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Unusual inclusions within olivine megacrysts in the Dar al Gani 735 shergottite

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Abstract: Unusual inclusions occur within olivine megacrysts in the DaG735 olivine-phyric shergottite. They consist of pyroxene and chromite in a ratio of about 2 : 1, and show strange textures. They are grouped into two types, symplectic and non-symplectic. The pyroxenes in unusual inclusions are similar in composition to those in the main lithology of DaG735, but the chromites differ in TiO_2 contents which are lower by half than those of chromites in the main lithology. The symplectic textures indicate exsolution origin of the unusual inclusions within olivine megacrysts, and the reaction to produce the unusual inclusions suggests that the original olivine megacrysts may have contained some amounts of Cr^{+2} in addition to Cr^{+3}, and the Cr^{+2} was oxidized to Cr^{+3} during the formation of the unusual inclusions.

key words: martian meteorites, olivine-phyric shergottites, DaG735, inclusions in olivine, chromite

1. Introduction

Dar al Gani 735 (DaG735) was recovered from the Saharan desert (Libya) in 1996/1997, and was recently identified as a shergottite (Grossman, 2000). It is suggested to be paired with other Libyan shergottites, DaG476/489/670/876/975 (Folco *et al*., 1999; Folco and Franchi, 2000), which are well studied by many authors. They contain zoned olivine megacrysts which have been discussed to be either xenocrysts or phenocrysts (Zipfel *et al*., 2000; Wadhwa *et al*., 2001; Mikouchi *et al*., 2001). The olivine megacrysts in the NWA1068 olivine-phyric shergottite are interpreted as disrupted cumulates (Barrat *et al*., 2002). Probably the olivine megacrysts in DaG735 may have been derived from olivine cumulates which were mixed with a basaltic magma.

The olivine megacrysts contain mineral inclusions of chromite in DaG476 (Zipfel *et al*., 2000; Mikouchi *et al*., 2001), DaG489 (Folco and Franchi, 2000), and in both (Wadhwa *et al*., 2001). Some of chromite inclusions within olivine megacrysts associate intimately with pyroxene (Zipfel *et al*., 2000; Wadhwa *et al*., 2001), and the inclusions were considered to be produced by exsolution from the host olivine (Ikeda, 2001). The curious inclusions within olivine megacrysts consist of chromite and pyroxene, and are defined here as ‘unusual inclusions’. The origin of the unusual inclusions will be discussed in this paper.

2. Petrography and mineralogy of DaG735

DaG735 is an olivine-phyric shergottite with a porphyritic texture, consisting of olivine megacrysts and groundmass (Fig. 1a). The groundmass consists mainly of olivine, pyroxene, maskelynite, chromite, ilmenite, phosphate, and sulfide. The mineral compositions were obtained using an electron-probe microanalyzer.

2.1. *Olivine*

Modal abundance of olivine in DaG735 was measured on BSE images of three thin sections (α, β, γ), and is about 17.3 vol% in average (Table 1). DaG476/489/670 contain olivine in similar amounts to DaG735 (Table 1). There are two types of olivine in DaG735, zoned olivine megacrysts ($>$~1 mm in size) and smaller homogeneous olivine grains ($<$~0.5 mm in size) (Fig. 1a). The volume ratio of the zoned olivine megacrysts to the homogeneous olivine grains is about 4 : 1.

The zoned olivine megacrysts range in composition from magnesian cores of Fo_{78} to ferroan rims of Fo_{58}, and contain (a) unusual inclusions and (b) normal mineral inclusions of pyroxene or chromite. The smaller homogeneous olivine grains occur in the groundmass and have a narrow range of composition from Fo_{63} to Fo_{58}, sometimes containing (c) magmatic inclusions and (d) normal mineral inclusions of the groundmassic minerals such as pyroxene, maskelynite, or chromite. The chemical compositions of a core and rim of a zoned olivine megacryst and a homogeneous olivine grain are shown in Table 2.

2.2. *Pyroxene*

Pyroxenes occur in the groundmass, and are composed of orthopyroxene (Opx), pigeonite (Pig), and augite (Aug). The pigeonite is dominant in the groundmass. The low-Ca pyroxene has chemical zoning from magnesian orthopyroxene ($En_{82}Wo_2$) to more ferroan pigeonite ($En_{56}Wo_{12\sim14}$), and ferroan orthopyroxene rarely occurs in rims of pigeonite. Augite occurs at rims of pigeonite of the groundmass, but it is minor. The chemical compositions of pyroxenes are shown in Table 2 and Fig. 2a.

Crystallization temperatures of pyroxenes are estimated from pairs of augite and pigeonite using the two-pyroxene geothermometer (Lindsley and Andersen, 1983). The temperatures are 1240°C for a magnesian pair and 1150°C for a ferroan pair.

2.3. *Maskelynite*

Maskelynite occurs as an interstitial phase in the groundmass and shows chemical zoning from calcic core ($An_{\sim70}$) to sodic rim (An_{48}). The chemical compositions of the core and rim of a maskelynite grain are shown in Table 2.

2.4. *Chromite*

Chromite occurs in contact with maskelynite in the groundmass and as inclusions in olivine and pyroxene. Most of chromite grains in the groundmass are larger than a few tens of μm, whereas most of chromite grains in olivine and pyroxene are smaller

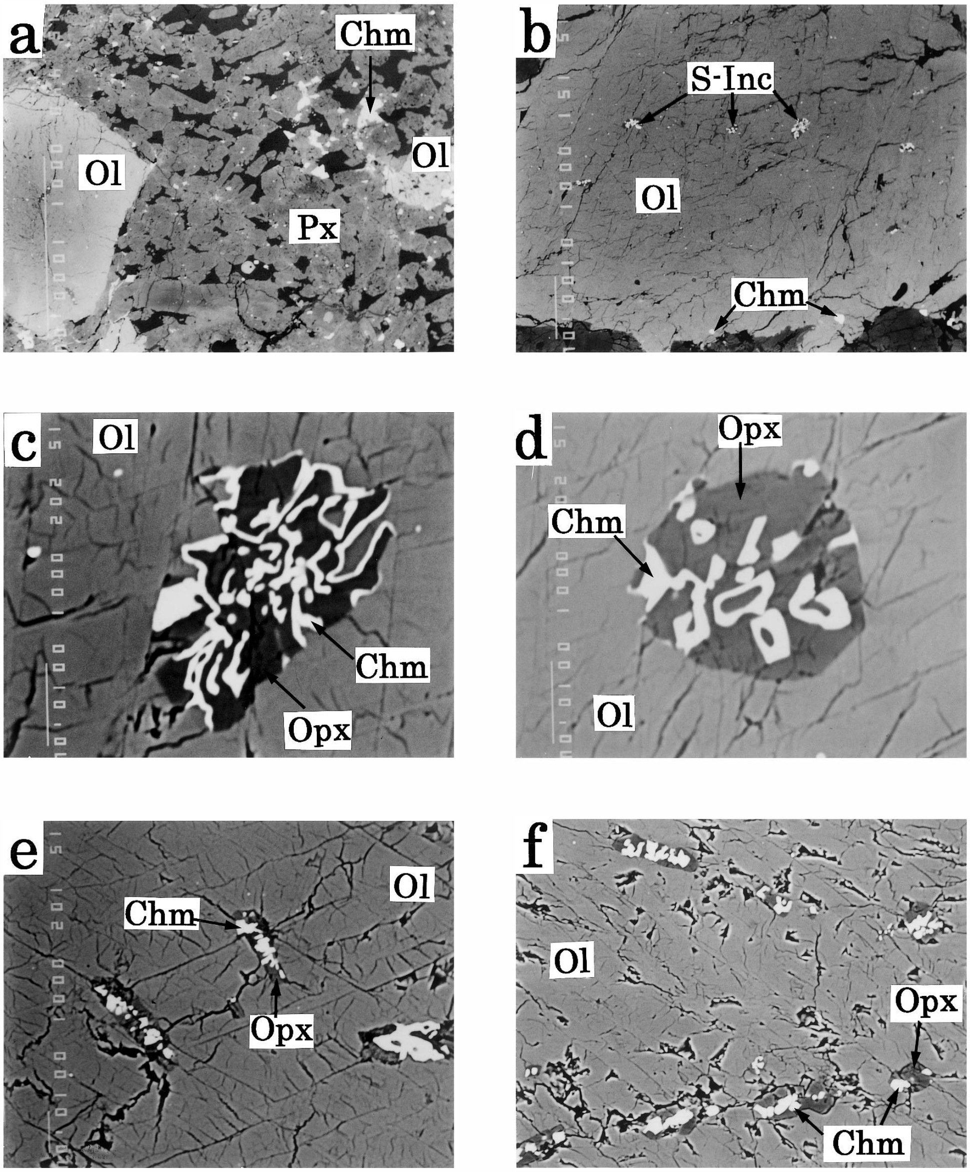

Fig. 1. Back-scattered electron (BSE) images of DaG735 and unusual inclusions within olivine megacrysts in DaG735. (a) A megacryst of olivine (Ol) set in the groundmass consisting mainly of smaller olivine (Ol), pyroxene (Px), maskelynite (a dark phase), and chromite (Chm). Width is about 2.5 mm. (b) Unusual inclusions (symplectic type, S-Inc) occur in the magnesian core of an olivine megacryst, and normal mineral inclusions (chromite, Chm) occur in the ferroan rim. Width is about 1.2 mm. (c) and (d) Symplectic inclusions consisting of orthopyroxene (Opx) and chromite (Chm). Width is about 56 μm. (e) Non-symplectic inclusions consisting of orthopyroxene (Opx) and chromite (Chm) occur within an olivine megacryst. An inclusion of intermediate type between symplectic and non-symplectic types occurs at right. Width is about 110 μm. (f) Non-symplectic inclusions occur in linear alignment. Width is about 110 μm.

Table 1. Modal% of olivines in DaG735 and other paired Libyan shergottites. Modal abundance of olivine in DaG735 was measured, using transparent section-papers put on BSE images of three thin sections (α, β, γ) of DaG735.

DaG735	α	14.8%
	β	14.7%
	γ	22.5%
	average	17.3%
DaG476	Zipfel *et al.* (2000)	14–17%
	Wadhwa *et al.* (2001)	10.4%
	Mikouchi *et al.* (2001)	24%
DaG489	Falco *et al.* (1999)	21%
	Wadhwa *et al.* (2001)	17.8%
DaG670	Folco and Franchi (2000)	11%

Table 2. Chemical compositions of the constituent minerals in DaG735.

	Ol Megacrysts		H. Ol	Pyroxenes				Maskelynite		Ilm	Whitl.	Chromite		
	Core	Rim		m.Opx	Pig	Aug	f.Opx	Core	Rim			(A)	(B)	(C)
SiO_2	39.35	36.83	35.77	56.00	53.87	53.22	53.34	51.56	56.10	0.00	0.07	0.00	0.00	0.00
TiO_2	0.00	0.00	0.00	0.00	0.07	0.65	0.30	0.01	0.16	53.44	0.00	0.42	1.99	21.65
Al_2O_3	0.00	0.00	0.00	0.59	1.07	1.48	0.82	30.79	26.99	0.04	0.00	5.84	10.35	3.78
Cr_2O_3	0.12	0.00	0.00	0.62	0.32	0.50	0.35	0.00	0.00	0.16	0.00	61.68	53.91	18.14
FeO	19.98	33.68	34.97	10.79	16.76	11.26	19.78	0.17	0.55	41.11	1.22	27.95	28.27	52.68
MnO	0.40	0.51	0.65	0.35	0.80	0.34	0.53	0.00	0.00	0.91	0.06	0.37	0.33	0.65
MgO	39.66	29.51	28.38	30.13	22.02	15.45	22.35	0.18	0.07	3.51	3.38	4.00	4.19	3.49
CaO	0.14	0.15	0.10	0.93	5.28	16.37	2.20	14.05	9.65	0.14	47.03	0.00	0.02	0.03
Na_2O	0.04	0.00	0.00	0.00	0.08	0.24	0.04	3.38	5.75	0.06	1.72	0.00	0.08	0.00
K_2O	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.03	0.19	0.03	0.00	0.00	0.00	0.00
P_2O_5	-	-	-	-	-	-	-	-	-	-	46.87	-	-	-
Total	99.70	100.67	99.87	99.45	100.26	99.52	99.71	100.18	99.45	99.41	100.34	100.26	99.14	100.42
mg	0.78	0.61	0.59	0.83	0.70	0.71	0.67			0.13	0.83	0.20	0.21	0.11
Ab								30	51					

Olivine (Ol), homogeneous (H.), ilmenite (Ilm), whitlockite (Whitl.), magnesian (m.), ferroan (f.), orthopyroxene (Opx), pigeonite (Pig), augite (Aug), Mg/(Mg+Fe) ratio (mg), albite components (Ab), Cr-rich chromite (A), Al-rich (B), and Ti-rich (C).

than a few tens of μm (Fig. 1b). Chromite occurs also in unusual inclusions within olivine megacrysts, which will be discussed in detail later.

Chromite in groundmass occurs mostly in contact with maskelynite, and zones in composition from Cr-rich cores to Ti-rich rims (Fig. 3a). The chemical compositions are plotted with a trend through (A)–(B)–(C) in Fig. 3b, where chromites in groundmass form a compositional trend from Cr-rich cores (A) via Al-rich chromite at a bending point (B) to Ti-rich rims (C). Their representative chemical compositions at (A), (B), and (C) are shown in Table 2.

The zoning trend of chromite may have been produced by the fractional crystallization of the DaG735 magma. The primary chromite was Cr-rich (A), and the crystallization of olivine and pyroxene changed the original magma to Al-rich residual magma, forming Al-rich chromites (B). Plagioclase began to crystallize, and suppressed the increase of Al, but Ti continued to increase in the residual magma,

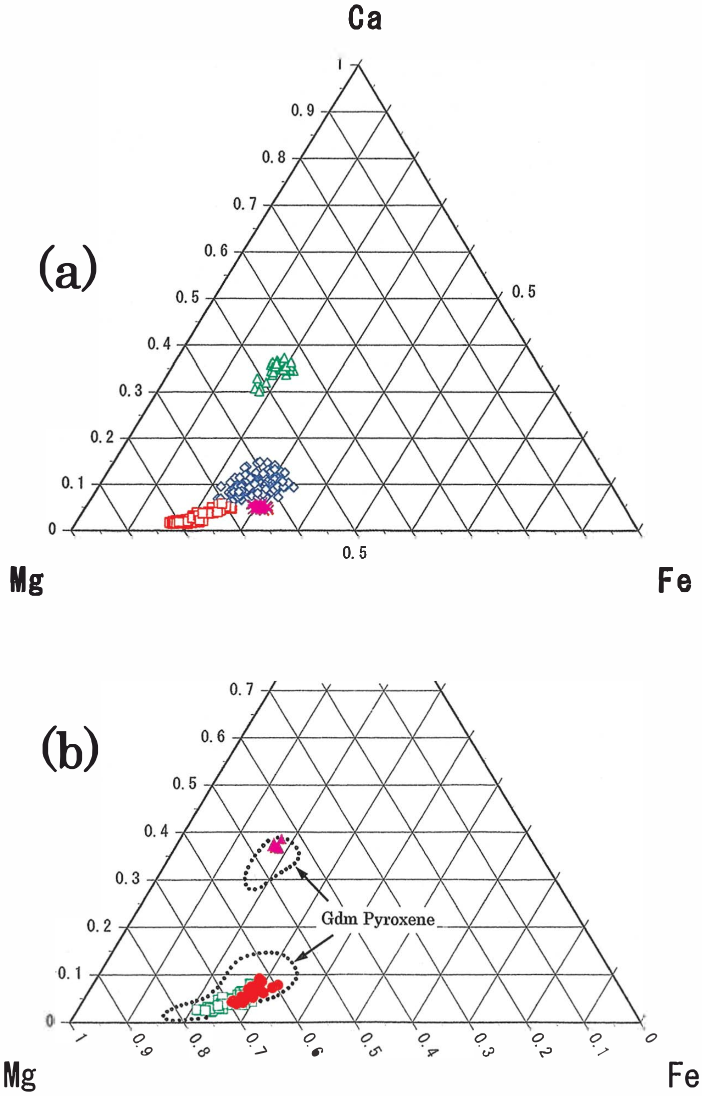

Fig. 2. *Pyroxenes in DaG735 are plotted in a diagram of Ca-Mg-Fe in atomic ratios. (a) Pyroxenes in the groundmass. Usually, the CaO contents of orthopyroxene and pigeonite in DaG735 are <3.0 wt% and >3.0 wt%, respectively. Red square (orthopyroxene), blue diamond (pigeonite), green triangle (augite), and purple cross (more ferroan orthopyroxene). (b) Pyroxenes in unusual inclusions are plotted. Green square (orthopyroxene in unusual inclusions, symplectic type), red circle (orthopyroxene and pigeonite in unusual inclusions, non-symplectic type), and purple triangle (augite in unusual inclusions, non-symplectic type). The compositional ranges of pyroxenes in the main lithology in DaG735 are shown by dotted lines designated by [Gdm Pyroxenes].*

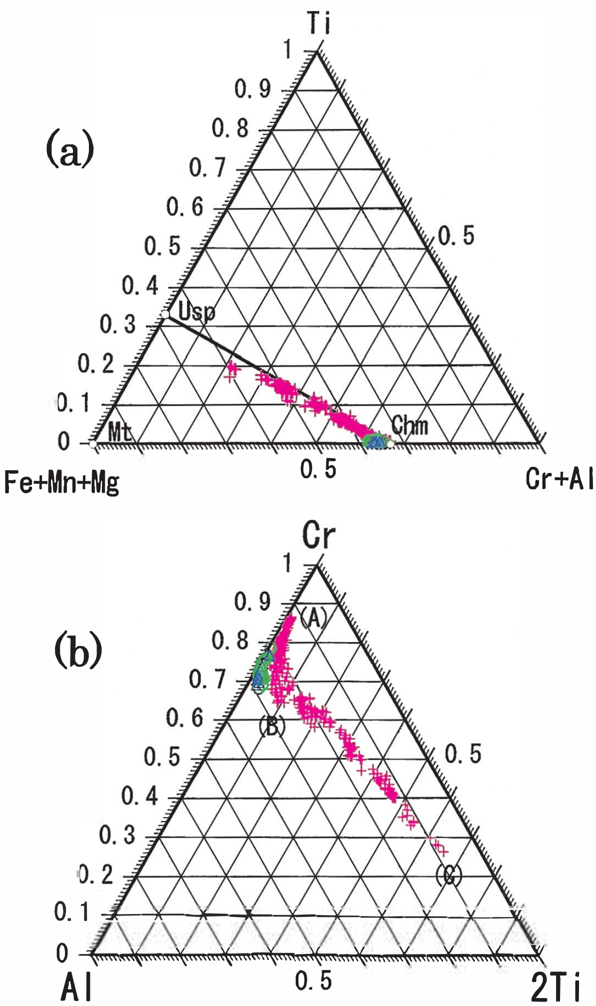

Fig. 3. Chromites are plotted in (a) Ti–(Fe+Mn+Mg)–(Cr+Al) and in (b) Cr–Al–2Ti in atomic ratios. Red symbol (chromite in contact with maskelynite), green circle (chromite in unusual inclusions, symplectic type), and blue triangle (chromite in unusual inclusions, non-symplectic type). The end components of chromite (Chm), ulvöspinel (Usp), and magnetite (Mt) are shown by open circles, and a solid solution between chromite and ulvöspinel is shown by a bold line in Fig. 3a. Cr-rich, Al-rich, and Ti-rich chromites are designated by (A), (B), and (C), respectively in Fig. 3b.

resulting in chromites (B) to (C). Finally, Ti-rich chromite (or ulvöspinel) (C) precipitated together with ilmenite at the latest stage of the fractional crystallization.

2.5. *Other minerals*

Ilmenite, phosphate, and sulfide occur in the groundmass. Ilmenite and whitlockite are rich in MgO (Table 2). Calcite veins, several to a few tens of μm in width, run through the meteorite, and they are terrestrial weathering products.

3. Unusual inclusions

Unusual inclusions often occur in olivine megacrysts zoned in composition from $Fo_{\sim 78}$ to $Fo_{\sim 62}$ in DaG735 (Fig. 1b). They are smaller than ~30 μm in width, and the ratios of unusual inclusions to the host olivine are 0.1–0.5% in area. They consist of pyroxene and chromite, and the volume ratio of pyroxene to chromite is about 2 : 1 (Figs. 1c, d, e and f). There are two types of unusual inclusions, symplectic and non-symplectic. Symplectic type occurs within magnesian olivine (Fo_{78} to Fo_{68}), 10–30 μm across in size, and consists of orthopyroxene and Ti-poor chromite. The symplectic type shows strange textures that orthopyroxene contains anhedral worm-like chromite grains (Figs. 1c and d). Non-symplectic type occurs mostly in olivine with intermediate compositions ($Fo_{\sim 70}$ to $Fo_{\sim 62}$) within zoned olivine megacrysts and is smaller than the symplectic type, 5–10 μm in width (Figs. 1e and f). It consists of pyroxenes and chromite without symplectic textures, although intermediate type between the two types rarely occurs (Fig. 1e). The pyroxenes are orthopyroxene in unusual inclusions within magnesian olivine, although those are pigeonite (or rarely augite) within more ferroan olivine. Non-symplectic inclusions sometimes occur in linear alignment (Fig. 1f). The chemical compositions of pyroxene and chromite in unusual inclusions are shown in Table 3 and plotted in Figs. 2b and 3b.

The pyroxene in unusual inclusions shows a good correlation in Fe/(Mg+Fe) atomic ratios to the host olivine (Fig. 4). This indicates that the unusual inclusions are in equilibrium with the host olivine. The partition coefficient of Fe-Mg between the host olivine and the pyroxene in unusual inclusions ($K^{Fe\text{-}Mg}_{Ol\text{-}Pyx}$) is about 1.2, suggesting that they were in equilibrium at magmatic temperatures.

Table 3. Chemical compositions of pyroxene and chromite in unusual inclusions within olivine megacrysts in DaG735.

	Opx	Pig	Opx	Pig	Aug	Chm	Chm	Chm	Chm
	S-type	S-type	N-type	N-type	N-type	S-type	S-type	N-type	N-type
SiO_2	55.56	54.02	54.09	54.05	52.70	0.10	0.00	0.07	0.22
TiO_2	0.00	0.06	0.00	0.06	0.43	0.11	0.48	0.49	0.84
Al_2O_3	0.61	0.75	0.67	0.60	1.45	11.81	13.27	10.66	13.04
Cr_2O_3	0.76	0.34	0.43	0.31	0.69	53.47	51.96	54.97	48.40
FeO	13.43	17.51	17.96	20.14	10.88	26.73	28.90	28.19	32.03
MnO	0.50	0.45	0.74	0.60	0.49	0.21	0.51	0.55	0.96
MgO	27.41	22.84	24.09	20.65	14.87	5.83	5.40	3.96	3.78
CaO	1.35	3.99	2.09	3.79	18.38	0.00	0.00	0.00	0.00
Na_2O	0.03	0.01	0.06	0.12	0.36	0.00	0.00	0.16	0.09
K_2O	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.01	0.00
Total	99.68	99.97	100.12	100.35	100.25	98.25	100.53	99.04	99.37
mg	0.78	0.70	0.71	0.65	0.71	0.28	0.25	0.20	0.17

Symplectic type (S-type) and Non-symplectic type (N-type).

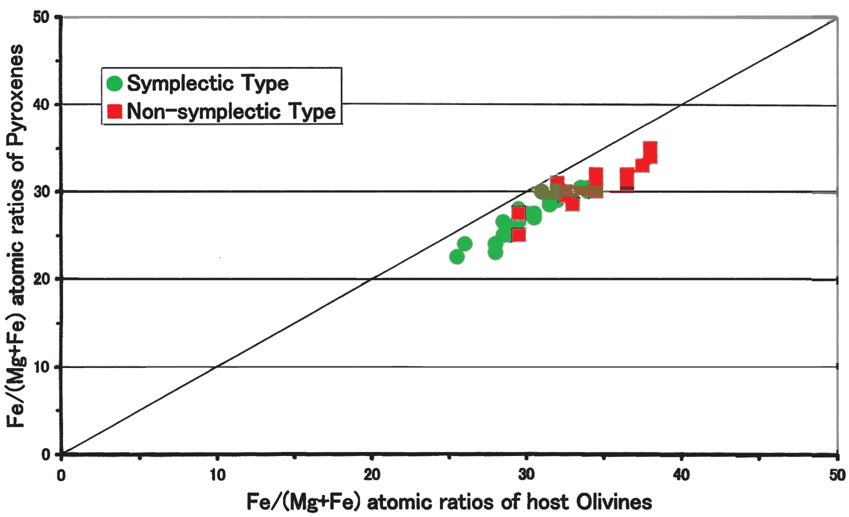

Fig. 4. Correlationship of mg ratios between pyroxenes in unusual inclusions and the directly contacting host olivines.

4. Origin of unusual inclusions

The symplectic textures (Figs. 1c, d) suggest that the unusual inclusions may have produced by exsolution of Cr-olivine components within the original olivine megacrysts. A possible reaction is;

$$(M_4Cr^{+2}{}_2)_6Si_3O_{12}+1/2O_2 \rightarrow M_3Si_3O_9+MCr^{+3}{}_2O_4, \quad (1)$$

Olivine → Pyroxene Chromite

where M is divalent ions such as Mg^{+2} and Fe^{+2}. The reaction takes place under an oxidized condition to introduce oxygen into the olivine megacrysts. The product consists of low-Ca pyroxene and chromite in ratio of about 2 : 1, because volume of minerals roughly correlates to the numbers of the constituent oxygen, and the ratio of pyroxene to chromite in the product of eq. (1) is 9 : 4.

Chromite in unusual inclusions contains small amounts of Al_2O_3, and the component can be introduced into the chromite according to following reaction;

$$(M_5T_2\square)_8Si_4O_{16} \rightarrow M_4Si_4O_{16}+MT_2O_4, \quad (2)$$

Olivine → Pyroxene Al-chromite

where T is trivalent ions such as Al^{+3} and Cr^{+3}, and $\square$ is defects in crystallographic olivine lattice (vacancy). As the ratio of pyroxene and chromite (4 : 1) in the products of eq. (2) differs from the ratio (2 : 1) for the unusual inclusions in DaG735, the reaction should be limited to minor contribution for formation of the unusual inclusions. TiO_2 contents of the chromite in unusual inclusions are less than 1 wt% and lower than the chromite (A) to (B) in the main lithology (Fig. 3b). The low TiO_2 contents of the chromite in unusual inclusions may be due to the low Ti contents of the original olivine megacrysts.

Exsolution lamellae within olivine are reported from Chassigny (Greshake *et al*., 1998), Governador Valadares (Mikouchi and Miyamoto, 1998; Greshake *et al*., 2000), and Yamato nakhlites (Imae *et al*., 2004). The exsolution lamellae are very thin, with less than 1 μm in width, and consist of augite and magnetite (Mikouchi *et al*., 2000). Original olivine in nakhlites may have contain high Ca contents, which exsolved under a cooling condition. A possible reaction is;

$$\underset{\text{Olivine}}{(CaMg_2Fe_3)_6Si_3O_{12}} + {}^{1/2}O_2 \rightarrow \underset{\text{Augite}}{(CaMg_2)_3Si_3O_9} + \underset{\text{Magnetite}}{Fe_3O_4}. \quad (3)$$

Equation (3) for nakhlites differs from eq. (1) for DaG735 shergottite; the difference may come from high Ca contents of original olivine in nakhlites, and magnesian olivines in DaG735 may have contained high Cr contents to produce chromite instead of magnetite.

Origin of symplectic exsolution in terrestrial olivines was discussed by Moseley (1984). He presented a reaction to produce symplectites consisting of pyroxene and magnetite in olivine grains;

$$\underset{\text{Olivine}}{(Fe^{+3}{}_4\square_2)_6Si_3O_{12}} + \underset{\text{Olivine}}{Fe^{+2}{}_2SiO_4} + \underset{\text{Olivine}}{M_8Si_4O_{16}} \rightarrow \underset{\text{Magnetite}}{Fe_6O_8} + \underset{\text{Pyroxene}}{M_8Si_8O_{24}}, \quad (4)$$

where M is Ca, Mg, and Fe^{+2}. If the unusual inclusions in DaG735 are produced by eq. (4), Fe^{+3} in the reactants must be replaced by Cr^{+3}. Then, the ratio (3 : 1) of pyroxene and chromite in the products of eq. (4) is similar to the ratio (2 : 1) for the unusual inclusions in DaG735. Therefore, eq. (4) is another candidate for formation of the unusual inclusions. The critical difference between eqs. (1) and (4) is the introduced oxygen during the reaction; eq. (1) is under an open system for oxygen, whereas eq. (4) is under a closed system for oxygen.

Nitsan (1974) reported stability of terrestrial olivines with respect to oxidation and reduction. His reaction is;

$$\underset{\text{Olivine}}{(M_3Fe_3)_6Si_3O_{12}} + {}^{1/2}O_2 \rightarrow \underset{\text{Pyroxene}}{M_3Si_3O_9} + \underset{\text{Magnetite}}{Fe_3O_4}. \quad (5)$$

This equation is almost the same as eq. (1), but differs in products; chromite in eq. (1) and magnetite in eq. (5).

The chemical compositions of chromites in DaG735 are obtained using an electron-probe microanalyzer, and the ferric iron contents are not known. However, the magnetite molecules (Fe_3O_4) of chromites are estimated on an assumption that chromites in DaG735 are stoichiometric in composition. The magnetite molecule contents of chromites (A) and (B) in the groundmass of DaG735 seem to be lower than 10 mole %. The magnetite molecules in chromite in unusual inclusions are also less than 10% (Fig. 3a), suggesting that these chromites were produced under a relatively lower oxygen fugacity in the early to middle stages of crystallization of DaG735. DaG476/489 seem to have experienced more reducing crystallization conditions than other shergottites except for QUE94201 (Wadhwa *et al*., 2001). The shergottite source region seems to have an oxidation state about 2 or 3 orders of magnitude below the quartz-fayalite-magnetite (QFM) oxygen reference buffer (Ghosal *et al*., 1998), and Herd (2003) estimated the oxygen fugacity of the DaG476 to be [QFM-2.5] at temperatures around 1018℃.

The olivine megacrysts in DaG735 may have derived from olivine cumulates which were mixed by a basaltic magma. The trend (A)–(B)–(C) of chromite in the groundmass was produced by fractional crystallization of the DaG735 magma, whereas the chromite in unusual inclusions was produced within olivine megacrysts which derived from olivine cumulates. However, the pyroxene and chromite in unusual inclusions have similar compositions to those in the main lithology of DaG735 except low TiO_2 contents of the chromite in unusual inclusions (Figs. 2 and 3), suggesting that original olivine megacrysts have saturated in the pyroxene and chromite components similar to magnesian low-Ca pyroxene and Cr-Al-rich chromite in the groundmass. This suggests that the olivine cumulates had co-genetic relationship with the basaltic magma for DaG 735. Probably the olivine cumulates had a fugacity of O_2 slightly lower than that for the basaltic magma of DaG735, and the olivines may have contained some amounts of Cr^{+2} in addition to Cr^{+3}. The mixing of the two resulted in oxidation of the olivine megacrysts to produce the unusual inclusions in them by eqs. (1) and (4).

Unusual inclusions in non-symplectic type often show linear alignments within olivine megacrysts in DaG735 (Fig. 1f). Olivine in DaG476 has shock metamorphic features (Greshake and Stöffler, 1999), suggesting that they have experienced plural shock events. Some olivine megacrysts in DaG476 contain planar fractures, which can be used for nucleation sites of unusual inclusions. Probably the linear alignment of non-symplectic unusual inclusions in DaG735 may be produced along shock-induced planar fractures within olivine megacrysts before the excavation of DaG735 from Mars.

5. Summary

(1) DaG735 contains unusual inclusions and normal mineral inclusions within zoned olivine megacrysts. The unusual inclusions consist of pyroxene and chromite in a ratio of about 2 : 1.

(2) Chromite in contact with maskelynite in the groundmass shows the magmatic trend (A)–(B)–(C). Chromite in unusual inclusions within magnesian zoned olivine megacrysts has compositions similar to chromites (A) to (B), but is poorer in TiO_2 contents.

(3) Unusual inclusions were produced by exsolution within their host olivine megacrysts. The original magnesian olivine megacrysts may have contained some amounts of Cr^{+2}, which was oxidized to produce unusual inclusions consisting of pyroxene and chromite. Equations (1) and (4) are possible candidates for the reactions to produce the unusual inclusions in DaG735.

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