Bonanza: An extremely large dust grain from a supernova

Frank Gyngard, Manavi Jadhav, Larry R. Nittler, Rhonda M. Stroud, Ernst Zinner

Abstract

We report the morphology, microstructure, and isotopic composition of the largest SiC stardust grain known to have condensed from a supernova. The 25-μm diameter grain, termed Bonanza, was found in an acid-resistant residue of the Murchison meteorite. Grains of such large size have neither been observed around supernovae nor predicted to form in stellar environments. The large size of Bonanza has allowed the measurement of the isotopic composition of more elements in it than any other previous presolar grain, including: Li, B, C, N, Mg, Al, Si, Ca, Ti, Fe, and Ni. Bonanza exhibits large isotopic anomalies in the elements C, N, Mg, Si, Ca, Ti, Fe, and Ni typical of an astrophysical origin in ejecta of a Type II core-collapse supernova and comparable to those previously observed for other presolar SiC grains of type X. Additionally, we extracted multiple focused ion beam lift-out sections from different regions of the grain. Our transmission electron microscopy demonstrates that the crystalline order varies at the micrometer scale, and includes rare, higher order polytype domains (e.g., 15 R). Analyses with STEM–EDS show Bonanza contains a heterogeneous distribution of subgrains with sizes ranging from <10 nm to >100 nm of Ti(N, C); Fe, Ni-rich grains with variable Fe:Ni; and (Al, Mg)N. Bonanza also has the highest ever inferred initial 26Al/27Al ratio, consistent with its supernova origin. This unique grain affords us the largest expanse of data, both microstructurally and isotopically, to compare with detailed calculations of nucleosynthesis and dust condensation in supernovae.

Keywords: Presolar grains; Supernovae; Nucleosynthesis; Silicon carbide; NanoSIMS; Transmission electron microscopy; Isotopic anomalies

1. INTRODUCTION

Primitive meteorites, interplanetary dust particles, Antarctic micrometeorites, and cometary material contain tiny grains of stardust that condensed in outflows of late-type stars and the ejecta of core-collapse supernovae (Clayton and Nittler, 2004; Lodders and Amari, 2005; Lugaro, 2005; Zinner, 2014). After a long interstellar history, these grains ended up in the molecular cloud from which our Solar System formed. The stellar origin of these so-called presolar stardust grains is inferred from their isotopic compositions, which are highly anomalous and completely different from those of the Solar System. Their detailed study in the laboratory provides information on stellar evolution and nucleosynthesis, the chemical evolution of the Galaxy, as well as physical and chemical conditions in stellar atmospheres and in the early Solar System. Silicon carbide is the most studied type of presolar grain (Hynes and Gyngard, 2009; Nittler and Ciesla, 2016). Different subtypes of presolar SiC have been defined based on their C, N, and Si isotopic ratios (Hoppe et al., 1994; Zinner, 2014). While most SiC grains have an origin in...
asymptotic giant branch (AGB) stars, type X and C grains, comprising only 1% and ~0.1%, respectively, of all SiC grains, condensed in the ejecta of core-collapse (Type II) supernovae (SNe) (Nittler et al., 1996; Hoppe et al., 2012). These grains are characterized by excesses in $^{26}$Si and $^{15}$N relative to solar, a wide range of $^{12}$C/$^{13}$C ratios (from ~15 to ~10,000) and very high inferred $^{26}$Al/$^{27}$Al ratios, ranging up to 0.8. A subset of grains that had their Ca-Ti isotopes measured show large $^{44}$Ca excesses from the decay of short-lived ($t_{1/2} = 60$ y) $^{44}$Ti (Nittler et al., 1996). Both $^{26}$Si and $^{44}$Ti are produced only in SNe; the first by oxygen burning (e.g., Meyer and Zinner, 2006) and the second by a $\alpha$-rich freezeout from nuclear statistical equilibrium (Timmes et al., 1996). Their presence in X grains provides direct evidence for their SN origin.

In spite of their relatively low abundance, a fairly large number of X grains has been located by ion imaging (e.g., Nittler et al., 1997 and Hoppe et al., 2000) and automatic isotopic measurements (e.g., Nittler and Alexander, 2003). However, because many of these grains were relatively small (<1 μm), not many isotopic analyses of different elements have been performed on them. Most isotopic measurements have been restricted to C and Si. Of the ~700 X grains that have been analyzed to date (e.g., Hynes and Gygard, 2009), the approximate percentages of grains analyzed for the following elements are: C 67%, Si 93%, N 44%, Al-Mg 20%, S 4.0%, Ca (40,42,44) 21%, Ti (46,48,50) 16%, Fe (54,56,58) 7%, Ni (58,60,61,62) 6%, Ba (135,136,137,138) 1.2%. The fractions for other trace elements, such as Sr, Zr, Mo, and Ru, analyzed by resonance ionization mass spectrometry (RIMS) are even smaller. There is also no overlap for many of these analyses. For example, none of the X grains that had their Fe and Ni isotopic ratios measured (Marhas et al., 2008) were analyzed for their Ti isotopic ratios.

We report the discovery of an extremely large X grain, named Bonanza, with a diameter of 25 μm. This corresponds to a volume some 15,000 times larger than that of a typical ~1 μm X grain. Such a large grain offers a unique opportunity to measure as many elements as possible for their isotopic compositions in the same grain and to explore the nucleosynthesis mixing and condensation conditions that occurred in a presolar Type II SN. Bonanza was found among grains from the size fraction LU of the Murchison L-series chemical and physical separation (Amari et al., 1994). Here we report transmission electron microscopy (TEM) and NanoSIMS isotopic data of this unique grain. Preliminary results have been presented by Zinner et al. (2010, 2011) and Stroud et al. (2014, 2015). Some Raman spectroscopic data have been also reported for this grain (Wopenka et al., 2010) but are not discussed in detail here.

2. SAMPLES AND ANALYTICAL TECHNIQUES

The chemical and physical procedures to separate the SiC grains studied here have been described by Amari et al. (1994). Grains from the Murchison SiC-rich size fractions LS (2–10 μm) and LU (>10 μm) were deposited from suspension in a water-isopropanol solution onto microscope slides. From these slides, candidates of SiC grains were moved with a micromanipulator onto a clean gold foil and pressed into the foil with a quartz disk. Optical and scanning electron microscope (SEM) maps were obtained for documentation and 2 SiC grains were identified by energy dispersive X-ray (EDS) analysis in the SEM. High-resolution SE images were obtained of these grains with the Washington University (WU) PHI 700 Scanning Auger Nanoprobe equipped with a field-emission electron gun.

2.1. Isotopic measurements

Whole grain isotopic measurements with the Washington University NanoSIMS 50 ion microprobe of C and Si were made on all 20 grains, of Al-Mg on 19 grains, of Li and B on 16 grains, and of N on 6 grains. All these measurements included LU-13, hereafter referred to as Bonanza. In addition, whole grain isotopic measurements of Ca-Ti and isotopic images of C, Si, Al-Mg, S, Ca-Ti, and Li and B were obtained for Bonanza. All C, Si, N, and S isotopic measurements were made with negative secondary ions produced by Cs$^+$ bombardment, and all Li, B, Mg, Al, Ca and Ti isotopic measurements with positive secondary ions produced by O$^-$ bombardment. Fine-grained synthetic SiC powder was used for normalization of the C and Si isotopes. Nitrogen isotopes were measured as CN$^-$ secondary ions and a fine-grained mixture of synthetic SiC and Si$_3$N$_4$ powder was used for standardization. Canyon Diablo troilite (FeS) grains were used as standards for the S isotope measurements. While the precise isotopic compositions of these standards are unknown, for the purposes of comparison with presolar grains containing extreme isotopic anomalies, such as in the present study, they should not be sufficiently different from terrestrial values as to affect any conclusions herein. A polished NIST SRM 610 glass reference material was used for standardization of the Li and B isotopes. It should be remarked, however, that the glass test tubes used in the chemical preparation of these L-series grains were not of the highest purity, and Li and B may have leached onto the grains’ surfaces from them. Burma spinel (MgAl$_2$O$_4$) grains were used for normalization of the Mg and Al isotopes and concentrations, while grains of perovskite (CaTiO$_3$) were used as standards for the Ca and Ti isotopes. In addition to Si isotopic images made with negative secondary ions, $^{28}$Si images with positive secondary ions were obtained along with Al-Mg and Ca-Ti images.

Isotopic analyses of Ti, Fe, and Ni on Bonanza were obtained with the NanoSIMS 50 L at the Carnegie Institution of Washington (CIW). Isotopic ratio distributions were calculated from ion images of positive secondary ions sputtered with an O$^+$ primary beam. For the Ti isotopic analysis, the five Ti isotopes and $^{48}$Ca and $^{52}$Cr were measured in multidetection on seven electron multipliers, with perovskite again used as a Ti standard. Thirty-five layers were summed for the analysis, followed automated alignment of layer-to-layer spatial shifts. For the Fe and Ni isotopic analysis, $^{52}$Cr, $^{54,56,57}$Fe and $^{58,60,61,62}$Ni were measured in combined mode, a combination of multidetection and magnetic peak jumping. Twenty-one layers were summed for
the analysis. A fine grained Fe-Ni alloy was used for normalization of the Fe-Ni results.

As we do not have a representative SiC standard with known concentrations of trace elements, matrix differences between our standards and presolar SiC allow us to only determine relative elemental concentrations, not absolute ones. For Ti, a relative sensitivity factor (RSF) was established by calculating the expected ion yield of Ti from the NIST SRM 610 glass by measuring its $^{48}\text{Ti}/^{52}\text{Si}$ ratio and comparing it with its known Ti concentration. The RSFs for Fe and Ni were determined in a similar manner by measuring the $^{56}\text{Fe}/^{52}\text{Si}$ and $^{58}\text{Ni}/^{52}\text{Si}$ ratios in the same NBS SRM 610. The Ti, Fe, and Ni RSFs used in this study were determined from NanoSIMS measurements performed at Washington University prior to this work. Variations between instruments and among tuning conditions for a given measurement session can have a significant impact on RSFs, particularly those determined by NanoSIMS, as its ion extraction optics are closer to the sample surface than on conventional SIMS instruments. These effects can combine to lead to uncertainties in the RSFs of up to 10% or more, thus affecting the accuracy of our reported elemental abundances.

2.2. Microstructural analyses

After completion of the isotopic analyses, additional elemental and structural analyses were performed. Imaging and energy dispersive spectroscopic (EDS) X-ray measurements were made with a JEOL 6500F scanning electron microscope at CIW. Three focused ion beam (FIB) lift-out sections for TEM analysis were extracted with the Nova 600 FIB-SEM at the Naval Research Laboratory. Two were extracted in situ (within the FIB-SEM) and attached directly to a Cu TEM grid; the third was extracted ex situ under an optical microscope and placed on a C-film coated Cu TEM grid. The sections were subsequently analyzed in the JEOL 2200FS field emission TEM and Nion UltraSTEM200-X aberration-corrected scanning transmission electron microscope (STEM), each operated at 200 kV. Selected area electron diffraction patterns (SAEDPs) were recorded on the Gatan Ultrascan1000 CCD on the JEOL 2200FS, with camera constants calibrated with polycrystalline Al diffraction standards. The patterns were analyzed using the CRISP and PHIDIO software packages, to obtain quantitative measurements of the quality of fit with SiC polytypes 2H, 3C, 4H, 6H, 15R, 21R and 33R. Diffraction patterns for comparison (Fig. 3a). Others (Fig. 3b) showed spacings characteristic of one or two crystallographic directions, indicative of intergrowth and/or stacking disorder. At least one SAEDP was obtained for each crystallite larger than 0.5 µm in each section, and where possible, as many as 6 patterns and the values of d-spacings for the common SiC polytypes, some SAEDPs could be indexed reasonably to multiple polytypes (Fig. 3a). Others (Fig. 3b) showed spacings characteristic of only 15R, or alternatively other higher order polytypes.

Elemental mapping and HAADF imaging of the sections (Fig. 4) demonstrates that there are abundant subgrains of the SiC grains on the grain mount containing Bonanza. Three focused ion beam (FIB) lift-out sections from the regions indicated with dashed lines in Fig. 1a. Fig. 2a corresponds to the dashed line at the bottom of Figs. 1a and 2b is from the dashed line through the outlined fragment 1. The ex situ lift-out section (not shown) was taken from the third dashed line (Fig. 1a upper left). The diffraction contrast in these images confirms that the grain is polycrystalline with crystallite sizes ranging from 10s of nms up to ~5 µm. The boundaries between crystallites are mostly flat and indicative of coherent polycrystalline growth in a single condensation event. However, voids and rounded boundaries between crystallites are also present that could indicate either coherent growth in a region outside the FIB section, or aggregation of separately condensed crystallites.

Selected area electron diffraction patterns (SAEDPs) from the individual crystallites reveal significant variation in the atomic-scale ordering (Fig. 3). Some of the SAEDPs have sharp spots that indicate well-ordered crystal structure. Others exhibit extra spots and/or streaking in one or two crystallographic directions, indicative of intergrowth and/or stacking disorder. At least one SAEDP was obtained for each crystallite larger than 0.5 µm in each section, and where possible, as many as 6 patterns and the angles between the zones were recorded. Due to the similar values of d-spacings for the common SiC polytypes, some SAEDPs could be indexed reasonably to multiple polytypes (Fig. 3a). Others (Fig. 3b) showed spacings characteristic of only 15R, or alternatively other higher order polytypes.

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3. RESULTS

The surface morphology and C, N, Mg, Si isotopic ratios and initial $^{26}\text{Al}/^{27}\text{Al}$ ratios (inferred from $^{26}\text{Mg}$ excesses) of the SiC grains on the grain mount containing Bonanza are given in Table 1. Note that a few of the measured grains (LS-4, LU-7, and LU-27) have terrestrial isotopic compositions and may not be presolar SiC. While this paper concentrates on Bonanza, results on the other grains will be mentioned occasionally for comparison.

3.1. Morphology and microstructure

Fig. 1a shows a secondary electron (SE) micrograph of Bonanza. While grains with sizes of up to 50 µm have been found in the Murchison LU fraction (Gyngard et al., 2009b; Virag et al., 1992), Bonanza is by far the largest X grain ever found. Previously located X grains range up to ~5 µm in size. The morphology of Bonanza is also unusual and appears to consist of an assemblage of smaller nodules, sub-to a few µm in size, which broke up when the grain was pressed onto the Au mount. It is very different from large euhedral grains such as grain LU-27, a mainstream (AGB) grain, shown in Fig. 1b.

Fig. 2 shows bright-field STEM images of two of the Bonanza lift-out sections from the regions indicated with dashed lines in Fig. 1a. Fig. 2a corresponds to the dashed line at the bottom of Figs. 1a and 2b is from the dashed line through the outlined fragment 1. The ex situ lift-out section (not shown) was taken from the third dashed line (Fig. 1a upper left). The diffraction contrast in these images confirms that the grain is polycrystalline with crystallite sizes ranging from 10s of nms up to ~5 µm. The boundaries between crystallites are mostly flat and indicative of coherent polycrystalline growth in a single condensation event. However, voids and rounded boundaries between crystallites are also present that could indicate either coherent growth in a region outside the FIB section, or aggregation of separately condensed crystallites.

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considerably thinner than the section thickness. For the largest Fe, Ni-rich grains, the elemental maps show corresponding reductions in the both Si and C intensity. Thus we infer that these grains are unlikely to be silicides or carbides. The subgrain sizes range from ~10 nm to ~100 nm. Many, but not all, of the grains appear to be spatially associated with voids. No significant difference in the types of subgrains was observed for the three different sections, although only HAADF, and not EDS maps, were obtained for the ex situ lift-out section.

3.2. Isotopic composition

The C, N, Al, and Si isotopic compositions of Bonanza (Table 1) identify the grain as a type X grain. In addition to the whole-grain data given in Table 1, we obtained isotopic images of various elements.

3.2.1. Carbon and silicon

Fig. 5 shows isotopic images (256 × 256 pixels) of 12C and 28Si along with ratio images of 29Si/28Si, 30Si/28Si, 13C/12C, and 28Si/28Si. In all these images, thresholds were set to exclude pixels with low values. In spite of this procedure, some extreme values in the ratio images are due to edge effects. Some variations in the intensity images of 13C and 28Si are undoubtedly caused by topographic effects, which can strongly influence secondary ion yields in the NanoSIMS. The isotopic ratio images show some variations and the question arises whether these variations indicate intrinsic variations in the C and Si isotopic ratios within the Bonanza grain. In order to investigate this more quantitatively, we averaged the isotopic ratios of 4 × 4 pixel areas within the grain into individual bins. The bin size is 0.59 × 0.59 μm². Fig. 6 shows plots of the Si and C isotopic ratios in individual bins. Also shown are the whole-grain ratios for Bonanza. These ratios are compared to the ratios measured for other SiC grains on the same grain mount (Table 1). The solid lines are unweighted least squares fits to the individual bin values. In Fig. 6a, the deviations of individual bin data points from this line are commensurate with errors on the ratios. In the Si 3-isotope plot (Fig. 6a), the fitted line is almost exactly a two-component mixture of isotopic compositions of the whole grain (Fig. 1) and of the solar composition (Fig. 2). In the C 3-isotope plot (Fig. 6b), the fitted line is almost exactly a three-component mixture of isotopic compositions of the whole grain (Fig. 1), of oxygen-carbonate material (Fig. 2), and of carbonaceous chondrites (Fig. 3).

Table 1

<table>
<thead>
<tr>
<th>Grain</th>
<th>Size μm</th>
<th>Morphology</th>
<th>12C/13C</th>
<th>14N/15N</th>
<th>δ29Si/28Si</th>
<th>δ30Si/28Si</th>
<th>δ25Mg/24Mg</th>
<th>δ26Mg/24Mg</th>
<th>26Al/27Al</th>
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<tbody>
<tr>
<td>Bonanza</td>
<td>25.5</td>
<td>eu-fine</td>
<td>190.2 ± 1.0</td>
<td>28 ± 0.4</td>
<td>−292.1 ± 3.8</td>
<td>−448.3 ± 4.0</td>
<td>2 ± 24</td>
<td>647.479 ± 10,799</td>
<td>5982.0 ± 5.7</td>
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<tr>
<td>LS-1</td>
<td>1.9</td>
<td>eu</td>
<td>76.3 ± 0.4</td>
<td>46.1 ± 5.7</td>
<td>49.4 ± 7.8</td>
<td>−1 ± 27</td>
<td>561 ± 40</td>
<td>6.9 ± 0.4</td>
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</tr>
<tr>
<td>LS-2</td>
<td>3.5</td>
<td>eu</td>
<td>40.0 ± 0.2</td>
<td>71.0 ± 5.6</td>
<td>83.8 ± 7.7</td>
<td>7 ± 16</td>
<td>83 ± 22</td>
<td>6.7 ± 1.6</td>
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<tr>
<td>LS-4</td>
<td>3.8</td>
<td>smooth</td>
<td>89.7 ± 0.6</td>
<td>13.9 ± 5.5</td>
<td>30.3 ± 7.6</td>
<td>1 ± 12</td>
<td>293 ± 22</td>
<td>5.5 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>LS-5</td>
<td>4.8</td>
<td>fine-gr</td>
<td>49.3 ± 0.2</td>
<td>−9.0 ± 5.3</td>
<td>5.5 ± 7.2</td>
<td>1 ± 12</td>
<td>293 ± 22</td>
<td>5.5 ± 0.3</td>
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<tr>
<td>LS-6</td>
<td>5.2</td>
<td>eu-fine</td>
<td>3.0 ± 0.0</td>
<td>116 ± 1</td>
<td>−10.4 ± 5.3</td>
<td>11.9 ± 7.4</td>
<td>−23 ± 9</td>
<td>11,612 ± 129</td>
<td>138.9 ± 0.3</td>
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<tr>
<td>LS-7</td>
<td>2.5</td>
<td>eu</td>
<td>93.9 ± 0.6</td>
<td>20.3 ± 5.6</td>
<td>53.0 ± 7.7</td>
<td>17 ± 32</td>
<td>3745 ± 107</td>
<td>14.2 ± 0.2</td>
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<tr>
<td>LS-8</td>
<td>2.9</td>
<td>eu</td>
<td>79.2 ± 0.6</td>
<td>18.3 ± 6.1</td>
<td>24.0 ± 8.1</td>
<td>20 ± 22</td>
<td>383 ± 32</td>
<td>11.0 ± 0.8</td>
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<tr>
<td>LS-9</td>
<td>3.4</td>
<td>eu</td>
<td>91.8 ± 0.5</td>
<td>27.0 ± 5.5</td>
<td>38.2 ± 7.5</td>
<td>−56 ± 26</td>
<td>6474 ± 117</td>
<td>10.5 ± 0.2</td>
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<td>LS-10</td>
<td>2.6</td>
<td>eu</td>
<td>51.3 ± 0.2</td>
<td>418 ± 9</td>
<td>142.6 ± 6.0</td>
<td>1219 ± 8.0</td>
<td>−4 ± 12</td>
<td>21 ± 18</td>
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<td>LS-11</td>
<td>3.4</td>
<td>eu-fine</td>
<td>57.5 ± 0.3</td>
<td>69.8 ± 5.8</td>
<td>65.4 ± 7.8</td>
<td>−7 ± 22</td>
<td>903 ± 35</td>
<td>11.6 ± 0.4</td>
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<td>3.3</td>
<td>eu</td>
<td>43.1 ± 0.3</td>
<td>481 ± 9</td>
<td>141.8 ± 6.4</td>
<td>107.7 ± 8.4</td>
<td>18 ± 10</td>
<td>94 ± 18</td>
<td>13.5 ± 2.3</td>
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<tr>
<td>LU-3</td>
<td>7.7</td>
<td>eu</td>
<td>27.0 ± 0.1</td>
<td>1753 ± 24</td>
<td>−5.0 ± 5.2</td>
<td>17.3 ± 7.3</td>
<td>−17 ± 26</td>
<td>13,249 ± 255</td>
<td>41.4 ± 0.3</td>
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<tr>
<td>LU-7</td>
<td>7.5</td>
<td>conch</td>
<td>90.2 ± 0.5</td>
<td>8.3 ± 5.4</td>
<td>11.6 ± 7.3</td>
<td>−8 ± 10</td>
<td>−14 ± 16</td>
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<tr>
<td>LU-9</td>
<td>6.6</td>
<td>eu</td>
<td>52.1 ± 0.3</td>
<td>95.5 ± 5.9</td>
<td>82.0 ± 7.9</td>
<td>−17 ± 22</td>
<td>2195 ± 48</td>
<td>24.7 ± 0.5</td>
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<tr>
<td>LU-11</td>
<td>7.4</td>
<td>eu</td>
<td>56.0 ± 0.3</td>
<td>110.2 ± 5.9</td>
<td>97.1 ± 8.0</td>
<td>−6 ± 22</td>
<td>175 ± 28</td>
<td>4.8 ± 0.7</td>
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<tr>
<td>LU-19b</td>
<td>6.4</td>
<td>eu</td>
<td>55.1 ± 0.3</td>
<td>99.7 ± 5.7</td>
<td>95.9 ± 7.8</td>
<td>6 ± 31</td>
<td>10,405 ± 224</td>
<td>12.6 ± 0.1</td>
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<td>LU-21</td>
<td>11.0</td>
<td>smooth</td>
<td>90.0 ± 0.5</td>
<td>10.5 ± 5.3</td>
<td>25.2 ± 7.3</td>
<td>31 ± 32</td>
<td>36 ± 34</td>
<td>&lt;0.5</td>
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<tr>
<td>LU-23</td>
<td>12.0</td>
<td>eu</td>
<td>122.0 ± 0.6</td>
<td>396 ± 4</td>
<td>−19.9 ± 5.1</td>
<td>25.2 ± 7.3</td>
<td>−19 ± 17</td>
<td>322 ± 26</td>
<td>5.7 ± 0.4</td>
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<td>LU-27</td>
<td>10.4</td>
<td>eu</td>
<td>47.4 ± 0.2</td>
<td>86.9 ± 5.7</td>
<td>96.8 ± 7.8</td>
<td>−1 ± 34</td>
<td>13 ± 36</td>
<td>&lt;1.6</td>
<td></td>
</tr>
</tbody>
</table>

Errors are ±1σ.

* Geometric average of the longest and shortest dimensions in the SEM image.

Fig. 5 shows isotopic images (256 × 256 pixels) of 12C and 28Si along with ratio images of 29Si/28Si, 30Si/28Si, 13C/12C, and 28Si/28Si. In all these images, thresholds were set to exclude pixels with low values. In spite of this procedure, some extreme values in the ratio images are due to edge effects. Some variations in the intensity images of 13C and 28Si are undoubtedly caused by topographic effects, which can strongly influence secondary ion yields in the NanoSIMS. The isotopic ratio images show some variations and the question arises whether these variations indicate intrinsic variations in the C and Si isotopic ratios within the Bonanza grain. In order to investigate this more quantitatively, we averaged the isotopic ratios of 4 × 4 pixel areas within the grain into individual bins. The bin size is 0.59 × 0.59 μm². Fig. 6 shows plots of the Si and C isotopic ratios in individual bins. Also shown are the whole-grain ratios for Bonanza. These ratios are compared to the ratios measured for other SiC grains on the same grain mount (Table 1). The solid lines are unweighted least squares fits to the individual bin values. In Fig. 6a, the deviations of individual bin data points from this line are commensurate with errors on the ratios. In the Si 3-isotope plot (Fig. 6a), the fitted line is almost exactly a two-component mixture of isotopic compositions of the whole grain (Fig. 1) and of the solar composition (Fig. 2). In the C 3-isotope plot (Fig. 6b), the fitted line is almost exactly a three-component mixture of isotopic compositions of the whole grain (Fig. 1), of oxygen-carbonate material (Fig. 2), and of carbonaceous chondrites (Fig. 3).

Likewise, the 12C/13C ratio of fragment 1 is 180.7 compared to the ratio of 190.2 obtained from the whole grain measurement (Table 1).

3.2.2. Magnesium and aluminum

Table 1 gives the $^{25,26}\text{Mg}/^{24}\text{Mg}$ values and inferred $^{26}\text{Al}/^{27}\text{Al}$ ratio obtained from the whole grain isotopic analysis of Bonanza and other LS + LU grains. However, much more information can be obtained from the isotopic images. Fig. 7 shows ion images of the three Mg isotopes and of $^{27}\text{Al}$ for Bonanza. Because the primary O$^+$ beam cannot be focused as well as the Cs$^+$ beam, the spatial resolution of these images is not as high as that of the C and Si images (Fig. 5). Furthermore, whereas the images in Fig. 5 have 256 x 256 pixels, those in Fig. 7 have 128 x 128 pixels. The $^{24}\text{Mg}$ and $^{25}\text{Mg}$ images are very similar. In contrast, $^{26}\text{Mg}$ is completely dominated by radiogenic $^{26}\text{Mg}$ from the decay of $^{26}\text{Al}$ ($t_{1/2} = 7.2 \times 10^5$ y) and its counts are much higher than those of $^{24}\text{Mg}$. The $^{26}\text{Mg}/^{24}\text{Mg}$ ratio is 97 averaged over the whole grain but reaches 770 in selected areas. This latter ratio corresponds to a $^{26}\text{Mg}/^{24}\text{Mg}$ value of $5.5 \times 10^6$‰. The $^{26}\text{Mg}$ image is roughly similar to that of $^{27}\text{Al}$ but differs in details. The inferred $^{26}\text{Al}/^{27}\text{Al}$ ratio image is shown in Fig. 7f. It is apparent that this ratio varies over the grain. This is also shown in Fig. 8 where the $^{26}\text{Mg}$ ion counts in 6 x 6 pixel bins (corresponding to 1.64 x 1.64 μm$^2$ areas) are plotted against the $^{27}\text{Al}$ ion counts. The $^{26}\text{Mg}$ counts are corrected for the different ion yields for Mg and Al so that the slope of a line between the origin and a selected data point would give the inferred $^{26}\text{Al}/^{27}\text{Al}$ ratio of this point. The point with the highest Al counts also corresponds to the maximum inferred $^{26}\text{Al}/^{27}\text{Al}$ ratio for a given bin of 0.9 (line). As can be seen, most data points deviate from this line. With the C and Si isotopic ratios, we can ask whether the $^{26}\text{Al}/^{27}\text{Al}$ ratio in Bonanza is heterogeneous or whether the variations can be explained by contamination with Al. In the case of the former, the STEM-EDS measurements described above indicate the presence of (AlMg)N subgrains which are spatially heterogeneous throughout the grain as well as Al in solid solution in the SiC, thus supporting the possibility of a heterogeneous $^{26}\text{Al}/^{27}\text{Al}$ ratio. If the variations are due to contamination, any given data point in Fig. 8 can be produced from the original intrinsic $^{26}\text{Al}/^{27}\text{Al}$ ratio, assumed to be uniform, i.e., from data points lying on the $^{26}\text{Al}/^{27}\text{Al} = 0.9$ line, by adding Al, which would shift the data points from the line to the right. Under the assumptions that the original intrinsic $^{26}\text{Al}/^{27}\text{Al}$ ratio is 0.9 and that the measured $^{27}\text{Al}$ counts were a sum of intrinsic Al and contamination, we calculated the distributions of the intrinsic Al containing $^{26}\text{Al}$ (Fig. 7g) and of possible Al contamination (Fig. 7h). We note that most of the calculated Al contamination appears at the boundary of the grain, and laboratory contamination might be expected to occur preferentially at grain surfaces which will be better preserved at the boundary since the main surface was already sputtered during the C and Si measurements. This contamination would not be indigenous to the grain or representative of the interior of the grain as observed by STEM-EDS. Thus, the Al-Mg data can plausibly be explained as either a mixture of Al with an initially homogeneous $^{26}\text{Al}/^{27}\text{Al}$ ratio of $\sim 0.9$ with variable amounts of contamination, a spatially heterogeneous distribution of (AlMg)N subgrains, or a combination of both and we cannot claim conclusive evidence for either a homogeneous or heterogeneous $^{26}\text{Al}/^{27}\text{Al}$ ratio in Bonanza.

Independent of the isotopic compositions, it is clear from Fig. 7 that there are large variations of the Al content (and thus of radiogenic $^{26}\text{Mg}$) in Bonanza. In the left upper

Fig. 1. (a) Secondary electron micrograph of Bonanza (LU-13). The grain broke into different fragments when it was pressed into a gold foil mount. One of the fragments discussed in the text and indicated in other figures is outlined in the image. Dashed lines indicate the locations of sections extracted with FIB lift-out. (b) Secondary electron micrograph of grain LU-9, a mainstream grain (see Table 1).
corner (Fig. 7 e), there is an especially Al-rich region where the $^{27}$Al content is 2.7 wt%, but the original Al content was 5.1 wt% if $^{26}$Al is included. Fragment 1 (Figs. 1a and 5), which, as discussed in the previous section, might have a Si isotopic composition different from the rest of the grain, yielded a higher $^{28}$Si signal (Fig. 8d) and has an Al content more than an order of magnitude lower (0.18 and 0.34 wt%, respectively). In the negative ion images, this fragment also has higher $^{14}$C and $^{28}$Si signals than the rest of Bonanza (Fig. 5a and b). It is not clear what causes these enhanced ion yields; it might be a surface morphology effect, influencing the extraction of secondary ions.

3.2.3. Calcium and titanium

Table 2 shows the results of measurements of $^{40,42,44}$Ca and $^{48}$Ti. The measurements were made in two ways. Two measurements were performed in isotope mode where the above isotopes and $^{28}$Si were measured in multideposition mode, one by rastering the primary O beam over the whole grain and one by rastering it over a 4 $\mu$m$^2$ area centered on a Ti-rich hotspot (identified in a rapid survey $^{48}$Ti scan). Whereas the whole grain analysis shows only a modest excess in $^{44}$Ca, the analysis on the hotspot yields a much larger excess. The $^{44}$Ca/$^{40}$Ca ratio is normal (terrestrial) in both analyses.

In addition, we obtained images of the whole grain in the above five isotopes. The $^{40,42,44}$Ca and $^{48}$Ti images are shown in Fig. 9. The $^{48}$Ti image is shown both on linear (Fig. 9d) and logarithmic scales (Fig. 9e). Also shown is an image of $^{30}$Si/$^{28}$Si (Fig. 9f). Titanium appears to be distributed heterogeneously into small subgrains. Calcium is also highly heterogeneous, but is not correlated with Ti. Calcium is isotopically normal in both ratios in all the areas and spots with high Ca concentrations. It is likely that all of that Ca is contamination. Calcium-44 excesses are found not only in the total grain but much higher excesses are found in areas with Ti-rich subgrains. Most prominent is spot 1 circled in Fig. 9e–f where the $^{44}$Ca/$^{40}$Ca reaches 1485‰. This is clearly seen in the $^{44}$Ca and $^{30}$Si/$^{28}$Si images, which show that the $^{44}$Ca excess is associated with Ti, providing unambiguous proof that the $^{44}$Ca excess originates from the decay of short-lived ($t_{1/2} = 60$ y) $^{44}$Ti, as previously seen for other presolar SiC-X and graphite grains (e.g., Nittler et al., 1996). Although not apparent in the $^{44}$Ca/$^{40}$Ca image, smaller $^{44}$Ca excesses are also present in the other Ti-rich spots encircled in Fig. 9e (Table 2).

Fig. 9 and Ti-isotopic analyses discussed further below have also shown that Ti in Bonanza is concentrated in subgrains, as previously seen in depth profiles during SIMS analysis (Lin et al., 2010), and TEM analysis of X grains (Hynes et al., 2010; Kodolányi et al., 2016). Most inferred $^{44}$Ti/$^{48}$Ti ratios in Bonanza are not very different from the value of $2.6 \times 10^{-3}$ found in spot 1 (Table 2). Notable exceptions are spot 4 and spot 5 with ratios of $0.5 \times 10^{-3}$ and $5.4 \times 10^{-3}$ respectively (Fig. 10). Zinner and JadHAV (2013) discussed the possibility of $^{44}$Ti/$^{48}$Ti heterogeneity among different TiC subgrains in presolar graphite grains from supernovae. They considered two processes that can lead to apparent differences in the $^{44}$Ti/$^{48}$Ti ratio among TiC subgrains: contamination with Ti and/or loss of radiogenic $^{44}$Ca. In our case, it is possible that most of the Ti in spot 4 is contamination, leading to a lower inferred $^{44}$Ti/$^{48}$Ti ratio. However, if the true $^{44}$Ti/$^{48}$Ti ratio in all subgrains is the highest observed value of $5.4 \times 10^{-3}$, found in spot 5, explaining the rather homogeneous $^{44}$Ti/$^{48}$Ti of the other spots would require a fine tuning of just the right amount of Ti contamination and/or radiogenic $^{44}$Ca loss in each spot, which is highly unlikely. We thus argue this is
convinced evidence that the $^{44}\text{Ti}/^{48}\text{Ti}$ ratio of subgrain 5 was different from that of the other subgrains or that of the rest of the whole Bonanza grain. Fig. 10 compares the $^{44}\text{Ti}/^{48}\text{Ti}$ ratio inferred from the five hotspots identified by ion imaging and $^{29}\text{Si}/^{28}\text{Si}$ with those of other X grains. As can be seen, the Bonanza data fit into the general trend of roughly correlated $^{44}\text{Ti}/^{48}\text{Ti}$ ratios with $^{28}\text{Si}$-enrichments, as exhibited by the other X grains.

### 3.2.4. Titanium

Fig. 11 shows the Ti isotopic images that were used to determine Ti isotopic ratios. As has already been seen in Figs. 9 and 4, Ti is contained in small subgrains. The subgrains seen in Fig. 9 have apparently been sputtered away during subsequent analysis and the new subgrains seen in Fig. 11 have been exposed. As has been previously found for X grains (Amari et al., 1995; Lin et al., 2010), the concentration of Ti in Bonanza is quite low. During the Ti isotopic measurements, Si was not measured as a reference, but we can obtain an estimate of the Ti concentration from the Ca-Ti measurement of the whole grain, when $^{28}\text{Si}$ was also measured and from the images when a $^{28}\text{Si}$ image was obtained along with the $^{40},^{42},^{44}\text{Ca}$ and $^{48}\text{Ti}$ images. To make a comparison with the Ti concentration data of Amari et al. (1995) data easier, we express the Ti concentration as atomic ratios relative to Si and normalized to the solar system abundances of the two elements (Asplund et al., 2009). For the two measurements, we obtain ratios of 0.16 and 0.17, respectively. This compares to upper limits of 0.09 and 0.04 obtained by Amari et al. (1995) for two X grains. Lin et al. (2010) obtained for X grains ratios varying from 0.002 to 1.1, with a median value of 0.1.

The Ti isotopic ratios, expressed as $\delta$-values in Bonanza are given in Table 3 and shown in Fig. 12. A correction for contributions from $^{50}\text{Cr}$ to the measured $^{50}\text{Ti}$ signal was made from the measured $^{52}\text{Cr}$ by assuming a normal $^{50}\text{Cr}/^{52}\text{Cr}$ ratio. This correction amounts to 7‰, smaller than the experimental uncertainty on the $^{50}\text{Ti}/^{48}\text{Ti}$ ratio (Table 3). Chromium is relatively volatile and is not expected to condense into SiC. Thus, the Cr detected during the analysis is probably contamination from Cr-rich meteoritic phases dissolved during preparation of the SiC residue. Even if there should be some intrinsic Cr present, the SN zones that appear to contribute most to the X grain
compositions (Section 4) are predicted to have solar to slightly sub-solar $^{50}$Cr/$^{52}$Cr ratios, and our $^{50}$Cr correction is thus probably an upper limit.

In Fig. 12a, the $\delta$-values in Bonanza are compared to those of other X grains (Hynes and Gyngard, 2009). The isotopic pattern exhibited by Bonanza, a large $^{49}$Ti excess and smaller $^{50}$Ti excess, is also seen in other X grains (Nittler et al., 1996; Besmehn and Hoppe, 2003) and low-density graphite grains from supernovae (Jadhav et al., 2013). It is the isotopic signature found in the He/C zone of SN models, the same zone thought to contribute many of the observed isotopic signatures in X grains (Section 4). Similar to most SiC X grains analyzed by Lin et al. (2010), a contribution from the decay of short-lived $^{49}$V (t$_{1/2}$ = 330 d), as suggested by Hoppe and Besmehn (2002), is not needed in order to explain the Ti isotopic ratios of Bonanza. Below in Section 4, we shall try to match the Ti isotopic ratios of Bonanza by performing SN mixing calculations.

In Fig. 12b, we plot the Ti isotopic ratios of individual subgrains labeled in Fig. 11. The Bonanza data points were obtained from the total Ti counts in the $^{46,49,50}$Ti isotopic images. The averages of the subgrains were obtained by adding the counts in the individual subgrains. By subtracting these sums from the total counts in the images, we obtained the ratios for the remaining area (“Rest” on Fig. 12b). As can be seen, the subgrains, on average, have different isotopic compositions than the remaining region, with the subgrains having larger isotopic anomalies than the host grain. Individual subgrains have also different ratios amongst themselves, which in both panels plot along lines. As we have seen above for other isotopic systems, the question arises whether these differences indicate isotopic heterogeneity among subgrains and between Ti-rich subgrains and the host SiC grain. In principle, the differences could be the result of mixing with isotopically normal Ti, as we have argued for in the case of the Si isotopes. In the lower panel, the individual subgrains, as well as their average, and the host grain lie within errors on a line through the Bonanza average and isotopically normal Ti (the origin of the $\delta$-value 3-isotope plot). In the upper panel, the best-fit line through the individual subgrains does not go through isotopically normal Ti. This could indicate intrinsic isotopic heterogeneity among subgrains. Unfortunately, measurement errors (based on counting statistics) are fairly large and the deviation from a line through the origin is marginal. Even if mixing with normal Ti is indeed the cause for the distributions in the two plots, we still do not know the nature of this isotopically normal component. If it is contamination, the contamination must be confined to the Bonanza grain because there is hardly any Ti signal from areas outside the grain in the images (Fig. 11), which would not be surprising if the contamination is from a surface coating obtained during the preparation of the sample residue.

3.2.5. Iron and nickel

Because Fe and Ni isotopic measurements were made from images obtained during the same measurement, we present the Fe and Ni analyses together. Fig. 13 shows the isotopic images of $^{58,60}$Ni and $^{54,56,57}$Fe. As for Ti (Fig. 11), Fe and Ni is concentrated in small subgrains. This co-occurrence has previously been observed in other X grains (Marhas et al., 2008). In many, but not all, cases, the Fe and Ni signals are correlated. Unfortunately, the counts are so low that it was not possible to determine whether there is any isotopic heterogeneity among any of the subgrains. One difference to the measurements by Marhas et al. (2008) is that the Ni concentration in
Bonanza is much lower than that of Fe. After normalizing the ion ratio from the ion images to atomic ratios by applying a relative sensitivity factor of 3.9 (Fe is more sensitive than Ni), we obtain an average Ni/Fe atomic ratio of 0.44 across the whole grain. However, there are variations among individual spots, as, for example, the Ni/Fe atomic ratio for the Ni-rich spot on the lower left of the main group is 0.66, consistent with the variability observed by STEM-EDS. These ratios are upper limits because we corrected for the $^{58}\text{Fe}$ interference on $^{58}\text{Ni}$ with the assumption that the $^{58}\text{Fe}/^{56}\text{Fe}$ ratio is normal. If, as discussed below, the true $^{58}\text{Fe}/^{56}\text{Fe}$ ratio is much larger, the Ni/Fe ratios would be lower. All of these ratios are much lower than the average Ni/Fe atomic ratios of 3.3 for X grains and 4.7 for mainstream grains determined by Marhas et al. (2008). As we shall see below, the low Ni/Fe ratio introduces large uncertainties in the correction for the $^{58}\text{Fe}$ interference with $^{58}\text{Ni}$.

The Fe isotopic ratios in Bonanza are given in Tables 3 and 4 and plotted in Fig. 14a, where they are compared with the Fe isotopic ratios measured by NanoSIMS in other X grains (Marhas et al., 2008). Bonanza has a small $^{54}\text{Fe}$ deficit and a large $^{57}\text{Fe}$ excess of 780‰, larger than that of most other X grains. The $\delta^{54}\text{Fe}/^{56}\text{Fe}$ value includes a correction of 3.4‰ if a normal $^{54}\text{Cr}/^{52}\text{Cr}$ ratio (0.028) is assumed. Even if we assume a $^{54}\text{Cr}/^{52}\text{Cr}$ ratio of 0.077, which can be obtained from SN models calculated by Rauscher et al. (2002) and described in detail below, the correction would be 9.2‰, still smaller than the experimental uncertainty.

Similar to Ti, we determined the Fe isotopic ratios in individual subgrains, their average and the Fe isotopic ratios for the remaining area (Fig. 14b). The errors for subgrains are even larger than for the Ti isotopic ratios. Here the difference between the whole grain average and the “Rest” region (grain area outside subgrains) is much smal-
Fig. 6. (a) Si 3-isotope δ-value plot of individual 4 × 4 pixel (0.59 × 0.59 µm²) bins of the Si ion images shown in Fig. 5. Also plotted is the whole-grain composition and the isotopic ratios of mainstream grains on the same sample mount. δ-values are deviations from the normal (Solar System) isotopic ratios in parts per thousand (permil, ‰). (b) δ²⁹Si/²⁸Si values of individual 4 × 4 pixel bins of the Bonanza images are plotted against their ¹²C/¹³C ratios. Ratios of the whole Bonanza grain and of mainstream grains are also shown. The solid lines in both panels are linear fits to the bin data.

In contrast to the corrections for interfering ⁵⁸Cr where we argued that Cr is isotopically normal and, if not, corrections are small, Fe in Bonanza is clearly not isotopically normal and corrections are expected to be large. Marhas et al. (2008) made corrections for the ⁵⁸Fe interference in the X grains they analyzed by using SN predictions for the ⁵⁸Fe/⁵⁶Fe ratio based on the ⁵⁷Fe/⁵⁶Fe ratios measured in the grains. We will do the same in the context of the SN mixing calculations presented below.

3.2.6. Lithium, boron, nitrogen, and sulfur

In addition to the isotopic analyses described above, we made measurements of N, S, Li, and B isotopic measurements on Bonanza. Nitrogen isotopic measurements were made on Bonanza and five other LS + LU grains (Table 1). Besides ¹²C₁⁴N and ¹³C₁⁵N, we measured ¹⁴C, ¹⁵C, and ³⁰Si and obtained thus another determination of the C isotopic ratios. Unfortunately, we did not obtain N isotopic images of Bonanza. Carbon and N isotopic measurements were made before any analyses with positive secondary ions. In retrospect, in view of the large variation of the Al abundance within Bonanza, it would have been interesting whether N also shows such a large variation.

It has variously been proposed that Al and N in SiC grains are contained as AlN subgrains or as AlN in solid solution; AlN is isostuctural with SiC (Zinner et al., 1991; Lodders and Fegely, 1995; Kobayashi and Komatsu, 2008). The STEM-EDS observations of subgrains of (Al, Mg)N and Al and N in the host SiC in two FIB lift-out sections described in Section 3.1 indicate that both hypotheses are true. Future whole grain measurements in which we obtain N isotope images along with ion images of MgO and AlO are planned in order to map the spatial heterogeneity of (Al, Mg)N subgrains in Bonanza and investigate any correlation in the abundances of Al and N. However, as Bonanza has been heavily sputtered through many measurements, a significant portion of small grains may have been lost. Nitrogen and Al images obtained by atom-probe tomography in a presolar SiC grain show a correlation, even though imperfect, in the distribution of these two elements (Stadermann et al., 2011).

We obtained two sets of ³²S⁻ and ³⁴S⁻ images together with Si isotopic images (Fig. 15). As can be seen, S is concentrated in small subgrains. The ³⁴S/³²S values obtained from the two sets of image analyses are −12 ± 5 ‰ and −15 ± 5 ‰, respectively. Much larger ³⁴S (and ³³S) depletions in X grains have previously been reported (Hoppe et al., 2012; Xu et al., 2012). However, the uncertainties in the S isotopic calibration for the Bonanza image analysis and in the correction for the quasi-simultaneous arrival (QSA) effect (Slodzian et al., 2004) are much larger than the measurement errors and we thus cannot claim any unambiguous ³⁴S depletion (or ³₂S excess) for Bonanza. Within errors, there are no S isotopic heterogeneities among S-rich subgrains. Some of the subgrains, e.g., those at the lowest part of the images, are located at the edges of Bonanza and are most likely contamination. However, most subgrains are within the borders of Bonanza. Results of the STEM-EDS analysis indicate that S is present in both Ti-rich subgrains and Fe, Ni-rich subgrains, and below EDS detection limits in the host SiC.
Whole-grain isotopic measurements of Li and B were made on Bonanza and 15 other LS + LU grains. The Li and B isotopic ratios are normal within measurement errors for all grains. However, none of the analyzed grains have the large, platy, anhedral morphology like the grains analyzed by Gyngard et al. (2009a,b). Furthermore, we did not try to clean the analyzed grain by pre-sputtering with the primary O beam nor did we obtain counts only from interior regions of the grains the way Gyngard et al. (2009a,b) had done. On Bonanza, we obtained two sets of images of $^{6,7}$Li$^+$, $^{10,11}$B$^+$, and $^{30}$Si$^+$. We observed variations in the concentrations of Li and B over the surface of the grains but we could not determine whether any of the Li and B was intrinsic or due to contamination. We estimate the Li concentrations to be 5.7 and 4.8 ppm by weight in the first and second set of images, respectively, and the B concentrations to be 58 and 34 ppm by weight. These values are much higher than what Gyngard et al. (2009a,b) found in their analysis, indicating that the two elements are dominated by contamination. This is not surprising, because as mentioned above in Section 2, the glass test tubes used in the preparation of the L-series contained significant trace amounts of Li and B.

4. DISCUSSION: BONANZA, MODELS OF SUPERNOVAE AND SUBGRAINS

4.1. Type II supernovae

Prior to exploding as Type II SNe, massive stars have an onion-shell structure with chemically distinct zones, with the composition of each zone set by the stellar evolutionary history of the material (Meyer et al., 1995). Deeper layers experienced more advanced stages of nuclear burning and thus are dominated by increasingly heavy elements. As is typically done, we have labeled the zones by their two most abundant elements, e.g., a zone dominated by Si with S as its second most abundant element is termed the Si/S zone. Thus, moving from the outside in, stars of $\sim$10–25 M$_\odot$ generally consist of the following structure: a massive H-dominated envelope; a He- and N-rich zone (He/N) that has experienced H-burning; a He/C zone that has experi-
enced partial He-burning; several O-rich zones with various amounts of C, Ne, and Si (O/C, O/Ne, and O/Si, respectively); and, finally, a Si/S zone surrounding an Fe-Ni core. More massive stars may have lost their envelopes and He-rich zones in strong Wolf-Rayet winds. The major chemistry of each zone is set by the pre-SN evolution of the star and is largely homogenized by convection, but can be modified by additional nuclear reactions occurring as the SN shock wave passes through the ejecta.

It was recognized early that no single SN zone can explain all of the isotopic characteristics of presolar grains from SNe. For example, high $^{26}\text{Al}/^{27}\text{Al}$ ratios in X grains point to a contribution from the He/N zone, but SiC condensation chemistry points to material from the C-rich He/C zone and $^{26}\text{Si}$ and $^{44}\text{Ti}$ excesses require material from the very deep Si/S zone. This has long been taken as evidence for heterogeneous mixing of various layers in the SN progenitors and there have been many SN mixing calculations aimed at reproducing the isotopic signatures of X grains (Nittler et al., 1996; Hoppe et al., 2000; Yoshida and Hashimoto, 2004; Yoshida, 2007; Marhas et al., 2008; Fedkin et al., 2010; Lin et al., 2010), SN graphite grains (e.g., Travaglio et al., 1999; Jadhav et al., 2013), and SN oxide grains (e.g., Choi et al., 1998; Nittler et al., 2008; Gyngard et al., 2010).

4.2. Comparison of Bonanza with Rauscher et al. (2002) model calculations

The large number of elements analyzed in Bonanza provides a unique opportunity to constrain the mixing that occurred in its parent SN and test SN nucleosynthesis predictions. We base our considerations here on the SN models of Rauscher et al. (2002), for several reasons. While we acknowledge the models of other authors (e.g., Hashimoto et al., 1995; Limongi and Chieffi, 2003; Chieffi and Limongi, 2004), it is outside the scope of this paper to compare and contrast the entire parameter space, such as different masses, metallicities, rotation rates, etc., of all published and unpublished model calculations. In fact, many of the models from different authors do not agree with each other within the precision of the data we report. Additionally, much of the input physics (e.g., reaction cross-sections and estimates of solar abundances) for all of the calculations have been updated since publication; however, generally we prefer the Rauscher et al. (2002) calculations for comparison as they have become, for better or for worse, a sort of standard candle for which to compare the grain data in the presolar grain community (e.g., see mixing calculations by Nittler et al. (2008), Lin et al. (2010), Jadhav et al. (2013), etc. that use the Rauscher et al. (2002) SN models). We refer the interested reader to Jadhav et al. (2013) for a detailed comparison of different SN models as regards mixing between the He/N and He/C zones (see their Section 4.1.2.4).

Table 2
Calcium isotopic ratios and inferred $^{44}\text{Ti}/^{48}\text{Ti}$ ratios of Bonanza.

<table>
<thead>
<tr>
<th></th>
<th>$\delta^{42}\text{Ca}/^{40}\text{Ca}$ (%)</th>
<th>$\delta^{44}\text{Ca}/^{40}\text{Ca}$ (%)</th>
<th>$^{44}\text{Ti}/^{48}\text{Ti}$ (inferred) ($10^{-5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulk analysis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Whole grain</td>
<td>16 ± 24</td>
<td>46 ± 15</td>
<td>17.7 ± 5.7</td>
</tr>
<tr>
<td>Hotspot</td>
<td>25 ± 22</td>
<td>686 ± 12</td>
<td>23.9 ± 0.4</td>
</tr>
<tr>
<td><strong>Image analysis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Whole image</td>
<td>7 ± 6</td>
<td>47 ± 8</td>
<td>19.7 ± 3.2</td>
</tr>
<tr>
<td>Spot 1</td>
<td>70 ± 83</td>
<td>1485 ± 31</td>
<td>26.2 ± 0.6</td>
</tr>
<tr>
<td>Spot 2</td>
<td>−61 ± 94</td>
<td>230 ± 47</td>
<td>22.9 ± 4.6</td>
</tr>
<tr>
<td>Spot 3</td>
<td>60 ± 90</td>
<td>262 ± 47</td>
<td>27.3 ± 4.9</td>
</tr>
<tr>
<td>Spot 4</td>
<td>106 ± 93</td>
<td>112 ± 53</td>
<td>5.1 ± 2.4</td>
</tr>
<tr>
<td>Spot 5</td>
<td>74 ± 67</td>
<td>302 ± 35</td>
<td>54.1 ± 6.2</td>
</tr>
</tbody>
</table>

Errors are 1σ; in the case of the image analysis, based solely on counting statistics.
We note also two recent theoretical developments that bear directly on the origin of supernova SiC grains. First, Pignatari et al. (2013) investigated explosive nucleosynthesis occurring at the bottom of the He/C and top of the O/C zones of a 15 M\(_\odot\) SN model during the passage of the shock wave through these layers. They considered higher shock velocities than one would reach in a standard symmetric SN model (Woosley and Weaver, 1995; Rauscher et al., 2002) by arguing that such velocities could be reached in asymmetric explosions. At the resulting high temperatures and in the presence of abundant He, nucleosynthesis is dominated by \(a\)-captures, resulting in production of \(a\)-nuclei along the \(a\)-capture chain starting with \(^{16}\text{O}\) and reaching up to \(^{44}\text{Ti}\). This results in a zone with high abundances of \(^{12}\text{C}\) and \(^{28}\text{Si}\), called the C/Si zone by Pignatari et al. (2013). The authors proposed that SiC X grains could originate from the C/Si zone or from mixtures of this zone with other layers. One benefit of this model is that the C/Si zone is not rich in \(^{54}\text{Fe}\), avoiding the problem of the lack of \(^{54}\text{Fe}\) in X grains.

Second, Pignatari et al. (2013) explored the effect of ingestion of H into the He-rich shell of a massive star during the presupernova phase, leading to the occurrence of explosive H-burning within the He-rich shell during the SN explosion. This process can explain low \(^{12}\text{C}/^{13}\text{C}\) and \(^{14}\text{N}/^{15}\text{N}\) ratios observed in many SiC X grains, as well as some highly \(^{13}\text{C}\)- and \(^{15}\text{N}\)-rich SiC C grains, some grains previously thought to have originated in novae, and \(^{15}\text{N}\)-rich SiC AB grains (Liu et al., 2016, 2017a). This model also produces high \(^{26}\text{Al}/^{27}\text{Al}\) ratios. A detailed comparison of these models with the Bonanza data is beyond the scope of the present paper, but their development indicates the general need for a broader consideration of the parameter space of supernova nucleosynthesis models when confronting the presolar SiC data.

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**Fig. 9.** Positive \(^{40},^{42},^{44}\text{Ca}\) and \(^{48}\text{Ti}\) ion images of Bonanza. Also shown is an image of \(\delta^{44}\text{Ca}/^{40}\text{Ca}\). Each ion image is the sum of 12 individual 128 x 128 pixel layers. The color bars to the right of the images indicate counts/pixel or \(\delta\)-values in \(\text{‰}\) for the \(\delta^{44}\text{Ca}/^{40}\text{Ca}\) image. Panel (d) shows the \(^{48}\text{Ti}\) image on a linear scale and panel (e) on a logarithmic scale. In panel (e), Ti-rich spots for which Ca isotopic ratios had been determined (Table 2) are labeled by circles, for spot 1 this is also shown in panels (c), (d), and (f).

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**Fig. 10.** The inferred initial \(^{44}\text{Ti}/^{48}\text{Ti}\) ratio and \(\delta^{29}\text{Si}/^{28}\text{Si}\) values of Ti-rich hotspots in Bonanza (Table 2) are compared with those of other X grains (e.g., Nittler et al., 1996; Hoppe et al., 2000; Besmehn and Hoppe, 2003; Lin et al., 2010; Zinner, 2014 and references therein).

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We note also two recent theoretical developments that bear directly on the origin of supernova SiC grains. First, Pignatari et al. (2013) investigated explosive nucleosynthesis occurring at the bottom of the He/C and top of the O/C zones of a 15 M\(_\odot\) SN model during the passage of the shock wave through these layers. They considered higher shock velocities than one would reach in a standard symmetric SN model (Woosley and Weaver, 1995; Rauscher et al., 2002) by arguing that such velocities could be reached in asymmetric explosions. At the resulting high temperatures and in the presence of abundant He, nucleosynthesis is dominated by \(a\)-captures, resulting in production of \(a\)-nuclei along the \(a\)-capture chain starting with \(^{16}\text{O}\) and reaching up to \(^{44}\text{Ti}\). This results in a zone with high abundances of \(^{12}\text{C}\) and \(^{28}\text{Si}\), called the C/Si zone by Pignatari et al. (2013). The authors proposed that SiC X grains could originate from the C/Si zone or from mixtures of this zone with other layers. One benefit of this model is that the C/Si zone is not rich in \(^{54}\text{Fe}\), avoiding the problem of the lack of \(^{54}\text{Fe}\) in X grains. Second, Pignatari et al. (2013) explored the effect of ingestion of H into the He-shell of a massive star during the presupernova phase, leading to the occurrence of explosive H-burning within the He-rich shell during the SN explosion. This process can explain low \(^{12}\text{C}/^{13}\text{C}\) and \(^{14}\text{N}/^{15}\text{N}\) ratios observed in many SiC X grains, as well as some highly \(^{13}\text{C}\)- and \(^{15}\text{N}\)-rich SiC C grains, some grains previously thought to have originated in novae, and \(^{15}\text{N}\)-rich SiC AB grains (Liu et al., 2016, 2017a). This model also produces high \(^{26}\text{Al}/^{27}\text{Al}\) ratios. A detailed comparison of these models with the Bonanza data is beyond the scope of the present paper, but their development indicates the general need for a broader consideration of the parameter space of supernova nucleosynthesis models when confronting the presolar SiC data.
4.2.1. \(^{26}\)Al and \(^{12}\)C/\(^{13}\)C

Fig. 16 compares the \(^{12}\)C/\(^{13}\)C and \(^{26}\)Al/\(^{27}\)Al ratios of Bonanza with those of other SiC X grains (Hynes and Gyngard, 2009). Bonanza has the highest \(^{26}\)Al/\(^{27}\)Al ratio of any X grain found so far. Also shown in the figure are mixing lines between material of selected layers of the He/N and He/C zone of the 15 M\(_{\odot}\) SN model by Rauscher et al. (2002). The red line is for a mixture between a layer at 3.506 M\(_{\odot}\) internal mass in the He/C zone and 4.178 M\(_{\odot}\) internal mass in the He/N zone, where the maximum \(^{26}\)Al/\(^{27}\)Al ratio is found. The blue line sloping to lower values in the He/C zone is for a mixture between the 3.061 M\(_{\odot}\) layer with the same He/N layer, and the green line is for a mixture between the averages of the He/C and He/N zones. As has been discussed before (Lin et al., 2010; Jadhav et al., 2013), some SiC grains of type X and low-density graphite have higher \(^{26}\)Al/\(^{27}\)Al ratios than can be explained by SN models. The ratio for the Bonanza grain is higher than the ratio in any SN layer; most SN models predict comparable or lower \(^{26}\)Al/\(^{27}\)Al ratios. For example, predicted \(^{26}\)Al/\(^{27}\)Al ratios in the 25 M\(_{\odot}\) SN model of Rauscher et al. (2002) are lower (see Fig. 17 of Lin et al., 2010) and the Limongi and Chieffi (2003) models predict even lower ratios. The recently measured new \(^{25}\)Mg(p, \(\gamma\))\(^{26}\)Al reaction rate (Straniero and 30 co-authors, 2013) is expected to result in even lower predicted \(^{26}\)Al abundances than those based on the old rate. Measured ratios lower than those predicted by SN models can in principle be explained by Al contamination, but the high \(^{26}\)Al/\(^{27}\)Al ratios observed in Bonanza, some other SiC X grains, and low-density graphite grains remain a puzzle. One possible explanation is the explosive H burning scenario of Pignatari et al. (2013) discussed above at the beginning of Section 4.2, though it is unlikely that this model is needed to explain Bonanza’s \(^{12}\)C-rich composition.

The variations in the Al concentrations from 0.1 wt% to several wt%, are difficult to explain. The different fragments making up Bonanza may have formed under very different conditions, either with different Al gas concentration or at different temperatures, which are likely to also be reflected in the amount of \(^{26}\)Al incorporated into various components of the grain. That the C and Si isotopic ratios (and to some degree the \(^{26}\)Al/\(^{27}\)Al ratios), of Bonanza are so uniform, suggests that the Al heterogeneity may alternatively result from post-condensation diffusion of the Al and formation of AlN subgrains ex-solution.

4.2.2. Ti, Fe, Ni, and \(^{12}\)C/\(^{13}\)C

Interestingly, the Ti, Fe, and Ni isotopic ratios in the He/N zone are normal and one has to go to the He/C zone or more interior zones to find anomalies in these elements. The \(^{12}\)C/\(^{13}\)C ratio in the He/N zone is very low (3.6, the equilibrium value of the CNO cycle during core and shell H-burning), whereas this ratio in the He/C zone exceeds 10\(^5\). Mixing is thus required to obtain the ratio of 190 observed in Bonanza. The Si in the Si/S zone is dominated by \(^{28}\)Si and a contribution from this zone is required to reproduce the \(^{28}\)Si excesses, which are characteristic for X grains.
As a first step, we will mix the whole He/C zone with the whole He/N zone. This will ensure that the mixture has C > O. This condition is required for equilibrium condensation of carbonaceous phases (e.g., Lodders and Fegley, 1995). Clayton and coworkers have proposed that in SN ejecta carbonaceous phases can condense from regions where O greatly exceeds C (Clayton et al., 1999, 2001; Clayton, 2013). Specifically, Deneault et al. (2003) conjectured that SiC grains condensed in the outer O/Si and inner O/Ne SN zones where O/C ratios vary from 50 to 100. It is still not established whether SiC grains can condense under such conditions (Ebel and Grossman, 2001). For example, although a mechanism involving C chains isomerizing to rings has been proposed to explain graphite growth in O-rich supernova layers (Clayton et al., 1999), no comparable mechanism has been suggested for SiC condensation. More importantly, the observed isotopic compositions of SiC grains cannot be explained if the grains condensed in these regions, though small contributions from these zones may be required to explain some isotopic signatures (Meyer et al., 2000).

Fig. 17 shows selected Ti, Fe, and Ni isotopic compositions in the He/C zone of three SN models with different masses by Rauscher et al. (2002). As can be seen, anomalies increase with decreasing interior mass in the zone. They even become larger as one crosses into the C/O zone. We mix the He/N and He/C in different proportions in order to become even larger as one crosses into the O/C zone. We increase with decreasing interior mass in the zone. They include that in the He/C zone of the 25 M\(_\odot\) SN model 62Ni abundances would be lowered by between 6 and 28%. This would result in a better match between the Bonanza Ni data and the SN mixing models. However, the relatively low Ni/Fe ratio in Bonanza leads to large uncertainties in its Ni isotopic ratios, which depend on what mixture is used for the Fe correction. We hope that in the future we will be able to make Fe and Ni isotopic measurements on Bonanza by resonance ionization mass spectrometry (RIMS). This technique allows for the detection of ions of only one element at the exclusion of isobaric interferences from another element. A new generation RIMS instrument, the Chicago Instrument for Laser Ionization (CHILI), has successfully measured Fe and Ni isotopes simultaneously in presolar SiC grains to greater precision and sensitivity than has previously been possible by SIMS analyses (Trappitsch et al., 2017). With CHILI, we thus should be able to detect 58Fe and 58Ni independently and, in addition to obtaining an unequivocal 58Fe/56Fe ratio, shed some light on the true Ni isotopic composition of Bonanza (see also Kodolányi et al., in press).

The reason for the mismatch of the 12C/13C ratio for mixtures that match 58Ni independently and, in addition to obtaining an unequivocal 58Fe/56Fe ratio, shed some light on the true Ni isotopic composition of Bonanza (see also Kodolányi et al., in press).
topic ratios. The $^{58}\text{Fe}$ corrections for all cases are larger than those for most X grains analyzed by Marhas et al. (2008), because in Bonanza the Ni/Fe ratio is smaller than that in most other X grains.

However, there are still several remaining problems. First, the $^{12}\text{C}/^{13}\text{C}$ ratios for the Ti, Fe, and Ni matches are still not the same, although the relative differences are reduced. Second, the isotopic patterns of Ti and Ni cannot be reproduced as well as they can be with the mixture between the whole He/C and He/N zones. For example, the $\delta^{48}\text{Ti}/^{46}\text{Ti}$ value of the mixture with up to 3.1 M$_{\odot}$ interior mass of the He/C zone is 372‰, much higher than the observed value and the value obtained from mixing the whole zones (Table 4). The reason is that, with
decreasing interior mass the $\delta^{50}$Ti/$^{48}$Ti value increases more rapidly than the $\delta^{49}$Ti/$^{48}$Ti value; in the O/C zone, it actually overtakes it. Thus, adding contributions from the O/C zone does not help, but rather produces a pattern with $\delta^{50}$Ti/$^{48}$Ti > $\delta^{49}$Ti/$^{48}$Ti. In addition, since the $^{13}$C abundance sharply increases as one crosses from the He/C zone into the O/C zone, adding material from the O/C zone does not help with the $^{12}$C/$^{13}$C ratio problem and only increases this ratio. Finally, and perhaps most importantly, this mixing exercise of selecting certain regions is completely ad hoc as there is no simple guiding principle that would tell us why certain regions should be selected preferentially.

In the 25 M$_\odot$ SN model, we encounter the opposite problem. There, mixing of the whole He/C zone with the whole He/N zone produces $^{12}$C/$^{13}$C ratios that are smaller than the measured ratio, if one matches the measured $\delta^{50}$Ti/$^{48}$Ti, $\delta^{57}$Fe/$^{56}$Fe, and $\delta^{59}$Ni/$^{58}$Ni values (Table 4). The reason is that in this model the Ti, Fe, and Ni anomalies become prominent much farther out in the He/C zone than in the 15 M$_\odot$ SN model (Fig. 17a and c). In order to increase the $^{12}$C/$^{13}$C ratio relative to the Ti, Fe, and Ni anomalies, we mixed material from outer regions of the He/C zone, between the 7.4 and 7.5 M$_\odot$ interior masses and the He/C-He/N boundary, with the whole He/N zone. This mixing does result in an increase of the $^{12}$C/$^{13}$C ratios for the various matches; however, whereas for the region from 7.8 M$_\odot$ interior mass the $^{12}$C/$^{13}$C ratio for the Ti match is still smaller than the measured ratio, for the Fe and Ni matches it is much larger (Table 4). In other words, the discrepancy in the $^{12}$C/$^{13}$C ratios increases. Another result of mixing only outer layers of the He/C zone is that the match for the Ti isotopic pattern becomes much worse: whereas for the whole zone mixing, $\delta^{50}$Ti/$^{48}$Ti is 224‰, identical with the measured value within errors, it is only 98‰ for the mixture from 7.8 M$_\odot$ interior mass (Table 4).

We expected that a SN model with an intermediate mass between 15 and 25 M$_\odot$ might produce a better fit to the $^{12}$C/$^{13}$C ratio of Bonanza but this is not the case. Table 4 shows that for the 19 M$_\odot$ SN model of Rauscher et al. (2002) the mixture of the whole zones results in a $^{12}$C/$^{13}$C ratio for the Ti fit that is approximately the same as that for the 15 M$_\odot$ mixture, while $^{12}$C/$^{13}$C ratios are much larger for the Fe and Ni fit. Since the Ti, Fe, and Ni anomalies are fairly constant throughout the He/C zone of this model (Fig. 17b), selecting only an inner region does not help much. The anomalies sharply increase in the O/C zone, however, the $^{13}$C abundance increases even more. When we mixed the region between 4.4 (in the O/C zone) and 4.8 M$_\odot$ interior mass with the He/N zone, the $^{12}$C/$^{13}$C ratio of the mixture that reproduces $\delta^{50}$Ti/$^{48}$Ti is 503, larger than that for the whole-zone mixture.

In the lower part of Table 4, we present the corresponding N, Al, and Si isotopic ratios for the same various SN mixtures described above. Similar to the case for the $^{26}$Al/$^{27}$Al ratio, the $^{14}$N/$^{15}$N ratio of Bonanza cannot be obtained by any SN mixture, in line with the findings of other authors for both type X SiC grains in general (e.g., Lin et al., 2010) and supernova graphites (e.g., Jadhav

Fig. 13. Positive $^{58,56}$Ni and $^{54,56,57}$Fe ion images of Bonanza. Each ion image is the sum of 21 individual 128 $\times$ 128 pixel layers. Maximum pixel intensities (in counts per pixel) for the images are $^{58}$Ni: 9, $^{56}$Ni: 4, $^{54}$Fe: 14, $^{56}$Fe: 220, and $^{57}$Fe: 10.
Table 4

Results of supernova mixing between the He/C and He/N zones compared with Bonanza’s isotopic composition.

|        | $^{29}$Ti | $^{30}$Ti | $^{31}$C/$^{32}$C match $^{30}$Ti | $^{32}$C/$^{33}$C match $^{30}$Ti | $^{34}$Fe | $^{35}$Fe | $^{36}$Fe | $^{36}$Ni | $^{37}$Ni | $^{38}$Ni | $^{39}$Ni | $^{40}$Ni | $^{41}$C/$^{42}$C match $^{30}$Ni |
|--------|------------|-----------|----------------------------------|----------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|-------------------|-------------------|
| Measured | 3         | -55       | 570                               | 229                               | 190      | -59      | 781      | 190      | -40       | 1212     | 98       | 190    |                   |
| SN-15  |            |           |                                   |                                   |          |          |          |          |           |          |          |        |                   |
| He/C-He/N | 17        | -12       | 570                               | 215                               | 335      | -34      | 781      | 3545     | 561       | 103      | 1541     | 261      | 312      | 1541               | 387               |
| to 3.4$^a$ | 14        | -1        | 570                               | 271                               | 255      | -33      | 781      | 4354     | 371       | 142      | 1631     | 306      | 153      | 1631               | 505               |
| to 3.2$^a$ | 11        | 8         | 570                               | 320                               | 209      | -33      | 781      | 5027     | 281       | 176      | 1710     | 345      | 170      | 1710               | 537               |
| to 3.1$^a$ | 9         | 15        | 570                               | 372                               | 197      | -32      | 781      | 5755     | 253       | 216      | 1802     | 390      | 190      | 1802               | 650               |
| SN-19  |            |           |                                   |                                   |          |          |          |          |           |          |          |        |                   |
| He/C-He/N | 25        | -32       | 570                               | 93                                | 330      | -36      | 781      | 1506     | 823       | 16       | 1341     | 162      | 84       | 1341               | 219               |
| 4.4 to 4.8$^b$ | 38       | -22       | 570                               | 152                               | 503      | -37      | 781      | 2603     | 1016      | 61       | 1445     | 213      | 120      | 1445               | 364               |
| SN-25  |            |           |                                   |                                   |          |          |          |          |           |          |          |        |                   |
| He/C-He/N | 18        | -3        | 570                               | 224                               | 55       | -34      | 781      | 3637     | 81        | 107      | 1551     | 266      | 142      | 1551               | 457               |
| from 7.4$^a$ | 25       | -18       | 570                               | 113                               | 95       | -34      | 781      | 1754     | 165       | 26       | 1363     | 173      | 20       | 1363               | 299               |
| from 7.5$^a$ | 27       | -29       | 570                               | 99                                | 145      | -35      | 781      | 1556     | 321       | 18       | 1345     | 164      | 90       | 1345               | 516               |
| from 7.8$^a$ | 27       | -31       | 570                               | 98                                | 159      | -35      | 781      | 1568     | 378       | 19       | 1346     | 164      | 91       | 1346               | 234               |
| Measured | 28        | 28        | 28                                | 0.9                                | 0.9      | 0.9      | 292      | 292      | 292       | 0.9      | 0.9      | 292      | 0.9      | 292                | 0.9               |
| SN-15  |            |           |                                   |                                   |          |          |          |          |           |          |          |        |                   |
| He/C-He/N | 201       | 130       | 115                               | 0.16                               | 0.14     | 0.13     | 104      | 118      | 144       | 164      | 157      | 178      | 157      | 178                |                   |
| to 3.4$^a$ | 155       | 109       | 99                                | 0.18                               | 0.17     | 0.16     | 110      | 141      | 146       | 187      | 158      | 202      | 158      | 202                |                   |
| to 3.2$^a$ | 136       | 102       | 93                                | 0.20                               | 0.19     | 0.19     | 116      | 160      | 149       | 207      | 161      | 223      | 161      | 223                |                   |
| to 3.1$^a$ | 168       | 131       | 120                               | 0.21                               | 0.21     | 0.20     | 124      | 180      | 156       | 227      | 168      | 244      | 168      | 244                |                   |
| SN-19  |            |           |                                   |                                   |          |          |          |          |           |          |          |        |                   |
| He/C-He/N | 2253      | 998       | 641                               | 0.12                               | 0.07     | 0.05     | 89       | 71       | 133       | 107      | 153      | 124      | 153      | 124                |                   |
| 4.4 to 4.8$^b$ | 2180     | 1138      | 795                               | 0.14                               | 0.10     | 0.08     | 98       | 100      | 147       | 151      | 157      | 180      | 157      | 180                |                   |
| SN-25  |            |           |                                   |                                   |          |          |          |          |           |          |          |        |                   |
| He/C-He/N | 610       | 526       | 488                               | 0.16                               | 0.14     | 0.13     | 102      | 127      | 139       | 172      | 160      | 200      | 160      | 200                |                   |
| from 7.4$^a$ | 627     | 510       | 377                               | 0.13                               | 0.11     | 0.079    | 73       | 66       | 104       | 95       | 139      | 126      | 139      | 126                |                   |
| from 7.5$^a$ | 592       | 418       | 317                               | 0.11                               | 0.076    | 0.056    | 89       | 77       | 131       | 114      | 154      | 134      | 154      | 134                |                   |
| from 7.8$^a$ | 654       | 475       | 354                               | 0.11                               | 0.069    | 0.048    | 90       | 76       | 134       | 114      | 158      | 134      | 158      | 134                |                   |

Notes. The “measured” Ni isotopic ratios are corrected for $^{56}$Fe interference with a normal $^{56}$Fe/$^{56}$Fe ratio. The first set of model Ni isotopic ratios are corrected with an $^{56}$Fe/$^{56}$Fe ratio derived from the SN mixture that reproduces the $^{57}$Fe/$^{56}$Fe ratio. The second set of model Ni isotopic ratios are obtained from the SN mixture that reproduces the $^{59}$Ni/$^{58}$Ni ratio. The columns labeled “$^{12}$C/$^{13}$C match” give the resultant $^{12}$C/$^{13}$C ratio calculated for mixing that reproduces either the $^{49}$Ti, $^{57}$Fe, or $^{61}$Ni value of the Bonanza. See text.

$^a$ Mixture of the whole He/N zone with material from the base of the He/C zone to the given interior mass coordinate ($M_{\odot}$); see text and Fig. 17.

$^b$ Mixture of the whole He/N zone with the O/C-He/C zones between the interior mass coordinates 4.4 $M_{\odot}$ and 4.8 $M_{\odot}$; see text and Fig. 17.

$^c$ Mixture of the whole He/N zone with material from the given mass coordinate ($M_{\odot}$) to the He/C-He/N zone boundary; see text and Fig. 17.
et al., 2013). The $\text{^{14}N}/\text{^{15}N}$ ratio in the He/N zone is very high as a result of H burning in the CNO cycle, and the high $\text{^{14}N}$ abundance cannot be overcome by the $\text{^{15}N}$ found in the inner layers of the He/C zone. The 25 M$_{\odot}$ model by Rauscher et al. (2002) features a $\text{^{15}N}$ spike in the middle of the He/N zone in the layer where H becomes exhausted. There, $\text{^{15}N}$ is produced by explosive He burning during

Fig. 14. (a) The Fe isotopic ratios of Bonanza are compared with those of other X grains (Marhas et al., 2008). Also plotted are isotopic ratios obtained from mixing between the whole He/C and He/N zones of the 15 and 25 M$_{\odot}$ SN models of Rauscher et al. (2002) and mixing with the Si/S zones (see text and Table 5). (b) Iron isotopic ratios of individual subgrains. Also plotted are the ratios obtained from the whole images (Bonanza), the averages of the subgrains and the ratios for the rest of the images once the subgrains are subtracted out ("Rest"). A line connecting the Bonanza ratios to the Solar System ratios is shown. Errors are 1σ.

Fig. 15. Negative $\text{^{28}Si}$, $\text{^{32}S}$, and $\text{^{34}S}$ ion images of Bonanza. Each ion image is the sum of 100 individual 256 $\times$ 256 pixel layers. Maximum pixel intensities (in counts per pixel) for the images are $\text{^{28}Si}$: 90,000, $\text{^{32}S}$: 40,000, and $\text{^{34}S}$: 1800.
the passage of the shock (Meyer and Bojazi, 2011). However, similar mixing calculations as those performed by Lin et al. (2010) have shown that the C and N isotopic ratios measured in Bonanza cannot be reproduced even if one mixes 20% of the He/N zone centered on the 15N spike with a layer with the lowest 14N/15N ratio in the He/C zone. In addition, the 15 M_{\odot} model does not have such a 15N spike. Furthermore, the correlation of large 14N and 18O excesses in regions within SN graphite, which condensed from SN ejecta similar to those X grains condensed from, indicates that 15N excesses originate in the He/C zone, which is rich in 18O (Groopman et al., 2012). As can be seen in Table 4, mixtures of the 15 M_{\odot} model produce the lowest 14N/15N ratios, but still much higher than that measured in Bonanza.

We conclude that for the SN models considered here, no mixing between the material from the He/C and He/N zone (and any other zones) can simultaneously reproduce the C, N, Al, Ti, Fe, and Ni isotopic ratios measured in Bonanza. However, the 26Al/27Al ratio can be reproduced if one adds 20% of the He/N zone centered on the 26Al spike to the 15M_{\odot} model. In this case, the 14N/15N ratio measured in Bonanza is reproduced in the He/C zone.

Since Si is isotopically normal in the He/N zone and isotopically heavy in the He/C zone, any mixture has 29Si and 30Si excesses (Table 4). In order to achieve a 28Si excess, we have to add material from the Si/S zone, the only zone with a 28Si excess. Since C and N abundances in this zone are extremely low, mixing with Si/S material will not change the C and N isotopic ratios of any He/C-He/N mixture; however, it will potentially affect the isotopic compositions of other elements. As an exercise, we mixed two He/C-He/N mixtures with Si/S material: (1) a mixture between the whole He/C and He/N zones of the 15 M_{\odot} SN model that reproduces the Ti isotopic ratios quite well, and (2) a mixture between the whole He/C and He/N zones of a 25 M_{\odot} SN model that also reproduces the Ti isotopic ratios quite well. We have to point out that neither mixture reproduces the Fe and Ni isotopic ratios. In the 15 M_{\odot} SN case, 26Fe/28Fe is 563\%, instead of 781\%; and 58Ni/56Ni is 997\%, instead of 1541\%; in the 25 M_{\odot} SN case, 26Fe/28Fe is 571\%, instead of 781\%; and 58Ni/56Ni is 977\%, instead of 1551\%. For our purpose, this discrepancy is not important because we mainly want to see how the isotopic ratios of Al, Ti, Fe, and Ni change as a result of the addition of material from the Si/S zone that would approximate (see below) the Si isotopic ratios of Bonanza.

Table 5 shows the results of the mixing exercise with the Si/S zone. For either SN model, mixing with the Si/S zone shifts the Si isotopic composition on a Si 3-isotope plot such as in Fig. 6 toward a composition of pure 30Si (δ-Si values of -1000‰). This means that to first order 28Si/29Si = 29Si/30Si. This is in contrast to the Si isotopic ratios of Bonanza and most other X grains, which have larger 29Si/28Si ratios than 30Si/28Si ratios. This problem has previously been discussed in detail by many authors (e.g., Hoppe et al., 2000; Lin et al., 2010), who pointed out that mixing with the Si/S zone cannot reproduce the Si isotopic compositions of the majority of X grains (see Fig. 15 of Lin et al., 2010). In Table 5, we consider two different mixtures, one that reproduces the 28Si/29Si value and another that reproduces the 28Si/29Si value of Bonanza. Because of the large 28Si abundance in the Si/S zone, only ~1% of the Si/S zone has to be admixed to the He/C-He/N mix to match the Si isotopic ratios of Bonanza. Mixing with the Si/S zone does not affect the 26Al/27Al ratio or the 12C/13C and 14N/15N ratios (not shown in the table). However, it does affect the Ti, Fe, and Ni isotopic ratios. For Ti, it increases 46Ti/48Ti, slightly increases 49Ti/48Ti, and decreases 47Ti/48Ti and 48Ti/49Ti. The increase in 46Ti/48Ti is due to a large 48Ti abundance in the outer region of the Si/S zone. The major effect of the mixing is an increase in 26Fe/28Fe, the result of a large 54Fe abundance throughout most of the Si/S zone. The effect of the mixing on the Ni isotopes is a decrease in all the Ni ratios because of a large 58Ni abundance in the Si/S zone. We could improve the match with the Ti isotopic pattern if we take only material from the inner Si/S zone; however, this would not improve the mismatch of the Fe and Ni isotopic ratios.

The effect of mixing with the Si/S zone is also shown in the isotopic ratio plots of Figs. 12 and 14. In these figures, we first plot the isotopic ratios of the two 15 and 25 M_{\odot} He/C-He/N whole-zone mixtures that reproduce the 46Ti/48Ti, 26Fe/28Fe, and 58Ni/56Ni values, respectively. As can be seen, for Ti and Fe, these ratios are fairly close to the ratios measured in Bonanza. Next we plot the ratios resulting from the mixing with the Si/S zone for the four cases given in Table 5. As can be seen, this mixing results in large 46Ti and 54Fe excesses (Figs. 12 and 14, respectively). The situation is more complicated for the Ni isotopic ratios because of the 26Fe interference correction. In Fig. 18, we first plot the isotopic ratios obtained by correcting Ni under the...
assumption of a normal $^{58}\text{Fe}/^{56}\text{Fe}$ ratio. If we instead assume the larger $^{58}\text{Fe}/^{56}\text{Fe}$ ratio inferred from the $^{57}\text{Fe}/^{56}\text{Fe}$ ratio and SN models, this leads to a smaller amount of $^{58}\text{Ni}$ and larger Ni isotopic ratios as seen in the figure. The Ni isotopic ratios of the He/C-He/N whole zone mixtures that match $^{61}\text{Ni}/^{58}\text{Ni}$ are not very different from these corrected ratios and might be even closer if we take higher $^{62}\text{Ni}$ neutron-capture rates (Corvi et al., 2002;
The effect of mixing with the Si/S zone leads to a reduction in all Ni isotopic ratios but is not as drastic as for the $^{46}\text{Ti}/^{48}\text{Ti}$ and $^{54}\text{Fe}/^{56}\text{Fe}$ ratios (Figs. 12 and 14).

We conclude that even though the Ti, Fe and Ni isotopic ratios (but not the C, N, and Al isotopic ratios) of Bonanza can be matched fairly well by mixtures of material from the He/C and He/N zone, the agreement for these isotopic ratios goes away if we add material from the Si/S zone, necessary to reproduce the Si isotopic ratios. Various authors have invoked elemental fractionation in order to explain discrepancies between isotopic compositions measured in SN grains and the predictions of theoretical SN models (Marhas et al., 2008; Hoppe et al., 2012). Since SiC grains from AGB stars typically have somewhat higher-than-solar Ti/Si ratios, the low Ti/Si ratios in X grains are most likely the result of formation conditions. Titanium-to-Si ratios in the He/C and He/N zone are close to the solar ratio in SN models (Rauscher et al., 2002) and the addition of $^{28}\text{Si}$ from the Si/S zone in X grains, resulting in $^{28}\text{Si}$ excesses, can at best account for an overabundance of Si over Ti by a factor of two. In the case of Bonanza and other X grains, Ti, Fe, and Ni have to be separated from Si from the Si/S zone that was mixed with material from outer layers and condensed into SiC grains. A fundamental question is how material from the Si/S zone could be mixed into the outer C-rich He/C and He/N zones without the mixture being overwhelmed by the massive amount of the intermediate O-rich zones. However, astronomical observations of SNe provide numerous lines of evidence (e.g., Wooden, 1997; Hughes et al., 2000 and references therein) that SN ejecta are not a uniform mix but that “bullets” from inner zones can penetrate into outer layers. This is also the result of multi-dimensional SN explosion models which show that fingers of inner zone material reach into outer layers where they slow down and mix with local material (Kifonidis et al., 2003; Joggerst et al., 2009; Hammer et al., 2010). It is thus conceivable that material from the Si/S zone penetrates the O-rich SN zones and mixes with C-rich layers.

Given such a scenario, it is not clear what processes could result in the separation of Ti, Fe, and Ni from Si. Since the Si/S zone is rich in sulfur, these metals could have formed sulfides and were thus separated from the Si from this zone. Either sulfide grains were physically removed from the mixture from which the X grains condensed, or the metals remained in sulfide molecules and did not participate in the formation of SiC. However, Fedkin et al. (2010) calculated that in a gas with the composition of the Si/S zone, Ti, Fe, and Ni condense as silicides before any sulfides.

An alternative scenario is that of Pignatari et al. (2013) in which a higher-than-typical SN shock energy leads to development of a C/Si zone below the He/C zone. Whether such a model can better explain the isotopic data for Bonanza remains to be seen.

4.3. Reconciliation of microstructure and subgrains in Bonanza with supernova models

Bonanza is clearly somewhat of an outlier with regard to both size and crystal structure. The large size of the grain

<table>
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<th>Table 5</th>
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<tr>
<td>Results of supernova mixing between the Si/S, He/C, and He/N zones and comparison with Bonanza.</td>
</tr>
<tr>
<td>$^{28}\text{Si}$</td>
</tr>
<tr>
<td>Measured</td>
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<tr>
<td>SW/He/He/N mix</td>
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<tr>
<td>Mix with Si/S a</td>
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<td>He/C-He/N mix</td>
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<td>Mix with Si/S a</td>
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<tr>
<td>SN-25</td>
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<tr>
<td>He/C-He/N mix</td>
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<td>Mix with Si/S a</td>
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Notes: The values of the He/C-He/N mix are for a mix that matches $^{46}\text{Ti}/^{48}\text{Ti}$.

$^{46}\text{Ti}/^{48}\text{Ti}$.
indicates either rapid condensation at higher gas densities than the majority of presolar SiC, or longer residence time in the circumstellar condensation envelope. More rapid condensation is supported by the polycrystalline microstructure and the variable type and degree of ordering among its crystallites (Figs. 2 and 3). That some crystallites show diffraction patterns from higher order polytypes, such as 15R, also supports higher pressure and/or temperature condensation. The temperature and pressure stability of the various SiC polytypes remains a matter of significant debate, due to the very small differences in free energy (<1 meV in many cases), which increases the dependence of the phase fractions on other growth conditions such as gas composition (Si/C ratio), impurity incorporation, e.g., N, growth seed or surface. Despite ongoing debate regarding polytype stability (Ito et al., 2011), empirical evidence demonstrates 2H single crystal growth occurs at the lowest temperatures (1300–1600 °C), which transforms to 3C at 2000 °C, which in turn transforms to 6H at 2100 °C. Furthermore, it is possible to produce 4H, 15R and 21R as intergrowths with 6H, under nominally identical conditions (Feldman et al., 1968). However, such polytypes are very rare among presolar SiC. Daulton et al. (2002, 2003) showed that ~99% of presolar SiCs in the most common size range have either the 3C, 2H structures, or an intergrowth of these two structures, consistent with low temperature condensation conditions. In a recent conference abstract, Kodolányi et al. (2016) reported five out of seven X grains analyzed by TEM to have the 6H structure, but details of the diffraction analysis were not provided. Liu et al. (2017b) recently used Raman measurements to target presolar SiCs with rare structures, and identified 11/156 had either non-cubic polytypes, or more complex intergrowth and/or twinning than the predominant 3C polytype. Coordinated TEM analysis on two grains confirmed the presence of 6H and 15R polytypes. Similar to Bonanza, the Raman spectrum of the grain identified as of the 15R polytype had the primary TO peak shifted to 789 cm⁻¹ (Wopenka et al., 2010).

Bonanza is also unusual in the abundance of subgrains it contains (Figs. 4, 11 and 13). In a TEM study of six X grains, Hynes et al. (2010) found only one with subgrains: one Ti-rich and 7 Fe/Ni-rich; two X-grains studied by Stroud (2005) showed no subgrains. Kodolányi et al. (2016) reported one FeNi grain and one TiC subgrain, out of seven X grains studied by TEM. Evidence for subgrains inside of X grains has also been obtained from depth profiles during isotopic measurements (e.g., Marhas et al., 2008; Lin et al., 2010). Here the question arises whether these subgrains condensed as independent grains and were later included into the growing SiC host or whether they co-condensed with SiC or condensed into solid solution with SiC and subsequently formed subgrains from exsolution. Hynes et al. (2010) showed epitaxial relationships between the subgrains and host SiC that indicated formation by exsolution. In the case of at least one Bonanza (Al, Mg)N grain, there is also a clear argument for formation by exsolution, based on the depletion of Al and Mg in the SiC host in the immediate vicinity of the subgrain. In the case of the Ti, and Fe, Ni-rich grains, the evidence is less clear; the abundance of Fe, Ni and Ti in the SiC host outside the subgrains is below detection limits for STEM-EDS. That the subgrains appear to be preferentially located at grain boundaries between different SiC crystallites and near voids could be argued as evidence against condensation as separate grains prior to incorporation. One possible growth scenario is that the subgrains formed by co-condensation, i.e., that individual impurity atoms of Fe, Ni or Ti adsorbed onto the various growing SiC crystal facets served as preferential sticking sites for additional Fe and Ni, or Ti ad-atoms respectively, leading to contemporaneous secondary phase formation. Bernatowicz et al. (1992), based on epitaxial relationships of TiC subgrains within a SiC grain of unspecified stellar origin,
concluded that the subgrains had not condensed prior to SiC formation, but that host and subgrains formed simultaneously or the subgrains constituted exsolution. The subgrains may also have a role in stabilizing specific SiC stacking sequences, and thus in the structural variability among the individual crystallites.

Isotopic heterogeneity among subgrains and between subgrains and SiC host would seem to favor scenarios in which the subgrains condensed independently before SiC formation. Titanium-rich subgrains (Fig. 11) show variations in their Ti isotopic ratios (Fig. 12b) but, as already discussed, we do not have absolute proof that these variations are intrinsic and not the result of mixing with an isotopically normal component such as contamination. In fact, the STEM analysis clearly shows abundant subgrains at sizes too small to be individually resolved with NanoSIMS, making isotopic dilution with neighboring host SiC and other subgrains likely. Marhas et al. (2008) observed large variations in the $^{56}\text{Fe}/^{54}\text{Fe}$ ratio between subgrains within SiC X grains and between subgrains and host and these observations might be the best evidence for isotopic heterogeneity; however it is unknown whether subgrains $\ll 100$ nm were also present in those X grains.

If subgrains formed before SiC condensation, it is possible that they condensed from a He/C-He/N mixture before any contribution from the Si/S zone was admixed and thus do not show the expected concomitant anomalies from the Si/S zone ($^{46}\text{Ti}$ and $^{56}\text{Fe}$ excesses). Equilibrium condensation calculations by Lodders and Fegley (1995) show that at C/O ratios not much larger than unity and relatively high pressures, TiC condenses before SiC and graphite. This is likely to hold true for incorporation of small amounts of N into the carbides as well. However, in that case the SiC host outside the subgrains should still show Ti and Fe contributions from the Si/S zone (Figs. 12b and 14b). Alternatively, no Ti and Fe condensed into the SiC host, but this is highly unlikely in view of the expected condensation behavior (Lodders and Fegley, 1995). Thus, if all subgrains in X grains have indeed an origin as either co-formation or exsolution, rather than pre-condensation, we are again faced with the problem of how Ti, Fe, and Ni were physically separated from Si ejected from the Si/S zone. At present, all options are quite unsatisfying.

### 5. CONCLUSIONS

The fortuitous discovery of Bonanza, the largest stardust supernova grain ever found, has afforded us the opportunity to make isotopic measurements of a large suite of elements (i.e., Li, B, C, N, Si, Mg, Al, S, Ca, Ti, Fe, and Ni) all in the same grain. This has allowed for detailed comparisons with models of nucleosynthesis in supernovae of different masses with greater numbers of isotopic ratio constraints than was previously possible for smaller grains. Additionally, it was possible to extract multiple FIB lift-outs from different regions of Bonanza and analyze with TEM. This exhaustive combination of isotopic and microstructural analyses allows us to conclude:

1. Despite its unexpectedly large size for a SN condensate, Bonanza is not likely a mechanical aggregate, but rather represents polycrystalline growth in a single condensation event. SiC grains of such size are not predicted by models of grain condensation around either AGB stars or supernovae. Moreover, detection of such large grains in astrophysical environments by spectroscopic techniques is extremely difficult. However, Gall et al. (2014) used multi-wavelength methods to estimate that dust grains in one SN remnant reach sizes greater than 8 microns, providing independent evidence that large grains can grow in SNe.

2. Evidence for a variety of internal subgrains such as Ti(C, N)s, Fe-Ni-rich grains, and (Al, Mg)Ns were observed in all three FIB lift-out sections. The observation of (Al, Mg)Ns represents an unequivocal detection of these subgrains in presolar SiC from a supernova, lending supporting evidence to the idea that Al and N are present in the grains as subgrains, and not only in solid solution.

3. Bonanza shows evidence for multiple polytypes among the individual constituent crystallites, including rare higher-order polytypes (e.g., 15R). This implies condensation under higher pressure and/or temperature than most other presolar SiCs, including both AGB and supernova grains. This lends support to the approach of Liu et al. (2017b) to search for rare SiC grains using coordinated Raman, TEM and SIMS, in order that the full range of circumstellar SiC condensation conditions be determined.

4. NanoSIMS whole grain isotopic imaging shows heterogeneous distributions of Al, Ti, Fe, and Ni, with the highest inferred $^{26}\text{Al}/^{27}\text{Al}$ ratio ever observed, even higher than predicted from SN models.

5. Similar to the situation for other stardust grains from supernovae, detailed mixing calculations of the model ejecta from various SNe of different masses fail to reproduce the isotopic composition and observed elemental abundances of Bonanza.

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