Earth and Planetary Science Letters 399 (2014) 128–138

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Assessment of alteration processes on circumstellar and interstellar grains in Queen Alexandra Range 97416

Maitrayee Bose [a,*], Thomas J. Zega [b], Peter Williams [a]

[a] Arizona State University, Department of Chemistry and Biochemistry, Physical Sciences Building, Room D-57, PO Box 871604, Tempe, AZ 85287, United States
[b] Lunar and Planetary Laboratory, University of Arizona, 1629 East University Blvd., Tucson, AZ 85721, United States

ARTICLE INFO

Article history:
Received 27 November 2013
Received in revised form 25 April 2014
Accepted 9 May 2014
Available online 29 May 2014
Editor: B. Marty

Keywords:
organic matter
NanoSIMS
TEM
XANES
QUE 97416
CO3 chondrite

ABSTRACT

Insight into the presolar and interstellar grain inventory of the CO3 chondrite Queen Alexandra Range (QUE) 97416 is gained through correlated secondary ion mass spectrometry (SIMS), transmission electron microscopy (TEM), and synchrotron-based X-ray absorption near-edge structure spectroscopy (XANES). Only one presolar silicate grain [$^{17}O/^{16}O = (9.96 \pm 0.75) \times 10^{-4}$; $^{18}O/^{16}O = (19.49 \pm 0.96) \times 10^{-4}$] that may have formed in a low-mass Red Giant or Asymptotic Giant Branch star occurs in the coarse-grained matrix of QUE 97416. No other presolar grains were identified. Although presolar grains are rare in QUE 97416, numerous (898 ± 259 ppm) ^{15}N-rich domains ($\delta^{15}N \sim +1447‰$ to $+3069‰$) occur in the thin section. Based on TEM of an extracted section, two ^{15}N-rich domains are amorphous, C-bearing, and texturally uniform, and they are embedded in a ferromagnesian silicate matrix with varied grain sizes. The individual ^{15}N-rich organic regions with high $\delta^{15}N$ ($+2942 \pm 107‰$ and $+2341 \pm 140‰$) exhibit diverse carbon functional groups, such as aromatic, vinyl-keto, amidyl, and carboxylic functionality, while the nitrogen XANES reveals traces of nitrile functionality. QUE 97416 appears to have escaped aqueous alteration based on the absence of hydrated minerals but is thermally altered, which could have resulted in the destruction of presolar grains. However, this process at $>400\,^{\circ}C$ metamorphic temperatures was inefficient in destroying the carriers of N isotope anomalies, which may indicate the resistant nature of the organic carriers and/or the limited extent of thermal metamorphism on the QUE 97416 parent body.

1. Introduction

Refractory dust grains formed during later stages of stellar evolution were injected into the local part of our galaxy where our solar system formed over 4.5 billion years ago. These *presolar* circumstellar materials were preserved in asteroids, the physical relics leftover from the birth of our solar system. Probing these materials can provide information on nucleosynthetic processes in stars, the thermodynamics of the circumstellar envelopes, transport and irradiation processes within the interstellar medium, and secondary processes during solar system evolution (i.e., either in the nebular phase or on the asteroid parent bodies). Many types of circumstellar grains have been identified since their discovery over 25 years ago; see the review by Zinner (2013) and references therein.

Presolar silicate grains constitute one of the most abundant (up to 210 ± 25 ppm in CO3 DOM 08006; Nittler et al., 2013) presolar phases in carbonaceous chondrites (CCs), exhibit highly anomalous oxygen isotopic compositions relative to solar values (e.g., Nguyen et al., 2007, 2010; Floss and Stadermann, 2009a, 2012; Vollmer et al., 2009a; Bose et al., 2010a, 2010b, 2012; Leitner et al., 2012; Zhao et al., 2013), and have been found in all types of extraterrestrial materials including meteorites, interplanetary dust particles (IDPs), and Antarctic micrometeorites (Messenger et al., 2003; Nguyen and Zinner, 2004; Nagashima et al., 2004; Yada et al., 2008). A range of isotope ratios (O, Si, Mg, and Fe), elemental compositions, mineralogy, and abundances has been reported (e.g., Nguyen et al., 2007, 2010; Vollmer et al., 2009a, 2009b; Floss and Stadermann, 2009a, 2012; Stroud et al., 2008, 2009; Bose et al., 2010a, 2010b, 2012; Leitner et al., 2012; Zhao et al., 2013; Haenecour et al., 2013). These studies show that the majority (>80%) of presolar silicate grains condensed in envelopes and circumstellar disks of low–mass ($M \leq 2M_{\odot}$) asymptotic giant branch (AGB) stars (early in the first and second thermal pulses) and the remaining fraction of grains formed in the turbulent outflows of massive supernovae ($M > 8M_{\odot}$) and novae (O/Ne or O/C). The silicate grain-types include olivine and pyroxene; a vast number of which (>500 silicate grains, Hynes and Gyngard, 2009) exhibit non-stoichiometric ferromagnesian compositions, and several are complex aggregates of amorphous and nanocrystalline material.

* Corresponding author.
E-mail address: maitrayee.bose@asu.edu (M. Bose).

http://dx.doi.org/10.1016/j.epsl.2014.05.007
0012-821X/

A significant fraction of the presolar silicate grains in primitive CCs exhibit Fe-rich compositions, whereas the abundance of Ca- and/or Al-bearing ferromagnesian grains is low. The significantly higher Fe-content in the silicate grains is either due to non-equilibrium condensation reactions in the circumstellar envelopes or elemental exchange between the presolar grains and surrounding Fe-rich matrix during parent-body processing. The studies on presolar silicate grains have also revealed conditions leading to the survival of presolar silicates in the early solar system. Laboratory analyses of silicate dust complement spectroscopic observations of stars. For example, the 9.7 μm and 18 μm emission features in the envelopes of evolved stars and circumstellar disks around young stellar objects have been attributed to amorphous silicates (Waters et al., 1996; Waelkens et al., 1996; Demyk et al., 2000).

The organic carbon in primitive CCs contains soluble and insoluble organic matter (IOM) fractions. Both fractions can have isotopic anomalies, mainly enrichments in D and ^{15}N, but occasionally ^{13}C enrichments or depletions (Epstein et al., 1987; Busemann et al., 2006; Floss et al., 2006; Floss and Stadermann, 2009b; Bose et al., 2012). The isotopic variations in the soluble organics amongst individual compounds and meteorites are considerable (e.g., Pizzarello et al., 2008). The H, C, and N isotopic anomalies have been reported both in IOM separates and residues, and as sub-micron to micron-sized *in situ* "hotspots" within primitive meteorites and IDPs (e.g., Alexander et al., 2007, 2010; Busemann et al., 2006; Floss and Stadermann, 2009b; Remusat et al., 2009; Zega et al., 2010; Bose et al., 2012). The hotspots are not always associated with discrete domains, e.g., nanoglobules, which are typically sub-micrometer, roughly spherical objects that are often hollow and can be isotopically anomalous (Garvie and Buseck, 2004; Nakamura-Messenger et al., 2006; De Gregorio et al., 2010, 2013). Instead, amorphous material with short-range order and aromatic functionality can also carry ^{15}N anomalies (e.g., Zega et al., 2010; Floss et al., 2011). It is now universally accepted that the large D and ^{15}N enrichments are products of low temperature chemistry in the interstellar medium or the early outer solar system (Terzieva and Herbst, 2000; Sandford et al., 2001; Clayton, 2002; Rodgers and Charnley, 2002, 2008a). The isotopic variations of IOM in different classes of CCs are complex, and may be related to parent-body processes, if the precursor of the IOM is common to all CCs (Alexander et al., 2010). The IOMs from even the most pristine Type 3 CCs, Semarkona (LL), ALHA 77307 (CO), Kaba (CV), and Acfer 094 (C), appear to be modified by parent-body processes and/or terrestrial weathering (Alexander et al., 2007). There is no strong correlation between the isotopic compositions of the IOM with degree of aqueous alteration in CM and CR chondrites (Alexander et al., 2007). The IOM of ordinary chondrites exhibit large D enrichments ($\delta D \sim 12\,000‰$) that increase with increasing thermal metamorphism, unlike the IOM of CO chondrites (Alexander et al., 2010). In CH and CB chondrites whole rock ^{15}N enrichments up to $\delta^{15}N \sim 1500‰$ are seen in chondritic clasts (Grady and Pillinger, 1990; Bonal et al., 2009; Briani et al., 2009) and are possibly produced by shock metamorphism (Krot et al., 2005).

Here we search for presolar grains in the unexplored CO chondrite Queen Alexandra Range 97416 (hereafter QUE 97416) by isotopic imaging with the NanoSIMS. We also map the sample in N for N-anomalous organics and report on the nature of the carrier phase. The chemical and isotopic compositions, abundances and molecular makeup of these phases are used as tools to probe nebular and parent-body processes in the early solar nebula, and decipher the chondrite's history on Earth. This work expands on prior investigation of the effects of thermal annealing on presolar silicate compositions in CO CC (Bose et al., 2012, 2013; Bose and Williams, 2012). It will also allow a comparison of the grain inventories with other CO's studied to date, namely ALHA 77307, LaPaz 031117 and DOM 08006 (Nguyen et al., 2010; Bose and Williams, 2012; Haenecour and Floss, 2011; Nittler et al., 2013). CO CCs have experienced secondary alteration processes including thermal metamorphism and aqueous alteration (Huss and Lewis, 1994; Huss et al., 2003; Rubin, 1998), which can significantly affect presolar grain and organic abundances. Large variations can also be a result of heterogeneous incorporation of these phases. This study on QUE 97416 elucidates the relative importance and complexity of these processes.

2. Experimental conditions

A thin section of QUE 97416 was obtained from the Antarctic Meteorite Collection in Johnson Space Center, Houston. QUE 97416 is classified as a *find* from the Scoraine moraine ice field in Antarctica and the original mass weighed about 12.3 g. The thin section consists of abundant small chondrules, chondrule fragments, and mineral grains set in a dark matrix. The extent of the parent-body aqueous and thermal alteration effects is unknown because this chondrite has not been extensively studied. This stone was classified as a petrologic type 3 (<3.2), based on the criteria of Scott and Jones (1990) with a weathering grade of B/C (moderate to severe rustiness). The sample was imaged in reflected and transmitted light using an Olympus BX60 optical microscope, and suitable matrix areas (dark contrast, fine-grained), including regions around calcium–aluminum-rich inclusions and chondrules, were chosen for isotopic imaging.

2.1. NanoSIMS analysis

Isotopic analysis was performed using a Cameca Ametek NanoSIMS (Secondary Ion Mass Spectrometry) 50L at Arizona State University. A gold coating, estimated to be several nanometers thick, was deposited on top of the thin section to make it conductive for NanoSIMS measurements. The distribution of presolar grains is often heterogeneous, and therefore several (nine) different fine-grained matrix areas in QUE 97416 were scanned. We pre-sputtered areas measuring 12×12 μm^2 or 15×15 μm^2 using a high ($\sim$30 pA Cs$^+$) beam current in order to remove the Au coat and implant Cs into the sample to a steady state. Automated measurements of negative secondary ions $^{16}O^-$, $^{17}O^-$, $^{18}O^-$, $^{28}Si^-$, $^{29}Si^-$, $^{30}Si^-$ (set 1) and $^{12}C^-$, $^{13}C^-$, $^{16}O^-$, $^{17}O^-$, $^{18}O^-$, $^{28}Si^-$ (set 2) were made using a $\sim$1 pA Cs$^+$ primary ion beam current (beam size $\sim$75 nm). Samples were imaged simultaneously in secondary ions (6 species only) and secondary electrons. The primary beam was rastered over 10×10 μm^2 areas during analysis, and 256×256 pixel images were acquired for 6 to 10 frames ($\sim$20 minutes per frame). The total non-contiguous areas analyzed for O- and C-anomalous grains were 9000 μm^2 (set 1 and 2) and 15250 μm^2 (set 2 and 3, see below), respectively. Nitrogen in the sample was measured as CN$^-$. A total area of 5350 μm^2 was imaged in $^{12}C^-$, $^{13}C^-$, $^{12}C^{14}N^-$, $^{12}C^{15}N^-$, $^{28}Si^-$, and $^{30}Si^-$ (set 3) to search for material with C, N and Si anomalies. Set 3 was measured in close proximity to the areas scanned for presolar grains.

San Carlos olivine (for O) and cyanoacrylate 'Krazy glue' (for C and N) were used as secondary isotopic standards for tuning purposes with terrestrial isotopic compositions, namely $^{13}C/^{12}C = 1.12 \times 10^{-2}$, $^{17}O/^{16}O = 3.81 \times 10^{-4}$, $^{18}O/^{16}O = 2.00 \times 10^{-3}$, $^{29}Si/^{28}Si = 5.06 \times 10^{-2}$, and $^{30}Si/^{28}Si = 3.36 \times 10^{-2}$. An entrance slit was chosen to attain sufficient mass-resolving power to separate the isobaric peaks of $^{12}C^{14}N$, $^{13}C^{13}C$, and $^{12}C^{13}C^{1}H$; and $^{12}C^{15}N$ and $^{13}C^{14}N$. The $^{11}B^{16}O$ peak at mass 27 is absent because of low B content in the meteorite matrix. Data were processed as quantitative isotopic ratio images using custom software (WinImage) and were corrected for effects of detector dead-time and