PRESOLAR SILICA GRAINS IN METEORITES: IDENTIFICATION OF A SUPERNOVA SILICA GRAIN IN THE CO3.0 CHONDRITE LAPAZ 031117. P. Haenecour[1,2] and C. Floss[1,3]. [1]Laboratory for Space Sciences, [2]Department of Earth and Planetary Sciences, [3]Physics Department, Washington University, St. Louis, MO 63130, USA (haenecour@wustl.edu).

INTRODUCTION. The use of Auger spectroscopy to characterize the elemental compositions of presolar grains in primitive extraterrestrial materials (meteorites, interplanetary dust particles, Antarctic micrometeorites, and cometary samples) has led to the identification of new presolar phases, such as FeO, MgO, and SiO_2 grains [e.g., 1–4]. Presolar silica grains constitute the latest phase added to the presolar silicate inventory. SiO_2 has been called a "mythical condensate" [5] because it is not expected to condense in circumstellar shells according to thermochemical equilibrium calculations and its origin remains unclear.

Here we report on the identification of the first Group 4 silica grain in LaPaz 031117 and discuss models of silica dust formation in circumstellar environments.

EXPERIMENTAL METHODS. The presolar silica grain was identified by NanoSIMS 50 raster ion imaging during our search for oxygen- and carbon-anomalous grains in a thin section of LAP 031117. A focused Cs^+ primary beam of ~1 pA (~100 nm in diameter) was rastered over areas of 10×10 μm^2 (256^2 pixels). Secondary ions of $^{12,13}C^-$ and $^{16,17,18}O^-$, as well as secondary electrons, were simultaneously acquired in multicollection mode. Subsequently, high-resolution secondary electron images, and elemental spectra (from 30 to 1730 eV) were acquired for most of the grains using the PHI 700 Auger Nanoprobe.

PRESOLAR SILICA GRAINS IN METEORITES. To our knowledge only five other presolar silica grains have been identified so far, one in QUE 99177 (CR3) [2], and four in ALHA77307 (CO3.0) [3, 4]. These five grains have similar isotopic compositions, with enrichments in ^{17}O relative to solar and close to solar $^{18}O/^{16}O$ ratios (Fig. 1) and are classified as Group 1 grains [6]. Within errors, they all exhibit O/Si ratios consistent with SiO_2. Although Auger spectroscopy provides compositional information, it does not provide the structural information needed to determine whether the grains are crystalline or amorphous. TEM study of one presolar silica grain [4] indicated that it was amorphous. It is not clear whether the grain condensed as an amorphous phase, or was initially crystalline (e.g., quartz, tridymite, or cristobalite) and was later amorphized. Amorphous silicon dioxide grains with large enrichments in both ^{17}O and ^{18}O (with ratios of about 0.07 and 0.11, respectively) have also been reported from within insoluble organic matter (IOM) isolated from the Murchison CM meteorite [7]. However, these authors argued that the grains have a solar system origin with production of the oxygen isotopic anomalies through irradiation by high energy particles accelerated during an active phase of the protosun [7].

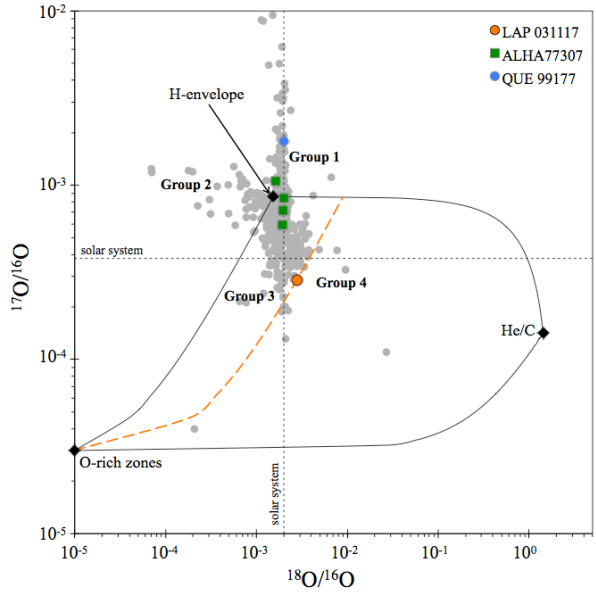

Figure 1. Oxygen three-isotope plot showing the silica grains identified in LAP 031117 (this study), QUE 99177 [2]*, and ALHA 77307* [3, 4]*. Other data (grey) are from the Presolar Grain Database (http://presolar.wustl.edu/PGD/Presolar_Grain_Database.html). Group classifications are from [6]. Black dimonds corresponds to the* 15 $M_\odot$ SN zones from *[18] and the black lines corresponds to mixing calculations between different SN zones.*

Based on its differentiated Auger spectrum, one of the oxygen-anomalous grains identified in LAP 031117, LAP-53, appears to consist only of Si and O (Fig. 2). While the O/Si ratio of this grain is slightly higher (O/Si = 2.8 ± 0.6) than what would be expected for SiO_2, no other elements are detectable in the Auger spectrum (Fig. 2). Although the higher O/Si ratio could reflect residual surface oxygen contamination, it is also possible that the grain really does have a higher O/Si ratio than SiO_2, as many presolar silicates are also non-stoichiometric. Unlike the five presolar silica grains previously reported, this grain belongs to group 4, with an enrichment in ^{18}O relative to solar and a subsolar $^{17}O/^{16}O$ ratio (Fig. 1). Like the silica grains previously

reported, the silica grain identified in LAP 031117 is relatively small, with a size of only 190 nm.

SILICA GRAINS FROM LOW- TO INTERMEDIATE-MASS RED GIANT OR AGB STARS. The five presolar silica grains previously identified are Group 1 grains (Fig. 1) and originated in the envelopes of low- to intermediate-mass red giant or asymptotic giant branch (AGB) stars. IR spectroscopy studies of AGB stars have suggested that SiO_2 could be the carrier of the 13 μm feature observed in about half of the oxygen-rich AGB stars [e.g., 8]; however other species, such as corundum (α-Al_2O_3) and spinel ($MgAl_2O_4$), have also been proposed as possible carriers of this feature [8].

According to thermodynamic calculations for equilibrium condensation from a solar composition gas, silicon is completely consumed in circumstellar environments by the formation of Mg- and/or Fe-rich silicates, mainly olivine and pyroxene [e.g., 5]. However, thermodynamic condensation calculations [e.g., 9, 10] suggest that $MgSiO_3$ and SiO_2 could constitute significant dust components in the atmospheres of stars characterized by Mg/Si < 1. Observations suggest that only about 10% of all stars are characterized by Mg/Si ratios favorable for the condensation of SiO_2 grains [9], which would explain the low number of silica grains identified so far. Close to 450 oxygen-anomalous grains have been analysed with the Auger Nanoprobe so far, but only six (~1%) are silica grains.

SILICA GRAIN FROM A SUPERNOVA. The silica grain identified in our study belongs to Group 4 (Fig. 1) and most probably originated in a Type II supernova (SN) [e.g., 11].

Both equilibrium and non-equilibrium condensation models in supernova ejecta predict the condensation of silica grains. On the one hand, high-temperature equilibrium condensation sequence calculations [12] show that graphite and SiO_2 should be produced in abundance in the massive O-dominated SN zones, in the absence of polyatomic gaseous molecules (e.g., CO). Another model, based on equilibrium condensation calculations for the different layers of a $21M_\odot$ SN, indicates that tridymite, a high-temperature polymorph of quartz, is a possible condensate in the O/Si zone [13]. On the other hand, non-equilibrium condensation calculations, based on a non–steady state nucleation and grain growth, indicate that SiO_2 grains might condense from SiO molecules left over after the formation of Mg-silicate grains [14].

Recent astronomical observations by the NASA *Spitzer* Space telescope indicated the presence of silica in supernova remnants. The features of several species, including SiO_2, $MgSiO_3$, and SiC were identified in *Spitzer* IRS spectra of the Cassiopeia A SN remnant [15], and the young SN remnant 1E0102-7219 in the Small Magellanic Cloud (SMC) [16]. Spectral fitting of the 21μm feature implies the presence of both SiO_2, Mg-protosilicates, and FeO grains, likely originating from the inner O and Si/S layers of the supernova [15].

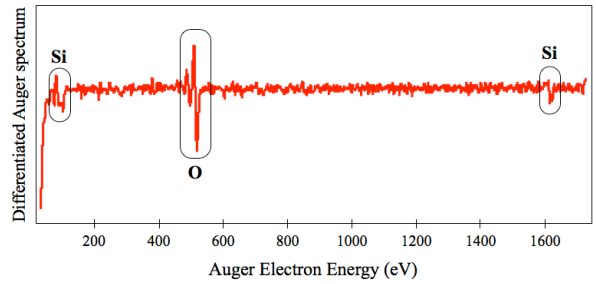

Figure 2. Differentiated Auger elemental spectra of the silica grain (LAP-53).

If silica grains condensed in O-rich layers of supernova as suggested by both thermodynamic calculations and astronomical observations, these grains should exhibit enrichments in ^{16}O relative to solar. However, the silica grain identified in LAP 031117 exhibits an excess in ^{18}O and a subsolar $^{17}O/^{16}O$ ratio, and its oxygen isotopic composition can be reproduced by mixing only a very small amount of ^{16}O-rich material from the O-rich zones with material from both the outer He/C zone and H-envelope (orange dotted line in Fig. 1).

CONCLUSION. Both theoretical models and astronomical observations have suggested the presence of silica dust in supernovae. The identification of a Group 4 silica grain in LAP 031117 provides evidence that condensation of silica dust does occur in supernova environments.

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