

SI ISOTOPES OF BROWNLEEITE. K. Nakamura-Messenger^{1,2}, S. Messenger¹, M. Ito^{1,3}, L. P. Keller¹, S. J. Clemett^{1,4}, J. H. Jones¹, W. Klöck⁵, M. E. Zolensky¹ and H. Tatsuoka⁶. ¹Astromaterials Research and Exploration Science Directorate /NASA Johnson Space Center, Houston, TX 77058, USA, ²ESCG/ Jacobs Engineering, TX 77058, USA, ³LPI-USRA, Houston TX 77058, USA, ⁴ESCG/ ERC Inc., TX 77058, USA, ⁵Röntgenanalytik Messtechnik GmbH, Tausnusstein, D-65232, Germany, ⁶Faculty of Engineering, Shizuoka University, Hamamatsu, Japan. (keiko.nakamura-1@nasa.gov)

Introduction: Brownleeite is a manganese silicide, ideally stoichiometric MnSi, not previously observed in nature until its discovery within an interplanetary dust particle (IDP) that likely originated from a comet [1]. Three discrete brownleeite grains in the IDP L2055 I3 (4 μm in size, hereafter IDP I3) were identified with maximum dimensions of 100, 250 and 600 nm and fully analyzed using scanning-transmission electron microscopy (STEM) [1]. One of the grains (100 nm in size) was poikilitically enclosed by low-Fe, Mn-enriched (LIME) olivine. LIME olivine is epitaxial to the brownleeite with the brownleeite (200) parallel to the olivine c^* [1]. LIME olivine is an enigmatic phase first reported from chondritic porous IDPs and some unequilibrated ordinary chondrites [2], that is commonly observed in chondritic-porous IDPs. Recently, LIME olivine has been also found in comet Wild-2 (Stardust) samples [3], indicating that LIME olivine is a common mineral component of comets. LIME olivine has been proposed to form as a high temperature condensate in the protosolar nebula [2].

Brownleeite grains also likely formed as high-temperature condensates either in the early Solar System or in the outflow of an evolved star or supernova explosion [1]. The isotopic composition of the brownleeite grains may strongly constrain their ultimate source. To test this hypothesis, we performed isotopic analyses of the brownleeite and the associated LIME olivine, using the NASA/JSC NanoSIMS 50L ion microprobe.

Sample & Analytical Methods: Brownleeite-bearing IDP I3 was embedded in low-viscosity epoxy and 70 nm-thick sections were obtained using ultramicrotomy. The biggest brownleeite grain (600 nm in size) occurred in three consecutive thin sections, two of which were on C supportive films and observed by using STEM, while the middle section ended up on the Cu TEM grid bar. The center section was the target for isotopic studies. Mn and Si isotopic images were taken simultaneously, acquiring images of ^{12}C , ^{16}O , $^{28,29,30}\text{Si}$, $^{55}\text{Mn}^{16}\text{O}$, and $^{55}\text{Mn}^{28}\text{Si}$ in multidetection with electron multipliers. The images were obtained by rastering a 0.12 pA, <100 nm Cs^+ beam over a 6 μm field-of-view that covered the entire IDP section including the MnSi target grain. These images were repeatedly acquired for a total of 30 image layers. Sample charging was mini-

mized with the use of an electron flood gun. A Si wafer was used as an external isotopic standard. The isotopic compositions of the brownleeite grain, LIME olivines, and standard minerals were determined using custom image processing software, in which corrections are made for electron multiplier deadtime, QSA, and instrumental mass fractionation. The outlines of the brownleeite grain were determined in each image layer to minimize isotopic dilution effects from adjacent material.

Unfortunately, the brownleeite grains found in IDP I3 are too small to measure Mn-Cr isotopes even with the NanoSIMS 50L.

Brownleeite & Associated Minerals: The major components of brownleeite-bearing IDP I3 include GEMS grains (*glass with embedded metal and sulfides*), enstatite, forsterite, and sulfides bound together by abundant carbonaceous material. Mineral grain sizes range from 20 to 200 nm. Individual enstatite and forsterite grains contained up to 5 wt.% of MnO, consistent with composition of LIME olivines and pyroxenes [2,4]. Magnetite rims, which are an indicator of strong heating during atmospheric entry, were not developed on the surfaces of mineral grains. Solar flare tracks were not detected in any I3 enstatite grains (~200 nm in size), consistent with a short space exposure time. IDP I3 also contains C-rich spherical hollow objects similar to the ^{15}N -rich organic globules reported from many carbonaceous chondrites and IDPs [5].

Si Isotopes of Brownleeite: Figure 1 shows an elevated Si/O ratio where the brownleeite grain (600nm in size) is located in the secondary electron image taken in the STEM. The MnO image in the Figure indicates that LIME olivine is associated with the brownleeite grain, consistent with our previous observation of the adjacent sections. According to the isotopic imaging, the brownleeite grain has $\delta^{29}\text{Si} = -18 \pm 23 \text{‰}$, $\delta^{30}\text{Si} = -44 \pm 36 \text{‰}$ (1σ) and LIME olivine has $\delta^{29}\text{Si} = -6 \pm 16 \text{‰}$, $\delta^{30}\text{Si} = -21 \pm 13 \text{‰}$ (1σ). These isotopic data indicate that the brownleeite and LIME olivine are probable Solar System products rather than stardust.

Brownleeite Forming Environment in early Solar Nebula: Our new isotopic results reinforce our earlier evaluation [1] that brownleeite could have formed locally in the early solar nebula, as well as the LIME

olivine. A limiting f_{O_2} calculation for brownleeite formation yields a $\log f_{O_2}$ of -15.5, which is very close to that of a gas of solar composition. Brownleeite could have formed under more reducing conditions, but our calculations indicate that conditions more reducing than solar are not necessary. Although silicides are predicted solar nebula condensates [6], MnSi is clearly extremely rare and the conditions for its formation must have been unusual to account for the lack of other elements in solid solution (e.g. Fe).

It is important that one of the brownleeite grains we observed is poikilitically enclosed in LIME olivine. This enclosure gives a stratigraphy: brownleeite formed first and the olivine formed later. The epitaxial nature of the brownleeite-olivine interface strongly suggests that the brownleeite acted as a nucleus for LIME olivine condensation from a gas. Since LIME olivine encloses brownleeite, it seems very unlikely that brownleeite was somehow formed by the reduction of olivine. In this eventuality, we would expect that brownleeite would enclose olivine instead.

Figure 1: NanoSIMS Isotopic imaging of a brownleeite-bearing thin section of IDP L205513 cluster #7 on a TEM Cu grid bar.

References: [1] Nakamura-Messenger K. et al. (2010) *American Mineralogist*, in press. [2] Klöck, W., et al. (1989) *Nature*, 339, 126-128. [3] Zolensky, M.E. et al. (2006) *Science*, 314, 1735-1739. [4] Weisberg, M. K. et al. (2004) *MAPS* 39, p.1741-1753 [5] Nakamura-Messenger, K., et al. (2006) *Science*, 314, 1439-1442. [6] Petaev P.I. & Wood J. A. (1998) *LPS XXIX*, #1474.

