Observation of internal structure of carbon grains in Dar al Gani 999 ureilite.

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Introduction: Ureilite is one of the achondrite mainly consist of coarse-grained olivine and pyroxene. Majority of them are thought to be igneous rocks after partial melting based on petrologic, chemical composition, and Oxygen isotope composition analyses. One of the unique characteristic of ureilite is relatively large amount of carbonaceous materials up to ~10 vol. %. It is well known that those carbonaceous grains are composed by graphite, diamond, and rare lonsdaleite (hexagonal diamond) [1]. At the present, there are some hypothesis for diamond formation in ureilite. Well accepted hypothesis is the shock origin models in which diamonds formed by shock pressure when parent body suffered catastrophic disruption [1,2]. On the other hand, recent studies reveal that micro sized diamond occur in some ureilites and proposed that such micro diamond is not likely to be shock origin [3].

On the other hand, basic texture of carbon grain is still not well understood, in contrast chemical and crystallographic characteristics were eagerly investigated. The main reason that prevent the understanding is technical problem. Graphite is one of the softest material and diamond is the hardest material. Thus, it is impossible to make smooth surface of carbon grain in ureilite that is mixture of graphite and diamond. Thus commonly used surface analysis such as SEM observation is not suitable to understand texture of carbon grain in ureilites. To investigate such material, 3D textural investigation such as CT analysis is the most powerful tool. However, conventional CT analysis with absorption contrast is difficult to visualize precise texture of graphite-diamond composite because of too small difference of absorption coefficient between graphite and diamond.

To overcome those problems, we developed investigation procedure with scanning/imaging X-ray microscope (SIXM) and electron and ion probes. Focused ion beam machine enable us to make micro sized sample by chemical process. Thus it is very suitable for carbon grain in ureilite which is impossible to make micro sample by mechanical process. SIXM enable us to investigate internal structure of light element materials such as carbon allotropes. In this study, we report the detail internal structure of carbon grains in ureilite Dar al Gani (DaG) 999 by newly developed methods, and discuss its formation history.

<u>Sample and Methods</u>: We prepared a thin section of DaG 999. Based on the surface observation by optical microscope and electron microscope, we choose 4 carbon grains for SIXM analysis. Micro samples (~30x30x20 um in size) were prepared by using FIB. SIXM analysis was conducted at BL47XU, SPring-8. In addition to SIXM analysis, we also conducted dual energy tomography (DET) with 7 keV and 7.35 keV to obtain high resolution image and reveal 3D Fe distribution.

Result and Discussion

The observed grains (grain1-4) have different occurrence at the thin section surface. Grain1 is a flatten shaped grain which occurs among mineral fragments in the brecciated region. Grains2-4 occur in the large lithic clast (~1 cm) which resembles olivinepigeonite monomict ureilite. The shock stage is U-S3 in the classification of shock metamorphism [4]. Grain2 has amoeboid shape which occur between silicate grain. Grain3, 4 have blade shape.

CT analysis reveals that there are two types of texture present among carbon grains. Grain1, 2 have texture where wide spread graphite enclose micron sized diamonds (Type1 texture). Some micro diamond has hexagonal shape



Fig. 1. CT images of carbon grain. (a) CT image of grain2. Micro diamond enclosed in graphite. Micro diamond with twinning-like occurrence is shown in upper of image. (b) CT image of grain3. Foliation texture is well developed (up-down) with Fe-bearing sheet. Planar diamond occur perpendicular to foliation (right-left) and cut by foliation. Scale bars show 10µm.

which is likely the euhedral shape. Fig. 1a shows a typical type1 texture. Fe-bearing material occur in all samples and they are selectively rich in micro diamond rather than graphite-rich region. Some samples have micro diamond with unique occurrence. One is twining-like occurrence of diamond (Fig. 1a). The other is planar aggregate of micro diamond with width up to 20µm.

Grain3, 4 have very fine-grained texture with well oriented foliation (Type2 texture). Fig. 2b shows a typical type2 texture. Grain sized is estimated to be less than 100 nm which is spatial resolution of X-ray microscope. Although precise estimation is difficult because of small size, those grains are thought to be graphite and diamond. Orientation of foliation is well matched to elongation direction of host carbon grain. In the fine grained texture, micro diamond was also present. Those micro diamonds have plate shape and include Fe-bearing inclusions as the case of Type1 texture. In addition to inclusions, Fe-rich sheets are present among all sample. Those shape are likely to be disk and align parallel to foliation texture and elongation of host carbon grain. There is no relationship with those Fe-rich sheet and occurrence of diamond. In contrast to those well oriented components, we observed planar diamond across over the micro sample nearly perpendicular to foliation. This planar diamond is cut by foliation texture.

Coexistence of type1 and type2 texture in single clast indicate that formation condition of carbon grain is not so simple. Type2 texture resemble the texture of carbon grain in highly shocked ureilite [1]. Thus, it is likely to be related to shock event. In addition, both grain3 and grain4 has blade shape which is typical euhedral shape of graphite. This coincident imply that formation of type2 texture related to shape of precursor, although more investigation needed to conclude this hypothesis. In addition, complex fault relationship in type2 texture indicates, at least, they experience 2 texture formation event.

For the origin of micro diamonds, abundant Fe-bearing inclusions in micro diamond imply the relationship between iron and diamond. Possibly Fe worked as catalyst for them as previously proposed [1]. However, if this is the case, diamond should be crystallized from carbon-rich iron melt. It means that solid-solid (martensitic) transformation often proposed for phase transformation during shock deformation is not likely for those micro diamonds. Therefore, micro diamond in type1 and possibly in type2 texture might not be the result of shock deformation.

We propose that diamond formation process is not limited in single process previously assumed but more complex e.g. multi shock formation or mixture of previously proposed scenario such as shock modification of pre-existence micro diamond.

Reference: [1] Nakamuta et al. (2016) JMPS, 111, 252-269. [2] Nestola et al. (2020) PNAS, 117, 41, 25310-25318. [3] Miyahara et al. (2015) GCA, 163, 14-26. [4] Stöffler et al. (2018) MAPS, 53, 5-49.