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Origins of Al-rich chondrules: Clues from a compound Al-rich chondrule in the Dar al Gani 978 carbonaceous chondrite

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ABSTRACT

Aluminum-rich chondrules are one of the most interesting components of primitive chondrites, because they have characteristics that are similar to both CAIs and ferromagnesian chondrules. However, their precursor and formation history remain poorly constrained, especially with respect to their oxygen isotopic distributions. In this study, we report on the petrography, mineralogy, oxygen isotope ratios, and rare-earth-element compositions of a sapphirine-bearing Al-rich chondrule (SARC) in the ungrouped chondrite Dar al Gani (DaG) 978. The SARC has a complex core-mantle-rim texture; while both the core and the mantle are mainly composed of Al-rich enstatite and anorthite with minor amounts of mesostasis, these regions are distinguished by the presence of Fe-rich spinel and sapphirine in the core and their absence in the mantle. The rim of the SARC consists mainly of Fe-rich olivine, enstatite, and Fe-Ni metal. Spinel and some olivine grains in the SARC are $^{16}O$-rich, with $\Delta^{17}O$ values down to $-20\%$ and $-23\%$, respectively. Enstatite, sapphirine, and most olivine grains have similar $\Delta^{17}O$ values ($\sim -7\%$), which are lower than those of anorthite and the mesostasis (including augite therein) ($\Delta^{17}O: \sim -3\%$). Mesostasis from both the core and mantle have Group II rare-earth-element (REE) patterns; however, the core mesostasis has higher REE concentrations than the mantle mesostasis. These observations provide a strong indication that the SARC formed by the melting and crystallization of a mixture of materials from Group II Ca,Al-rich inclusions (CAIs) and ferromagnesian chondrules. Both spinel and olivine with $^{16}O$-rich features could be of relict origin. The $^{16}O$-poor isotopic compositions of most components in Al-rich chondrules can be explained by oxygen isotopic exchange between the melt and $^{16}O$-poor nebular gas ($\Delta^{17}O: \sim -7\%$) during melting in chondrule-forming regions; whereas the anorthite and mesostasis could have experienced further oxygen isotopic exchange with a relatively $^{16}O$-poor reservoir ($\Delta^{17}O: \sim -3\%$) on the parent body, likely during fluid-assisted thermal metamorphism. During the same thermal metamorphism event, spinel, olivine, some enstatite, and the mesostasis experienced Mg-Fe exchange to various extents.
INTRODUCTION

Aluminum-rich chondrules are defined as round objects in chondrites with igneous textures and high bulk Al_2O_3 contents (≥10 wt%; Bischoff and Keil, 1984). They have been observed in most groups of chondrites and have diverse textures and mineralogy (ordinary chondrites, Bischoff and Keil, 1984; Bischoff et al., 1989; Russell et al., 2000; Rubin, 2004; MacPherson and Huss, 2005; enstatite chondrites, Guan et al., 2006; carbonaceous chondrites, Sheng et al., 1991; Krot and Keil, 2002; Krot et al., 2002; Akaki et al., 2007; Zhang and Hsu, 2009). The bulk Al_2O_3 contents of Al-rich chondrules are intermediate between those of Ca,Al-rich inclusions (CAIs) and ferromagnesian chondrules (Russell et al., 2005). Because of this compositional feature, Al-rich chondrules can be used to assess possible genetic relationships between CAIs and ferromagnesian chondrules, which are the two main high-temperature crystallization products from the solar nebula preserved in chondritic meteorites.

Previous investigations have suggested that Al-rich chondrules could have formed by melting and crystallization of precursor mixtures composed of CAIs and ferromagnesian chondrules (Bischoff and Keil, 1984; Sheng et al., 1991; Krot and Keil, 2002; Krot et al., 2002; MacPherson and Huss, 2005; Zhang and Hsu, 2009), although Rubin (2004) proposed that amoeboid olivine aggregates (AOAs) could also be the precursor materials of some Al-rich chondrules. The key evidence for this conclusion includes high bulk Al_2O_3 contents, relict fragments of CAIs, and fractionated rare-earth-element (REE) patterns (e.g., Misawa and Nakamura, 1988; Sheng, 1992; Krot and Keil, 2002; Krot et al., 2006). In contrast, the oxygen isotopic compositions of most Al-rich chondrules in ordinary and enstatite chondrites (δ^{17,18}O: ~−15 to +5 ‰; Russell et al., 2000; Guan et al., 2006) are closely related to those of ferromagnesian chondrules (Krot et al., 2006). This led Russell et al. (2000) and Guan et al. (2006) to suggest that Al-rich chondrules were not significantly influenced by remelting of a hybrid mixture of ferromagnesian chondrules and 16O-rich CAI materials, which have δ^{17,18}O values down to −70 ‰ (Gounelle et al., 2009). However, oxygen isotopic compositions of minerals are subject to resetting during thermal events (e.g., chondrule formation and parent body metamorphism). Therefore, without combining with other geochemical parameters, such as REE patterns, that can be diagnostic of CAIs, it is difficult to determine from these studies alone whether Al-rich chondrules have the same oxygen isotopic compositions as those of their precursors, or have experienced oxygen isotope exchange during melting of their precursors and/or after accretion onto the parent body.
The main purpose of this study is to constrain the precursor and formation history of Al-rich chondrules by studying the petrography, mineralogy, bulk composition, and \textit{in situ} oxygen isotopes and REE compositions of a sapphirine-bearing Al-rich chondrule (abbreviated as SARC) with a core-mantle-rim texture from the Dar al Gani (DaG) 978, an ungrouped carbonaceous chondrite (Zhang and Yurimoto, 2013). The combination of REE with oxygen isotope ratios is used as indicators of CAI origin, and diffusion modeling of oxygen and Fe-Mg in minerals is used to constrain thermal history on the parent body. Preliminary results of this study were reported as conference abstracts (Zhang et al., 2011, 2013).

**SAMPLE AND ANALYTICAL METHODS**

Dar al Gani 978 is a type 3 ungrouped carbonaceous chondrite found in Libya (Choi et al., 2010; Zhang and Yurimoto, 2013). Zhang and Yurimoto (2013) reported detailed petrography and mineralogy of this ungrouped chondrite. Most grains of spinel and olivine in this chondrite are highly FeO-rich. Zhang and Yurimoto (2013) suggested that DaG 978 could have experienced parent-body thermal metamorphism temperature up to 850-950 K.

The petrography of the SARC from DaG 978 was studied using scanning electron microscopy (SEM; Hitachi 3400N II) at Nanjing University and field emission-SEM (FE-SEM; JEOL JSM-7000F) at Hokkaido University. Mineral chemistry of the SARC was determined by using electron probe micro-analysis (EPMA; JEOL 8100) at Nanjing University. The operating conditions employed for EPMA measurements were 15 kV accelerating voltage, 20 nA beam current, and a beam size of 1-2 µm. Natural and synthetic standards were used. The typical detection limits for oxides of most elements were better than 0.02 wt%. EPMA data were reduced using the ZAF correction procedure.

Bulk compositions of the core and mantle in the SARC and their respective mesostasis, were obtained using FE-SEM following the procedure of Zhang and Hsu (2009) under the analytical mode for irregularly outlined materials of the Point&ID Navigator in the X-ray spectroscopy (EDS; Oxford-INCA) system. The energy dispersive spectrometer scans a selected area and outputs the average results of elements in the selected area. Spinel and anorthite grains in sapphirine-bearing objects were used as standards for Si, Mg, Fe, Ca, Al, Cr, Na, and Ti with 100 s counting time; the compositions of these spinel and anorthite grains were previously measured by EPMA, and have confirmed homogeneous compositions among different grains.
Oxygen isotopic compositions of minerals in the SARC were measured using the Cameca IMS-1270 instrument at Hokkaido University. The primary ion beam was mass filtered positive Cs⁺ ions of 20 keV and the beam spot size was ~ 3 µm in diameter. A primary beam current of ~ 20 pA was used to obtain a count rate of negative ¹⁶O ions of ~ 1×10⁷ cps. A normal-incident electron gun was utilized for charge compensation of the sputtered area. Negative ¹⁶O ions were detected with an axial Faraday cup, while negative ¹⁷O, ¹⁶OH, and ¹⁸O ions were detected with an axial electron multiplier, in magnetic peak jumping mode. A mass resolving power of ~ 5500 was used to separate ¹⁷O from ¹⁶OH. The instrumental mass fractionation effect was corrected using terrestrial spinel, anorthite, olivine, and augite standards (Yurimoto et al., 1994; Katayama et al., 2012; Kawasaki et al., 2012; Wakaki et al., 2013). The reported uncertainties of the individual analyses are expressed in 2σ, which were estimated by considering both the internal error of each measurement and the reproducibility of the standard measurements. After the measurements, all spots were evaluated using FE-SEM. Data from spots that overlapped undesirable minerals and/or cracks were rejected.

The REE concentrations of mesostasis in the SARC were determined with the Cameca IMS-6f instrument at Hokkaido University. The procedure was similar to that described in Yurimoto et al. (1989) and Wang and Yurimoto (1993). The primary beam was mass filtered ¹⁶O⁻ of 14.5 keV and irradiated on the sample surface to a diameter of ~ 30 µm. Kinetic energy filtering was achieved by offsetting the sample acceleration voltage (~60 eV) while keeping the electrostatic analyzer voltage, as well as the width and position of the energy slit, constant. The energy bandwidth was 20 eV. The exit slit was set to a mass resolving power of ~ 500. Positive secondary ion intensities were counted, typically for 10 s, using the peak jumping mode. Each analysis included 20 cycles. Relative sensitivity factors between secondary ion intensity and concentration for each REE (relative to Si) were determined using the Takashima augite, for which REE contents have been well determined by instrumental neutron activation analysis (INAA) (Onuma et al., 1968).

RESULTS

Petrography and mineralogy of the SARC

The sapphirine-bearing Al-rich chondrule from DaG 978 has a round shape of approximately 1.5 mm in diameter. It has a complex core-mantle-rim texture (Fig. 1) based on the change of constituent minerals.
The core is approximately 700 µm in diameter and consists mainly of anhedral to euhedral enstatite and anorthite. The enstatite crystals contain thin and parallel cracks perpendicular to the elongated c-axis (Fig. 2a). These parallel cracks could have formed during the transformation from high-temperature protoenstatite into clinoenstatite (Yasuda et al., 1983). The most important characteristics of the core are the dense distribution of fine-grained spinel (<10 µm) and the presence of euhedral sapphirine in the mesostasis (Fig. 2a). The subhedral to euhedral spinel grains are enclosed not only by Al-rich enstatite and anorthite, but also by euhedral sapphirine (Fig. 2b). Sapphirine occurs mainly in the mesostasis (Fig. 2b). Besides sapphirine and spinel, the mesostasis in the core contains very fine-grained high-Ca pyroxene and anorthite (Fig. 2b). The spinel is FeO-rich, with Mg# values [mol. % MgO/(MgO + FeO)] of 58-60 (Table 1). The anorthite has a composition of An87-An89. Most Al-rich enstatite grains in the core contain low Fs and Wo components (En96.5-98.0Fs0.6-2.1Wo1.4) and have high Al2O3 contents (~11.0 wt%). The sapphirine has a composition close to its stoichiometry (Mg2Al4SiO10) and contains low FeO (0.39-0.51 wt%). Its TiO2 and Cr2O3 contents are 1.44-1.75 wt% and 1.09-1.42 wt%, respectively (Table 1). EDS results for the average compositions of the bulk core and its mesostasis are given in Table 2. Both the bulk core and its mesostasis have high average contents of Al2O3 (29.3 and 27.2 wt%, respectively) and FeO (5.4 and 4.6 wt%, respectively). The average Na2O contents in the bulk core and its mesostasis are both 1.1 wt% (Table 2).

The mantle of the SARC is approximately 400 µm thick and is mainly composed of Al-rich enstatite, anorthite, and mesostasis (Fig. 3a). The core and the mantle are distinguished by the presence of spinel (core) and the lack of spinel (mantle) in the mineral assemblage (Fig. 3b). Unlike their counterparts in the core, Al-rich enstatite and anorthite in the mantle are coarser-grained (Fig. 3a), with some anorthite grains that are approximately 60 µm wide. Most Al-rich enstatite grains also contain thin and parallel cracks perpendicular to the c-axis, whose formation could be related to the transformation from high-temperature protoenstatite into clinoenstatite. The mesostasis in the mantle consists mainly of relatively coarse-grained high-Ca pyroxene (up to 20 µm in diameter) and anorthite than those in the core mesostasis. Chemically zoned and Al-poor enstatite grains often occur in or adjacent to mesostasis in the mantle (Fig. 3c). It is noteworthy that some anhedral to subhedral olivine grains and FeNi metals (10-60 µm in size) occur locally in the mantle, close to the margin of this chondrule (Fig. 3d). Anorthite grains in the mantle contain slightly lower An components (An82-87) than those in the core of the SARC (Table 1). Most coarse Al-rich enstatite grains (En97.7-97.9Fs0.6-
0.8Wo1.4-1.6) contain high Al2O3 (8.13-10.7 wt%) and low FeO (0.37-0.50 wt%) (Table 1). However, the zoned enstatite grains (En77.4-97.6Fs1.1-21.2Wo0.8-1.7) in and adjacent to mesostasis contain lower Al2O3 (3.71-7.11 wt%) and higher FeO (0.73-14.0 wt%). The high-Ca pyroxene grains (En31.6-48.5Fs17.6-18.5Wo34.0-50.7) in the mantle mesostasis are FeO-rich (Mg#=64.1-73.4) and have large variations in Al2O3 and TiO2 contents (0.43-4.91 and 0.14-3.06 wt%, respectively). Olivine in the mantle is FeO-rich (Mg#=68.1-71.2). The average bulk compositions of the mantle and its mesostasis are also given in Table 2. Compared to the bulk core and its mesostasis, the bulk mantle and its mesostasis have higher average amounts of SiO2 and CaO and lower average amounts of MgO and Al2O3 (Table 2). The bulk mantle and its mesostasis contain high FeO (4.5 and 6.6 wt%, respectively) and Na2O (1.8 and 1.7 wt%, respectively).

The rim of the SARC is mainly composed of olivine, enstatite, and Fe-Ni-metal and occurs discontinuously (Figs. 1 and 4a). A few fine and irregular grains of anorthite are present in the rim; however, no apparent mesostasis was observed. At some sections, the olivine-enstatite assemblages are partially enclosed in the mantle (Fig. 4b). The texture and mineralogy of the rim, with round-shaped olivine and FeNi metal grains enclosed by enstatite, are almost the same as those of porphyritic olivine-pyroxene chondrules observed in DaG 978 (Zhang and Yurimoto, 2013). Olivine in the rim is also Fe-rich (Mg#=68.7-69.3) and is almost identical in composition to olivine in the mantle (Table 1). Enstatite grains (En74.0-92.6Fs6.5-24.3Wo0.9-1.7) in the rim are usually low in Al2O3 (~ 1 wt%) and have a large variation in Mg# (75.3-93.4).

**Oxygen isotopic compositions of the SARC**

Minerals in the SARC have a large variation in oxygen isotopic composition (Table 3) and almost all data lie along the carbonaceous chondrite anhydrous minerals (CCAM) line (Fig. 5).

The oxygen isotopic compositions of more than ten spinel grains from the core of the SARC were measured. However, nine of the ten measurements, that show 16O-enrichments to various degrees, were contaminated by surrounding minerals or cracks due to the small spinel grain sizes and were rejected. One spinel grain was successfully measured without contamination from surrounding minerals and cracks, and the result indicated 16O-enrichment (Δ17O = −19.9‰; Table 3). Sapphirine in the core mesostasis of the SARC has a small grain-to-grain variation in Δ17O from −7.7 to −5.8‰ (Fig. 5; Table 3). The Al-rich enstatite grains in
the core of the SARC have oxygen isotopic compositions ($\Delta^{17}O = -7.5$ to $-3.7\%$) similar to those of sapphirine. Anorthite from the core of the SARC is $^{16}O$-poor (Table 3; Fig. 5) and has a small variation of oxygen isotopic compositions ($\Delta^{17}O = -4.6$ to $-2.7\%$). The core mesostasis (not overlapping sapphirine) has oxygen isotopic compositions ($\Delta^{17}O = -4.2$ to $-1.0\%$) similar to those of anorthite.

Aluminum-rich enstatite in the mantle of the SARC has oxygen isotopic compositions ($\Delta^{17}O = -8.8$ to $-3.8\%$) similar to those in the core of the SARC. Oxygen isotopic compositions of anorthite ($\Delta^{17}O = -4.7$ to $0.2\%$) and mesostasis (including a 20-µm-size augite grain @95 therein shown in Fig. 3c) ($\Delta^{17}O = -3.3$ to $-0.6\%$) in the mantle are also similar to those in the core of the SARC, respectively. Oxygen isotopic compositions of most olivine grains ($\Delta^{17}O = -8.8$ to $-3.8\%$) in the mantle are similar to those of Al-rich enstatite (Table 3; Fig. 5); however, one analysis (@46, which is in the same olivine#1 grain with @49 and @51) shows a $^{16}O$-rich oxygen isotopic composition with the $\Delta^{17}O$ value down to $-11.6\%$ (Table 3).

Enstatite in the rim of the SARC has oxygen isotopic compositions ($\Delta^{17}O = -8.2$ to $-6.6\%$) generally similar to those in the core and the mantle. Differing from enstatite, olivine in the rim of the SARC has a large variation of oxygen isotopic composition among different grains, with $\Delta^{17}O$ varying from $-23.0\%$ to $-4.5\%$. Similar to those in olivine#1 grain, variable oxygen isotopic compositions within a few single olivine grains were observed (e.g., spots @132, @133, and @135 in olivine#3 grain; Table 3). However, based on the few measured spots of single olivine grains, it is difficult to determine whether there is gradual zoning of the oxygen isotopic compositions.

In summary, spinel and some olivine grains in the SARC are $^{16}O$-rich, with $\Delta^{17}O$ down to $-19.9\%$ and $-23.0\%$, respectively. Al-rich enstatite, sapphirine, enstatite, and most olivine grains have oxygen isotopic compositions similar to each other ($\Delta^{17}O: \sim -7\%$). Meanwhile, anorthite and mesostasis (including the 20-µm-size augite therein) have similar oxygen isotopic compositions and are even more $^{16}O$-poor ($\Delta^{17}O: \sim -3\%$) than those of Al-rich enstatite, sapphirine, enstatite, and most olivine grains.

**Rare-earth-element compositions of mesostasis**

Analytical results for REE in eight mesostasis samples from the core and the mantle of the SARC are given in Table 4 and the CI-normalized abundances of the REEs are plotted in
Fig. 6 (Anders and Grevesse, 1989). Both mesostasis in the core and mantle are enriched in REE and have Group II REE patterns with a flat light REE (LREE) pattern and a fractionated heavy REE (HREE) pattern (Fig. 6). However, the REE abundances of the core mesostasis (La ~ 102-157 × CI) are higher than those of the mantle mesostasis (La ~ 65-132 × CI; Fig. 6).

DISCUSSION

Precursor materials and melting environment of the Al-rich portion in the SARC

The precursor materials of an Al-rich chondrule are one of the key constraints to its origin. Previous investigations have suggested that some Al-rich chondrules are related to a mixture of CAIs and ferromagnesian chondrules, based on the bulk chemistry, the presence of relict fragments of CAIs, and fractionated REE patterns (e.g., Sheng, 1992; Russell et al., 2000; Krot and Keil, 2002; Krot et al., 2002; MacPherson and Huss, 2005; Zhang and Hsu, 2009). However, oxygen isotopic compositions ($\delta^{17,18}$O: ~ –15 to +5 ‰) of minerals in Al-rich chondrules from ordinary chondrites (Russell et al., 2000) and enstatite chondrites (Guan et al., 2006) are closely related to those of ferromagnesian chondrules. These results led them to suggest that the precursor materials of Al-rich chondrules are not simple mixtures of materials from CAIs and ferromagnesian chondrules (e.g., Russell et al., 2000; Guan et al., 2006). In this section, we will discuss our observations with respect to the possibility that the precursor materials of the Al-rich core and mantle in SARC are mixtures of materials from CAIs and ferromagnesian chondrules.

First, the Al-rich portion (including the core and the mantle) of the SARC has intermediate bulk chemistry and mineralogy between those of CAIs and ferromagnesian chondrules. On one hand, both the core and mantle of the SARC contain much higher Al$_2$O$_3$ (up to 29 wt%), relative to the amount in ferromagnesian chondrules. This is due to the dominance of Al-rich minerals (spinel, anorthite, and Al-rich pyroxene) in the core and mantle of the SARC. On the other hand, the core and mantle have lower CaO contents than typical CAIs, which are due to the presence of low-Ca pyroxene, rather than high-Ca pyroxene in SARC core and mantle. Olivine and FeNi-metal, the common minerals of ferromagnesian chondrules, are also present in the mantle. Thus, the petrography, bulk compositions, and mineralogy support that the precursor material of the Al-rich portion (core and mantle) of the SARC is a mixture of materials from CAIs and ferromagnesian chondrules.
Second, mesostasis from both the core and mantle of the SARC have REE patterns similar to those of Group II refractory inclusions. The Group II REE pattern is usually explained by fractional removal of some ultra-refractory elements, which could have concentrated in early condensed solids from a nebula (Boynton, 1975; Davis and Grossman, 1979; Palme et al., 1982). This REE pattern is only consistent with an origin of refractory inclusions, although it does not occur in all refractory inclusions. Thus, although the REE patterns of the bulk Al-rich portion in the SARC could be slightly different from those of mesostasis, due to the igneous fractionation of pyroxene and anorthite, REE pattern should still be similar to that of Group II refractory inclusions because REEs are incompatible in anorthite and enstatite; therefore REEs should be concentrated in mesostasis. The Al-rich portion of the SARC contains very minor amounts of olivine, so that it seems unlikely that amoeboid olivine aggregate (AOA) precursor material is a main contributor to the precursor materials of the Al-rich portion in SARC. Thus, the REE patterns of mesostasis from the core and mantle strongly suggest that the precursor materials of the Al-rich portion in the SARC are related to materials from Group II CAIs.

Third, it is well accepted that primitive refractory inclusions are $^{16}$O-rich, whereas chondrules are usually $^{16}$O-poor (Yurimoto et al., 2008). Of course, in the literature (e.g., Maruyama et al., 1999; Yurimoto and Wasson, 2002; Maruyama and Yurimoto, 2003; Jones et al., 2004; Nagashima et al., 2012), there are a few reports that some minerals in chondrules also have $^{16}$O-rich oxygen isotopic compositions. However, most of these investigators suggested that the $^{16}$O-rich features could be related to relict materials from Ca,Al-rich inclusions or amoeboid olivine aggregates. Alternatively, Jones et al. (2004) also proposed that the earliest nebular solids from which chondrules formed are $^{16}$O-rich as discussed by Kobayashi et al. (2003), since no petrographic and mineralogical supporting a relict origin from refractory inclusions was observed in their study. In this study, we favor that the $^{16}$O-rich feature of the spinel in the SARC is additional evidence that supports the precursor material of the core in the SARC is related to materials from CAIs.

Thus, it is concluded that the precursor of the Al-rich portion in the SARC must have been a mixture of materials from CAIs with a Group II REE pattern and ferromagnesian chondrules. The materials from CAIs should be dominant in the mixture. We can also infer that the minerals (e.g., Al-rich enstatite and sapphirine) crystallized from in the Al-rich portion of the SARC were more $^{16}$O-rich than those of the minerals crystallized from ferromagnesian chondrules (e.g., enstatite and most olivine grains in the rim of the SARC).
and those of the ferromagnesian chondrule components in most chondrites (e.g., Krot et al., 2006; Yurimoto et al., 2008; Ushikubo et al., 2012; Tenner et al., 2013). Instead, in contrast to this inference, the oxygen isotope compositions of Al-rich enstatite and sapphirine in the SARC are similar to those of enstatite and most olivine grains in the rim. This observation is similar to those from previous investigations (Russell et al., 2000; Guan et al., 2006). It is very likely that the oxygen isotopic compositions of most minerals in the Al-rich portion of the SARC had been reset during melting of the Al-rich portion of the SARC precursor materials and/or after accretion into the parent body. In this study, we suggest that the oxygen isotopic compositions of most minerals crystallized from the Al-rich portion of the SARC (except the \(^{16}\)O-rich spinel) had been reset during the heating and melting event of their precursor materials in the nebula; whereas the oxygen isotopic compositions of anorthite and mesostasis were further modified on the parent body. In addition, the ferromagnesian components (including the rim and olivine and metal in the mantle) in the SARC could have formed in a separate process (will be discussed in detail later on), which is not related to the precursor materials of the Al-rich portion of the SARC and their melting.

Yu et al. (1995) performed high-temperature oxygen isotopic exchange experiments, which indicated that oxygen isotopic compositions between a chondrule analogue melt and water vapor could reach equilibrium on a scale of minutes. Therefore, if the precursor materials of the Al-rich portion in the SARC were melted, the melt could readily approach oxygen isotopic equilibrium with the surrounding \(^{16}\)O-poor nebular gas. Meanwhile, the \(^{16}\)O-rich spinel could be of relict origin during melting of the precursor. The self-diffusion speed of oxygen in solid spinel is very slow (Ryerson and McKeegan, 1994). At 1400 K, an oxygen diffusion length of 1 \(\mu\)m in spinel could require ~ 170 years, which is much longer than the duration of high temperature in chondrule-forming events (probably tens of hours, Desch et al. 2012). Thus, it is reasonable that relict spinel can retain its \(^{16}\)O-rich feature during the chondrule-forming event, while minerals crystallized from the melt adopt \(^{16}\)O-poor features \((\Delta^{17}\text{O}: \sim -7\%\)) due to melt-gas oxygen isotopic exchange in the nebula. The similarity between oxygen isotopic compositions of Al-rich enstatite and sapphirine in the SARC and those of ferromagnesian chondrule materials from other chondrites (e.g., Krot et al., 2006; Yurimoto et al., 2008; Ushikubo et al., 2012; Tenner et al., 2013) also supports this inference.

**Crystallization of the Al-rich core and mantle in the SARC**

The ferromagnesian rim in SARC has a distinctly different texture and mineral assemblages, relative to those of the Al-rich portion in the SARC. Ferromagnesian
components in the rim, as well as Fe-rich olivine in the mantle, were probably attached onto
the mantle of SARC during solidification of the mantle. Their formation will be discussed
separately in the following section. In this section, we focus mainly on the crystallization of
the Al-rich portion in the SARC. The boundary between the core and mantle of the SARC
implies three possible interpretations for the core-mantle texture of the Al-rich portion: 1) The
core and mantle may have formed during two heating/melting events in the nebula (e.g.,
Akaki et al., 2007). 2) The core and mantle formed under a single heating/melting event in
the nebula and crystallization proceeded from the mantle to the core. 3) The core and mantle
formed under a single heating/melting event in the nebula and crystallization proceeded from
the core to the mantle.

Akaki et al. (2007) studied a compound Al-rich chondrule from Allende, which also
contains distinct textural domains. They proposed a model of two heating/melting events to
interpret the texture and oxygen isotopic distribution of olivine in that Al-rich chondrule. In
the model, the core, which is considered as the primary chondrule, was formed during the
first heating/melting event, and the mantle was then formed by the melting of core
plagioclase and a porous dust clump that surrounded the primary chondrule. For the case of
the SARC, this model can explain the decrease in the REE concentrations of mesostasis from
the core to the mantle, assuming that the dust clump is REE-poor. However, this model may
have difficulty in explaining the presence of sapphirine in the core. Crystallization
experiments conducted by Sheng (1992) suggested that sapphirine is a metastable phase in
Al-rich chondrules. Thus, if the core was reheated to ~ 1260 °C, sapphirine would likely have
disappeared from the phase assemblage. In this study, we observed that most Al-rich enstatite
grains in the core and mantle of the SARC are clinoenstatite that transformed from high-
temperature protoenstatite, based on their parallel cracks perpendicular to the c axis (Yasuda
et al., 1983). This indicates that, at a minimum, both the core and mantle crystallized above
1000 °C (Yasuda et al., 1983). If the temperature were significantly higher, sapphirine would
have disappeared during a second heating/melting event, which is clearly inconsistent with its
presence in the core. Thus, it is unlikely that the core and mantle of the SARC were formed
by two separate heating/melting events.

The model that the core and mantle of the SARC formed under a single heating/melting
event is supported by the similarity of REE patterns of the core and mantle mesostasis,
especially one of the REE analyses of the mantle mesostasis overlaps with those of the core
mesostasis. Meanwhile, the variation of REE concentrations in the mesostasis would also be
a powerful indicator of the crystallization sequence. Anorthite and enstatite are the major
components in the Al-rich portion of the SARC and are incompatible for REEs; therefore, the
REE concentrations of the melt should tend to increase with the fractionation of anorthite and
enstatite during crystallization. Also fractionation of primary anorthite during crystallization
would cause deeper negative Eu anomaly of core mesostasis vs. mantle mesostasis. Therefore,
the variation of REE concentrations of the mesostasis supports that the crystallization
proceeded from the mantle to the core (e.g., Fig. 6). This conclusion is also consistent with
the euhedral shape and large grain sizes of most anorthite and enstatite in the mantle; whereas
the anhedral to euhedral shape and small grains of anorthite and enstatite in the core could be
due to space limitations during crystallization. The slightly lower An value of anorthite in the
mantle could be due to a higher degree of secondary sodium-metasomatism in the mantle,
relative to that in the core. The slightly higher Na$_2$O content in mesostasis of the mantle,
relative to that of the core also supports this interpretation. However, this crystallization
sequence (from the mantle to the core) seems to conflict with the presence of relict spinel,
because relict spinel grains are the preferred nucleation sites if there is no significant
temperature gradient between the core and the mantle.

If the crystallization of the Al-rich portion started from the core by nucleation on relict
spinel, then the variation of the anorthite An values from the core to the mantle is consistent
with the crystallization sequence, meaning that no secondary sodium-metasomatism was
required. However, to explain the relatively low REE concentrations of the mantle mesostasis,
when compared to those from the core, would require the addition of REE-poor material
during crystallization of the mantle. The olivine and FeNi-metal could represent this REE-
poor material; however, the minor amount of olivine and FeNi-metal observed in the mantle
of the SARC does not seem sufficient to explain the dilution effect of REE in the mantle.

Based on the discussion above, melting under a single heating/melting event and
crystallization that proceeded from the mantle to the core seems to be the most likely scenario
for the formation and crystallization of the Al-rich portion in the SARC. This single stage
heating event model is also consistent with the almost same oxygen isotopic compositions of
Al-rich enstatite from the core and the mantle; chondrules formed during heating events at
different local regions may preserve various primary oxygen isotopic compositions
(Ushikubo et al., 2012). The different bulk composition and mineralogy in mesostasis from
the core and mantle could be due to the formation separate melt pockets during crystallization
of enstatite and anorthite.
Tronche et al. (2007) have performed experiments to understand the effects of bulk compositions, peak temperatures, and cooling rates on the mineralogy and texture of Al-rich chondrules. They concluded that the textures of anorthite-rich compositions are more sensitive to peak temperatures than they are to cooling rates. In their run products, higher peak temperatures response to coarser textures; meanwhile, at the same peak temperatures, slower cooling rates lead to lower aspect ratios of anorthite laths. For the case of the Al-rich portion of the SARC, which is anorthite-rich (Fig. 1), the sizes of anorthite laths in the mantle are comparable to those of run products cooled from a peak temperature of 1475 °C (Tronche et al., 2007) and are much coarser than those of experiments cooled from a peak temperature of 1401 °C and 1452 °C (Tronche et al., 2007). And, the aspect ratios of anorthite grains are comparable to those of run products cooled at 5-10 °C/h. This indicates that the mantle of the SARC could have crystallized from a peak temperature between 1452-1475 °C and at cooling rates of 5-10 °C/h. In addition, as pointed out by Sheng (1992), sapphirine is a metastable phase during crystallization and not stable at 1253-1260 °C. Therefore, the presence of sapphirine in the core mesostasis implies that the core could have completed its crystallization below 1253 °C. This inference is consistent with the various textures of run products cooled from different peak temperatures (Tronche et al., 2007).

**Formation of ferromagnesian components in the SARC**

The ferromagnesian components in the SARC include the chondrule-like rim, and olivine and FeNi metal grains observed in the mantle. The olivine grains in the mantle have similar petrographic, mineralogical, and oxygen isotopic features to those in the rim, which suggests that the ferromagnesian components in the mantle and the rim have a common origin.

All olivine grains in the SARC have sub-rounded to rounded shapes and all olivine grains in the rim are embedded in enstatite. This feature is similar to that of most porphyritic olivine-pyroxene chondrules (Zhang and Yurimoto, 2013), which implies similar formation processes. Most olivine grains have $^{16}$O-poor oxygen isotopic compositions similar to that of enstatite, which is also a typical feature of porphyritic olivine-pyroxene chondrules from unmetamorphosed carbonaceous chondrites (Ushikubo et al. 2012; Tenner et al., 2013). Therefore, the oxygen isotopic compositions of enstatite may represent those of the chondrule-forming region. Interestingly, a few olivine grains are $^{16}$O-rich to various degrees. Similar $^{16}$O-rich isotopic compositions in chondrule olivine have also been previously reported (e.g., Hiyagon and Hashimoto, 1999; Jones et al., 2004; Nagashima et al., 2012;
Ushikubo et al., 2012; Tenner et al., 2013) and are likely of relict origin, although Jones et al. (2004) also proposed an alternative interpretation that the earliest nebular solids from which chondrules formed had $\delta^{17}$O and $\delta^{18}$O values around $-50\%$. The relict origin for these olivine grains could be similar to the origin of the $^{16}$O-rich spinel discussed earlier or of the $^{16}$O-rich olivine of a $^{16}$O-rich chondrule (Kobayashi et al., 2003), as both phases have similarly slow oxygen diffusion rates under chondrule-forming conditions (Ryerson et al., 1989; Ryerson and McKeegan, 1994). The $^{16}$O-rich olivine in the SARC could also be of relict origin due to incomplete melting during the chondrule-forming event (not the event that caused melting of the precursor of the Al-rich portion in SARC). Analyses that indicate intermediate $\Delta^{17}$O probably reflect various contributions from $^{16}$O-rich (e.g., $\Delta^{17}$O = $-23\%$) and $^{16}$O-poor (e.g., $\Delta^{17}$O = $-7\%$) domains within each measurement spot. However, one olivine grain in the SARC has an extremely low $\Delta^{17}$O ($-23\%$) that is almost identical to that of olivine in pristine CAIs and AOAs (Hiyagon and Hashimoto, 1999; Komatsu et al., 2001; Yurimoto and Wasson, 2002; Imai and Yurimoto, 2003; Itoh et al., 2004; Itoh et al., 2007). In addition, olivine grains from DaG 978 AOA have similar CaO contents (<0.1 wt%) to those in the SARC (Zhang and Yurimoto, 2013), and both are lower in CaO contents than olivine from CAIs (CaO >0.1 wt%) in the same sample (Zhang and Yurimoto, 2013). This indicates that the $^{16}$O-rich feature of some olivine grains in the SARC could have been derived from AOAs.

**Post-crystallization processes in the SARC**

One post-crystallization process recorded in SARC involves iron-enrichment in the oxide and silicate minerals. For example, enstatite along cracks and grain boundaries is FeO-enriched, which indicates that Fe-Mg interdiffusion occurred after the crystallization of enstatite. This interpretation is supported by the fact that sapphireine and most enstatite (Al-rich and Al-poor) grains in the SARC are FeO-poor, with Mg# values up to 99, suggesting that they initially formed in a FeO-depleted system. Spinel and olivine are also FeO-rich (Mg#: ~60 and 70, respectively) and are highly unequilibrated with FeO-poor enstatite. The Mg# values of spinel and olivine are instead similar to those of other grains of spinel and olivine from DaG 978 (Zhang and Yurimoto, 2013). Therefore, the FeO-rich features of spinel and olivine indicate secondary processes involving Mg-Fe exchange in the oxides and silicates, probably due to thermal metamorphism on the parent body. Zhang and Yurimoto (2013) suggested that the metamorphic temperature on the parent body of DaG 978 could be up to 850-950 K, based on spinel-olivine geothermometric calculations.
The other post-crystallization process recorded in the SARC involves the exchange of oxygen isotopes in anorthite and mesostasis (including a relatively coarse mesostasis augite grain up to 20 µm in size). The Al-rich portion in the SARC has an igneous texture; therefore, its components, except for relict spinel, should have nearly identical $\Delta^{17}O$ (c.f., Ushikubo et al., 2012). However, the present data indicate that anorthite and mesostasis (very fine-grained augite and anorthite/glass therein) have higher $\delta^{18}O$ and $\Delta^{17}O$ than enstatite, olivine, and sapphirine. This oxygen isotopic difference cannot be explained by melt-gas oxygen isotopic exchange during crystallization of the SARC, because the oxygen isotopic distribution in different minerals is not correlated with their crystallization sequence. For instance, sapphirine in mesostasis and enstatite have similar $\Delta^{17}O$ values that are lower than those of anorthite and mesostasis. Oxygen usually has faster diffusion rates in anorthite and mesostasis when compared to in pyroxene, olivine, and spinel (Ryerson et al., 1989; Ryerson and McKeegan, 1994); therefore, it is likely that the high $\Delta^{17}O$ of anorthite and mesostasis in the SARC is due to secondary oxygen isotope exchange after the solidification of the SARC (e.g., Wasson et al., 2001; Krot et al., 2008; Rudraswami et al., 2011). In addition, it is also possible that oxygen isotopic exchange in both anorthite and mesostasis, as well as the Mg-Fe exchange in minerals in the SARC, occurred during the same thermal metamorphic event on the parent body.

To further evaluate the feasibility of and conditions for O-isotope and Fe-Mg exchange on the parent body of DaG 978, the diffusion of oxygen and Fe-Mg in different minerals under anhydrous and hydrous conditions was calculated based on elemental diffusion coefficients for different minerals available in the literature and with various assumptions (Giletti et al., 1978; Freer and O’Reilly, 1980; Hallwig et al., 1982; Jaoul et al., 1983; Elphick et al., 1988; Farver, 1989; Ryerson et al., 1989; Ryerson and McKeegan, 1994; Hier-Majumder et al. 2005; Chakraborty, 2010). The minimum temperatures and durations (solid curves in Fig. 7) are constrained according to the estimated oxygen and Fe-Mg diffusion lengths in various minerals (30 and 10 µm for oxygen diffusion in anorthite and augite, respectively; 5, 15, 10, and 5 µm for Fe-Mg interdiffusion in spinel, olivine, augite, and in Al-poor enstatite, respectively).

The required diffusion temperatures and durations (dashed curves in Fig. 7) were also calculated for 1 µm diffusion of oxygen in spinel and olivine. These diffusion temperatures and durations likely represent upper limits because no oxygen isotopic compositions of spinel...
and olivine were observed to be similar to those of anorthite and mesostasis, even if spinel
and olivine were measured near the grain boundaries.

Diffusion calculations under anhydrous conditions (Fig. 7a) have two major implications.
First, for a given temperature and time duration, the diffusion distance of oxygen in anorthite
is approximately twice the distance of Fe-Mg interdiffusion in forsterite. This suggests that
the oxygen isotopic composition of anorthite was changed when the Mg-Fe content of olivine
was re-equilibrated during metamorphism on the parent body. However, it is difficult to
explain the $^{16}$O-poor composition of augite in the mesostasis by oxygen diffusion during the
metamorphic event because the required temperature and duration for oxygen diffusion in
augite is above those for oxygen diffusion in spinel and olivine (Fig. 7a). One possibility is
that the augite is a metamorphic crystal crystallized during the metamorphic event (e.g.
Rudraswami et al., 2011).

Second, in order to achieve equilibrium of the oxygen isotopic composition in anorthite,
as well as the Fe-Mg compositions in spinel, forsterite, and for Fe to penetrate into Al-poor
enstatite by diffusion, the estimated diffusion duration is around 1 Myr at a temperature of
850-950 K, which seems to be likely for a chondrite with a petrologic type of 3.6 (Zhang and
Yurimoto, 2013). Therefore, if the large augite grain with high $\Delta^{17}$O ($\sim$3‰) in the mesostasis
crystallized during thermal metamorphism on the parent body, then it is likely that the oxygen
isotopic exchange in anorthite and the Fe-Mg diffusion in spinel, olivine, and enstatite
occurred under anhydrous metamorphic conditions.

All the diffusion curves measured under aqueous fluid saturated conditions (Fig. 7b)
have significant shifts to lower temperatures at a given time duration, when compared with
those measured under anhydrous conditions. This indicates that the Mg-Fe and oxygen
isotopic exchange in minerals of the chondrule could have occurred easily under some degree
of hydrous conditions because the presence of aqueous fluid significantly enhances the
diffusion rates of oxygen and Fe-Mg in minerals. However, it should be noted that the
diffusion coefficients under water saturated conditions used in Fig. 7 may be too large to
constrain the O isotopic exchange of $^{16}$O-rich minerals and that the experimental diffusion
coefficients have high uncertainties compared with those under anhydrous conditions.
Considering the presence of low-temperature alteration products (e.g., secondary nepheline)
in DaG 978 (Zhang and Yurimoto, 2013), it is possible that the presence of water during
thermal metamorphism under hydrous conditions assisted elemental and isotopic exchange in
minerals.
Model for the formation of the SARC and comparison with other Al-rich chondrules

These discussions indicate that the SARC in DaG 978 has experienced multiple formation processes, which involved the mixing and melting of materials from refractory inclusions and ferromagnesian chondrules. The most probable model for the formation of the SARC includes the following stages (Fig. 8). a) Condensation of a CAI from $^{16}$O-rich nebular gas ($\Delta^{17}$O < –20‰) where ultra-refractory components have been removed. This process resulted in the Group II REE pattern of the CAI. b) The Group II CAI was then transported into the chondrule-forming region, where it mixed with ferromagnesian material (that forms chondrule and/or matrix of chondrites). c) The hybrid between the Group II CAI and ferromagnesian material was melted, probably by a heating event related to chondrule-forming events, and experienced oxygen isotope exchange in a $^{16}$O-poor chondrule-forming region ($\Delta^{17}$O = –7‰). Based on the texture comparison between SARC and those of experimental run products by Tronche et al. (2007), the peak crystallization temperature of the Al-rich portion of SARC was likely between 1452-1475 °C. However, in this heating event, spinel grains were not melted and retained their original $^{16}$O-rich oxygen isotopic compositions. d) Upon cooling, the Al-rich melt crystallized from the mantle to the core. Some ferromagnesian chondrule materials were attached on the Al-rich melt and some fragments are partly or totally encapsulated in the Al-rich melt. e) After accretion into the parent body of DaG 978, anorthite and mesostasis in the SARC experienced oxygen isotopic exchange with relatively $^{16}$O-poor fluid ($\Delta^{17}$O: –3‰) during fluid-assisted thermal metamorphism; during this process, spinel, olivine, some enstatite, and mesostasis experienced Mg-Fe exchange.

Interestingly, two other sapphirine-bearing Al-rich chondrules (USNM 3510 and BG82CLII) and a few previously reported cordierite-bearing Al-rich chondrules (Fuchs, 1969; Sheng et al., 1991; Akaki et al., 2007) also have similarly complex textures and mineral assemblages. All of these sapphirine and cordierite-bearing Al-rich chondrules have complex core-mantle features and their dominant Al-rich minerals are anorthite and Al-rich enstatite, rather than Al-rich diopside. In addition, small spinel grains are typically enclosed by anorthite, Al-rich enstatite, sapphirine or cordierite. The main difference among these complex Al-rich chondrules is the variation in the abundance of primary olivine from these Al-rich melts. The similarity in petrographic texture, mineral assemblage, and even oxygen isotopic composition among these sapphirine-bearing and cordierite-bearing Al-rich chondrules may indicate that they have experienced similar formation processes. The
differences in mineralogy between these Al-rich chondrules could be due to variety in the 
bulk compositions of their precursor materials. Compared to the Al-rich chondrules with 
complex textures, Al-rich chondrules with simple textures could have experienced high 
enough temperatures that would have melted all precursor materials, which would have 
allowed for near-complete oxygen isotope exchange with surrounding nebular gas in 
chondrule-forming regions. If correct, it could well explain the similarity in the oxygen 
isotopic compositions of most Al-rich chondrules when compared to those of ferromagnesian 
chondrules. However, although our oxygen isotope and REE data show that Al-rich 
chondrules could have formed by melting of hybrid of materials from CAIs and chondrules, 
some Al-rich chondrules contain no diagnostic evidence for the existence of CAI precursors. 
For example, MacPherson and Huss (2005) measured trace-element compositions for eleven 
Al-rich chondrules from unequilibrated ordinary chondrites. And no Group II REE patterns 
were observed for these 11 Al-rich chondrules. Thus, it suggests that some of these Al-rich 
chondrules, if not all, cannot be explained by the hybrid model inferred from this study.

CONCLUSIONS

A sapphirine-bearing Al-rich chondrule (SARC) was observed in the DaG 978 
ungrouped type 3 carbonaceous chondrite. Petrographic, mineralogical, and SIMS oxygen 
isotope and REE geochemical analyses were conducted and the following conclusions were 
drawn:

1) The $^{16}$O-rich spinel and olivine in the SARC are of relict origin.

2) The high bulk Al$_2$O$_3$ contents, the presence of relict spinel, and the characteristic 
Group II REE composition in mesostasis strongly indicate that the precursor of the 
Al-rich portion of the SARC is a mixture of materials from CAIs and ferromagnesian 
chondrules.

3) The Al-rich portion of the SARC experienced melt-gas oxygen isotope exchange in 
the chondrule-forming region, which could well explain why the oxygen isotopic 
compositions of most Al-rich chondrules are similar to those of ferromagnesian 
chondrules.

4) The presence of $^{16}$O-rich olivine indicates that AOAs contributed in some manner to 
the formation of ferromagnesian chondrules.
5) After accretion onto the parent body of DaG 978, components in the SARC experienced oxygen and Fe-Mg exchange to various degrees, likely during fluid-assisted thermal metamorphism.

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REFERENCES


Figure Captions

Figure 1. Back-scattered electron (BSE) image of the sapphirine-bearing Al-rich chondrule in DaG 978. The dashed and solid lines indicate the core-mantle and mantle-rim boundaries, respectively.

Figure 2. BSE images of the core in the SARC. (a) Small spinel grains are included in anorthite, Al-rich enstatite, and sapphirine. (b) Euhedral sapphirine grains are randomly distributed in mesostasis.

Figure 3. BSE images of the mantle in the SARC. (a) Typical area in the mantle, which contains euhedral anorthite, enstatite, and mesostasis. (b) Transition zone between the core and mantle, distinguished by the presence or lack of spinel, respectively. (c) Augite grain in mesostasis up to 20 µm in size and the Fe-rich, low-Al enstatite in mesostasis is approximately 5 µm thick. (d) Several anhedral olivine grains and FeNi metal in the mantle.

Figure 4. BSE images of the SARC rim, which mainly contains of Fe-rich olivine, enstatite, and FeNi metal. Al-en: Al-rich enstatite; an: anorthite; meso: mesostasis; sp: spinel; spr: sapphirine; en: enstatite; ol: olivine.

Figure 5. Oxygen isotopic compositions of minerals and mesostasis presented on oxygen three-isotope diagrams. Error bars denote two standard deviation (2σ). En: enstatite; an: anorthite; meso: mesostasis; sp: spinel; spr: sapphirine; ol: olivine.

Figure 6. REE pattern of mesostasis in the SARC from DaG 978. Error bars denote one standard deviation (1σ).

Figure 7. Curves showing diffusion time as a function of temperature for various diffusion lengths. Solid curves represent minimum temperatures and diffusion times for the estimated oxygen and Fe-Mg diffusion lengths observed in this study. Dashed lines represent the upper limits of temperature and diffusion time, based on estimated upper limits of O diffusion lengths in olivine and spinel. (a) Under anhydrous conditions. The diffusion coefficients for oxygen in spinel, anorthite, forsterite, and diopside under anhydrous conditions are from Ryerson and McKeegan (1994), Elphick et al. (1988), and Hallwig et al. (1982). The diffusion coefficients for Fe-Mg in spinel, forsterite, Al-poor enstatite, and diopside under anhydrous conditions are from Freer and O’Reilly (1980), Ganguly and Tazzoli (1994), Dimanov and Wiedenbeck (2006), and Chakraborty (2010). (b) Under hydrous conditions. The diffusion coefficients for oxygen in anorthite, forsterite, and diopside under hydrous conditions are from Giletti et al. (1978), Jaoul et al. (1983), and Farver (1989).
Figure 8. Schematic diagram for the formation of SARC in DaG 978. Diamond and rectangle symbols represent spinel and olivine, respectively.
Figure 1.
Figure 2.
Figure 3
Figure 4
Figure 5.
Figure 6.
Figure 7.
Figure 8.

(a) Condensation

(b) Mixing with ferromagnesian materials

(c) Melting and oxygen isotopic exchange in the chondrule forming region

(d) Attachment of chondrule materials and crystallization

(e) Accretion into the parent body: Fe-Mg and oxygen isotopic exchange on the parent body
Table 1. Representative chemical compositions (wt%) of minerals in SARC from DaG 978

<table>
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<tr>
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<th>Core minerals</th>
<th>Mantle minerals</th>
<th>Rim minerals</th>
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<tr>
<td></td>
<td>sp</td>
<td>spr</td>
<td>an</td>
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<tr>
<td>SiO₂</td>
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Calculated based on 24 oxygen atoms

Ti: 0.040 0.150 0.006 0.160 0.004 0.006 0.162 0.115 0.165 0.007 0.016 0.010 0.019
Al: 11.907 8.999 5.645 1.738 5.725 5.435 1.703 0.624 0.780 bd 0.078 bd 0.004 0.175
Cr: 0.164 0.120 bd 0.027 0.003 bd 0.037 0.032 0.050 bd 0.006 bd 0.017
Mg: 3.405 4.953 bd 7.033 bd 0.037 6.783 6.093 7.552 8.341 2.582 8.313 7.612
Mn: 0.016 0.009 0.002 0.008 bd bd 0.013 0.031 0.027 0.038 0.014 0.053 0.008
Fe: 2.332 0.046 0.024 0.042 0.027 0.036 0.043 1.669 0.082 3.426 1.447 3.719 0.533
Ca: 0.017 0.024 2.666 0.099 2.689 2.541 0.109 0.113 0.100 0.009 4.133 bd 0.077
Na: bd bd 0.412 0.005 0.413 0.569 bd 0.011 0.008 bd 0.036 bd bd

Table 2. SEM-EDS bulk compositions (wt%) of the core and mantle and their respective mesostasis in SARC

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<th>Core Mesostasis</th>
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Table 3. Oxygen isotopic compositions (permil) of minerals and mesostasis in SARC 858

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<th>( \delta^{17}O_{SMOW} )</th>
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Individual measurements are from different grains except anorthite grain#1 and olivine grains #1, #2, and #3. Intra-grain heterogeneities are observed in olivine grains #1 and #3.
Table 4. REE concentrations (ppm) in the core and mantle mesostasis of SARC

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