**HYDROUS IRON PHOSPHATES IN THE CHONDRITIC IMPACT MELT BRECCIA NWA 4218.** D.D. Badjukov<sup>1</sup>, Brandstaetter<sup>2</sup>, G. Kurat<sup>2</sup>, and J. Raitala<sup>3</sup>, <sup>1</sup>V.I. Vernadsky Institute RAS, Kosygin str. 19, 119991, Moscow, Russia, <u>badyukov@geokhi.ru</u>, <sup>2</sup>Naturhistorisches Museum, Burgring 7, A-1010 Wien, Austria, <u>franz.brandstaetter@nhm-wien.ac.at</u>, <sup>3</sup>Astronomy, University of Oulu, PO BOX 3600, Finland, <u>jraitala@oulu.fi</u>

The chondritic melt rock NWA 4218 contains within the melt matrix regions rich in an iron phosphate mineral. We suggest that the hydrous phosphate was formed either (i) directly by terrestrial weathering in an acid environment or (ii) by terrestrial alteration of a certain primary phosphate (e.g. sarcopside, graftonite?).

Samples and analytical procedures: NWA 4218 was purchased at St. Marie aux Mine, France in 2005 and was classified as an L chondrite impact melt breccia [1]. We studied four polished thin sections of the meteorite with a total area of  $\sim$ 12 cm<sup>2</sup>. Standard analytical techniques such as optical microscopy, ASEM, and EPMA were used for the study.

**Description and results:** The rock is a melt breccia and consists of ordinary chondrite clasts set in a melt matrix. The rock has some porosity due to the presence of 0.1 - 3 mm-wide vugs and 1 - 10-µm-sized vesicles and voids. Subrounded chondritic clasts are usually less than 3 cm in size and their abundance is estimated to be approximately 15-20 vol.%. Clasts are commonly transected by thin veins of fine-grained melt matrix. Average Fa and Fs contents in olivine and low-Ca pyroxene from the clasts are  $23.5\pm0.4$  and  $19.5\pm0.3$  mol%, respectively. The clast minerals are darkened. Shock metamorphic effects include highly undulose and mosaic extinction of olivine and pyroxene grains, planar fractures and rare planar deformation features in olivine, partial isotropization of feldspar, and the presence of one or two sets of PDFs in large feldspar grains.

One clast is composed mainly of coarse-grained olivine and pyroxene grains and occasionally chondrule fragments embedded in a molten groundmass. Only vague shadows of chondrule outlines are visible. Average Fa and Fs contents in relic olivine and low-Ca pyroxene from the clast are  $21.8\pm0.6$  and  $19.0\pm0.9$  mol%, respectively. The brownish groundmass consists of fine-grained (2 - 40 µm-sized) olivine, pyroxene and interstitial glass and shows igneous textures. The relict olivine grains show planar fractures, mosaicism and are often re-crystallized to aggregates of domains that have roughly similar crystallographic orientation.

The impact-melt hosting the chondritic clasts also contains relict (> 20 µm-sized) olivine and pyroxene grains that contain numerous tiny droplets of troilite. The olivine grains display shock effects such as undulose extinction, strong mosaicism, planar fractures and incipient re-crystallization that correspond to shock stages ranging from moderate to strong (~20 - 50 GPa). Some relict grains have sharp contacts with the matrix whereas others appear to be overgrown by small grains that crystallized from the melt. The melt matrix has textures varying from microporphyritic to microgranular and consists mainly of euhedral to subhedral (1 - 30) $\mu$ m-sized) olivine grains and subhedral to anhedral (1 – 40 µm-sized) pyroxene grains embedded in a glass mesostasis containing sulfide and metal dust commonly converted to oxides. Olivines and pyroxenes that crystallized from the melt are compositionally slightly poorer in Fe as compared to the minerals in the chondritic clasts but have wider ranges.

Olivine has an average Fa content of 21.6 mol% (range 21.2-24.7 mol%) with Mn as the only detectable minor element (range 0.4-0.5 wt% MnO). The average Fs content in low Ca-pyroxene is 18.1 mol% and ranges from 14.4 to 21.7 mol% and Wo contents vary from 1.2 to 4.3 mol%. The low Ca-pyroxene contains some Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> with concentrations below 0.7 wt% and usually lower than 0.5 wt%. Mesostasis glass has 70 -73 wt% SiO<sub>2</sub>, 20 - 24 % Al<sub>2</sub>O<sub>3</sub>, 1.5 - 2.5 % MgO, 1.5 % FeO, 2.5 % Na<sub>2</sub>O, and 0.5 % K<sub>2</sub>O. Opaque phases are troilite and products of its weathering, chromite, iron oxides, and occasionally dusty metal. Remelted chromites in the matrix differ from relict chromites by a slightly higher Fe/(Fe+Mg) atomic ratio (0.77) and lower Cr/(Cr+Al) atomic ratio (0.79) and, hence, are richer in hercynite component. Spherical aggregates with iron oxide cores and Ni-containing sulfide mantles are suggested to be former metal-trolite droplets. They are very similar in appearance to pyrrhotite-limonite/saponite aggregates in the Lappajärvi impact melt rocks, which are proposed to be shock-melted and altered remnants of troilite and metal of the Lappajärvi projectile [2,3].

Noteworthy, water-containing iron phosphates occur as minor secondary minerals in NWA 4218. The iron phosphate phase exhibiting a greenish colour in transmitted light clusters within 100-250  $\mu$ m-sized sub-rounded patches in the impact-melt matrix (Fig.1).



Fig. 1. Composite BSE-SE image of a region rich in Fephospate (grey) within the impact-melt matrix. Olivine and pyroxene are dark grey, Ni-containing (oxi?)sulfide is white, Fe-oxide is light grey. Holes and epoxy are black. The center of the area is occupied by a relic pyroxene grain.

In these patches the melt contains  $1-10 \ \mu\text{m-sized}$  phosphate grains of euhedral to subhedral shape resembling the outlines of olivine grains. Also, the outer zones of some

former olivine grains consist of iron phosphate and seem to be a product of substitution of olivine by this phosphate (Fig. 2). The posphate-rich regions are not abundant and a thin section with an area of 4 - 5 cm<sup>2</sup> usually contains only a few of them.



Fig.2. Olivine – hydrous Fe-phosphate (light grey) assemblage, composite BSE-SE image. Interstitial glass is dark grey, voids are black

The greenish Fe-phosphate contains Mg and minor amounts of Mn, Ni, Co, Si, S, Al and EMPAs have low totals. Contents of Si are variable and correlate negatively with P and positively with totals. Neglecting Al2O3 as a component due to its very low abundance, one can calculate the formula of the phase as

(Fe, Mg, Ni, Co)<sub>3</sub>[PO<sub>4</sub>]<sub>2-(x,y)</sub>[SO<sub>4</sub>]<sub>x</sub>[SiO<sub>4</sub>]<sub>y</sub> \*(3-4)H<sub>2</sub>O, where x and y are ~0.04. Iron is the only main cation, Mg atomic contents are usually lower than 0.15 and Ni and Co contents are lower than 0.01. This formula roughly corresponds to that of phosphoferrite [Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>\*3H<sub>2</sub>O] or ludlamite [Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>\*4H<sub>2</sub>O].

Another iron phosphate present is vivianite which in contrast to the mode of occurrence of the greenish Fe-phosphate occurs in  $20 - 50 \mu$ m-wide vugs near chondritic clasts.

The whole meteorite is heavily weathered. Numerous iron hydroxide veins and associated veinlets intersect the rock. All lithologies show significant brown staining but glass and mafic silicates are unaltered. Metal is transformed to limonite and sulfide (troilite) is converted to Ni-containing sulfides (oxy-sulfides?) and oxide(s). Only tiny metal droplets survived in the impact-melt matrix in the central part of the rock mass. These features correspond to weathering grade W4.

**Discussion:** NWA 4218 contains an appreciable amount of relictic shocked chondritic material which indicates that the rock is an impact-melt breccia. The olivine and pyroxene compositions in all but one of the studied clasts correspond to L chondrites and the degree of chondrule recrystallization as well as the presence of low-Ca clinopyroxene are consistent with petrologic type 5. The observed shock effects in the clasts correspond to shock stage S4. The partially (anatec-

tic?) melted clast experienced stronger heating than these L5 clasts It contains relict olivine, which has a slightly lower Fe content than that of the L clasts. We suppose that the original compositions of olivines in the clast were similar to L chondrite olivines but that they were modified due to thermal reduction of Fe and/or interaction with the melt. Impact melt breccias dominate among impact melted meteorites and NWA 4218 is similar to other chondritic impact-melt breccias ([4], [5] and references therein) and resembles terrestrial impact-melt rocks. We suppose that NWA 4218 was derived from a melt breccia sheeet at the floor of a relatively large impact crater.

The origin of the phosphate-rich patches is unclear. It seems that the phosphate substitutes olivine and is a metasomatic reaction product. Terrestrial weathering itself could directly cause this olivine alteration. Under acidic conditions, olivine is a less stable phase than glass or pyroxene and the presence of orthophosphorous acid from a terrestrial source would produce dissolution of olivine and precipitation of the iron phosphate. However, this model does not explain (i) the uniform distribution of the phosphate patches through the meteorite mass and the lack of their preferred development near the surface of the meteorite and (ii) their insulated isometric but not vein-like outlines. Furthermore, there is a problem of a terrestrial source for the orthophosphorous acid.

On the other hand, the phosphate-rich patches could have on the NWA4218 parent body and were modified by terrestrial weathering. One way of contamination of an L chondrite by iron phosphate is dissemination of an iron projectile in the impact melt sheet. Similar terrestrial impactmelt rocks are contaminated by a projectile matter with contents up to 10-15 % [6,7]. If this projectile was relatively rich in iron phosphates (sarcopside, graftonite) then the phosphates could have been incorporated into the silicate melt by shock melting of the projectile. Segregation of metal melt from the immiscible silicate melt could explain the absence of metal nodules in NWA 4218. Following fluidal activity in the crater melt sheet might produce the substitution of olivine by some iron phosphate(s). The fluidal activity in impactite sheets on parent bodies has been proposed as the cause of origin of some varieties of black veins in ordinary chondrites [8]. Subsequent terrestrial alteration then led to hydration and incorporation of Ni, Co, and S into the phosphate phase.

Finally, vivianite is considered as alteration product formed by dissolution of the pre-existing phosphate (phosphoferrite or ludlamite) and precipitations in vugs. **Acknowledgments.** This study was supported by Austrian Academy of Sciences and Academy of Finland. **References** 

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