THE ORIGIN OF DIAMONDS IN UREILITES. C. A. Goodrich[1], F. Nestola[2], R. Jakubek[3], T. Erickson[3], M. Fries[4], A. M. Fioretti[5], D. K. Ross[3], and F. E. Brenker[6]. [1]Lunar and Planetary Institute, USRA, Houston, TX 77058 USA (goodrich@lpi.usra.edu); [2]Dept. Geosciences, Univ. of Padova, Padova I-35131 Italy; [3]Jacobs-NASA, JSC, Houston TX 77058 USA; [4]ARES, NASA, JSC, Houston TX 77058 USA; [5]CNR-Inst. Geosciences and Earth Resources, Padova I-35131 Italy; [6]Geoscience Inst., Goethe-Univ., Frankfurt 60323 DE.

Introduction: Recent studies have proposed that diamonds in ureilites formed at static pressures >20 GPa [1,2]. This would imply either that the ureilite parent asteroid was a Mercury- to Mars-sized embryo [2], or that diamonds in ureilites are exogenous [3].

Ureilites are ultramafic achondrites containing ~2-8 wt.% carbon [4]. The carbon is dominantly graphite, occurring in lath-shaped areas along silicate grain boundaries. In "unshocked" ureilites these areas consist of mm-sized graphite crystals [5,6]. In most ureilites (shocked to various degrees) they are polycrystalline. Diamonds are a minor component in graphite areas.

Hypotheses for the origin of the diamonds include: (1) high static pressure in a planetary-sized body [1,2,7]; (2) transformation from graphite by impact shock [8-13]; (3) chemical vapor deposition [14,15]. Most authors favor shock origin, but [1,2] argued that a ureilite (MS-170) from Almahata Sitta (AhS) contains large diamonds formed at high static pressures.

Here we investigate the origin of diamonds in ureilites Northwest Africa (NWA) 7983 and MS-170.

Methods: SEI/BEI, EMPA, Raman spectroscopy, and EBSD analyses were conducted at ARES, JSC. XRD was conducted at the University of Padova.

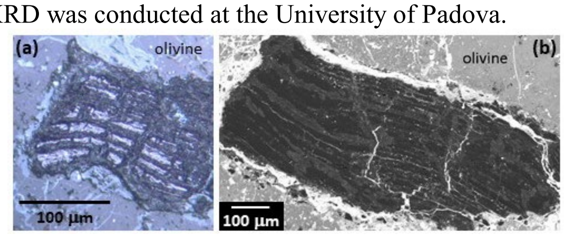

Fig. 1. Carbon masses in NWA 7983. (a) Reflected light. Stripes of high relief and reflectivity parallel the external shape of the carbon mass. (b) BEI. Dark & light stripes correlate with high & low relief, respectively. Diamonds occur in both dark and light areas

NWA 7983: NWA 7983 consists of olivine, pyroxene, and ~6 vol.% carbon phases. Olivine is mosaicized and the pyroxene has been extensively shock-smelted [16], indicating ~15 GPa [17]. The carbon occurs dominantly in lath-shaped masses (up to 1 mm) along silicate grain boundaries. They show a striped texture parallel to their external shapes. In reflected light, the stripes consist of alternating high relief, high reflectivity and low relief, low reflectivity (Fig. 1a). These are seen in BEI (Fig. 1b) as dark and light stripes, respectively. From EDS, the dark areas contain only C; light areas also contain Fe and S. Based on fluorescence, both light and dark areas contain diamonds. Micro-XRD of fragments removed from light areas showed nanodiamonds (9-50 nm), nanographite, and Fe and FeS. A 100 µm fragment from a dark area showed only diffraction spots (Fig. 2c) indicating a single diamond crystal. Other dark areas showed mixed large crystals and nanodiamonds.

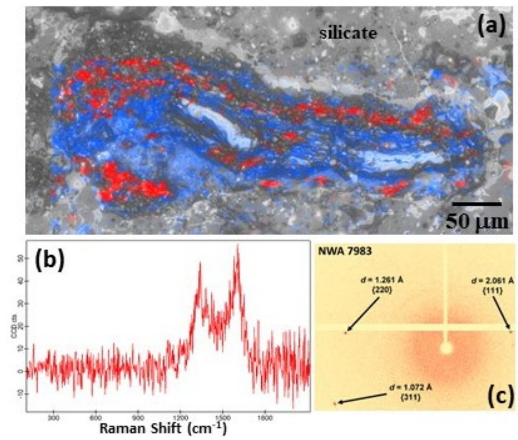

Fig. 2. (a) Carbon area in NWA 7983. Raman (red = diamond; blue = graphite) overlain on reflected light image. (b) Raman spectrum from high relief stripe in (a), consistent with nanodiamonds. (c) XRD pattern of ~100 µm-sized single diamond crystal from NWA 7983.

Raman images of carbon areas (Fig. 2a) show the distribution of diamond (1330 cm^{-1} band) and graphite (~1590 cm^{-1} G band). Large diamonds (contiguous "grains" up to 30 µm) are prevalent in low-relief areas but also occur in some high relief stripes (Fig. 2a). The high relief areas show mainly graphite. However, a subset of spectra yield broad, low intensity 1330 cm^{-1} diamond bands (Fig. 2b) consistent with nanodiamonds [18]. These bands derive from the sp2 hybridized carbon atoms at the diamond grain boundary and occur because smaller diamonds have a larger fraction of carbon atoms at grain boundaries [19].

EBSD mapping of most carbon areas in NWA 7983 are poorly indexed, with minimal diamond and graphite patterns detected. This may be due to the defect-rich nature of the phases, rough surface topography from polishing soft graphite mixed with hard diamond, or the crystallites being smaller than the interaction volume of the electron beam (~50 nm). However, in one carbon area (Fig. 3), EBSD shows regions of diamond (up to ~125 µm) in which diamonds all have similar orientation (Fig. 3c). The diamonds are internally twinned with both (111) and (112) habit planes (K1). Twin formation may be consistent with a transformation mechanism, supporting an origin through high deviatoric stresses, consistent with shock.

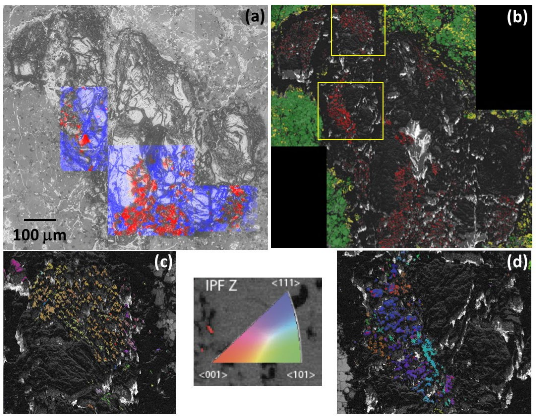

Fig. 3. NWA 7983 carbon area. (a) Raman image (red = diamond) superimposed on reflected light image. (b) EBSD map of diamond (red) distribution. (c,d) Inverse pole figure Z maps (key in middle) of areas outlined in yellow in (b).

MS-170: MS-170 is a typical olivine-pigeonite ureilite of medium shock level, with carbon phases in lath-shaped masses along grain boundaries. Diamonds occur as high relief, fluorescing grains (5-20 µm) within low relief, non-fluorescing areas (Fig. 4a).

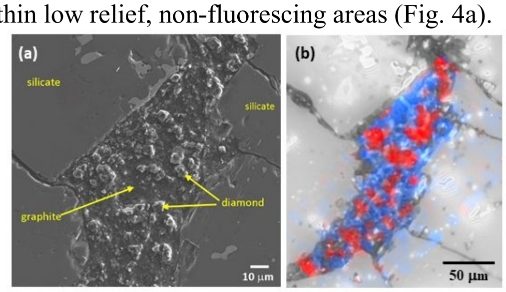

Fig. 4. Carbon area in MS-170. (a) SEI. (b) Raman map (red = diamond; blue = graphite).

Raman maps of the carbon masses (Fig. 4b) show large diamond areas and graphite corresponding to high and low relief. Compared to NWA 7983, the diamond ~1330 cm^{-1} band is more prevalent, indicating that MS-170 contains more large diamonds. We did not observe the broadened, low intensity 1330 cm^{-1} band, suggesting few or no nanodiamonds. XRD will be used to test this. EBSD indexing of the carbon areas was poor, likely due to large topographic relief. Grains that do index show evidence for (111) and (112) twins.

Discussion: NWA 7983 is highly shocked yet contains large (≥100 µm) diamonds. This suggests that large diamonds in ureilites were formed by shock, rather than simply having survived it [1,2]. The blade-shapes (graphite morphology) of the carbon masses in which diamonds occur support this interpretation. If the diamonds were remnants of larger crystals formed in a planetary mantle, the shapes of the carbon masses would be those of diamond. Instead, their shapes and striped textures suggest that the diamonds are pseudomorphing graphite (as in the Popigai impact [20]) because they formed by a rapid transformation.

NWA 7983 has a high abundance of nanodiamonds. Nanodiamonds are commonly formed in industrial detonation of oxygen-deficient carbon-bearing gases, which simultaneously produces diamonds up to 140 µm size [21]. We suggest that in NWA 7983 and other shock-smelted ureilites [13], large and small diamonds formed by shock detonation of carbon-rich gases produced in decompression-triggered smelting [16].

The carbon masses in which diamonds occur in MS-170 also have the shapes of graphite crystals. Thus, it is unlikely that diamonds in this sample formed during long residence in a planetary mantle [1,2]. Furthermore, the "large" diamonds reported by [1,2] were only inferred to have existed from unconnected segments of diamonds having the same orientation. Other explanations could account for multiple crystals with the same orientation, including impact shock origin [22]. The single crystal diamonds in NWA 7983 are larger than any observed in MS-170 by [1,2]. Diamonds of such sizes can form in solid state shock transformation from graphite [23], and do not require long growth times.

From results to-date, we find no evidence for formation of diamonds in MS-170 or any ureilites in a large planetary body.

References: [1] Miyahara M. et al. 2015. *GCA* 163, 14-26. [2] Nabiei F. et al. 2018. *Nature Commun*. 9, 1327, 1-6. [3] Desch S. et al. 2019 *LPSC* 50, #1646. [4] Goodrich C.A. et al. 2015. *MAPS* 50, 782-809. [5] Berkley J.L. & Jones J. 1982. *Proc. 13th LPSC, JGR* 87, A355-A364. [6] Treiman A.H. & Berkley J.L. 1994. *Meteoritics* 29, 843-848. [7] Urey H. 1956. *ApJ* 124, 623-627. [8] Lipschutz M. 1964. *Science* 143, 1431-1434. [9] Nakamuta Y. & Aoiko Y. 2000. *MAPS* 35, 487-493. [10] Hezel D. et al. 2008. *MAPS* 43, 1127-1136. [11] Le Gouillou C. et al. 2011. *GCA* 74, 4167-4185. [12] Ross A.J. et al. 2011. *MAPS* 46, 364-378. [13] Nestola F. et al. 2020. Submitted. [14] Fukunaga K. et al. 1987. *Nature* 328, 141-143. [15] Matsuda M. et al. 1995. *GCA* 59, 4939-1949. [16] Warren P.H. & Rubin A. 2010. *GCA* 74, 5109-5133. [17] Stöffler D. et al. 2018. *MAPS* 49, 5-49. [18] Zhou D. et al. 1998. *J. Appl. Phys.* 84(4), 1981-1989. [19] Birrell J. et al. 2005. *Diamond & Related Materials*, 86-92. [20] Koeberl C. et al. 1997. *Geology* 25, 967-970. [21] Efremov V.P. et al. 2017. *J. Phys. Conf. Ser.* 946, 1-8. [22] Erskine D.J. & Nellis W.J. 1991. *Nature* 340, 317-319. [23] De Carli P.S. et al. 2002. *GSA Spec. Paper* 356, 595-605.