

Meteoritics & Planetary Science 41, Nr 7, 1045–1057 (2006) Abstract available online at http://meteoritics.org

Petrology and geochemistry of the fine-grained, unbrecciated diogenite Northwest Africa 4215

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(Received 31 January 2006; revision accepted 13 April 2006)

Abstract–We report on the petrology and geochemistry of Northwest Africa (NWA) 4215, an unbrecciated diogenite recovered in the Sahara. This single stone, weighing 46.4 g, displays a well-preserved cumulative texture. It consists of zoned xenomorphic orthopyroxene grains on the order of 500 μ m in size, along with a few large chromite crystals (<5 vol%, up to 3 mm). Accessory olivine and scarce diopside grains occur within the groundmass, usually around the chromite crystals. Minor phases are cristobalite, troilite, and metal. Unlike other diogenites, orthopyroxenes (En_{76.2}Wo_{1.1}Fs_{22.7} to En_{68.6}Wo_{5.5}Fs_{25.9}), olivines (Fo₇₆ to Fo₇₁), and chromites (Mg# = 14.3 44.0, Cr# = 42.2–86.5) are chemically zoned. The minor element behavior in orthopyroxenes and the intricate chemical profiles obtained in chromites indicate that the zonings do not mirror the evolution of the parental melt. We suggest that they resulted from reaction of the crystals with intercumulus melt. In order to preserve the observed zoning profiles, NWA 4215 clearly cooled significantly faster than other diogenites. Indeed, the cooling rate determined from the diffusion of Cr in olivine abutting chromite is in the order of 10– 50 °C/a, suggesting that NWA 4215 formed within a small, shallow intrusion.

The bulk composition of NWA 4215 has been determined for major and trace elements. This meteorite is weathered and its fractures are filled with calcite, limonite, and gypsum, typical of hot desert alteration. In particular, the FeO, CaO abundances and most of the trace element concentrations (Sr, Ba, Pb, and REE among others) are high and indicate a significant contribution from the secondary minerals. To remove the terrestrial contribution, we have leached with HCl a subsample of the meteorite. The residue, made essentially of orthopyroxene and chromite, has similar major and trace element abundances to diogenites as shown by the shape of its REE pattern or by its high Al/Ga ratio. The connection of NWA 4215 with diogenites is confirmed by its O-isotopic composition ($\delta^{17}O = 1.431 \pm 0.102\%$, $\delta^{18}O = 3.203 \pm 0.205\%$, $\Delta^{17}O = -0.248 \pm 0.005\%$).

INTRODUCTION

The howardite, eucrite, and diogenite (HED) suite are thought to sample the early igneous activity on the same small body, probably the asteroid 4 Vesta (Drake 2001). Eucrites have magmatic textures and chemical compositions indicating formation as lava flows, or intrusions, and are widely believed to be samples of the main upper crustal lithologies from the parent body. Diogenites are orthopyroxene-rich cumulates, which probably represent material from deeper crustal levels that was excavated and exposed by large impacts (e.g., Takeda 1979). Howardites are polymict breccias consisting mainly of eucritic and diogenitic lithologies.

HED meteorites have been extensively studied because they offer a unique opportunity to understand the igneous processes operating on small asteroids in the early solar system. Unfortunately, most HED meteorites also record a complex post-crystallization history that includes a prolonged stage of thermal metamorphism and many impact events. Thus, these meteorites are usually breccias consisting of a mixture of strongly metamorphosed crystal debris and rock fragments. For example, the vast majority of pyroxene crystals found in eucrites lack magmatic zoning and contain lamellae exsolution that formed during thermal metamorphism. Diogenites are no exception. They contain orthopyroxenes and chromites that have homogeneous major element compositions as a result of metamorphism. In addition, most diogenites show evidence of brecciation. Unbrecciated examples, such as Grosvenor Mountains (GRO) 95555 or Tatahouine, are extremely rare.

Until a few months ago, the possibility of finding an unbrecciated diogenite exhibiting crystals that preserved chemical zoning seemed to us to be fairly remote. We were therefore very surprised to identify Northwest Africa (NWA) 4215, a new diogenite that displays all of these features. In this paper, we present a petrological and chemical study of this unique orthopyroxenite. It will be shown that it clearly cooled much faster than the other diogenites and probably formed within a small, shallow magma body.

ANALYTICAL METHODS

Petrographic observations and quantitative chemical analyses of the various mineral phases of NWA 4215 were made on two polished sections of about 1 cm² each. Electron microprobe analyses were carried out at Ifremer (Centre de Brest) with a Cameca SX50. Analyses were generally obtained at 15 kV accelerating voltage with a sample current of 12 nA.

Major and trace element concentrations were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS), respectively, in Brest according to the procedures described, respectively, by Cotten et al. (1995) and Barrat et al. (2000). The accuracy of major and trace element concentrations is better than 5% (probably better than 3% for all the REEs), except for W (from 10–30% for the lowest concentrations) based on various standards and sample duplicates.

Oxygen isotope analyses were carried out using an infrared laser fluorination system following the methods and procedures of Miller et al. (1999). O₂ was analyzed using a Micromass Prism III dual inlet mass spectrometer. System precision (1 σ), based on replicate analyses of international (NBS-28 quartz, UWG-2 garnet) and internal standards, is approximately ±0.04‰ for δ^{17} O; ±0.08‰ for δ^{18} O; ±0.024‰ for Δ^{17} O (Miller et al. 1999). Quoted precision (1 σ) for NWA 4215 is based on replicate analyses. Results are reported in standard notation where δ^{18} O has been calculated as: δ^{18} O = ((18 O/ 16 Osample/ 18 O/ 16 Oref) – 1) × 1000 and similarly for δ^{17} O using 17 O/ 16 O ratio. Δ^{17} O has been calculated as: Δ^{17} O = 1000 ln (1+ (δ^{17} O/1000)) – λ 1000 ln (1+ (δ^{18} O/1000))) where λ = 0.5247 (Miller 2002).

RESULTS

Petrography

NWA 4215 is an unbrecciated brown rock weighing 46.4 g and coated by a dark film of desert varnish. A few fusion crust patches have been preserved. Weathering is significant, with a mixture of terrestrial calcite, limonite, and accessory gypsum filling fractures.

The sawn surfaces display a few large chromite crystals (<5 vol%, up to 3 mm) irregularly dispersed in a finemedium-grained groundmass. SEM observations and chemical mapping of sections (Fig. 1) indicate that NWA 4215 has a well-preserved cumulative texture (adcumulate). The groundmass is essentially composed of xenomorphic orthopyroxene grains on the order of 500 µm in size, which contain numerous inclusions (sometimes composite), of troilite, metal, and silica. Accessory olivine and scarce diopside grains occur within the groundmass, usually around the large chromite crystals. Interestingly, the shape of the chromite crystals is irregular, sometimes amoebiform (Fig. 1) and occasionally have offshoots (up to 100 µm in length). Additionally, chromite crystals contain numerous metal and troilite inclusions, and composite pyroxene inclusions (orthopyroxene + diopside \pm metal and troilite).

Mineral Compositions

Representative analyses of the mineral phases are given in Tables 1 and 2.

Pyroxene

Groundmass pyroxenes are normally zoned (Fig. 2). Their compositions range from En_{76.2}Wo_{1.1}Fs_{22.7} in the most Mg-rich cores to En_{68 6}Wo_{5 5}Fs_{25 9} in the rims (Fig. 3), and are similar to typical diogenitic pyroxenes (e.g., Mittlefehldt 1994a; Fowler et al. 1994). Interestingly, the highest wollastonite contents are found in the rims of the grains located close to the large chromite crystals, as illustrated by the detailed chemical mapping (Fig. 1). Minor elements are also zoned from core to rim (Fig. 2). The compositions of the cores closely resemble those of diogenitic pyroxenes (Fig. 4), although many NWA 4215 pyroxene rims are significantly richer in Al₂O₃ (up to 3 wt%) and TiO₂ (up to 0.5 wt%), while Cr₂O₃ displays rather homogeneous abundances. The composite pyroxene inclusions found in chromite crystals are made of orthopyroxene (En77-71Wo1-4Fs18-25) and diopside $(En_{45-49}Wo_{41-44}Fs_{9-12})$, whose compositions overlap those of the groundmass pyroxenes (Table 1; Fig. 3).

Olivine

Olivine grains are zoned from Fo_{76} to Fo_{71} (average Fo_{73}). A limited Cr enrichment has been detected in rims when crystals abut chromite, although their Cr_2O_3 contents



Fig. 1. Mg, Al, and Ca distribution maps of a selected area of a polished section of NWA 4215 (Chr = chromite, Ol = olivine, and Opx = orthopyroxene).

are always lower than 1 wt%. Chemical profiles obtained on two separate olivine grains in contact with the same chromite crystal are consistent with diffusive reequilibration with chromite over a few tens of microns (Fig. 5).

Chromite

In NWA 4215, chromite displays an astonishing range of compositions. The abundances of Cr_2O_3 varies from 34.5 to 61.6 wt%, Al_2O_3 from 6.2 to 31.6 wt%, FeO from 22.5 to 37.3 wt%, and MgO from 2.7 to 10 wt%. As a consequence the Mg# (=100 Mg/(Mg + Fe), atomic), and Cr# (=100 Cr/(Cr + Al), atomic) numbers vary from 14.3 to 44.0 and from 42.2 to 86.5, respectively. Chromites always have low Ti (TiO₂ < 1.55 wt%) and V (V₂O₃ < 0.8 wt%) abundances and their Fe³⁺ content is negligible (calculated using a spreadsheet provided by Stephen J. Barnes). The large chromite crystals have a prominent, fairly homogeneous core (typically Cr# = 75, Mg# = 24–29), with a complexly zoned rim, about 150 µm

thick (Figs. 1 and 6). It is notable that the compositional profiles are variable from crystal to crystal and from rim to rim. Between core and rim, profiles show a succession of increases and decreases in Cr# number (Fig. 6). Furthermore, the Al enrichment (and the associated decrease in the Cr# number) of the chromite rims is accompanied by a Ti enrichment, and importantly by a Mg# number increase (Figs. 6 and 7). The origin of this chromite zonation will be discussed below.

Troilite and Metal

Troilite is the only sulfide observed in NWA 4215. It is essentially pure FeS and contains occasionally traces of Co (0-0.09 wt%) or Cu (0-0.16 wt%). Metal grains are made of Fe containing only minor amounts of Ni (0.76-2.43 wt%) and Co (0.38-1.96 wt%). They are similar in composition to pristine metal found in diogenites (e.g., Gooley and Moore 1976; Mittlefehldt 2000).

Table 1. Electron microprobe analyses (wt%) of representative silicates in NWA 4215 (n.d. = not detected).

	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	Total	
Orthopyroxene	54.50	0.11	0.92	0.72	15.00	0.52	26.22	1 40	<0.01	<0.01	<0.01	100.42	
Average $(n = 182)$	54.50	0.11	0.82	0.72	15.88	0.53	26.33	1.49	< 0.01	<0.01	< 0.01	100.42	$En_{72.5}Wo_{3.0}Fs_{24.5}$
Mg-rich core	55.90	0.02	0.19	0.65	14.92	0.42	27.94	0.59	n.d.	n.d.	< 0.02	100.65	En _{76.1} Wo _{1.2} Fs _{22.8}
Rim1	53.13	0.48	3.39	0.84	16.23	0.50	24.42	2.56	< 0.05	< 0.01	< 0.07	101.68	En _{69.1} Wo _{5.2} Fs _{25.7}
Rim2	53.23	0.27	1.98	0.87	16.41	0.57	25.33	2.30	< 0.01	< 0.02	< 0.02	101.02	En70.0Wo4.6Fs25.5
Rim3	53.56	0.31	1.75	0.83	15.42	0.56	24.31	3.21	n.d.	n.d.	0.01	99.95	En _{68.9} Wo _{6.5} Fs _{24.5}
Diopside $(n = 5)$	51.69	0.39	2.44	0.89	8.02	0.37	15.07	20.07	0.22	< 0.01	< 0.01	98.89	$En_{44.3}Wo_{42.4}Fs_{13.2}$
Pyroxene inclusions in chromites													
opx $(n = 10)$	54.70	0.13	0.70	1.69	14.51	0.53	27.50	1.51	< 0.02	< 0.01	< 0.01	101.31	En74.9Wo2.9Fs22.2
$\operatorname{cpx}(n=3)$	53.58	0.17	0.76	1.71	6.79	0.22	16.94	20.84	0.18	n.d.	< 0.03	101.22	$En_{47.4}Wo_{41.9}Fs_{10.7}$
Olivine													
Average $(n = 29)$	38.19	0.02	0.02	0.07	25.02	0.53	37.14	0.05	< 0.01	< 0.01	< 0.01	101.06	Fo _{72.6}
Ol1	38.23	n.d.	0.02	0.08	25.93	0.38	36.20	0.06	n.d.	n.d.	< 0.03	100.94	Fo _{71 3}
012	38.99	n.d.	n.d.	0.40	21.71	0.44	39.43	< 0.01	< 0.01	n.d.	< 0.02	101.00	Fo _{76.4}
Cristobalite $(n = 2)$	98.55	0.08	0.85	< 0.01	0.70	0.04	0.02	0.21	0.13	0.05	n.d.	100.65	

Table 2. Electron microprobe analyses (wt%) of representative chromites in NWA 4215.

	SiO ₂	TiO ₂	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	V_2O_3	Total	Cr#	Mg#
Crystal 1											
Rim	0.02	1.24	26.02	41.26	22.77	0.38	8.61	0.29	100.60	51.54	40.27
5 µm	0.02	1.00	31.12	35.19	23.09	0.37	9.29	0.54	100.62	43.13	41.78
76 µm	0.04	0.73	8.33	60.22	24.71	0.44	5.02	0.28	99.79	82.90	26.58
129 µm	n.d.	0.92	11.06	55.74	25.67	0.65	5.64	0.38	100.07	77.17	28.16
150 μm	0.01	1.09	11.76	56.72	25.27	0.46	5.76	0.68	101.75	76.39	28.90
489 µm	n.d.	0.99	11.62	55.51	25.40	0.49	5.94	0.45	100.42	76.22	29.44
Core $(n = 9)$	0.05	1.19	12.28	55.05	25.57	0.48	5.83	0.43	100.87	75.05	28.89
Crystal 2											
Rim	0.11	0.98	10.96	53.45	26.32	0.60	5.58	0.46	98.45	76.59	27.43
58 µm	0.21	0.92	8.82	58.74	25.60	0.40	5.14	0.34	100.16	81.71	26.35
116 µm	0.02	0.98	11.63	53.64	26.08	0.54	5.45	0.28	98.60	75.58	27.13
454 μm	0.11	1.11	11.77	54.50	24.47	0.42	5.65	0.22	98.24	75.65	29.14
Core $(n = 11)$	0.10	1.07	11.87	54.82	25.23	0.45	5.66	0.38	99.59	75.59	28.56
Crystal 3											
Rim	0.07	1.27	16.16	48.55	27.19	0.54	4.91	0.27	98.97	66.84	24.35
24 µm	0.04	1.31	25.96	38.80	25.39	0.39	7.02	0.28	99.20	50.07	33.01
77 µm	0.19	0.77	8.63	57.85	27.19	0.58	4.32	0.45	99.98	81.82	22.08
103 µm	n.d.	1.01	11.23	54.16	26.05	0.52	4.79	0.48	98.25	76.39	24.67
177 μm	0.13	1.23	11.47	55.60	26.07	0.52	4.74	0.49	100.26	76.48	24.47
Core (<i>n</i> = 19)	0.03	1.15	11.23	54.91	26.37	0.50	4.75	0.45	99.40	76.63	24.30

Silica and Silica-Rich Phases

Many inclusions in groundmass pyroxenes contain nearly pure silica (Table 1). It was characterized by microRaman spectroscopy, and corresponds to wellcrystallized cristobalite. Electron microprobe analyses obtained in a small composite inclusion (40 μ m in diameter) suggest the presence of plagioclase in addition to cristobalite and metal. Although its composition cannot be precisely determined, it is close to An₇₅. No other plagioclase-bearing inclusion has been detected despite a careful search.

Whole Rock Geochemistry

Major and Trace Elements

Two chips of the NWA 4215 meteorite were ground using a boron carbide mortar and pestle. The powder from the first chip was analyzed without further treatment; the second was leached for one hour in hot (90–100 °C) sub-boiled 6 N HCl and rinsed five times in ultrapure water prior to analysis. The aim of this procedure was to remove any contribution from terrestrial alteration (mainly carbonate and limonite).

The results obtained for the two fractions are markedly different, especially for the trace elements (Table 3). The differences can be explained by variability in the proportions of chromite present in the two fractions and by removal of the secondary phases, metal and troilite, during the leaching step.

As shown by the Cr_2O_3 abundances, the chromite proportions in the two subsamples are different. This result is not surprising in view of the small size of the samples and because the chromite crystals are large and sparsely distributed within the rock. The involvement of the chromite cannot of course explain all the differences between the two subsamples. Least-square calculations (not shown) demonstrate that the composition for major elements can be easily explained by a mixture of about 92 wt% orthopyroxene, 1.5 wt% chromite, 4 wt% limonite, and 2.5 wt% calcite for the unleached sample, and about 96.5 wt% orthopyroxene and 3.5 wt% chromite for the leached one. It is well known that the trace element budget of hot desert meteorites can be severely modified by the contribution of alteration phases (e.g., Barrat et al. 1999, 2003; Crozaz et al. 2003; Al-Kathiri et al. 2005 and references therein). NWA 4215 is no exception, and the high Sr (14 μ g/g), Ba (84 μ g/g), and Pb (0.88 µg/g) abundances displayed by the unleached sample are clearly the fingerprint of terrestrial alteration. This conclusion can be extended to most of the other trace elements we have determined. Thus, for an orthopyroxenite the unleached sample is rich in REEs (Table 3; Fig. 8). Its REE pattern exhibits a pronounced LREE enrichment (Lan/ $Sm_n = 2.76$), and a significant positive Ce anomaly (Ce/Ce* = 1.29) which clearly reflect the contribution of secondary phases, as shown previously for the Tatahouine diogenite (Barrat et al. 1999). We would conclude from this that the trace element abundances of the unleached fraction of NWA 4215 cannot be used to discuss its petrogenesis.

Because NWA 4215 is devoid of REE-rich phases that can be eliminated by leaching (e.g., phosphates), this procedure gives a better picture of the composition of the whole rock before weathering for most major and trace elements, including the rare earth elements (REE). It can be pointed out that the Ba, Sr, and Pb abundances, which are sensitive indicators of Saharan weathering (e.g., Barrat et al.



Fig. 2. Chemical zoning of NWA 4215 orthopyroxene.

1999, 2003; Crozaz et al. 2003), are very low in the leached powder. This suggests that the secondary minerals have been nearly totally removed. Unfortunately, part of the metal and troilite were certainly attacked during the leaching step. This does have a significant impact on Ni, Co, Cu, Zn, and W concentrations, which are given just as indicative values.

Trace element abundances in the leached NWA 4215 sample are comparable to those in other analyzed diogenites (e.g., Fukuoka et al. 1977; Wolf et al. 1983; Mittlefehldt 1994a, 2000; Fowler et al. 1995). With the exception of Sc, V, Co, and Ni, all trace elements have concentrations $<4 \mu g/g$. NWA 4215 is extremely depleted in incompatible trace



Fig. 3. Quadrilateral pyroxene composition of NWA 4215. The fields of diogenitic pyroxenes are drawn using the data of Berkley and Boynton (1992), Mittlefehldt (1994a, 2000), Fowler et al. (1994), and Papike et al. (2000). The curves are the calculated isotherms for equilibrium relationships between coexisting pyroxenes in the Wo-Fs-En system (Lindsley 1983).

elements, as shown by the low U, Th, Nb, Zr, Rb, and REE abundances, which indicates that interstitial melt was efficiently expelled during the crystallization of this cumulate. Its REE pattern is characterized by an LREE depletion (Lan/Smn = 0.49), a marked negative Eu anomaly (Eu/Eu* = 0.44), and a pronounced heavy REE enrichment (Gdn/Lun = 0.17) (Fig. 8). It resembles the pattern obtained on Tatahouine (Barrat et al. 1999 and references therein) and some Yamato-74 diogenites (Masuda et al. 1979). On the other hand, the REE abundances in NWA 4215 are unlike those obtained for the Martian orthopyroxenite ALH 84001, which exhibits less pronounced LREE depletion, negative Eu anomaly, and heavy REE enrichment (Lan/Smn = 0.91, Eu/ $Eu^* = 0.81$, Gdn/Lun = 0.47, e.g., Dreibus et al. 1994). Indeed, the connection of NWA 4215 with diogenites is strengthened by its high Al/Ga ratio close to 23,000 (Al/Ga > 20,000 in diogenites (e.g., Wänke et al. 1977; Barrat et al., in preparation), and only 2070 in ALH 84001 (Dreibus et al. 1994).

Oxygen-Isotopic Composition

The bulk oxygen isotopic composition was determined in duplicate using the leached sample of NWA 4215. The results obtained were (1 σ): $\delta^{17}O = 1.431 \pm 0.102\%$, $\delta^{18}O = 3.203 \pm 0.205\%$, $\Delta^{17}O = -0.248 \pm 0.005\%$. The $\Delta^{17}O$ value of NWA 4215 is within error of the eucrite fractionation line ($\Delta^{17}O = -0.239 \pm 0.007$) defined by Greenwood et al. (2005) and the $\delta^{18}O$ value is well within the range of previous measurements from diogenites (Clayton and Mayeda 1996; Wiechert et al. 2004; Greenwood et al. 2005).



Fig. 4. Variations of TiO_2 , Cr_2O_3 , and CaO relative to Al_2O_3 (in wt%) in groundmass pyroxenes in NWA 4215. The field of diogenitic pyroxenes is shown for comparison (Berkley and Boynton 1992; Mittlefehldt 1994a, 2000; Fowler et al. 1994; Papike et al. 2000).

DISCUSSION

NWA 4215: A Unique Diogenite

In comparison with known extraterrestrial orthopyroxenites, NWA 4215 displays remarkable features. Unbrecciated diogenites are scarce (e.g., Tatahouine and GRO 95555). Most diogenites exhibit a cataclastic texture or are breccias principally composed of a recrystallized assemblage of orthopyroxene fragments. Furthermore, evidence from the unbrecciated diogenites, large clasts, and the largest crystal debris within the breccias suggests that the original orthopyroxene grain size ranged from about 1–2 mm to 5 cm. ALH 84001, the sole known Martian orthopyroxenite, displays a cataclastic texture with an initial



Fig. 5. Cr_2O_3 abundances across two olivine grains in contact with a large chromite crystal in NWA 4215. The calculated diffusion profiles are compared (see the text for more details).

grain size close to 5 mm. On the other hand, NWA 4215 is not only unbrecciated but exhibits an unusually fine grain size (about 500 μ m).

Moreover, the crystals in diogenites and in ALH 84001 are usually homogeneous in composition (e.g., Hewins 1980; Berkley and Boynton 1992; Mittlefehldt 1994a, 1994b; Fowler et al. 1994; Bowman et al. 1999). Crystals displaying a pronounced zoning are rare in diogenites. The only exceptions reported so far are a few orthopyroxenes in the Garland breccia, which range from $En_{74}Wo_2Fs_{24}$ in the cores to $En_{63}Wo_2Fs_{35}$ in the rims (Fowler et al. 1994), and large chromite crystals in Elephant Moraine (EET) 87530 and Thiel Mountains (TIL) 82410 that display a compositional zonation near the rim (Liermann and Ganguly 2001). The extensive compositional zonation shown by orthopyroxene and chromite crystals in NWA 4215 thus make it unique among known extraterrestrial orthopyroxenites

Despite these striking differences, NWA 4215 is unambiguously a diogenite. The composition of the NWA 4215 orthopyroxenes plot within the field of diogenites (Fig. 3) and their average FeO/MnO ratio (=30) is identical to that measured in other diogenites (e.g., Mittlefehldt 1994a) but lower than the value obtained for the ALH 84001 orthopyroxenes (=36, Mittlefehldt 1994b). The similarities with diogenites are strengthened by the lack of Fe³⁺ in chromite, the occurrence of metal, troilite, and traces of anorthite-rich plagioclase. The O-isotope composition of NWA 4215 and the trace element evidence discussed earlier provide further confirmation that this meteorite is a diogenite.



Fig. 6. The chemical zoning of NWA 4215 chromites.

Is NWA 4215 an Impact Melt?

Unequilibrated rocks are scarce among HED meteorites and it has been shown that some of them formed from impact melts (e.g., Barrat et al. 2003). Given that the fine-grained texture displayed by NWA 4215 is extremely unusual, one may argue that this stone formed from a quenched diogenite melt. This hypothesis can be easily ruled out:

- The Mg# number of a liquid produced by the total melting of a typical diogenite will be controlled by the composition of the orthopyroxenes (typically Mg# = 75); because the orthopyroxene KD is much lower than 1, the composition of the first crystallizing orthopyroxene will be much more Mg-rich than the liquid: close to En_{90} , assuming a K_D-value in the order of 0.25–0.3 as determined for eucritic or high-Mg eucritic systems (Stolper 1979; Bartels and Grove 1991), and in agreement with the pioneer work of Bowen and Schairer (1935) on the MgO-FeO-SiO₂ system. On the other hand, the compositions of the cores of the orthopyroxenes in NWA 4215 are well in the range of diogenitic values.
- It can be pointed out that the Ni abundance $(54 \ \mu g/g)$ measured on the NWA 4215 unleached sample (Table 3) seems high, and could be a projectile fingerprint; in fact, this concentration is in the range obtained for unbrecciated diogenites and orthopyroxene clasts (e.g., Floran et al. 1981; Mittlefehldt 2000; Barrat et al., in preparation).

Origin of the Compositional Zonings Shown by NWA 4215 Phases

The zonation shown by the NWA 4215 crystals is exceptional and merits further discussion. As a starting point it is assumed that this observed compositional zonation is of igneous origin and hence may record the chemical evolution of the residual melt.

The abundances of Al_2O_3 , TiO₂, and CaO in NWA 4215 orthopyroxenes are well correlated and appear to be consistent with a fractional crystallization process (Fig. 4). TiO₂ concentrations range from less than 0.05 wt% in the cores to about 0.5 wt% in some rims. Similarly, Al_2O_3 abundances range from about 0.2 wt% to more than 3 wt%. In both cases, these elements are incompatible during the crystallization of diogenites and their partition coefficients were undoubtedly very low probably less than 0.1 (e.g., Mittlefehldt et al. 1994a; Fowler et al. 1995). Taken at face value, these ranges require as much as 90% fractional crystallization. However, this seems unrealistic because neartotal crystallization of a single magma, irrespective of its initial composition, could not produce a cumulate composed essentially of only orthopyroxene.

High degrees of crystallization are in disagreement with the behavior of Fe and Mg. Assuming that orthopyroxene is the sole liquidus phase during a single fractional crystallization step, the range of FeO/MgO ratios (=0.529– 0.710) displayed by the NWA 4215 orthopyroxenes can be used to constrain the degree of fractional crystallization (see

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Appendix for the relevant calculations). For calculation purposes, the MgO abundance in the NWA 4215 parent melt is required. This parameter is impossible to constrain accurately, but assuming an unrealistic MgO content as high as 20 wt%, the full range of orthopyroxene compositions are produced with only 24% crystallization. This result can be considered as an upper limit because lesser crystallization degrees are calculated for MgO <20 wt%. Hence, Al₂O₃ abundances in the most evolved orthopyroxene in equilibrium with the related residual melts cannot exceed 0.30 wt%, assuming $D_{A1} = 0.1$. Taking into account the involvement of olivine, chromite, or the minor wollastonite component in orthopyroxene, or using lower DAl values does not substantially alter these estimates. However, fractional crystallization alone cannot explain the spread of the data shown on the Al₂O₃ versus FeO/MgO diagram (Fig. 9). An additional mechanism is required.

The zonation displayed by the chromites is not what would be expected from fractional crystallization processes (Figs. 6 and 7; Table 2). Of course, Cr# numbers are generally lower in the rims than in the crystal cores, but conversely Mg# numbers are often higher in the rims than in the cores. In detail, the chemical variations from core to rim are too complex to simply be a record of fractional crystallization processes. The Al-enrichment of the rims is strongly dependent upon very local conditions, so that compositional variation across the rims of crystals within the same polished section are often dissimilar (Fig. 6). To our knowledge, such intricate zoning has never been described before in achondrites. Interestingly, close compositional trends are well-known in chromites from terrestrial layered intrusions. For example, chromites from the Rhum intrusion (Scotland) sometimes exhibit marked Al enrichment accompanied by significant increases in Mg# number, which has been ascribed to post-depositional reactions of chromite with olivine, plagioclase, and/or the intercumulus melt (Henderson 1975; Henderson and Wood 1981). A similar explanation can be given for the NWA 4215 chromites, but of course the involvement of plagioclase is excluded here. Interestingly, the orthopyroxenes displaying the highest Al₂O₃ and CaO abundances are located in areas around the large chromite crystals. This is particularly obvious with the Ca distribution map (Fig. 1). This strongly suggests that reaction with evolved intercumulus melts was a major cause of the chemical zonation seen in chromite and orthopyroxene crystals. The low abundance of incompatible trace elements measured in the bulk rock suggests that these late melts were almost completely expelled during the crystallization of NWA 4215.

Thermal History of NWA 4215

Closure temperatures for NWA 4215 phases can be estimated from two-pyroxenes (Lindsley 1983), spinelorthopyroxene and spinel-olivine thermometry. As shown in



Fig. 7. Mg# and TiO₂ (wt%) versus Cr# in NWA 4215 chromites. The fields of diogenitic chromites are drawn using the data of Mittlefehldt (1994b, 2000) and Bowman et al. (1999).

Fig. 3, the pyroxene inclusions in chromites suggest temperatures as high as 1000 °C. These values are certainly not reliable because of the small size of the inclusions and the difficulties in avoiding electron beam overlap between the ortho- and clinopyroxenes. Temperatures in the order of 800-900 °C are deduced from the compositions of groundmass pyroxenes. Seventeen paired analyses of orthopyroxene and chromite yield calculated temperatures ranging from 760 to 1025 °C, with an average close to 890 °C, using the recent thermometric calibration of Liermann and Ganguly (2003). Five paired analyses of olivine and chromite yield temperatures ranging from 800 to 940 °C (average 845 °C) using the thermometric calibration of Sack and Ghiorso (1991a, 1991b). These closure temperatures are within the ranges observed in brecciated diogenites by Mittlefehldt (1994), Liermann and Ganguly (2001), and Domanik et al. (2004), and identical to the orthopyroxene-spinel temperature of the unbrecciated diogenite GRO 95555 (900 °C) (Stimpfl and Ganguly 2002).

A variety of approaches have been applied to HED materials in order to constrain their cooling rates, crystallization settings, burial depths, and excavation

Table 3. Major and trace element abundances in NWA 4215 (oxides in wt%, other elements in $\mu g/g$).

	IN WA 4215					
	Unleached	Leached				
Mass (g)	0.1103	0.535				
SiO_2	n.d.	51.4				
TiO ₂	0.13	0.16				
$Al_2 \tilde{O}_3$	1.12	1.26				
Cr_2O_3	1.47	2.57				
FeO	20.45	17.19				
MnO	0.53	0.53				
MgO	24.03	25.70				
CaO	2.15	1.56				
Sc	12.1	14.21				
V	118	150				
Со	39.67	18.6				
Ni	54.1	15.1				
Cu	16.6	2.2				
Zn	3.3	0.99				
Ga	0.41	0.29				
Rb	0.79	0.03				
Sr	14.21	1.24				
Y	1.83	0.82				
Zr	1.83	0.22				
Nb	0.20	0.060				
Ba	84.3	3.19				
La	1.16	0.0104				
Ce	2.93	0.0264				
Pr	0.281	0.0038				
Nd	1.21	0.0211				
Sm	0.265	0.0134				
Eu	0.072	0.0031				
Gd	0.284	0.0357				
Tb	0.0435	0.0099				
Dy	0.277	0.0997				
Но	0.062	0.0270				
Er	0.192	0.106				
Yb	0.221	0.147				
Lu	0.0368	0.0262				
Hf	0.047	0.010				
W	0.011	0.004				
Pb	0.88	0.009				
Th	0.18	0.003				
U	0.058	0.001				
(La/Sm)n	2.76	0.49				
(Gd/Lu)n	0.96	0.17				
Ce/Ce*	1.24	1.01				
Eu/Eu*	0.80	0.44				

histories. For example, the compositional gradient of Ca and the width of the augite exsolution lamellae in pigeonites indicate high temperature cooling rates (>700 °C) ranging from about 4 °C/a for the least metamorphosed noncumulate eucrites to 10^{-4} °C/a for the most equilibrated eucrites and cumulate eucrites (e.g., Miyamoto and Takeda 1977, 1994; Schwartz and McCallum 2005). In the case of diogenites, the



Fig. 8. REE patterns of NWA 4215. The reference chondrite is from Evensen et al. (1978). Also shown are the REE patterns for the ALH 84001 Martian orthopyroxenite (Dreibus et al. 1994), the Bilanga and Tatahouine diogenites (Barrat et al., in preparation).



Fig. 9. Al_2O_3 (wt%) versus FeO/MgO in NWA 4215 orthopyroxenes. The calculated fractional crystallization trend is shown for comparison (see the text for more details).

Fe²⁺-Mg ordering states of orthopyroxenes point to cooling rates ranging from 5×10^{-4} to 0.8 °C/a at temperatures in the order of 300–400 °C (Zema et al. 1997). Compositional zoning in a large chromite grain from diogenite TIL 82410 indicates similar values (Liermann and Ganguly 2001). Because most diogenites have experienced a complex thermal history involving brecciation events, this range has been ascribed to different burial depths under ejecta blanket materials. On the other hand, the occurrence of olivine abutting chromite in NWA 4215 offers another possibility to estimate the cooling rate from the diffusion of Cr in olivine at high temperatures. We have tentatively modeled the Cr distribution in olivine as a function of the cooling rates and compared the theoretical profiles with those obtained in two such grains (Fig. 5). Models were computed using an explicit finite difference method to solve the diffusion equation for a semi-infinite crystal bounded by a planar surface (Crank 1967), which approximates suitably the geometry of the contact of the olivine grains with the large chromite crystal:

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2} \tag{1}$$

C is the concentration, *t* is the time, and *x* is the distance from the crystal surface. *D* is the diffusion coefficient, which is temperature-dependent. The model assumes that i) the rim of the olivine crystal is in equilibrium with chromite and has a constant Cr concentration, and ii) the crystals were homogeneous before diffusion and devoid of Cr. Calculations were run at varying temperatures, using a linear cooling rate from a starting temperature T_0 .

Solving Equation 1 requires estimated values for i) the diffusion coefficient of Cr in olivine, and ii) the cooling rate and the initial temperature. The diffusion parameters for Cr in olivine have recently been determined experimentally. Ito and Ganguly (2006) have shown that the diffusion of Cr into olivine is significantly anisotropic but not dependent on the fO_2 between iron-wüstite and two orders of magnitude above this buffer. The temperature dependence of the diffusion coefficient D can be expressed according to an Arrhenian relation, $D = D_0 \exp(-E_a/RT)$, where D_0 is the diffusion coefficient at infinite temperature, E_a is the activation energy and R is the perfect gas constant. For calculation purposes, we have used the parameters available for diffusion parallel to the c-axis (log $D_0 = -6.65 \text{ m}^2/\text{s}$ and $E_a = 299 \text{ kJ/mol}$), because the diffusivity is slower parallel to this direction than to the other crystallographic axis (Ito and Ganguly 2006). For $T_0 =$ 1200 °C (corresponding to a realistic liquidus temperature), the cooling rate necessary to quench the Cr variations resulting from diffusion is in the order of 10–50 °C/a.

What environment could account for such a fast cooling rate? One possibility is that this diogenite was excavated from a deep crustal level in the parent body and then buried at a low depth under a blanket of ejecta. This model involves a complex thermal history with at least two distinct events: crystallization at depth (slow cooling rate) followed by the excavation/ejection (fast cooling rate). As the later rapid cooling event cannot reset the Cr distribution in the olivines this model can be directly ruled out. It would require the Cr abundances in the olivines abutting the chromites to be significantly higher and more uniform than is in fact the case (see Fig. 5). On the other hand, the calculated cooling rate more likely reflects the crystallization and subsolidus history of NWA 4215, and is consistent with its formation within a shallow intrusion. The diffusion of Cr into olivine is clearly a valuable tool for constraining cooling rates at high temperature, even though olivine crystals in contact with chromites are somewhat uncommon in diogenites

Summary and Implications for the Genesis of Diogenites

NWA 4215 is a unique orthopyroxenite. It is the least metamorphosed diogenite described so far, displaying an unbrecciated texture and remarkable mineralogical features. Its chromite and orthopyroxene crystals are chemically zoned. Our data suggests that these zonations do not purely result from intercumulus melt crystallization. More likely they reflect a more complicated process, involving reaction between crystals and intercumulus melt followed by efficient expulsion of this residual liquid prior to the complete solidification of the diogenite.

The vast majority of the HED meteorites are made of clasts that exhibit textural evidences for extensive thermal annealing (e.g., Metzler et al. 1995; Yamaguchi et al. 1996; Mittlefehldt et al. 1998 and references therein). Previous studies have shown that most of the other diogenites cooled slowly, possibly deep in the parent body, and contain crystals that have been homogenized for major elements (e.g., Mori and Takeda 1981; Mittlefehldt 1994a, 2000; Papike et al. 2000). NWA 4215 is clearly different from these diogenites having cooled much faster in order to preserve the observed mineral zonation patterns. The cooling rate determined from the diffusion of Cr in olivine abutting chromite is on the order of 10–50 °C/a, and suggests that NWA 4215 formed within a small and shallow intrusion.

The existence of diogenites that have not experienced the widespread thermal metamorphism of the 4 Vesta crust demonstrates that these orthopyroxenites are not necessarily deep crustal lithologies. At least some of them occasionally crystallized into the upper crust. Therefore, this strongly suggests that diogenites cannot be the early products of the asteroidal magmatic activity, but formed certainly after eucrites as previously proposed by age determinations (Takahashi and Masuda 1990) and trace element systematics (e.g., Barrat 2004). A better knowledge of the field relationships between diogenites and eucrites are necessary to validate these inferences, and will hopefully be achieved during the Dawn mission.

Acknowledgments–Bruno and Carine Fectay generously provided a sample of NWA 4215. We thank Dr. Randy Korotev for the editorial handling, Drs. Akira Yamaguchi, T. Burbine, and R. N. Taylor for constructive comments; and Pascale Barrat for her help. We gratefully acknowledge the Programme National de Planétologie (CNRS-INSU) for financial support. IAF and RCG supported by a PPARC grant. This research has made use of NASA's Astrophysics Data System Abstract Service.

Editorial Handling-Dr. Randy Korotev

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APPENDIX A: FeO-MgO FRACTIONATION DURING ORTHOPYROXENE CRYSTALLIZATION

The mathematical formulation of Albarède (1992) for olivine crystallization has been directly adapted to the orthopyroxene case. The reader is referred to this work for more details. Assuming that an orthopyroxene totally devoid of Ca was the sole liquidus phase in the system (i.e., neglecting the subsidiary wollastonite component in orthopyroxene, and the involvement of chromite and olivine), the liquid line of descent and the evolution of the composition of a crystal can be easily estimated using mass balance constraints and the behavior of Fe and Mg. Assuming K_D to be constant, introducing the variable Z as a function of the fraction of residual melt relative to the parent melt (*F*), and the concentrations of FeO and MgO in the parent and residual melts, we get:

$$Z = F.(MgO)_{liq1} / (MgO)_{liq0}$$
(A1)

$$(FeO/MgO)_{liq1} = (FeO/MgO)_{liq0}Z^{K_{D^{-1}}}$$
(A2)

$$(FeO/MgO)_{px1} = (FeO/MgO)_{px0} Z^{K_{D^{-1}}}$$

$$(1 - F) = [(FeO)_{liq0} / (FeO)_{fs}] . (1 - Z^{K_{D}})$$

$$+ [(MgO)_{liq0} / (MgO)_{en}] . (1 - Z)$$
(A3)

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liq0 and liq1 refer respectively to parent and residual melt, px0 and px1 to the pyroxenes in equilibrium with them, en and fs to the enstatite and ferrosilite end members.

The low-Ca pyroxene K_D (about 0.27) is well determined for eucritic or high-Mg eucritic systems (Stolper 1979; Bartels and Grove 1991). Hence, for a parental melt with known FeO and MgO contents, it is possible to estimate the FeO and MgO in a residual melt for a given *F* value. *Z* can be calculated from Equation A3 and the FeO and MgO abundances in the residual melt are deduced from equations A1 and A2.

In the case of a zoned orthopyroxene crystal produced by fractional crystallization, it is easy to estimate the fraction of residual melt relative to the parent melt (F) at the time of the crystallization of the rim. The FeO/MgO ratio in the core of the crystals (px0) provides directly a reasonable estimate of this ratio in the parent melt (liq0):

$$(FeO/MgO)_{liq0} = (FeO/MgO)_{px0}/K_D$$
 (A4)

Assuming that the MgO concentration in the parent melt is fixed, its FeO concentration can be deduced from Equation A4. Hence, the Z and F values between the core and the rim compositions are calculated successively from Equations A2 and A3. The knowledge of F allows the calculation of trace element abundances in the crystal, if their concentrations in the core and their orthopyroxene-melt partition coefficients are known.