PRESOLAR GRAINS FROM THE QINGZHEN (EH3) METEORITE

Yangting Lin,[1,2] Sachiko Amari,[2] and Olga Pravdivtseva[2]

ABSTRACT

A 28 g sample of the Qingzhen enstatite (EH3) chondrite was subjected to chemical and physical separation procedures to yield several grain-size residues. Ion mapping of isotopes of Si, O, and C in the ion microprobe of two size fractions (QZR4: 0.4–0.8 μm; QZR5: 0.8–2 μm) identified 55 ^{30}Si-depleted candidates out of 37,917 Si-rich grains and six ^{18}O-depleted grains out of 54,410 oxides. Subsequent isotopic analyses of C, N, and Si of 48 grains of the ^{30}Si-depleted candidates and additional randomly selected SiC and Si_3N_4 grains confirmed 36 of X-type SiC, nine of X-type Si_3N_4, and one of A+B–type SiC. The isotopic compositions of most X grains overlap those of previously measured X grains from the Murchison carbonaceous chondrite, but ~25% show more pronounced ^{29}Si deficits, suggestive of multiple stellar origins of X grains. Presolar Si_3N_4 grains have isotopic compositions similar to those of X SiC grains, except that their C isotopic ratios are close to solar. The relative abundances of various presolar grain types in Qingzhen are different from those in Murchison, suggestive of heterogeneity and/or size sorting in the primitive solar nebula.

Subject headings: dust, extinction — ISM: abundances — meteors, meteoroids — nuclear reactions, nucleosynthesis, abundances — supernovae: general

1. INTRODUCTION

Presolar grains from carbonaceous chondrites have been extensively studied (Anders & Zinner 1993; Zinner 1998a), especially the carbon-rich phases, such as diamond (Lewis et al. 1987), silicon carbide (Bernatowicz et al. 1987; Tang & Anders 1988), and graphite (Amari et al. 1990). The carbon-rich phases must have formed under reducing conditions with C/O ratios $\geq$1, different from the major constituent minerals of the host chondrites. In contrast, in carbonaceous chondrites only a few oxide grains have so far been confirmed to be of presolar origins (Huss et al. 1993; Hutcheon et al. 1994), probably in part because of dilution by abundant Ca-, Al-rich inclusions (CAIs). The majority of presolar oxide grains have been identified in ordinary chondrites (Nittler et al. 1994, 1997; Choi et al. 1998; Nittler & Alexander 1999; Nittler, Alexander, & Tera 2001; Krestina, Hsu, & Wasserburg 2002), most of them from Tieschitz (H3.6) by using ion imaging in the ion microprobe.

Studies of presolar grains from various chondrites have revealed that their abundances vary among the chondrite groups and are sensitive to thermal metamorphism (Alexander et al. 1990; Russell, Arden, & Pillinger 1992; Huss & Lewis 1994, 1995). Enstatite chondrites, formed under extremely reducing conditions, probably sampled presolar grains in different locations of the solar nebula than carbonaceous and ordinary chondrites. Most enstatite chondrites contain very few CAIs, hence presolar oxides (if they exist in these meteorites) may not be highly diluted by oxides from the CAIs. Indarch (EH4) is the most intensively studied enstatite chondrite, and it experienced moderate thermal metamorphism in the parent body. SiC isolated from Indarch is submicron sized (Russell et al. 1993; Gao et

al. 1995), distinctly smaller than that from Murchison. This is confirmed by the lower mean Ne-E(H)/Xe-s ratio of bulk SiC from Indarch than that of Murchison SiC (Russell et al. 1997). Ne-E(H) is an ^{22}Ne-rich component whose content is relatively constant in SiC grains of different grain size, while Xe-s is an Xe s-process–enriched component whose content is higher in smaller SiC grains (Lewis, Amari, & Anders 1990, 1994). Ion mapping on SiC from Indarch (Gao et al. 1995) suggested that it contains a similar fraction of the rare type X SiC from Murchison (Amari et al. 1992; Nittler et al. 1995). Presolar Si_3N_4 is much less abundant than type X SiC (Nittler et al. 1995; Hoppe et al. 1996a). Most Si_3N_4 grains in enstatite chondrites have normal isotopic compositions (Lee et al. 1992; Alexander, Swan, & Prombo 1994; Gao et al. 1995; Russell et al. 1995). They probably condensed in the solar nebula (Lee et al. 1992) and/or formed by exsolution from metallic Fe-Ni and schreibersite [(Fe, Ni)$_3$(P, Si); Alexander et al. 1994]. Recently, NanoSIMS isotopic analysis of submicron-sized grains (0.25–0.65 μm) from Indarch indicated the existence of presolar Si_3N_4 with the isotopic signatures of mainstream SiC (Amari et al. 2002).

Qingzhen is one of the most primitive EH3 chondrites (Lin & El Goresy 2002); hence, it might be a better sample than Indarch for the study of presolar grains in enstatite chondrites. Although no presolar oxides, Si_3N_4, nor any of the rare types of presolar SiC were reported from Qingzhen (Alexander 1993; Alexander et al. 1994; Choi, Huss, & Wasserburg 1999), a survey of presolar grains from a large sample of this meteorite is required. Two fragments of Qingzhen were collected; the larger one fell in a muddy field, and therefore it was heavily weathered and was never used for any geochemical, petrological, or mineralogical studies. However, weathering of the sample should have no significant effect on existing presolar grains; after all, presolar grains have previously been separated from other meteorites as acid residues. Furthermore, we expected presolar oxides from Qingzhen to be easier to find. Enstatite chondrites formed under more reducing conditions than other groups

[1] Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, P.O. Box 1131, Guangzhou 510640, China; linyt@gig.ac.cn.
[2] Laboratory for Space Sciences and the Department of Physics, Washington University, St. Louis, MO 63130-4899; sa@wuphys.wustl.edu, olga@wuphys.wustl.edu.

of meteorites and should have lower abundances of solar origin oxides that would survive the acid treatment and dilute the presolar oxides. Preliminary results of this study were reported by Lin, Amari, & Pravdivtseva (2000).

2. SAMPLE AND EXPERIMENTAL PROCEDURES

A sample of 27.9 g of the weathered portion of Qingzhen was subjected to the modified separation procedure described by Gao et al. (1995). The powdered sample was first reacted with 3N HCl at 85°C, then with 6N HCl at 60°C. After that, the sample was treated alternately with 10N HF–1N HCl and 6N HCl–0.6 M H_3BO_3 seven times at 70°C until all silicates were dissolved. The HCl/HF residue, after drying, weighed 0.42 g (i.e., 1.5% of the original mass). Most elemental sulfur (S^0) was dissolved in CS_2; the rest and organic carbon were then oxidized with 0.5N $Na_2Cr_2O_7$–2N H_2SO_4 at 85°C. Diamond was separated as colloid and purified by destroying all other carbonaceous phases with boiling 70% $HClO_4$. The remaining etched residue weighed 32 mg (i.e., 0.115% of the original mass). We performed a density separation on it, isolating a low-density fraction of carbonaceous grains (1.75–1.85 g cm^{-3}). The rest was oxidized with 70% $HClO_4$ at 203°C. The final separate was examined with a JEOL 840A scanning electron microscope (SEM) equipped with an ultrathin Be window and energy dispersive spectrometer (EDS). A total of 10% of the final residue was preserved for future study; the rest was separated into eight size fractions: QZR1 (<0.1 μm), QZR2 (0.1–0.2 μm), QZR3 (0.2–0.4 μm), QZR4 (0.4–0.8 μm), QZR5 (0.8–2 μm), QZR6 (2–4 μm), QZR7 (4–10 μm), and QZR8 (>10 μm).

In this work, two fractions, QZR4 and QZR5, were analyzed using the modified Cameca ims 3f ion microprobe at Washington University. Samples of these two size fractions were dispersed in 70% isopropanol/30% water and deposited on high-purity gold foils mounted on SEM stubs. The foils had been cleaned by HF etching and ion milling. Grains of Burma spinel and synthetic SiC grains were also placed on the mounts as standards using a micromanipulator. Secondary ion maps of $^{12}C^-$, $^{16}O^-$, $^{18}O^-$, $^{28}Si^-$, and $^{30}Si^-$ were made of one mount of QZR4 and two mounts of QZR5, following the description by Nittler (1996). Secondary ions were produced by bombardment of the samples with a primary Cs^+ beam of 5 nA. Highly anomalous grains were located by plotting ratios of $^{16}O^-/^{18}O^-$ and $^{28}Si^-/^{30}Si^-$ versus the intensities of $^{16}O^-$ and $^{28}Si^-$ for individual O-rich and Si-rich grains, respectively. High mass resolution isotopic analyses of C, N, and Si were made on most of the Si-rich candidates and some randomly selected grains of SiC and Si_3N_4, following the procedure described by Zinner, Tang, & Anders (1989).

3. RESULTS

3.1. Chemical Composition of the Residue

Diamond was the first presolar phase that we separated. After purification and baking, it weighed 2 mg, corresponding to a bulk content of 72 ppm. The bulk abundance of the final residue before size separation was 17.9 ppm. SEM observation indicated that it consisted predominantly of spinel, Si_3N_4, and SiC, with less Al_2O_3, accessory baddeleyite (ZrO_2), and TiC. The composition of the residue varies with grain size. Most of the micron-sized grains are spinel,

and the relative abundances of spinel, Si_3N_4, SiC, and Al_2O_3 are 42 : 15 : 10 : 2 based on the EDS examination of 69 randomly selected micron-sized grains. As the grains become smaller, the abundance of spinel relative to SiC decreases. This is confirmed by the ion mapping data that show the ratio of O-rich grains (predominantly spinel) to Si-rich (SiC and Si_3N_4) grains to be lower for the submicron-sized fraction QZR4 (1.1) than for QZR5 (1.8; see § 3.2). The Si_3N_4/SiC ratio also decreases as the grains become smaller, and of 12 randomly selected grains less than 0.3 μm, all were SiC.

3.2. Ion Imaging

Ion imaging data of O-rich grains were plotted as the $^{16}O^-/^{18}O^-$ ratio versus the intensity of $^{16}O^-$. Four of 23,177 O-rich grains from the QZR4 mount and two of 13,567 from one of the QZR5 mounts show significant ^{18}O deficits. These ^{18}O-deficient candidates have very low average intensities of $^{16}O^-$, suggestive of rather small grain sizes in comparison with the predominant isotopically normal grains. Among 17,666 O-rich grains from the second mount of the QZR5 fraction, no significantly ^{18}O-depleted grains were detected.

Similarly, ^{30}Si-deficient Si-rich grains were determined by plotting the $^{28}Si^-/^{30}Si^-$ ratio versus the intensity of $^{28}Si^-$. A total of 23 of 20,425 Si-rich grains from the QZR4 mount and 32 of 9677 + 7815 from both QZR5 mounts showed significant ^{30}Si deficits. A few of the Si-rich grains plot distinctly below the predominant trend, indicating ^{30}Si excesses. However, no ^{30}Si enrichments were confirmed by high mass resolution measurements of these grains.

3.3. High Mass Resolution Analyses

In this work, only Si-rich grains were analyzed under high mass resolution conditions to determine their C, N, and Si isotopic ratios (Figs. 1 and 2). The C, N, and Si isotopic compositions of the identified rare types of presolar SiC and Si_3N_4 are listed in Table 1. All 32 ^{30}Si-deficient candidates from QZR5 were confirmed to have ^{29}Si and ^{30}Si depletions (i.e., ^{28}Si excesses), similar to the X grains from Murchison. Although one of them (5B-81-21) has a higher than solar $^{14}N/^{15}N$ ratio (377 ± 76), its Si isotopic composition ($\delta^{29}Si$: −249 ± 12; $\delta^{30}Si$: −504 ± 10) is typical of X grains (see note in Table 1 for the definition of $\delta^i Si$). Of the 32 X grains, 26 are SiC and the other six are Si_3N_4, based on their distinct $^{28}Si^-/^{12}C^-$ and $^{12}C^{14}N^-/^{12}C^-$ ratios. This was confirmed by SEM examination of the grains after ion probe analysis. Only 16 ^{30}Si-deficient candidates on the QZR4 mount were analyzed for their C, N, and Si isotopic compositions, resulting in 10 grains of X SiC, three grains of X Si_3N_4, and three grains of mainstream SiC. One of the presolar Si_3N_4 grains (4A-107-16) shows an ^{29}Si enrichment relative to solar, but its nitrogen isotopic composition is typical of X grains (Table 1; Figs. 1 and 2). In addition to the ^{30}Si-deficient candidates, 32 randomly selected SiC grains (29 from the QZR5 mounts and three from the QZR4 mount) were also analyzed; they have isotopic compositions similar to those of mainstream SiC from Murchison, except for one A+B grain (Fig. 1). Another SiC grain (4A-272-2) has a low $^{14}N/^{15}N$ ratio (123.9 ± 4.4), with Si isotopic composition ($\delta^{30}Si$: 46 ± 14; $\delta^{29}Si$: 58 ± 13) indistinguishable from mainstream SiC. The mainstream SiC grains from Qingzhen plot along a line with a slope of 1.07 ± 0.13 ($r^2 = 0.70$), close to that of the mainstream SiC from Indarch (slope: 1.02 ± 0.10, $r^2 = 0.80$; Fig. 2b). Five random grains of
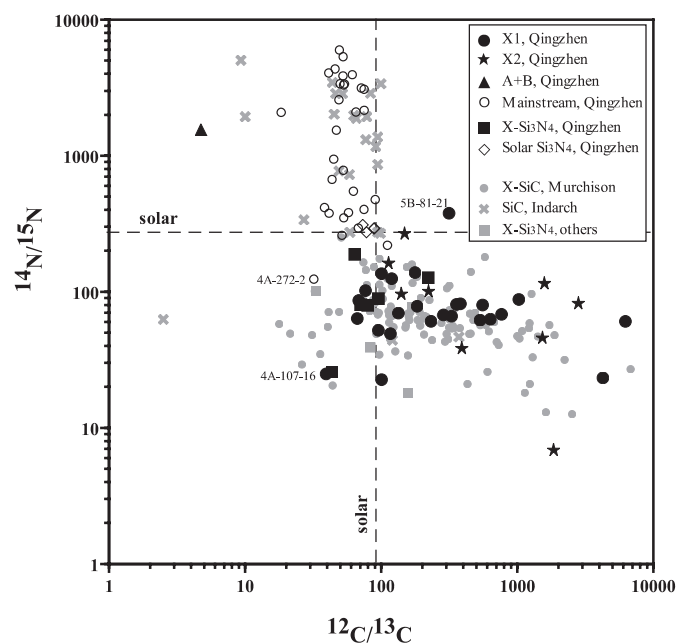
FIG. 1.—Plot of $^{14}N/^{15}N$ vs. $^{12}C/^{13}C$ of presolar SiC and Si_3N_4 grains from Qingzhen. All subtype X2 SiC grains have larger than solar $^{12}C/^{13}C$ ratios, while some subtype X1 SiC grains have lower than solar $^{12}C/^{13}C$ ratios, both overlapping with X SiC grains from Murchison (data from Amari et al. 1992; Nittler et al. 1995; Hoppe et al. 2000; L. Nittler 2002, unpublished). The C isotopic compositions of presolar Si_3N_4 grains from Qingzhen and X Si_3N_4 from other meteorites are closer to solar than those of the X SiC grains. The solar ratios of C (89) and N (272) are indicated by dashed lines.

Si_3N_4 from the QZR5 fraction show normal isotopic compositions of C, N, and Si, except for one with a small ^{29}Si deficit ($\delta^{29}Si$: -48 ± 25; $\delta^{30}Si$: -8 ± 25) and another one with a slight ^{30}Si deficit ($\delta^{29}Si$: 11 ± 10; $\delta^{30}Si$: -31 ± 11).

4. DISCUSSION

4.1. Subtypes of X SiC

On an Si three-isotope plot (Fig. 2a) the X grains of Qingzhen SiC appear to lie along two trends. Most of the grains plot well above the mixing line between solar Si and pure ^{28}Si. They plot along a line with a slope of 0.77 ($r^2 = 0.74$) and overlap with most X grains from Murchison SiC. These X grains are hereafter referred to as subtype X1. There are nine other grains of X SiC (i.e., 25% of the total) that show more significant ^{29}Si deficits than those of subtype X1. These nine grains plot close to another line with a slope of 1.23 ($r^2 = 0.74$), and they are hereafter referred to as subtype X2. The apparent gap in Si isotopic compositions intermediate between subtypes X1 and X2 is demonstrated in a histogram of the $\delta^{29}Si/\delta^{30}Si$ ratio (Fig. 3), which shows a bimodal distribution with peaks around 0.65 and 1.25, respectively. Interestingly, all nine grains of subtype X2 have larger than solar $^{12}C/^{13}C$ ratios (Fig. 1), while 20% of grains of subtype X1 have lower than solar $^{12}C/^{13}C$ ratios with the limited statistics. There is no visible difference in the N isotopic compositions of subtypes X1 and X2.

A deviation in Si isotopic compositions of X grains from the dominant trend has been previously reported for Murchison SiC. Hoppe et al. (1995) divided X grains from Murchison into subtypes A, B, and C, mainly according to
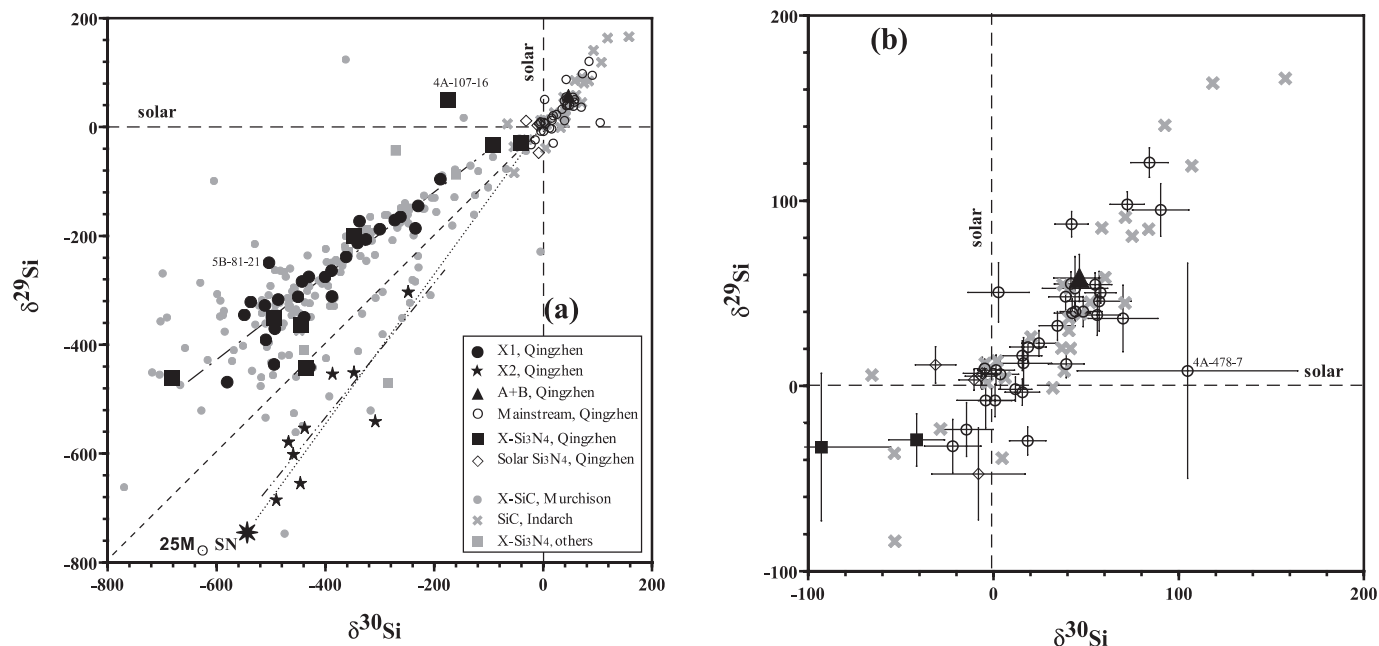

FIG. 2.—Plot of $\delta^{29}Si$ vs. $\delta^{30}Si$ of presolar SiC and Si_3N_4 grains from Qingzhen. (a) X SiC grains of subtypes X1 and X2 plotted along the two dot-dashed lines with different slopes (0.7 vs. 1.3). The Si isotopic ratios of subtype X1 grains are similar to those of the majority of X grains from Murchison. The predicted Si ratio for the Si/O zone of a 25 $M_\odot$ Type II supernova model (Meyer et al. 1995) is plotted for comparison. The slope of the mixing line between the theoretical ratio and solar is very similar to that of the regression line for the X2 grains. The mixing line between pure ^{28}Si and solar is also shown. Sources of the data: X SiC from Murchison from Amari et al. (1992), Nittler et al. (1995), Hoppe et al. (2000), Besmehn & Hoppe (2002), and L. Nittler (2002, unpublished); X Si_3N_4 from other meteorites from Alexander (1993), Hoppe et al. (1994b), Nittler et al. (1995), and Besmehn & Hoppe (2001); SiC from Indarch from Gao et al. (1995). (b) Subsection of the Si three-isotope plot. It shows similar isotopic compositions of mainstream SiC from Qingzhen and Indarch.

TABLE 1

Isotopic Compositions of C, N, and Si of Rare Types of Presolar SiC and Si_3N_4 from Qingzhen

Size Fraction	Grain	Type	$^{12}C/^{13}C$	$^{14}N/^{15}N$	$\delta^{29}Si^a$ (‰)	$\delta^{30}Si^a$ (‰)
QZR5	5B-90-8	A+B	4.7±0.1	1554±299	58±13	46±14
QZR4	4A-277-18	X1	77±4	102±10	−391±14	−510±12
	4A-280-3	X1	67±2	64±1	−165±10	−262±10
	4A-300-6	X1	556±42	80±4	−345±9	−549±8
	4A-430-14	X1	101±3	136±5	−186±10	−235±11
	4A-438-25	X1	134±11	70±3	−239±15	−362±14
	4A-454-27	X1	39±1	24.9±0.6	−350±12	−439±11
	4A-461-5	X1	101±3	22.6±0.5	−96±11	−189±11
	4A-482-20	X1	765±147	68±3	−370±23	−493±20
QZR5	5A-188-1	X1	357±9	81±2	−284±3	−443±3
	5A-247-4	X1	95±2	52±2	−469±5	−581±5
	5A-396-3	X1	177±6	138±7	−264±6	−389±5
	5A-564-14	X1	291±8		−317±6	−487±5
	5A-80-7	X1	1026±65	88±2	−436±5	−494±5
	5B-129-16	X1	68±2	86±6	−171±12	−273±12
	5B-154-16	X1	232±9	61±1	−311±10	−388±10
	5B-187-20	X1	4250±690	23.3±0.5	−173±17	−338±15
	5B-209-21	X1	381±15	82±2	−276±6	−401±6
	5B-212-2	X1	532±13	62±1	−275±4	−431±5
	5B-250-22	X1	329±22	66±2	−312±10	−450±9
	5B-340-18	X1	591±42		−321±10	−537±8
	5B-349-1	X1	286±12	68±1	−207±6	−326±7
	5B-350-22	X1	6227±1007	61±5	−441±9	−430±10
	5B-396-3	X1	119±2	125±2	−145±6	−230±7
	5B-45-11	X1	117±5	49±2	−188±12	−300±12
	5B-458-11	X1	634±103	63±1	−328±16	−512±13
	5B-58-12	X1	184±6	78±2	−213±8	−341±8
	5B-81-21	X1	314±31	377±76	−249±12	−504±10
QZR4	4A-134-9	X2	391±27	39±1	−452±9	−387±11
	4A-219-27B	X2	223±39	102±10	−600±18	−459±20
QZR5	5A-117-3	X2	1581±102	116±11	−684±3	−490±4
	5A-283-8	X2	1848±378	6.9±0.2	−540±9	−308±11
	5A-425-14	X2	140±10	97±10	−653±6	−446±7
	5A-551-24	X2	1528±270	46±2	−450±8	−348±9
	5B-276-2	X2	113±2	164±3	−302±8	−248±9
	5B-375-35	X2	148±10	271±22	−552±8	−438±9
	5B-77-15	X2	2807±886	83±10	−578±9	−468±10
QZR4	4A-107-16	Si_3N_4	43±5	25.7±0.9	50±23	−174±20
	4A-194-20	Si_3N_4	64±20	189±18	−29±14	−42±15
	4A-306-21	Si_3N_4	43±9		−363±22	−445±20
QZR5	5A-275-9	Si_3N_4	179±103		−201±11	−348±10
	5A-339-5	Si_3N_4	221±48	127±8	−442±9	−436±8
	5B-154-14	Si_3N_4	70±6	80±3	−351±13	−495±11
	5B-302-10	Si_3N_4	79±9	80±7		
	5B-51-9	Si_3N_4	95±19	89±3	−33±40	−93±37
	5B-85-9	Si_3N_4	241±61		−461±8	−681±6

Note.—Errors are 1 σ.

[a] $\delta^i Si() \equiv [(\delta^i Si/^{28}Si)_{grain}/(\delta^i Si/^{28}Si)_{solar} - 1] \times 1000$.

their Si isotopic compositions. The subtype A is most abundant and similar to our subtype X1 of Qingzhen. Subtype B grains have $\delta^{29}Si/\delta^{30}Si$ ratios close to unity and plot in a region between subtypes X1 and X2 in the $\delta^{29}Si$ versus $\delta^{30}Si$ diagram; subtype C is rarer, and it is ^{29}Si enriched relative to subtype A. In addition, a few X grains of Murchison SiC (e.g., X57; Hoppe et al. 1996b) have smaller than solar $^{29}Si/^{30}Si$ ratios, similar to grains of subtype X2 from Qingzhen. In Figure 3 we have included all available data of X SiC from Murchison (84 from Hoppe et al. 2000; 15 from Besmehn & Hoppe 2002; the other 82 from Amari et al. 1992, Nittler et al. 1995, and L. Nittler 2002, unpublished).

The main peak of Murchison X SiC is at a $\delta^{29}Si/\delta^{30}Si$ ratio of 0.6–0.7 and overlaps well with subtype X1. Murchison grains with $\delta^{29}Si/\delta^{30}Si$ ratios greater than 1.0 appear to have a different distribution of the $\delta^{29}Si/\delta^{30}Si$ ratio than Qingzhen X SiC grains: the first have a somewhat smaller average $\delta^{29}Si/\delta^{30}Si$ ratio. Of all 181 grains of Murchison X SiC, the relative abundance of the subtype with $\delta^{29}Si/\delta^{30}Si$ ratio greater than 1.0 is estimated to 17%. The Si isotopic data of Murchison X SiC also support the existence of subtypes.

The distinct Si isotopic compositions of subtypes X1 and X2 of Qingzhen SiC imply different stellar sources (e.g., Type II and Type Ia supernovae) or mixtures of materials
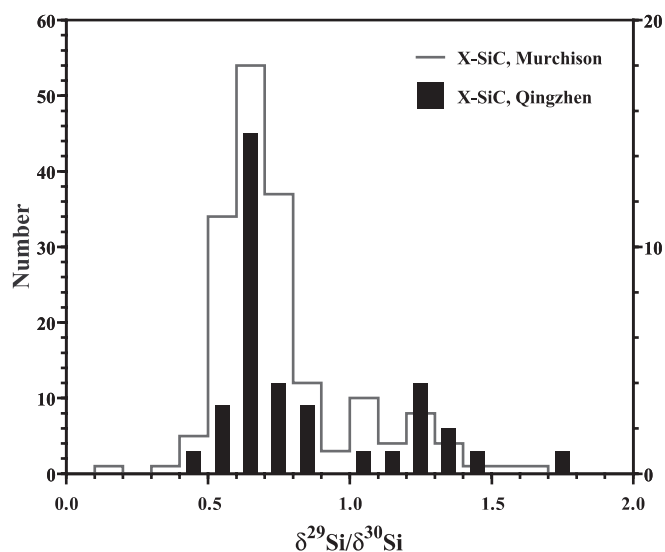
FIG. 3.—Histogram of the $\delta^{29}\mathrm{Si}/\delta^{30}\mathrm{Si}$ ratios of type X SiC grains from Qingzhen and Murchison. For the vertical axis the left scale refers to the Murchison and the right scale to the Qingzhen data. Data for both meteorites show a bimodal pattern. The peaks for Qingzhen seem to be more distinct than those for Murchison and are centered at the ratios 0.65 and 1.25. The first peak for Murchison is also centered at ~0.65, but the average ratio of the second is somewhat lower than that for Qingzhen. The data sources are the same as for Fig. 2.

from different inner zones of Type II supernovae where the Si isotopic compositions vary tremendously. Type II supernovae are the most likely sources of X grains (Amari et al. 1992; Anders & Zinner 1993; Hoppe et al. 1996b; Nittler et al. 1996), based on their large $^{28}\mathrm{Si}$ enrichments, as well as high $^{12}\mathrm{C}/^{13}\mathrm{C}$ and $^{14}\mathrm{N}/^{15}\mathrm{N}$ ratios. Additional evidence for a Type II supernova origin comes from high inferred initial $^{26}\mathrm{Al}/^{27}\mathrm{Al}$ and $^{44}\mathrm{Ti}/^{48}\mathrm{Ti}$ ratios in a few grains. However, Type II supernova models predict lower than solar $^{29}\mathrm{Si}/^{30}\mathrm{Si}$ ratios (Meyer, Weaver, & Woosley 1995; Timmes & Clayton 1996), in contrast to the ratios observed in most X grains from both Murchison and Qingzhen. This issue has been noted in previous studies of X-type grains (Nittler et al. 1995; Hoppe et al. 1996b, 2000; Zinner 1998a; Travaglio et al. 1999). Although the $^{29}\mathrm{Si}/^{30}\mathrm{Si}$ ratios of most X grains (i.e., subtype X1) are still not understood, the $^{29}\mathrm{Si}/^{30}\mathrm{Si}$ ratios of subtype X2 are consistent with bulk predictions of Type II supernova models. The grains of subtype X2 plot close to the mixing line between solar material and the undiluted ejecta from the O/Si zone of Type II supernovae with mass 25 $M_\odot$ ($\delta^{29}\mathrm{Si}$: -740‰; $\delta^{30}\mathrm{Si}$: -540‰; Meyer et al. 1995; see also Fig. 2a).

Another possible source of X2 grains are Type Ia supernovae. Clayton et al. (1997) calculated the chemical abundances and isotopic ratios of several elements as a function of the peak temperature during the explosive He burning of a Type Ia supernova. The $^{29}\mathrm{Si}/^{30}\mathrm{Si}$ ratio depends on the peak temperature, with $^{29}\mathrm{Si}/^{30}\mathrm{Si} < 1$ for $T_{\mathrm{peak}} \geq 1.0 \times 10^9$ K and $^{29}\mathrm{Si}/^{30}\mathrm{Si} > 1$ for $T_{\mathrm{peak}} < 1.0 \times 10^9$ K without any arbitrary changes of the yield rates of $^{29}\mathrm{Si}$ and $^{30}\mathrm{Si}$. Hoppe et al. (2000) made mixing calculations using the chemical and isotopic data of the Clayton et al. (1997) Type Ia supernova model. Although the expected isotopic patterns of the elements C, Al, and Ti are not very different between the Type Ia and Type II supernova mixing models, the $^{29}\mathrm{Si}/^{30}\mathrm{Si}$

ratios predicted by the Type Ia supernova model are significantly lower than the data of X1 SiC but overlap with those of X2 grains.

4.2. Presolar Si_3N_4

Presolar $\mathrm{Si_3N_4}$ is much less abundant than X SiC. Six grains have been found from Murchison (five grains by Nittler et al. 1995, one by Hoppe et al. 1994b) and three grains from Tieschitz (two grains by Nittler et al. 1995, one by Alexander 1993). Besmehn, Mostefaoui, & Hoppe (2001) reported three presolar $\mathrm{Si_3N_4}$ grains from Indarch. The isotopic compositions of Si, C, and N of these presolar $\mathrm{Si_3N_4}$ grains are characteristic of X grains; hence, a supernova origin has been proposed by these authors. Recently, small presolar $\mathrm{Si_3N_4}$ grains with the isotopic ratios of mainstream SiC were found from Indarch (Amari et al. 2002). Our data of presolar $\mathrm{Si_3N_4}$ from Qingzhen are consistent with the previous work on larger $\mathrm{Si_3N_4}$ grains. Moreover, we note the relatively narrow range of $^{12}\mathrm{C}/^{13}\mathrm{C}$ ratios of the presolar $\mathrm{Si_3N_4}$ grains from Qingzhen ($44 < {}^{12}\mathrm{C}/^{13}\mathrm{C} < 220$), in comparison with the large range for X SiC grains from the same meteorite ($67 < {}^{12}\mathrm{C}/^{13}\mathrm{C} < 6227$). This difference in $^{12}\mathrm{C}/^{13}\mathrm{C}$ ratio between presolar $\mathrm{Si_3N_4}$ and X SiC exists also for grains from Murchison and Tieschitz (Fig. 1). The different ranges of C isotopic ratios between presolar $\mathrm{Si_3N_4}$ and X SiC suggest distinct C ratios in supernova source zones from which these two species condensed.

Another possibility is that the $^{12}\mathrm{C}/^{13}\mathrm{C}$ ratio of presolar $\mathrm{Si_3N_4}$ was lowered by contribution of C from the outer zones (e.g., He/N, H) of Type II supernovae, which are predicted to be $^{13}\mathrm{C}$-rich (Meyer et al. 1995). This is possible because C is a minor element in $\mathrm{Si_3N_4}$. In contrast, the same process would not change the $^{12}\mathrm{C}/^{13}\mathrm{C}$ ratio of X SiC much because C is a major component. Contribution of material from the $^{14}\mathrm{N}$-rich outer zones may significantly affect the $^{14}\mathrm{N}/^{15}\mathrm{N}$ ratio of X SiC. However, this is not observed.

4.3. Heterogeneous Distribution of Presolar Grains in the Solar Nebula?

The abundance of X SiC among Si-rich grains is ~1/1000 according to the mapping data and high mass resolution analyses conducted on QZR4 and QZR5. As reported above, the $\mathrm{Si_3N_4}$/SiC abundance ratio is about 3:2 for micron-sized grains, but SiC becomes more abundant than $\mathrm{Si_3N_4}$ for smaller grains. Hence, the maximum abundance of X SiC is estimated to be ~1/400 relative to mainstream SiC for ≥ 1 μm grains. This is lower by a factor of 4 than the corresponding ratio for SiC from Murchison (~1%; Zinner 1998b). Although ion mapping of SiC from Indarch (Gao et al. 1995) suggested a similar fraction of X grains as for Murchison SiC, another survey of X SiC from Indarch found only two X grains out of 3500 SiC grains (Besmehn & Hoppe 2001). Furthermore, low abundances of X grains in enstatite chondrites were also confirmed by ion mapping on SiC from Sahara 97166 (EH3), which suggested an abundance of X grains of 0.36% relative to mainstream SiC (Besmehn et al. 2001).

As discussed above, the X grains from Qingzhen can be divided into subtypes X1 and X2, and the latter peaks at a $\delta^{29}\mathrm{Si}/\delta^{30}\mathrm{Si}$ ratio of ~1.25 (Fig. 3). In contrast, for Murchison X SiC there is a larger fraction of grains with ratios of 1.0–1.1 than for Qingzhen. In addition, the fraction of grains with $\delta^{29}\mathrm{Si}/\delta^{30}\mathrm{Si}$ ratios greater than 1.0 relative to all

X grains is lower in Murchison (∼17%) than in Qingzhen (28%).

For Qingzhen, the abundance of X Si_3N_4 relative to X SiC (9/36) is much higher than for Murchison (1/30). Besmehn & Hoppe (2001) found three presolar Si_3N_4 but only two X SiC grains from Indarch, indicating an even higher abundance of presolar Si_3N_4 than of X SiC. Gao et al. (1996) reported five candidates of presolar Si_3N_4 together with the discovery of 60 grains of X SiC from Acfer 094 (CM3), resulting in an abundance ratio of 1/12. This is also significantly lower than the ratio in enstatite chondrites.

Although high mass resolution analyses have not yet been conducted on the ^{18}O-deficient candidates from Qingzhen, it is obvious that the abundance of presolar O-rich grains in Qingzhen is very low. Only six ^{18}O-deficient candidates were found by imaging of 54,410 O-rich grains, implying a maximum abundance of ∼1/10,000 among all oxide grains. The rareness of presolar oxides in Qingzhen is consistent with earlier studies of enstatite chondrites (Choi et al. 1999). This is curious because refractory oxides are not expected to condense under the highly reducing conditions of enstatite chondrites. Recently, a few CAIs and their components were found in primitive enstatite chondrites (Fagan, Krot, & Keil 1999, 2000; Guan, McKeegan, & MacPherson 2000; Kimura, Lin, & Hiyagon 2000), but they are probably not in situ condensates in the region where enstatite chondrites formed.

The different abundances of various presolar grain types in Qingzhen and Murchison cannot be related to destructive processes in the solar nebula or to thermal metamorphism in the asteroidal parent bodies of these meteorites. Although these processes can explain the variation of presolar grains among various classes of chondrites and the negative correlation between the content of presolar grains and petrologic type of the chondrites (Russell et al. 1992; Huss & Lewis 1994, 1995), they cannot result in the different abundance ratios of X SiC to mainstream SiC and between subtypes X2 and X1 for Qingzhen and Murchison, since these SiC grains are distinguished only by their isotopic compositions. The very low fraction of presolar oxides in Qingzhen cannot be due to high dilution with condensates of solar system origin because CAIs and their fragments are much less abundant in enstatite chondrites than in Murchison. The residual oxides from Qingzhen consist predominantly of Mg-spinel, and the abundance ratio of Al_2O_3 to Mg-spinel is about 1 : 30, not significantly different from that of Murchison. Hence, the low fraction of presolar oxides in Qingzhen cannot be related to different modal compositions of the oxides.

Heterogeneity of the distribution of various types of presolar grains in the primitive solar nebula is a likely explanation for the differences in the abundance of presolar grains between Qingzhen and Murchison, since these meteorites formed under highly different redox conditions and, hence, probably in different regions of the solar nebula. Vanhala & Boss (2000) performed numerical simulations on the hypothesis of the triggered origin of the solar system and suggested that shock waves originating from a nearby explosive stellar event could inject significant amounts of freshly synthesized radioactivities into the collapsing protostellar system and result in temporal and spatial heterogeneities in the abundances of radioactivities (and thus also of other elements and isotopes) in the early solar system. Another scenario is related to size-sorting processes in the nebula. Mainstream SiC is considered to have formed in

asymptotic giant branch stars (Lewis et al. 1990, 1994; Hoppe et al. 1994a; Zinner 1998a), whereas the isotopic signatures of X grains point to a supernova origin (Amari et al. 1992; Nittler et al. 1995; Zinner 1998a; Hoppe et al. 2000). These are two very different stellar environments for the condensation of SiC, hence distinct size distributions of these different types of SiC might be expected, although no definitive evidence has yet been found. The distinct abundances of presolar grains from Qingzhen may be related to the smaller grain sizes of fractions QZR4 (0.4–0.8 μm) and QZR5 (0.8–2.0 μm) in comparison with the larger sizes of most Murchison SiC grains previously analyzed. Smaller average SiC grain sizes than in Murchison have been found in Indarch (Gao et al. 1995), a result that is confirmed by the relative abundances of noble gas components. The mean Ne-E/Xe-s ratio for bulk Indarch SiC is significantly lower than for bulk Murchison SiC (625 ± 7 vs. ∼3500; Russell et al. 1997) but is similar to that of the finest grain-size fractions (<1 μm) of the latter (Lewis et al. 1990, 1994).

A hint of possible size-dependent SiC abundances of different grain types is the lower abundance of X grains among Si-rich grains in the smaller size fraction QZR 4 (7/10,000) than in fraction QZR5 (15/10,000). This difference is enhanced if Si_3N_4 is taken into account because Si_3N_4 is more abundant in the larger size fraction QZR5 than in QZR4. However, such a correlation between abundance ratios and grain size of SiC types has not been observed in Murchison. In contrast, the study of different size fractions (0.67–3.0 μm) of Murchison SiC suggests a slight increase of the abundance of X SiC with decreasing grain size (Hoppe et al. 2000). In addition, the different abundance ratios of various types of grains between Murchison and Qingzhen cannot be related to grain size because the size range of the KJE fraction (0.5–1.5 μm) of Murchison, whose relative abundance of X grains is ∼0.8% (Hoppe et al. 2000), is comparable with those of the QZR4 and QZR5 fractions.

5. CONCLUSIONS

We performed a chemical and physical separation on an original amount of 28 g of the weathered portion of the EH3 chondrite Qingzhen. This procedure resulted in 72 ppm of diamond and 17.9 ppm of a final residue consisting of spinel+SiC+Si_3N_4 with minor Al_2O_3. This residue was separated into eight size fractions. Its composition depends on grain size. Spinel is dominant in large-size fractions (>2 μm), and SiC is the most abundant phase in submicronsized fractions, especially those with grains less than 0.3 μm. The Si_3N_4/SiC ratio decreases as the grains become smaller.

A total of 36 grains of SiC of type X were identified in size fractions QZR4 (0.4–0.8 μm) and QZR5 (0.8–2.0 μm) by isotopic imaging in the ion microprobe and were analyzed for their C, N, and Si isotopic compositions. This is the first report of type X SiC from Qingzhen. Based on their Si isotopic compositions we distinguish two subtypes of X SiC grains. A total of 27 grains of type X1 have $\delta^{29}Si/\delta^{30}Si$ ratios of ∼0.7 and overlap with their counterpart X grains from Murchison; the other nine grains of type X2 have $\delta^{29}Si/\delta^{30}Si$ ratios of ∼1.2 and on an Si three-isotope plot lie between solar Si and the Si isotopic composition of the Si/O zone of a 25 $M_\odot$ Type II supernova model (Meyer et al. 1995). Furthermore, all X2 grains have larger than solar $^{12}C/^{13}C$ ratios, while a fraction of X1 grains from both Qingzhen and Murchison have smaller than solar ratios.

The distinct isotopic compositions of subtypes X1 and X2 imply multiple stellar sources of X SiC.

In addition to SiC X grains, seven presolar Si_3N_4 grains were found. This is the first discovery of this grain type in an enstatite chondrite (Lin et al. 2000). Their C, N, and Si isotopic compositions are similar to those of X SiC, except that their C isotopic anomalies are smaller. Six ^{18}O-deficit candidates were found by ion mapping the O-rich grains but have not yet been analyzed in detail.

In comparison with Murchison and other carbonaceous and ordinary chondrites, Qingzhen contains much less X SiC ($\leq 0.25\%$ of mainstream SiC) and presolar oxides ($\sim 1/10,000$ of all oxide grains), but it has higher ratios of X2/X

$(9:36)$ and X Si_3N_4/X SiC $(9:36)$. These differences probably imply heterogeneity and/or size-sorting processes in the primitive solar nebula.

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