets. Unequilibrated carbonaceous, ordinary, enstatite and Rumuruti chondrites (e.g., Brearley & Jones, 1998; Bischoff et al., 2011) are important rocks that contain fine-grained materials consisting of both primitive and processed dust (Zinner, 2004; Brearley, 1996). The evolutionary path of this material is extremely complex, since it is relatively unequilibrated and formed under a wide range of PT-conditions. These PT-conditions may have fully or partially changed the chemical and/or mineralogical characteristics of the primary components within the protoplanetary nebula and subsequently within the parent bodies of meteorites.

A comparison of the major mineralogical characteristics of meteorites and terrestrial rocks indicates grain size as one of the distinguishing features resulting from the nature of minerals formed under different PT-conditions. Most terrestrial rocks have variable grain sizes ranging from fine to coarse-grained, although individual crystals can be very large, i.e. more than 1 m. For example, the largest quartz crystal found in Namibia, is ~50 m in size (Bukanov, 2001). In meteorites, the range of grain sizes is much narrower than in terrestrial rocks, and tends to be at the small end of the size distribution for individual crystals. In many extraterrestrial rocks mineral grains larger than 0.5 mm are rare. Complex processes of mineral formation (e.g., condensation, crystallization) and long-term evolution (e.g., thermal and shock metamorphism, aqueous alteration) in the gas-dust nebula, within

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meteorite parent bodies, and on Earth resulted in the formation of different genetic types of nanometer-sized grains representing an initial stage of structural ordering of solid matter. Using literature and original data, we define three major, genetically different types of nanometer-sized mineral grains in meteorites (e.g., Semenenko et al., 2010): (a) primitive condensates, (b) metamorphic, and (c) weathering.

A. PRIMITIVE CONDENSATES

Currently known isotopic data prove the existence of two major groups of mineral condensates: one group of presolar origin, and the other of solar origin (e.g., Lodders & Amari, 2005; Nittler et al., 2008; Zinner, 2004). The former assemblage is represented by a very small abundance of tiny minerals (Fig. 1a) in primitive chondrites including diamond, silicon carbide, silicon nitrides, Ti-, Zr-, Mo-rich carbides, oxides of Al and Ti, and silicates. Grain sizes of the presolar condensates vary from approximately nanometers to tens of micrometers. The largest presolar minerals are SiC-grains and graphites, which have been found existing with diameters in the µm-range. Other presolar grains are considerably smaller and are not larger than a few hundred nanometers. The smallest of these grains are diamonds that exhibit extraordinary constant sizes corresponding to ~1–2 nm. These data allow us to assume extremely complex and variable processes of mineral formation in stellar environments. In addition, it seems that the physical properties of minerals such as hardness have positively influenced the survival of especially diamonds throughout their long-term evolution.

Because grain sizes of other presolar minerals vary by 1–2 orders of magnitude, we cannot rule out incorrect estimates of mineral abundances for the lowest size fractions. Chemical treatment of samples for isotope analysis includes a chemical separation of the grains that promotes their fragmentation. This must be considered an important factor when taking the increased fragility of meteoritic minerals compared with terrestrial analogs into account. For example, the size of a rounded grain of hibonite (Fig. 1b), found in situ within the fine-grained carbonaceous xenolith BK13 in Krymka (LL3.1) chondrite, corresponds to $\leq 20 \times 10$ µm (Semenenko et al., 2001), while the hibonite grains (Fig. 1a), chemically isolated from the same meteorite for isotope studies (Nittler et al., 2008) have fragmented shapes and sizes of $\leq 5.5 \times 2$ µm. Sizes of the chemically pretreated oxides including the hibonites found in other chondrites vary between 0.15 – 3 µm (Zinner, 2004). Thus, we suggest that the true size

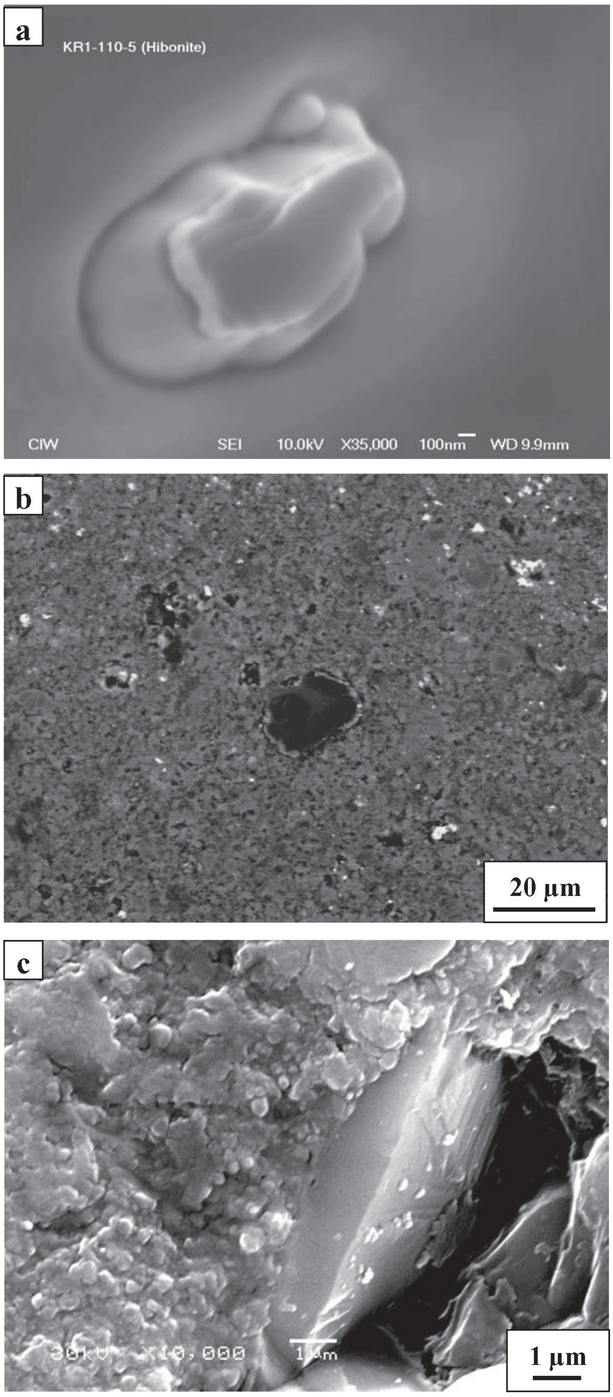

Fig. 1. Condensate type fine grains in the Krymka chondrite. (a): SEM image of presolar hibonite, chemically isolated from the meteorite for isotope studies. The grain is located on a gold plate. The image is kindly provided by Larry Nittler. (b): BSE image of hibonite grain located in situ within the Krymka fine-grained carbonaceous xenolith BK 13 (Semenenko et al., 2001). A polished section of the meteorite. (c): BSE image of a complicated globular structure of fine-grained silicates and metal-sulfide intergrowths in the Krymka xenolith BK14. A face of the large olivine crystal contains nanometer-sized inclusions of chromite crystals (white). A broken surface of the chondrite polished section

ranges of all types of presolar minerals are unknown. However, very hard and physically strong phases like diamond and carbides may have survived significant grain fragmentation and miniaturization.

Some fine-grained portions of primitive meteorites composed of silicates, metal, and some accessory high-temperature minerals (Larimer, 1988) are probably relics of solar condensates (Brearley, 1996). Our scanning electron microscopic (SEM) examination of fractured surfaces of fine-grained xenoliths BK14 from Krymka, studied previously by V. Semenenko et al. (2001), and AL1 from Allende, show evidence for a complicated globular structure of silicates and metal-sulfide-intergrowths (Fig. 1c), i.e. individual globules are composed of many smaller globules. The smallest globules are less than 10 nm in diameter. Based on these data, an initial globular nucleation of minerals is suggested here followed by agglomeration (accretion) of globules within a dusty environment. From our point of view, namely the enhanced accretional property of nanometric grains (Gusev, 2009) favored the formation of the complex globules as well as the accretion of the fine-grained material. The existence of an amorphous state of the primary globules cannot be ruled out. Mild metamorphic conditions may have triggered crystallization at a later stage. This seems to be the most likely formation mechanism of the fine-grained condensates.

B. METAMORPHIC TYPE

Nanometer-sized minerals mainly present in pores, cracks, interfaces or within the mineral phases as inclusions are widely distributed in meteorites of different groups that have undergone thermal, shock or aqueous metamorphism. For example, the presence of many fine inclusions of silica (Fig. 2a), chromites, phosphides, phosphates or silicates, as shown by our SEM studies, is typical for nickel-iron and iron sulfides of shocked ordinary chondrites Galkiv (H4) and Gruz'ke (H4). Although much previously published work has been performed on this topic (e.g., Barber, 1981; Zanda et al., 1994; Brearley & Jones, 1998), we describe some new and genetically important examples of nanometer-sized mineral grains of metamorphic origin that we observed in meteorites.

One example shows a low-Ca pyroxene-rich microchondrule containing uniformly distributed nanocrystals of magnesium spinel with euhedral morphology (Fig. 2b). This unique microchondrule was found within a fine-grained rim of a porphyritic chondrule from Krymka with the aid of SEM and energy dispersive spectroscopic (EDS) studies. Based on mineralogy and chemistry, we suggest a high-temperature-event for the formation of the microchondrule. Most likely, it formed due to high-energy processes within a dusty environment. We further suggest that a slight metamorphism is responsible for the solid-state diffusion of Mg^{2+}, Al^{3+} and uniform nucleation of the tiny Mg-spinel crystals in the pyroxene-rich microchondrule.

We also observed rare nanometer- and micrometer-sized crystals of graphite, which are associated with organic compounds and other C-rich materials (Semenenko et al., 2004; Semenenko et al., 2005) of high scientific interest. Elucidation of their formation processes may also help to better understand the origin of terrestrial organic material and graphite deposits. The crystals observed in this study have a regular lamellar shape with sizes ≤ 3 x 0.7 μm and are uniformly dispersed throughout the fine-grained silicates of a carbonaceous xenolith from the Krymka chondrite (Fig. 2c). In most cases, the crystals are restricted to the interphase boundaries of minerals. According to transmission electron microscopic investigations (Weber et al., 2003), even small flakes of graphite with a thickness of less than 100 nm show a crystalline character. The occurrence of carbon within the carbonaceous xenoliths in three different forms (isolated crystals, organics, and C-rich material) suggests a genetic relationship of the graphite crystals with organic compounds. In accordance with Buseck and Bo-Jun (1985), the formation and ordering of the crystal structure of graphite is due to a mild thermal metamorphism of organics-containing material. The Krymka chondrite has been affected by significant shock metamorphism (Semenenko & Perron, 2005). We surmise that the metamorphic growth of graphite within the xenoliths was likely triggered by the collision of meteorite parent bodies in space. This conclusion is further corroborated by the enlargement of the graphite crystals, correlating with the degree of metamorphic processing of the xenolithic materials (Semenenko et al., 2004; Semenenko et al., 2005). The xenoliths represent a new kind of meteoritic component and some astrophysicists (e.g., Campins & Swindle, 1998) have speculated about a probable genetic relationship with mineral components of comets. Although the relationship between cometary and known meteoritic material is certainly an open question, a similar environment for the accretion of the xenolithic material in the protoplanetary disk and for comets cannot be excluded (Semenenko et al., 2005).

In the Knyahinya (L5) chondrite, some of the rare shock-melted structures observed can be best explained as high-temperature complexes of lyophilic emulsions composed of taenite and tiny, silicate-rich globules (Fig. 2d). The complicated structure and the extremely small size of the smallest globules indicate that the intensive shock was followed by high-temperature melting of metal and silicates, which nearly corresponds to a critical temperature of their mixing in some areas of the chondrite. Distinct shock features are also seen in the form of planar fractures and the start of weak mosaicism in olivines.

Unfortunately, we do not fully understand the formation processes of unique inclusions of native

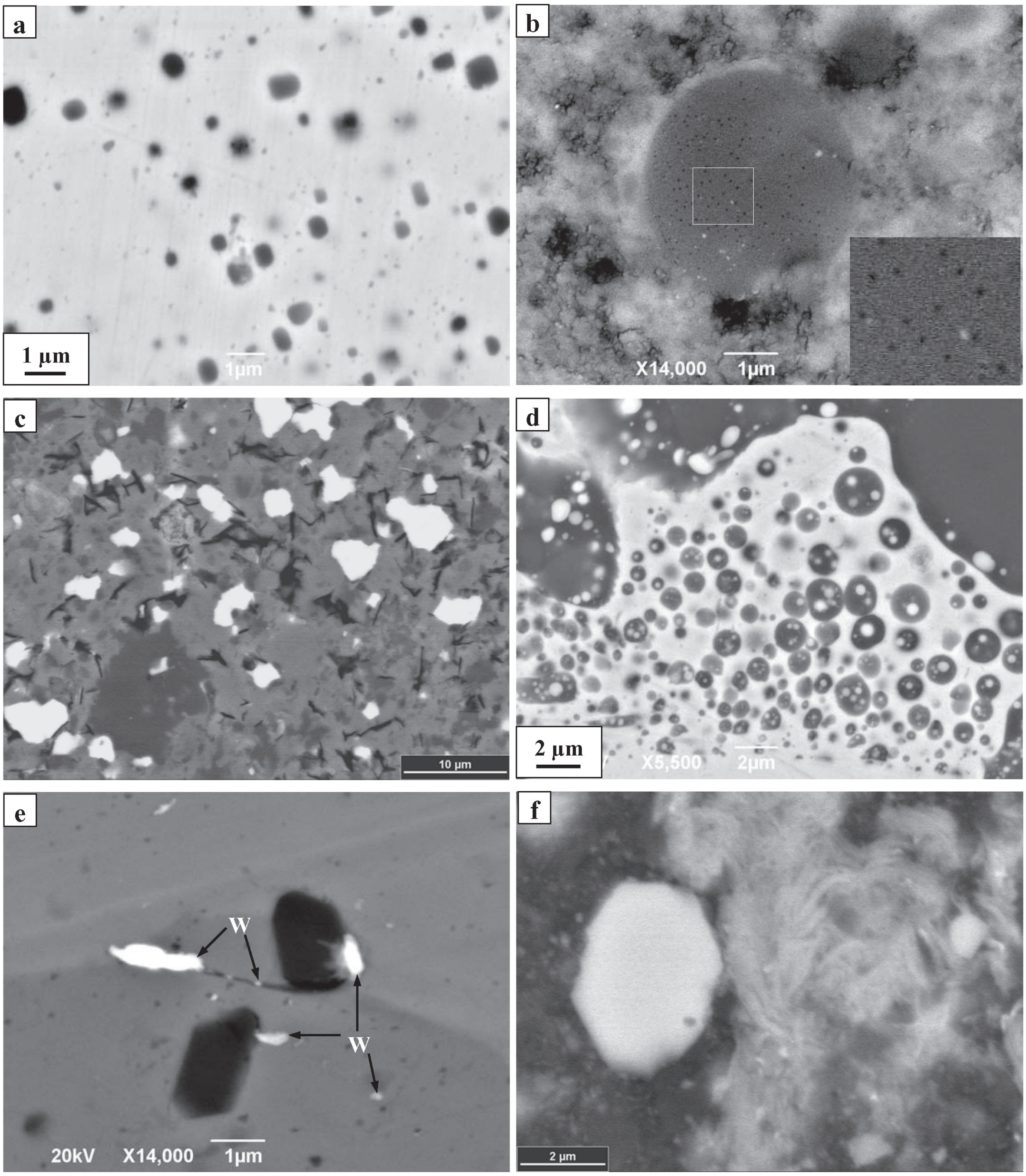

Fig. 2. BSE image of nanometer-sized grains of metamorphic type in polished sections of meteorites. (a): inclusions of silica (dark grey) within kamacite from the Galkiv (H4, shock stage S3) chondrite. (b): inclusions of spinel crystals in a low-Ca pyroxene-rich microchondrule embedded within fine-grained silicates from the Krymka chondrite. The enlarged part of the microchondrule with spinel (quadrangular black points) is presented in the right corner. (c): uniform distribution of graphite crystals (black) within the Krymka xenolith K1 (Semenenko et al., 2005). Silicates are light gray and gray, metal and sulfides are white. (d): lyophilic emulsion composed of taenite (white) and silicate-rich globules (gray) in the Knyahinya (L5) chondrite. (e): Unique inclusions of native tungsten (white) located within a kamacite globule (gray) found within a porphyritic chondrule from Krymka. Euhedral dark gray crystals are chromites. (f): Aggregates of fibrous crystals of phyllosilicates and magnetite crystals (white) within the Krymka fine-grained xenolith BK 1 (Girich & Semenenko, 2004).

tungsten (Fig. 2e) in the Krymka chondrite, which we found within a porphyritic chondrule with SEM and EDS study. Although W-bearing, refractory metal alloys are known from CAIs (MacPherson et al., 1988), to our knowledge, this is the first report of pure W-grains in meteorites. The inclusions are arranged within kamacite spherules embedded within the glass of a porphyritic chondrule, concentrated within cracks, pores and interfaces. The size of the smallest tungsten grain is ~50 nm. Their arrangement points towards a native origin. We do not consider these grains to be the result of contamination. The textural and mineralogical characteristics of the grains allow us to speculate on their formation process. The close connection between native tungsten and nickel iron indicates their genetic relationship. Although the very refractory grains of W condense at a higher temperature than nickel iron, we cannot exclude the following incorporation of W, for example, as nitrides or carbides, into nickel iron condensates. As high-temperature minerals, the W-bearing Fe,Ni-metals must have survived the melting process during chondrule formation. Later, stress-related shock metamorphism was probably favorable to the solid-state diffusion of W and formation of its inclusions within the kamacite cracks, pores and interfaces.

Aggregates of abundant cubic crystals of magnetite, i. e. framboids, as well as aggregates of fibrous crystals of phyllosilicates, comprise the most interesting secondary minerals that formed during low-temperature aqueous alteration of meteorite parent bodies (Zolensky & McSween, 1988). They occur in many CI and CM chondrites. These fibers within the Krymka fine-grained xenolith BK1 (Fig. 2f) are so thin ($\leq$ 10 nm) that we were not able to obtain precise data on the chemical composition of these phyllosilicates (Girich & Semenenko, 2004). Microprobe analyses revealed that they contain Fe, Mg, Si, and minor amounts of S. It should also be mentioned that some fine-grained, water-bearing alteration products are regarded to be of pre-accretionary origin (Bischoff, 1998).

C. WEATHERING TYPE

Nanometer-sized secondary minerals that result generally from terrestrial weathering are widespread in meteorites. Our SEM and EDS studies show that different morphological types of iron hydroxide crystals occur mainly as clusters of globules, very thin fibers and needles (Fig. 3a-b), platelets of goethite or akaganeite (Fig. 3c). These dominate on surfaces of mineral grains of all types of weathered meteorites. Nanometer-sized hexagonal plates, likely of hematite, were observed in a few cases as oriented crystals on the surface of an olivine grain from the Omolon pallasite, probably along shear deformations (Fig. 3d). Laboratory monitoring of the weathering products in meteorite collections indicates that predominantly fibrous and lamellar nanocrystals with high surface energy are developed. Inasmuch as the nanocrystals are characterized by enhanced adsorptional properties (Gusev, 2009), this morphological feature of the secondary mineral grains promotes subsequent intensive degradation of meteoritic material.

Native silver belongs to one of the most interesting weathering products formed most likely in a terrestrial environment. It was found as separate fine grains (Fig. 3e) and dendritic-like agglomerates (Fig. 3f) in a polished section of the Krymka chondrite (Semenenko, 2010a, b). In most cases, the silver grains consist of nanoglobules with diameters $\leq$ 100 nm (Fig. 3f). They are located within Fe, Ni, S – hydroxides, which replace a remelted metal-troilite rim around a porphyritic olivine chondrule. According to energy dispersive data, the highest measured Ag content is 95.6 wt. %, where the other elements detected reflect contamination by the surrounding Fe, Ni, S – hydroxides. We also noted the presence of a few micrometric crystals of corundum adjacent to the silver grains.

Based on the tight association of the native silver with the Fe, Ni, S – hydroxides, its formation is most probably the result of weathering of hypothetic Ag-bearing metal-sulfides as is the case within the oxidation zones of terrestrial sulfides (Boyle, 1968; Latysh, 1997). This common process of terrestrial weathering includes two main stages: 1. transformation of Fe^0 and Fe^{2+} to Fe^{3+}, 2. solid-state diffusion of Ag and formation of native silver inclusions within the hydroxides due to the discrepancy of its atomic radius with the ionic radius of Fe^{3+}. The data allow us to speculate on a possible condensation origin of Ag-bearing pristine minerals. We suppose that nickel iron and/or iron sulfides (Palme et al., 1988), accreted to the chondrule surface from a dusty environment. In light of the fact that presolar corundum has been chemically separated from Krymka and isotopically characterized (Nittler et al., 2008), the presolar nature of both the corundum crystals and an Ag-bearing precursor of the extremely rare grains of native silver is not excluded (Semenenko, 2010a, b).

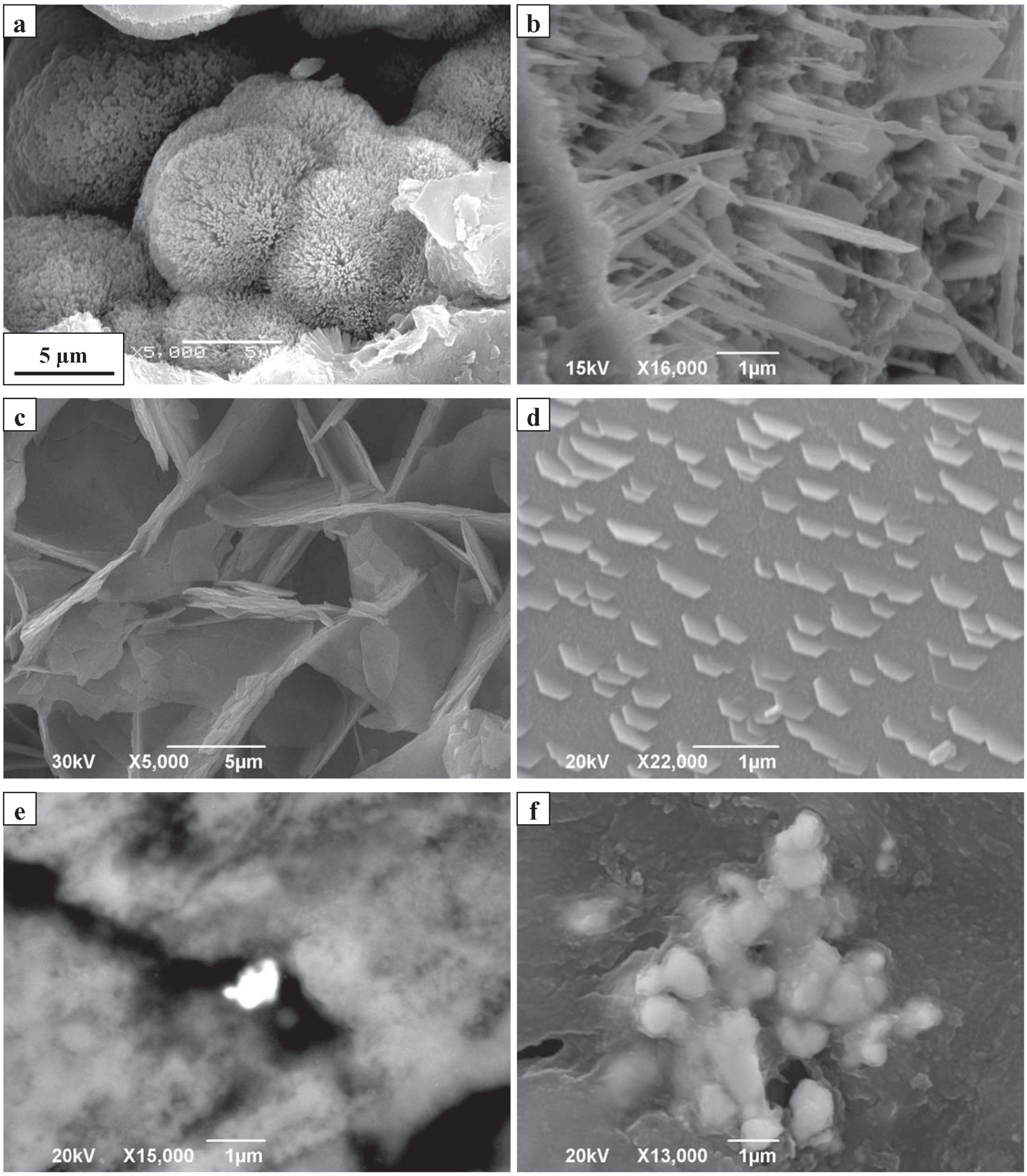

Fig. 3. SE and BSE (e) images of nanometer-sized grains of weathered type on fractured surfaces and in polished sections (e, f) of meteorites. (a, b): fine, fibrous needles of goethite within the ungrouped ataxite Chinga (a) and in the Galkiv chondrite (b). (c): very thin platelets of iron hydroxides with ~15 wt. % NiO arranged on a surface of the intensively weathered Berdyansk (L6) chondrite. (d): hexagonal plates, likely hematite, probably located along shear deformations on the surface of an olivine grain from the pallasite Omolon. (e): Separate grain of native silver in the Krymka meteorite. The grain is located within a crack in Fe,Ni,S-hydroxides belonging to weathering products of metal-troilite. (f): complicated globular structure of an agglomerate of native silver within iron hydroxides of the Krymka meteorite

CONCLUSIONS

1. Nanometer-sized mineral grains are ordinary constituents of all types of meteorites. Most of them occur within the fine-grained silicate material of primitive meteorites.

2. Complicated globular morphology is typical for condensing nanometer-sized grains, whereas fibrous or lamellar morphology is common for weathering products.

3. Enhanced accretional properties of nanometer-sized grains could be responsible for the accretion of primary condensed nanoglobules within a protoplanetary nebula.

4. Morphological features of weathered products promote subsequent intensive degradation of meteoritic material due to their enhanced adsorptional properties.

5. Only the primitive meteorites contain different genetic types of nanometer-sized grains that resulted from the structural ordering of solid matter as a fundamental process in the formation of minerals in stellar, nebular or solid bodies environments.

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