

Ca-, Al-Rich Inclusions in Two New Carbonaceous Chondrites from Grove Mountains, Antarctica

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Abstract Two new carbonaceous chondrites, GRV 023155 and GRV 050179, collected from the Grove Mountains (GRV), Antarctica, have been classified as the oxidized CV3 and CM2 chondrites, respectively. A total of 9 Ca-, Al-rich inclusions (CAIs) were found in the two meteorites. Most of the inclusions are extensively altered, with phyllosilicates commonly found in the alteration assemblages of CAIs, chondrules and matrix in the GRV 050179 CM2 chondrites, suggesting that aqueous alteration occurred on the host meteorite parent body. In contrast, feldspathoids and hedenbergite were identified in the CAIs from GRV 023155. The FeO-rich phases in the CAIs from GRV 023155 indicate alteration of these CAIs happened under high oxygen fugacity. All 9 inclusions can be classified as Type A or spinel-pyroxene rich inclusions, and they probably represent a continuum of solar nebular condensation. The survey of Ca-, Al-rich inclusions in GRV 023155 (CV3) and 050179 (CM2) suggests that Type A and spinel-pyroxene inclusions are common in these two meteorites.

Keywords Antarctica · Carbonaceous chondrite · Ca-, Al-rich inclusion · CAI · Nebula

1 Introduction

Ca-, Al-rich inclusions (CAIs) have a mineralogy consistent with predictions of condensation from a nebula gas of solar composition (Grossman 1972; Connelly et al. 2012). CAIs may be texturally divided into coarse-grained and fine-grained inclusions (Grossman and

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Ganapathy 1976a, b; Lin et al. 2006). Most coarse-grained CAIs are compact Type A (melilite-spinel rich), Type B (melilite-fassaite rich) and Type C (anorthite-fassaite rich) (Grossman 1975; Wark and Lovering 1982; Wark 1987; Sheng et al. 1991; Krot et al. 2006). The most common fine-grained inclusions are melilite-spinel rich (fluffy Type A) and spinel-pyroxene rich inclusions (MacPherson and Grossman 1984; Lin et al. 2006). The most extensive studies of CAIs have been performed on carbonaceous chondrites.

Lin and Kimura (2003) found that a large number of CAIs from the Ningqiang carbonaceous chondrite, classified as an unknown chondrite (Wang et al. 2007), revealed a continuum of fluffy Type As, spinel-pyroxene rich inclusions and amoeboid olivine aggregates (AOAs) with the bulk compositions following the predicted gas–solid condensation trajectory from a gas of solar composition. Furthermore, the discovery of a new type of CAI, namely the anorthite spinel-rich inclusion (ASI), bridges a genetic relationship between Type A and Type C inclusions (Lin and Kimura 1998). The size distribution patterns of the single inclusions and the individual nodules of conglomerated ones in various carbonaceous chondrites are similar to each other, and to those in ordinary and enstatite chondrites, except for the anomalously large CAIs found in CV3 chondrites. Comparable size, petrographic type distribution patterns, oxygen isotopes, Al–Mg isotopic systems and rare earth elements of CAIs in different groups of chondrites argue for a same reservoir of CAIs (Guan et al. 2000a, b; Kimura et al. 2002; Lin and Kimura 2003; Lin et al. 2003, 2006). During and/or after formation, CAIs were transported into different disk regions and subsequently underwent alteration.

Since the discovery of 9 meteorites on blue ice in Antarctica by the Japanese Antarctic Research Expedition in 1969, the number of Antarctic meteorites has vastly exceeded the total number of meteorites from other regions. The Grove Mountains consist of nunataks, and are located at the eastern edge of Antarctica. A total of ~11,400 meteorites were collected from the region by the Chinese Antarctic Research Expedition (CHINARE). In this paper, we report on the petrography and mineral chemistry of CAIs from two new carbonaceous chondrites from Grove Mountains, Antarctica, *i.e.* GRV 023155 (CV3) and GRV 050179 (CM2).

2 Samples and Experiments

Samples of the two carbonaceous chondrites were embedded in epoxy, and then cut into $\sim 1 \text{ mm}$ thin slices. Polished thin sections were prepared from the both slices without water. The surface areas of the sections of GRV 023155 and GRV 050179 are 1.08 and 1.31 cm² (Fig. 1), respectively.

CAIs were mainly located using the back-scattered electron (BSE) image mode of the electron probe microprobe analyzer (EPMA) JXA-8230 in the College of Earth Sciences, Guilin University of Technology. Textural observations and quantitative analyses of individual minerals in these CAIs were carried out using the same EPMA. Natural and synthetic minerals were used as standards. The operating conditions were 15 keV accelerating voltage and 20 nA beam current. Overlaps of the K_{α} lines of V and Mn by the K_{β} lines of Ti and Cr were corrected. The analyses were corrected using the conventional ZAF program.

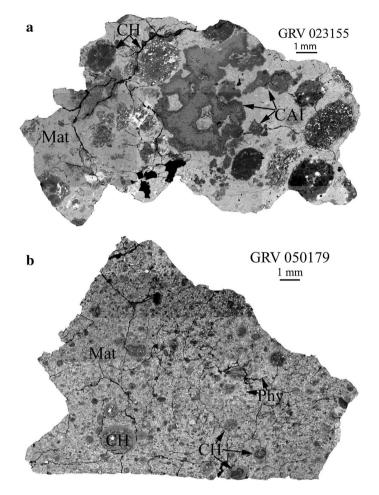


Fig. 1 Back-scattered electron image mosaic of two carbonaceous chondrites. The scale bars are 1.0 mm. **a** GRV 023155 has many large chondrules, CAIs and amoeboid olivine aggregates (AOAs). It is a CV3 chondrite; **b** GRV 050179, a typical CM2 chondrite. *Note* small chondrules and high abundance of matrix. Phyllosilicates are abundant within the matrix, chondrules and CAIs. *CH* chondrule, *Mat* matrix, *Phy* phyllosilicates

3 Results

3.1 Petrography

3.1.1 Grv 023155

Figure 1a is a BSE image mosaic of GRV 023155. Chondrules and refractory inclusions are large in GRV 023155. The diameter of chondrules falls in a range of 0.5–3.0 mm, and the largest CAI has a diameter up to 5.0 mm. The major minerals of chondrules are olivine, low-Ca pyroxene and troilite. Most of the matrix of GRV 023155 are opaque metallic Fe–Ni, troilite, and silicate, except for minor microcrystalline grains of olivine and pyroxene

(1–5 μ m). The abundance ratio of matrix/(chondrules + refractory inclusions) is ~1.0. The modal abundance of metallic Fe–Ni and sulfides is ~3.0 vol%, and 5 CAIs, with a total surface of ~ 0.3 cm², were found in the section, suggesting a modal abundance of ~28 vol%.

Type A inclusions 4 out of 5 CAIs are classified as Type A inclusions. The sizes of the 4 inclusions are $3000 \times 5000 \mu m$, $500 \times 1600 \mu m$, $260 \times 420 \mu m$ and $140 \times 350 \mu m$, respectively. The 4 inclusions are irregularly shaped, consisting of spinel + melilite/feldspathoids cores and Ca-pyroxene rims. In GRV 023155-CAI2, feldspathoids occur mainly between the spinel + melilite cores and the Ca-pyroxene rims. The largest CAI, GRV 023155-CAI1 has several concentrically zoned objects that have spinel + melilite cores and Ca-pyroxene rims, respectively. Accessory perovskite is enclosed in melilite and spinel (Fig. 2).

Spinel-pyroxene rich inclusions Only one spinel-pyroxene rich inclusion (GRV023155-CAI4) was found in the section. The size of the inclusion is $150 \times 400 \ \mu\text{m}$. It is irregularly shaped, consisting of spinel cores and Ca-pyroxene rims. Accessory perovskite is enclosed in spinel (Fig. 2).

3.1.2 Grv 050179

Shown in Fig. 1b, this chondrite contains much more abundant phyllosilicates-bearing matrix (74 vol%) and fewer chondrules (25 vol%, <2 mm and most <500 μ m in diameter) than GRV 023155 (Fig. 1). Phyllosilicates are common in CAIs, chondrules and matrix. Most chondrules have porphyritic textures and FeO-poor compositions (type I); they are surrounded by the fine-grained accretionary rims. The other major minerals of the chondrules are olivine, low-Ca pyroxene and troilite. Metallic Fe–Ni is rare (~0.4 vol%), and the modal abundance of sulfide is 1.5 vol%. Four CAIs were found in the section, giving a modal abundance of 0.29 vol%.

Type A inclusions All 4 CAIs are similar to Type A inclusions, although they are all heavily altered, as indicated by the presence of abundant phyllosilicates, and these CAIs have a size range of $250 \times 400 \mu m$, $50 \times 130 \mu m$, $50 \times 100 \mu m$, $130 \times 130 \mu m$, respectively. Most of these inclusions are irregularly shaped and loose assemblages of concentrically zoned objects, each of which consists of a core of fine-grained spinel and needle-shaped phyllosilicates and rims of Ca-pyroxene. One inclusion (GRV 050179-CAI4) has an outermost layer of forsterite (Fig. 3). The presence of phyllosilicates and absence of melilite (one of the most common primary phases in CAIs) indicate that these CAIs have been nearly completely altered. Assuming the precursor of the phyllosilicates is melilite (Greenwood et al. 1994; Lin et al. 2006), the primary mineral assemblages are similar to typical Type A inclusions.

3.2 Mineral Chemistry

3.2.1 Spinel

Spinel is the most common phase in all types of CAIs in the two chondrites. The grains in GRV 050179 are FeO-poor (<1.04 wt%) and show similar compositions between Type A and spinel-pyroxene rich inclusions (Table 1). However, spinel grains in all 5 CAIs from GRV 023155 are FeO-rich (up to 12.7 wt%) and ZnO-bearing (up to 0.26 wt%). The ZnO grains content are positively correlated with the FeO content. Other minor elements are TiO₂ (0.16–0.49 wt%, except for an analysis of 2.98 wt% probably due to alteration) and

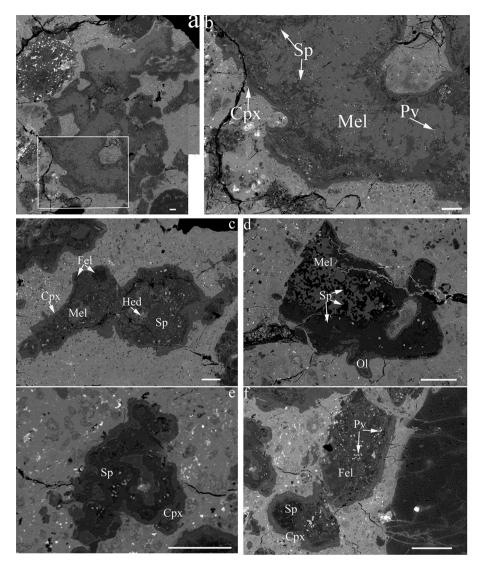


Fig. 2 BSE images of CAIs from GRV 023155. Scale bars at the bottom are 100 μ m. **a**, **b** A typical type A inclusion (GRV 023155-CAI1), consisting of many irregular concentrically zoned objects that have melilite (Mel) and spinel (Sp) cores and Ca-pyroxene (Cpx) rims. A few grains of perovskite (Pv) are enclosed in spinel and melilite; **c** A type A inclusion (GRV 023155-CAI2), consisting of a spinel core and a thin Ca-pyroxene (Cpx) rim. A layer of feldspathoids (Fel) occurs between the core and the rim. Minor melilite (Mel) is partially replaced by hedenbergite (Hed) in the center of the inclusion. A few white grains are perovskite (Pv); **d** A fragment of type A inclusion (GRV 023155-CAI3), consisting of a spinel and melilite core and a thin olivine (OI) rim. A few grains of perovskite are enclosed in spinel mainly close to the rim; **e** A spinel-pyroxene rich inclusion (GRV 023155-CAI4), consisting of a spinel core and a thin Ca-pyroxene rim. A few of small grains of perovskite occur in the center of the inclusion; **f** A type A inclusion (GRV 023155-CAI5), consisting of a thin layer of Ca-pyroxene rim. Spinel are perovskite (Fel) and spinel at the core and a thin layer of Ca-pyroxene rim spinel are perovskite occur in spinel and period (GRV 023155-CAI5), consisting of a the core and a thin layer of Ca-pyroxene rime and the rime reducts feldspathoids (Fel) and spinel at the core and a thin layer of Ca-pyroxene. Small white spots in spinel are perovskite

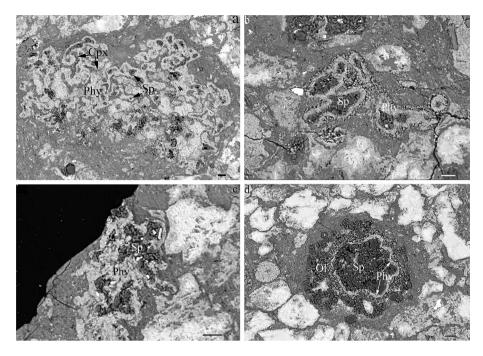


Fig. 3 BSE images of CAIs from GRV 050179. Scale bars at the bottom are 10 μ m. **a** A type A-like inclusion (GRV050179-CAI1), consisting of many irregular concentrically zoned objects that have phyllosilicate (Phy) and spinel (Sp) cores and Ca-pyroxene (Cpx) rims. The whole inclusion is strongly altered. **b**, **c** Both GRV 050179-CAI2 and GRV 050179-CAI3 are similar with GRV050179-3CAI1, consisting of many irregular concentrically zoned objects that have phyllosilicate (Phy) and spinel (Sp) cores and Ca-pyroxene (Cpx) rims. **d** A type A-like inclusion (GRV050179-CAI4), consisting of a spinel (Sp) cores and Ca-pyroxene (Cpx) rims. **d** A type A-like inclusion (GRV050179-CAI4), consisting of a spinel core and a thin olivine (OI) rim, consisting of alteration products phyllosilicate (Phy) at the core and a thin layer of olivine

 Cr_2O_3 (0.07–0.32 wt%, except for a few analyses of 2.15–2.78 wt% probably due to alteration), showing no significant differences between types of CAIs and/or the chondrites (Table 1).

3.2.2 Other Phases

Ca-pyroxene occurs as rims around CAIs of both Type A and spinel-pyroxene rich types. Most Ca-pyroxene rims in all CAIs contain low TiO₂ (<1.31 wt%) (Table 2). Analyses conducted on a few thick Ca-pyroxene rims show an increase of Al₂O₃ and TiO₂ toward the cores. Other minor elements are FeO (0.03–0.68 wt%) and Cr₂O₃ (<0.15 wt%).

Phyllosilicates are very common in all CAIs in GRV 050179. Quantitative analyses show low totals (79–85 wt%), suggestive of the presence of OH and/or H₂O. Besides SiO₂ (14.5–28.3 wt%), MgO (8.26–20.9 wt%) and Al₂O₃(4.05–15.8 wt%), phyllosilicates are highly FeO-rich (23.6–40.5 wt%). Only a few grains of melilite are available to analyze, and they are all gehlenitic (Åk < 40). Other minor elements are FeO (<0.20 wt%) and Na₂O (<0.26 wt%). Olivine occurs as a layer in GRV 023155-CAI3 and GRV 050179-CAI4, with a composition of forsterite (Fo_{96–100}). Hedenbergite is nearly pure FeCaSi₂O₆, with minor amounts of Al₂O₃ (0.47 wt%) and MnO (0.38 wt%).

Table 1	Table 1 Representative analyses of	ative analy:		opmen, m week											
	GRV 02	GRV 023155 (CV3)	()								GRV 05	GRV 050179 (CM2)	()		
	1	2	3	4	5	9	7	8	6	10	1	2	3	4	5
SiO_2	0.05	0.10	0.14	0.48	0.06	0.10	0.05	6.45	2.95	0.08	0.03	0.16	0.86	0.14	0.35
TiO_2	0.41	0.37	0.36	0.38	0.42	0.45	0.39	0.37	0.39	0.33	0.16	0.28	0.49	0.31	2.98
Al_2O_3	72.60	73.0	71.8	70.7	72.4	70.2	70.9	70.3	64.1	72.9	6.69	71.5	67.4	68.9	65.5
Cr_2O_3	0.17	0.31	0.08	0.13	0.10	0.04	0.30	0.00	0.15	0.07	0.32	0.21	2.78	2.61	2.15
FeO	4.13	0.67	3.94	7.17	0.82	8.52	6.53	10.44	12.7	0.67	0.31	0.4	1.04	0.73	0.78
MnO	0.04	0.00	0.00	0.04	0.03	0.03	0.00	0.00	0.02	0.00	0.03	0.02	0.12	0.16	0.19
MgO	24.6	26.2	24.4	22.0	26.3	21.2	22.5	12.6	16.4	26.7	27.0	27.6	26.2	27.4	25.9
CaO	0.22	0.11	0.14	0.29	0.12	0.09	0.10	1.67	1.29	0.06	0.14	0.17	0.19	0.08	0.40
ZnO	0.04	0.00	0.00	0.18	0.04	0.08	0.06	0.26	0.14	0.01		0.03		0.06	
Na_2O	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.58	0.00	0.00	0.03	0.01	0.04	0.02	0.32
Total	102.0	100.4	100.7	101.2	100.5	100.8	100.8	102.3	98.0	100.7	99.1	100.6	98.8	100.2	99.4
Cation per unit	er unit														
Si	0.001	0.002	0.003	0.012	0.002	0.002	0.001	0.154	0.075	0.002	0.001	0.004	0.021	0.003	0.009
Ti	0.007	0.007	0.006	0.007	0.007	0.008	0.007	0.007	0.007	0.006	0.003	0.005	0.009	0.006	0.055
Al	2.015	2.021	2.016	2.007	2.017	2.017	2.017	1.974	1.928	2.018	1.994	1.990	1.919	1.937	1.883
Cr	0.003	0.006	0.001	0.003	0.002	0.001	0.006	0.000	0.003	0.001	0.006	0.004	0.054	0.050	0.042
Fe	0.081	0.013	0.078	0.144	0.016	0.173	0.132	0.208	0.271	0.013	0.006	0.008	0.021	0.015	0.016
Mn	0.001	0.000	0.000	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.001	0.000	0.002	0.003	0.004
Mg	0.868	0.925	0.872	0.797	0.934	0.776	0.815	0.453	0.630	0.941	0.982	0.979	0.951	0.982	0.949
Ca	0.006	0.003	0.004	0.008	0.003	0.002	0.003	0.043	0.035	0.001	0.004	0.004	0.005	0.002	0.010
Zn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.027	0.000	0.000	0.001	0.000	0.002	0.001	0.015
Sum	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000

	GRV 0	23155 (CV	/3)					GRV 0	50179 (CM	2)
	Mel		Срх		Hed	Fel	Ol	Срх	Phy	Ol
SiO ₂	24.9	24.7	48.9	50.6	47.2	49.6	38.4	51.0	25.9	42.4
TiO_2	0.05	0.15	1.31	0.65	0.15	0.12	0.00	1.19	0.13	
Al_2O_3	33.7	33.7	9.57	6.84	0.47	42.0	0.03	6.91	8.01	0.01
Cr ₂ O ₃	0.00	0.02	0.07	0.05	0.04	0.00	0.01	0.12	0.01	0.37
FeO	0.03	0.00	0.03	0.17	27.1	1.63	22.4	2.25	32.3	0.51
MnO	0.00	0.00		0.00	0.38	0.00	0.45	0.12	0.21	0.18
MgO	1.96	1.98	15.2	16.1	0.16	0.76	38.9	16.2	14.7	55.3
CaO	39.2	39.6	25.2	23.9	26.3	1.52	0.01	20.9	0.73	0.38
ZnO				0.01		0.00		0.00	0.06	0.01
Na ₂ O	0.18	0.22	0.00	0.03	0.06	5.70	0.03	0.28	0.24	0.02
Total	99.8	100.0	100.3	98.5	101.9	102.9	100.3	99.1	82.7	99.2
Cation]	per unit									
Si	1.206	1.188	1.763	1.856	0.002	0.002	0.995	1.866	3.009	1.015
Ti	0.001	0.004	0.035	0.018	0.007	0.008	0.000	0.033	0.011	0.000
Al	1.840	1.836	0.407	0.295	2.017	2.017	0.001	0.298	1.095	0.000
Cr	0.000	0.001	0.002	0.001	0.002	0.001	0.000	0.003	0.001	0.005
Fe	0.001	0.000	0.001	0.005	0.016	0.173	0.483	0.069	3.135	0.010
Mn	0.000	0.000	0.000	0.000	0.001	0.001	0.010	0.004	0.020	0.004
Mg	0.114	0.115	0.817	0.880	0.934	0.776	1.514	0.882	2.545	1.955
Ca	1.832	1.847	0.975	0.938	0.003	0.002	0.000	0.820	0.090	0.010
Zn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.000
Na	0.014	0.017	0.000	0.002	0.000	0.000	0.002	0.020	0.053	0.001
Sum	5.000	5.000	4.000	4.000	3.000	3.000	3.000	4.000	10.000	3.000

 Table 2
 Representative analyses of melilite (Mel), Ca-pyroxene (Cpx), hedenbergite (Hed), feldspathoids (Fel), olivine (Ol) and phyllosilicates (Phy), in wt%

4 Discussion

4.1 Classification of the 2 Carbonaceous Chondrites

Chondrules and CAIs in CM chondrites are small—typically <0.5 mm in diameter—and have a narrow size-range. The modal abundance of matrix and chondrule in CMs are 70 and 20 vol%, respectively (King and King 1978), and the bulk of CMs are composed of extremely fine-grained hydrous matrix. Members of the CVs have abundant large (~ 1 mm) chondrules and prominent CAIs (Van Schmus 1969). Compared with CMs and COs, chondrules and CAIs are strikingly large in CVs. The modal abundance of matrix and chondrule are 40 and 45 vol%, respectively. McSween (1977) recognized two subgroups, oxidized and reduced, based on the metal/magnetite ratio and the Ni contents of the sulfides. Spinel grains in oxidized CVs are significantly enriched in FeO in comparison with those in the reduced subgroups (Kimura et al. 2002).

GRV 023155 appears to be a typical CV3 chondrite. The size range of chondrules (0.5–3.0 mm) are within the range of CV3 (\sim 1 mm) (Van Schmus 1969). The observed abundance ratio of matrix/(chondrules + refractory inclusions) \sim 1.0 is consistent with the

classification of CV3. In addition, the intense alteration of CAIs and the FeO-enrichment of spinel in GRV 023155 are similar to CAIs in oxidized CV3, but distinct from those in the reduced subgroups. This is supported by the paucity of metallic Fe–Ni in the meteorite. We classify GRV 023155 as an oxidized CV3 chondrite.

GRV 050179 contains small chondrules embedded in phyllosilicate-bearing matrix. The sizes of chondrules (most <500 μ m) and modal abundance ratio of matrix/chondrule (3.0) are typical for CM2 chondrites, but different from CO3, CV3 and other carbonaceous chondrites (Van Schmus and Wood 1967; Van Schmus 1969). The common occurrence of phyllosilicates in the matrix, chondrules and CAIs further confirms that GRV 050179 is a CM2 chondrite.

4.2 Formation of CAIs

CAIs in the two carbonaceous chondrites are most likely assemblages of solar nebular condensates. The Type A inclusions are similar to fluffy Type A (or referred to as melilite-spinel rich) inclusions in the extensively studied Allende (MacPherson and Grossman 1984), Ningqiang (Lin and Kimura 2003) and other Antarctic carbonaceous chondrites (Dai et al. 2004), because of their fluffy accretion of concentrically zoned objects, mineral assemblages and mineral chemistry (with the assumption that melilite has been altered to phyllosilicate). This is supported by the gehlenitic compositions of a few relict melilite grains, which are within the range of fluffy Type A inclusions (MacPherson and Grossman 1984; Lin and Kimura 2003) and similar to predictions of solar nebular condensation (Åk < 40, Yoneda and Grossman 1995). In contrast, melilite in once-molten CAIs, *e.g.* Compact Type A, Type B and C, is usually Åkermanitic (Åk < 90) (Lin and Kimura 1998, 2000).

Supporting the previous observations by Lin and Kimura (2003) and Russell and Howard (2013), the Type A inclusions and spinel-pyroxene rich inclusions show a continuous variation in modal composition. In fact, some CAIs cannot be clearly defined as Type A or as spinel-pyroxene-rich (Fig. 2c, f). Furthermore, compositions of spinel and Ca-pyroxene rims are indistinguishable between both occurrences (Tables 1, 2). Another line of evidence for gas–solid condensation of these CAIs is the mineral sequence of perovskite, melilite, spinel and Ca-pyroxene/forsterite, from core to rim. The fine-grained assemblages are likely alteration products of melilite that is one of the major constituent phases of Ca–Al-rich inclusions. Hence, the precursor of the fine-grained assemblages (*e.g.* phyllosilicate, feldspathoids and hedenbergite) can usually be referred to as melilite. This sequence is consistent with the prediction of solar nebular condensation (Grossman 1972; Yoneda and Grossman 1995), but different from crystallization sequences of melts with compatible compositions (Lin and Kimura 2003).

Another scenario is that these CAIs are high-temperature evaporating residues of MgO– FeO-rich silicates heated by intense irradiation from the proto-Sun (Shu et al. 1997, 2001). Such a model expects these CAIs to have more refractory rims than the cores, and to have typical textures of crystallization from liquids, different from the observations. Most CAIs in the two meteorites have Ca-pyroxene/olivine rims that are identical to Wark-Lovering rims (Wark and Lovering 1977). Wark and Boynton (2001) suggested that these rims were formed by flash heating, and one of the main lines of evidence is the enrichment of refractory elements in the rims relative to the interiors. However, all six CAIs they analyzed are coarse-grained and compact, hence probably crystallized from melts. This is different from the CAIs reported here, especially some of them have even less refractory forsterite rims. Figures 2d and 3d show inclusions with olivine layer. Forsterite accretionary rims have been reported around CAIs in many other CV3, too (*e.g.* Allende, Efremovka, Ningqiang) (Lin et al. 1999).

4.3 Alteration of CAIs

Most CAIs in the two carbonaceous chondrites are heavily altered, as indicated by the presence of abundant fine-grained secondary minerals. Only a few small grains of melilite were found in the CAIs, whereas melilite is typically one of the most common minerals in CAIs in other carbonaceous chondrites. The lack of melilite and presence of fine-grained secondary minerals, such as feldspathoids in the CV3, and phyllosilicates in CM2 are results of intense alteration, with melilite reacted with gaseous and/or aqueous phases to produce the fine-grained phases. Ca-pyroxene and spinel are much more resistant to alteration, hence remained.

Although the two meteorites were collected from Antarctica and experienced some terrestrial weathering, alteration of the CAIs cannot be results of the weathering. It is noticed that alteration products of the CAIs are different from meteorite to meteorite. As described above, most CAIs in GRV 050179 contain fine-grained and needle-shaped phyllosilicates in the cores, which are typical aqueous alteration products and are common in CM carbonaceous chondrites (Lee and Greenwood 1994). In contrast, phyllosilicates were not observed in CAIs in GRV 023155. Instead, feldspathoids and hedenbergite were identified, which is similar to CV carbonaceous chondrites (MacPherson and Grossman 1984; Lin et al. 2006). If the alteration of CAIs took place after the fall of the meteorites, phyllosilicates would have been found in CAIs of GRV 023155. Another line of evidence against terrestrial weathering is the distinct FeO contents of spinel in GRV 050179. Spinel grains in GRV 023155 are significantly enriched in FeO in comparison with those in GRV 050179. The high FeO contents of spinel indicate alteration of the CAIs in GRV 023155 happened under high oxygen fugacity (Kimura et al. 2002; Lin and Kimura 2003; Dai et al. 2004). This is similar to the common occurrence of FeO-rich spinel in altered CAIs from oxidized subgroups of CV3 chondrites (Kornacki and Wood 1985) and ordinary chondrites (Kimura et al. 2002). Terrestrial weathering does not produce such a systematic difference between the two Antarctic meteorites.

Where and when the alteration took place is a controversial issue. Very low abundances or absence of extinct radionuclides (e.g. 26 Al) in the alteration products of CAIs suggests that the secondary processes took place >5 Ma after the earliest CAI formation (Huss et al. 2001). Such a long interval points to an asteroidal origin of the alteration, because it is too long for residence in the solar nebula. The recent discovery of significant 36 Cl (half life of 0.3 Ma) in sodalite in alteration assemblages of a Ningqiang CAI (Lin et al. 2005) suggests that CAI alteration could have took place as early as ~2 Ma, hence probably in the nebula. Another evidence for a nebular origin of the alteration is very high heterogeneity of CAI alteration in some carbonaceous chondrites. However, phyllosilicates are commonly found in the alteration assemblages of CAIs, chondrules and matrix in the GRV 050179 CM chondrites, suggesting aqueous reactions probably occurred in the parent body.

4.4 Type Distribution Patterns of CAIs

The most extensively studied CAIs in CV chondrites, especially in Allende, are coarsegrained inclusions, such as Types B, C and compact Type A. This gave an impression of high abundances of the coarse-grained inclusions in these meteorites. The coarse-grained CAIs are usually millimeter- or centimeter-sized, so they can be easily recognized. In

Table 3 Summary of refractory inclusions in various chondrites	of refracto	ory inclusio	ns in vario	us chondri	ites										
Groups	EH3	Ordinary	Ordinary chondrite	CO3			CM2		CV3		CV3-like	CR	CH	Unique	CO/CM
Meteorites	Sahara 97159	Yamato 792947	Others	GRV 021579	Yamato 81020	others	Murchison	GRV 050179	Allende	GRV 023155	Ningqiang		NWA 739	Acfer 094	MAC 87300, 88107
Number of sections	2	5	18	1	1	10	2	1	4	1	21	12	1	1	2
Total areas (mm ²)	310	267	1390	62	6.1	858	210	1080	1090	1310	1740		100	34	270
Type A/A-like	35	15	14	4	42	51	6	4	40	4	31	14	14	95	55
Sp-Px/Sp fragment	26	20	6	8	23	145	7	1	20		79		13		174
ASI/AnPx					22	1					7	5		14	
Gro/Hib-rich						9			1			4	23	19	2
Sp/Hib/Fas															
Spherule/fragment	5	2	1	1	1	12	1		1					1	
B/C/POI	2										9			3	
Total	68	37	24	13	88	215	17		62		123	23	50	132	231
Reference ^a	6	б	1	1	1	4	1	0	1	0	5	9	٢	8	6
Sp spinel, Px Ca-pyroxene, An anorthite, Hib hibonite, Fas fassaite, B Type B, C Type C, ASI anorthite-spinel-rich, POI plagioclase-olivine-rich ^a 0 = this work, 1 = Lin et al. (2006), 2 = Lin et al. (2003), 3 = Kimura et al. (2002), 4 = Russell et al. (1998), 5 = Lin and Kimura (2003), 6 = Aléon et al. (2002),	roxene, <i>Ai</i> = Lin et a	1 anorthite, d. (2006), 2	<i>Hib</i> hibon $2 = \text{Lin et}$	iite, Fas fa al. (2003),	ssaite, $B T$, $3 = Kim$	ype B, <i>C</i> ura et al.	Type C, <i>AS</i> (2002), 4 =	I anorthite Russell et	-spinel-ricl al. (1998)	h, <i>POI</i> pla), 5 = Lin	gioclase-oliv and Kimura	ine-ricl (2003)	h), 6 = A	léon et al.	(2002),
V = Krot et al. (2006), $8 = $ Krot et al. (2004), $9 = $ Kussell et al. (2000)	(0), 8 = K	rot et al. (2	2004), $9 =$	Kussell et	al. (2000)										

contrast, hibonite-rich inclusions are the most intensely studied CAIs in CM chondrites (Ireland 1988), because hibonite is one of the earliest condensates and its typical blue color can be easily recognized. However, it is obvious that the two GRV meteorites in this paper contain similar CAIs. The two predominant petrographic types of CAIs are Type A and spinel-pyroxene rich inclusions.

A survey of CAIs in the ordinary chondrites, carbonaceous chondrites, enstatite chondrites, together with the paper, our previous data and literature, suggests that Type A (or A-like) and spinel-pyroxene inclusions are the common petrographic types in all chondrites summarized in Table 3.

It is also noticed that relative abundance ratios between Type A (or A-like) and spinelpyroxene inclusions may vary among chondrites (Table 3). The variation may partly be due to assignment of the petrographic types, because they are continuous in both petrography and bulk compositions (Lin and Kimura 2003). CH chondrites contain more hibonite and/or grossite-rich inclusions. Krot et al. (2006) reported 23 hibonite/grossiterich inclusions out of 50 refractory inclusions in NWA 739 (CH). The unique carbonaceous chondrite Acfer 094 also has a high abundance of hibonite/grossite-rich inclusions, with 19 out of 132 inclusions (Krot et al. 2004). Hibonite/grossite-bearing, Type A and spinelpyroxene inclusions represent continuous condensate assemblages of the solar nebula from high to low temperature, because their bulk compositions in Ningqiang follow the condensation trajectory of the solar nebula (Stolper 1982; Lin and Kimura 2003; Lin et al. 2006).

5 Conclusions

Two new carbonaceous chondrites from Grove Mountains, Antarctica, were classified as CV3 (GRV 023155) and CM2 (GRV 050179), respectively. Based on the intense alteration of the CAIs and the FeO-enrichment of spinel in GRV 023155, this meteorite is further classified as oxidized subgroup of CV3.

A total number of 9 CAIs have been found in thin sections of the two carbonaceous chondrites. Most of them have been extensively altered. CAIs in GRV 050179 commonly contain phyllosilicates, similar to those in other CM2 chondrites; spinel in CAIs from GRV 023155 is FeO-rich, distinct from the FeO-poor spinel in the GRV 050179 CAIs. The similarity of distinct alteration assemblages with chemical groups of the host meteorites excludes the possibility of terrestrial weathering of the CAIs. Phyllosilicates are commonly found in the alteration assemblages of CAIs, chondrules and matrix in the GRV 050179 CM2 chondrites, suggesting aqueous reactions in the parent body. FeO-rich spinels in the CAIs from GRV 023155 CV3 chondrites indicates alteration of these CAIs happened under high oxygen fugacity.

All of the CAIs are classified as Type A and spinel-pyroxene rich, respectively. These CAIs represent continuous gas–solid condensate assemblages, supporting the previous work by Lin and Kimura (2003).

The survey of CAIs in GRV 023155 (CV3), 050179(CM2) and other various chemical groups chondrites, suggests that Type A and spinel-pyroxene inclusions are common in these two meteorites.

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References

- J. Aléon, A.N. Krot, K.D. McKeegan, Calcium–aluminum-rich inclusions and amoeboid olivine aggregates from the CR carbonaceous chondrites. Meteorit. Planet. Sci. 37, 1729–1755 (2002)
- J.N. Connelly, M. Bizzarro, A.N. Krot, Å. Nordlund, D. Wielandt, M.A. Ivanova, The absolute chronology and thermal processing of solids in the solar protoplanetary disk. Science 338, 651–654 (2012)
- D. Dai, Y. Lin, B. Miao, W. Shen, D. Wang, Ca-, Al-rich inclusions in three new carbonaceous chondrites from the Grove Mountains, Antarctica: new evidence for a similar origin of the objects in various groups of *chondrites*. Acta Geol. Sinica 78, 1042–1051 (2004)
- R.C. Greenwood, M.R. Lee, R. Hutchison, D.J. Barber, Formation and alteration of CAIs in Cold Bokkeveld (CM2). Geochim. Cosmochim. Acta 58, 1913–1935 (1994)
- L. Grossman, Condensation in the primitive solar nebula. Geochim. Cosmochim. Acta 36, 597-619 (1972)
- L. Grossman, Petrography and mineral chemistry of Ca-rich inclusions in the Allende meteorite. Geochim. Cosmochim. Acta 39, 433–454 (1975)
- L. Grossman, R. Ganapathy, Trace elements in the Allende meteorite. I—coarse-grained, Ca-rich inclusions. Geochim. Cosmochim. Acta 40, 331–344 (1976a)
- L. Grossman, R. Ganapathy, Trace elements in the Allende meteorite. II—fine-grained, Ca-rich inclusions. Geochim. Cosmochim. Acta 40, 967–977 (1976b)
- Y. Guan, K.D. McKeegan, G.J. MacPherson, Oxygen isotopes in calcium–aluminum-rich inclusions from enstatite chondrites: new evidence for a single CAI source in the solar nebula. Earth Planet. Sci. Lett. 181, 271–277 (2000a)
- Y. Guan, G.R. Huss, G.J. MacPherson, G.J. Wasserburg, Calcium–aluminum-rich inclusions from enstatite chondrites: indigenous or foreign? Science 289, 1330–1333 (2000b)
- G.R. Huss, G.J. MacPherson, G.J. Wasserburg, S.S. Russell, G. Srinivasan, ²⁶Al in CAIs and chondrules from unequilibrated ordinary chondrites. Meteorit. Planet. Sci. 36, 975–997 (2001)
- T.R. Ireland, Correlated morphological, chemical, and isotopic characteristics of hibonites from the Murchison carbonaceous chondrite. Geochim. Cosmochim. Acta **52**, 2827–2839 (1988)
- M. Kimura, H. Hiyagon, H. Palme, B. Spettel, D. Wolf, R.N. Clayton, T.K. Mayeda, T. Sato, A. Suzuki, H. Kojima, Yamato 792947, 793408 and 82038: the most primitive H chondrites, with abundant refractory inclusions. Meteorit. Planet. Sci. 37, 1417–1434 (2002)
- T.V.V. King, E.A. King, Grain size and petrography of C2 and C3 carbonaceous chondrites. Meteoritics **13**, 47–72 (1978)
- A.S. Kornacki, J.A. Wood, Mineral chemistry and origin of spinel-rich inclusions in the Allende CV3 chondrite. Geochim. Cosmochim. Acta 49, 1219–1237 (1985)
- A.N. Krot, T.J. Fagan, K. Keil, K.D. McKeegan, S. Sahijpal, I.D. Hutcheon, M.I. Petaev, H. Yurimoto, Ca, Al-rich inclusions, amoeboid olivine aggregates, and Al-rich chondrules from the unique carbonaceous chondrite Acfer 094: I. mineralogy and petrology3. Geochim. Cosmochim. Acta 68, 2167–2184 (2004)
- A.N. Krot, M.I. Petaev, K. Keil, Mineralogy and petrology of Al-rich objects and amoeboid olivine aggregates in the CH carbonaceous chondrite North West Africa 739. Chem. Erde 66, 57–76 (2006)
- M.R. Lee, R.C. Greenwood, Alteration of calcium- and aluminium-rich inclusions in the Murray (CM2) carbonacoeus chondrite. Meteoritics 29, 780–790 (1994)
- Y. Lin, M. Kimura, Anorthite-spinel-rich inclusions in the Ningqiang carbonaceous chondrite: genetic links with Type A and C inclusions. Meteorit. Planet. Sci. 33, 435–446 (1998)
- Y. Lin, M. Kimura, Two unusual Type B refractory inclusions in the Ningqiang carbonaceous chondrite: evidence for relicts, xenoliths and multi-heating. Geochim. Cosmochim. Acta 64, 4031–4047 (2000)
- Y. Lin, M. Kimura, Ca–Al-rich inclusions from the Ningqiang meteorite: continuous assemblages of the nebular condensates and genetic link to Type Bs. Geochim. Cosmochim. Acta 67, 2251–2267 (2003)
- Y. Lin, A.E. Goresy, Z. Ouyang, Ca-, Al-rich inclusions and Pt-metal nuggets in the Ningqiang carbonaceous chondrite. Chin. Sci. Bull. 44, 725–731 (1999)
- Y. Lin, M. Kimura, H. Hiyagon, A. Monoi, Unusually abundant refractory inclusions from Sahara 97159 (EH3): a comparative study with other groups of chondrites. Geochim. Cosmochim. Acta 67, 4935–4948 (2003)
- Y. Lin, M. Kimura, B. Miao, D. Dai, A. Monoi, Petrographic comparison of refractory inclusions from different chemical groups of chondrites. Meteorit. Planet. Sci. 41, 67–81 (2006)

- Y. Lin, Y. Guan, L.A. Leshin, Z. Ouyang, D. Wang, Short-lived chlorine-36 in a Ca–Al-rich inclusion from the Ningqiang carbonaceous chondrite. Proc. Natl. Acad. Sci. 102, 1306–1311 (2005)
- G.J. MacPherson, L. Grossman, "Fluffy" Type A Ca-, Al-rich inclusions in the Allende meteorite. Geochim. Cosmochim. Acta 48, 29–46 (1984)
- H.Y. McSween Jr, Carbonaceous chondrites of the Ornans type: a metamorphic sequence. Geochim. Cosmochim. Acta 41, 477–491 (1977)
- S.S. Russell, A.M. Davis, G.J. MacPherson, Y. Guan, G.R. Huss, Refractory inclusions from the ungrouped carbonaceous chondrites MAC 87300 and MAC 88107. Meteorit. Planet. Sci. 35, 1051–1066 (2000)
- S.S. Russell, L. Howard, The texture of a fine-grained calcium–aluminium-rich inclusion (CAI) in three dimensions and implications for early solar system condensation. Geochim. Cosmochim. Acta 116, 52–62 (2013)
- S.S. Russell, G.R. Huss, A.J. Fahey, R.C. Greenwood, R. Hutchison, G.J. Wasserburg, An isotopic and petrologic study of calcium–aluminum-rich inclusions from CO3 meteorites. Geochim. Cosmochim. Acta 62, 689–714 (1998)
- Y.J. Sheng, I.D. Hutcheon, G.J. Wasserburg, Origin of plagioclase-olivine inclusions in carbonaceous chondrites. Geochim. Cosmochim. Acta 55, 581–599 (1991)
- F.H. Shu, H. Shang, A.E. Glassgold, T. Lee, X-rays and fluctuating X-winds from protostars. Science 277, 1475–1479 (1997)
- F.H. Shu, H. Shang, M. Gounelle, A.E. Glassgold, T. Lee, The origin of chondrules and refractory inclusions in chondritic meteorites. Astrophys. J. 548, 1029–1050 (2001)
- E. Stolper, Crystallization sequences of Ca–Al-rich inclusions from Allende—an experimental study. Geochim. Cosmochim. Acta 46, 2159–2180 (1982)
- W.R. Van Schmus, J.A. Wood, A chemical-petrologic classification for the chondritic meteorites. Geochim. Cosmochim. Acta 31, 747–765 (1967)
- W.R. Van Schmus, The mineralogy and petrology of chondritic meteorites. Earth Sci. Rev. 5, 145–184 (1969)
- G. Wang, Y. Lin, D. Dai, Bulk Mg isotopic compositions of Ca-, Al-rich inclusions and amoeboid olivine aggregates. Meteorit. Planet. Sci. 42, 1281–1289 (2007)
- D.A. Wark, Plagioclase-rich inclusions in carbonaceous chondrite meteorites: liquid condensates? Geochim. Cosmochim. Acta 51, 221–242 (1987)
- D.A. Wark, J.F. Lovering, Marker events in the early evolution of the solar system: evidence from rims on Ca–Al-rich inclusions in carbonaceous chondrites. Proceedings on Lunar and Planet Science Conference 8th, 95–112 (1977)
- D.A. Wark, W.V. Boynton, The formation of rims on calcium–aluminum-rich inclusions: step I—flash heating. Meteorit. Planet. Sci. 36, 1135–1166 (2001)
- D.A. Wark, J.F. Lovering, The nature and origin of type B1 and B2 Ca–Al-rich inclusions in the Allende meteorite. Geochim. Cosmochim. Acta 46, 2581–2594 (1982)
- S. Yoneda, L. Grossman, Condensation of CaO–MgO–Al₂O₃–SiO₂ liquids from cosmic gases. Geochim. Cosmochim. Acta 59, 3413–3444 (1995)