Northwest Africa 6693: A new type of FeO-rich, low-$\Delta^{17}$O, poikilitic cumulate achondrite

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Received 31 May 2012; accepted in revised form 24 December 2012; available online xxxx

Abstract

Northwest Africa 6693 is a new type of achondrite, with a unique combination of oxygen-isotopic composition (low $\Delta^{17}$O: $-1.08^{\text{wt%}}$, also $\delta^{17}$O = 1.19$^{\text{wt%}}$) and FeO-rich, low Mg bulk composition. A mode (in vol%) shows 70% pyroxene, 16% olivine and 13% feldspar, along with 0.6% Cr-spinel, and 0.4% NiFe metal (awaruite). Its coarse-poikilitic texture, with pigeonite oikocrysts up to 14 mm, as well as the subchondritic MgO/SiO$_2$ of the rock’s bulk composition, indicate origin as an igneous cumulate. The cumulus phases included pigeonite and olivine, and the parent magma was probably also saturated with feldspar, which occurs mainly as anhedral, yet optically continuous, grains intergrown with the pyroxene. The mafic silicates are uniformly ferroan: pigeonite near En$_{57}$Wo$_{3.2}$ and olivine near Fo$_{49}$. The feldspar is uniformly albitic, near Ab$_{92}$, except for a single tiny grain of Ab$_{57}$-Or$_{43}$. However, the albite features diverse K/Ca (Or/An) ratios: ranging from consistently $\sim$0.46 in one end of the oblong NWA 6693 stone, to 5.2 in an olivine-rich enclave that consists mostly of micrographic olivine–feldspar intergrowth. Also, siderophile and incompatible element data show heterogeneity among samples from different regions of this large cumulate. The rock was probably neither an orthocumulate nor an adcumulate, and the proportion of “trapped liquid” probably varied from place to place. After initial crystallization, a shock event caused very minor brecciation, and pervasively mobilized linear-arcuate trails of microinclusions (minute oxides, mostly) and bubbles. A minor proportion of additional melt was formed within, and/or infiltrated into, the rock and formed discrete overgrowth mantles, recognizable based on unusual scarcity of microinclusions, on some pyroxenes. Final cooling, based on mineral-equilibration temperatures, occurred at a moderate rate by intrusive-igneous standards.

Olivine, metal, and sulfide phases are all very Ni-rich (e.g., olivine NiO averages 0.77 wt%). Evidently the partitioning of NiO into the parent melt was extraordinarily high, which suggests a commensurately high oxygen fugacity. The V/(Al + Cr) ratio within spinel suggests that $f_{O_2}$ was IW $\pm$ 2. The bulk-rock composition features strong depletions in sulfur and chalcophile elements, but nonvolatile lithophile elements are only subtly fractionated from chondritic. Even siderophile element concentrations are near-chondritic; Co, Ni, Ir and Os are all at 0.7–1.0 $\times$ CI chondrites, and Au at 0.55 $\times$ CI. The limited fractionation of the siderophile elements may reflect igneous processing in a parent body so pervasively oxidizing that FeNi metal did not play its usual planetary role as agent for efficient sequestration of siderophile elements. More generally, the limited fractionation among nonchalcophile, nonvolatile elements suggests that the parent melt was not produced by extensive fractional crystallization; i.e., the high FeO and low Mg of NWA 6693 were probably in large measure already properties of the original primary magma, produced from an extremely oxidized (FeO-rich) variety of primitive material. NWA 6693 indicates that high oxygen fugacity inherited from oxidized-chondritic building blocks may persist within small bodies, despite melting extensive enough to engender igneous cumulates.

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http://dx.doi.org/10.1016/j.gca.2012.12.025
1. INTRODUCTION

Northwest Africa (NWA) 6693 is a recent achondrite find with distinctive compositional traits. The meteorite was reportedly found as a single mass of 5.1 kg, near Amazrou, Morocco, circa May 2010. Collector Edwin Thompson generously donated samples to UCLA for initial classification (Warren et al., 2011). Many strong resemblances suggest that NWA 6693 is paired with the similarly massive NWA 6704 (Irving et al., 2011), and also with NWA 6926.

Even macroscopically, NWA 6693 appears distinctive. A thin brown weathering rind, possibly in part a layer of adhering desert soil, covers much of the exterior. But the interior appears fresh with mostly vitreous grains in various shades of green. The lustrous green macroscopic appearance bears a striking, albeit superficial, resemblance to terrestrial mantle xenoliths, in particular the xenoliths from San Carlos, Arizona, a rock type for which many good images are available on the internet.

Ungrouped achondrites are rare. In the current Meteoritical Bulletin database, there are more than 2000 named achondrites, of which only 40 (2%) are listed as ungrouped (these numbers ignore the frequent issue of pairing among all types of achondrites). Only a handful of original parent bodies are believed to account for the vast majority of non-planetary achondrites. About half of all achondrites, 1000 named HEDs, are linked, most meteoritcists now believe, to a single large asteroid, 4 Vesta. The 300 named ureilites also probably come, ultimately, from a single large planetary space, the correlation between original parent bodies and chemistry of NWA 6693. Our study included thin sections, including one of brief duration for quick, on-site measurements of gamma-ray activity for shorted-lived nuclides, allowing us to determine V and improve/verify data for five other major and minor elements (Mg, Al, Ca, Ti, Mn). Glass beads fused from 20 to 30 mg aliquots of the powders produced as the first step in INAA are also studied by an application of EPMA we call MFBA (microprobe fused bead analysis). MFBA is our sole method for determining SiO₂, plus our main method for MgO and Al₂O₃. It is also a useful adjunct to INAA for 8 additional major and minor elements.

It should be noted that the peculiar composition of NWA 6693 presents unusual difficulties for analysis of lithophile trace elements by INAA. High contents of both Na and Co, along with lithophile trace elements at very low concentration, by achondrite standards, are an adverse combination: ²⁴Na (early) and ⁶⁰Co (later) generate Compton scattering that degrades counting statistics for all nuclides with gamma energies below their own high-energy peaks, at 1.368 MeV and 1.333 MeV, respectively. The combined effect is significant for most, and annihilative for some, of our customary target gamma peaks. Thus, our analyses did not constrain elements such as Ga, Sr, Ba, Ta, Th, U and the rare earth elements (REE) nearly as well as usual with modern INAA of achondrites.

Oxygen isotopic measurements were obtained from an interior sample, free of brown desert-weathered surface matter. Two separate masses of 3.42 mg and 2.56 mg were subjected to analysis. Oxygen gas was extracted from the samples and measured for isotopic compositions with the CO₂ laser-BrF₅ fluorination technique at the Korea Polar Research Institute (Ahn et al., 2012). Each sample or standard is placed in a small (2.5 mm diameter, 1.5 mm depth) hole in a pure Ni holder, fitted with 8 such holes. Juan de Fuca basalt glass (JFB, Kusakabe and Matsushita, 2008) is used as a solid standard. The samples and standard in the Ni holder are placed in a reaction chamber made of stainless steel with a BaF₂ window. The chamber is then evacuated and heated up to ~180 °C for ~12 h in order to remove surface contamination, followed by pre-fluorination for extra surface cleaning. Each sample is heated with a CO₂ laser in the presence of ~100 hPa of BrF₅ gas. Extracted gaseous species are purified through cryogenic traps at liquid nitrogen temperature and by the fluorine getter, which comprises coarse-grained KBr crystals kept at 150 °C. The purified O₂ gas is collected by a Molecular Sieve 13X cold finger at liquid nitrogen temperature. Oxygen isotopic compositions of the collected O₂ gases were measured using the mass spectrometer, PRISM (VG Isotech, UK), equipped with a dual inlet system. JFB standards were measured prior to and after the samples in order for volatilization-prone phases (feldspars) broader beams and currents as low as 4 nA were employed. A few additional semiquantitative analyses were obtained using an EDAX system on the SEM.

Bulk compositional data were obtained for five separate chips of NWA 6693, using the methodology of Warren et al. (2009), which uses primarily instrumental neutron activation analysis (INAA). The INAA procedure involves two separate irradiations at the UC-Irvine reactor facility, including one of brief duration for quick, on-site measurements of gamma-ray activity for shorted-lived nuclides, allowing us to determine V and improve/verify data for five other major and minor elements (Mg, Al, Ca, Ti, Mn). Glass beads fused from 20 to 30 mg aliquots of the powders produced as the first step in INAA are also studied by an application of EPMA we call MFBA (microprobe fused bead analysis). MFBA is our sole method for determining SiO₂, plus our main method for MgO and Al₂O₃. It is also a useful adjunct to INAA for 8 additional major and minor elements.
to check the daily performance of the line. Standard deviations ($2\sigma$) of four JFB measured on the same day are $0.09\%_{\text{o}}$ in $\delta^{18}\text{O}$, $0.03\%_{\text{o}}$ in $\delta^{17}\text{O}$ and $0.04\%_{\text{o}}$ in $\Delta^{17}\text{O}$.

3. TEXTURE AND MINERALOGY

3.1. General

The rock is dominated by pigeonite oikocrysts mostly over 5 mm, and up to 11 mm, in maximum dimension, based on unambiguous optical continuity in crossed-nicols viewing (Fig. 1; also Figs. EA-1 and EA-2 in the Electronic annex to this paper). This is a very low-Ca pigeonite ($\text{Wo}_3$, Table 1), and Irving et al. (2011) and Jambon et al. (2012) described it as orthopyroxene. However, we find consistently inclined extinctions. The maximum length of optical continuity is 14 mm, when expanses that are very nearly in optical continuity (i.e., we suspect slightly displaced by mild brecciation) are included.

To derive a thin-section mode, we employed a combination of point counting and BSE image analysis. Cr-spinel, metal and total silicates were determined by counting, with reflected-light microscopy applied to three sections, 8000 random points (statistical error in a point count is simply the square root of the number of points for a given constituent). Sulfide was directly measured from the total area of the few tiny grains present. Finally, pyroxene:olivine:feldspar proportionality was measured by digital processing of BSE images. The resultant mode has (by volume) 70% pyroxene, 16% olivine and 13% feldspar, along with 0.6% Cr-spinel, 0.4% NiFe metal (awaruite), a trace of Ca-phosphate (merrillite), and a far tinier proportion, 0.001%, of Ni-rich Fe-sulfide. This mode does not include one unusual olivine-rich clast that was conspicuous on a sawn surface and thus targeted for special study (see below). The pyroxene is nearly all monoclinic (i.e., pigeonite), although locally, mainly in the outer 0.1–0.3 mm of the oikocrysts, small-scale exsolution has occurred (Fig. EA-3). Pyroxene compositions (Table 1, Fig. 2) are consistently ferroan and, except for the very minor, rim-associated exsolution lamellae, CaO-poor.

In most of the rock (again, not including the olivine-rich clast), olivine occurs as blocky, equant grains scattered within (i.e., as chadacrysts) or between the pigeonite oikocrysts. Maximum dimension for these grains is usually $>>0.1$ mm but less than 1 mm. In rare instances there is apparent optical continuity between nearby outcrops as far as 3 mm apart. In places, particularly in the End 1 portion of the meteorite (see below), pyroxene forms a thin mantle around olivine (Figs. 3, EA-4, EA-5). In a few places, rounded pyroxene occurs as an inclusion within olivine (Fig. 3). Olivine compositions (Table 1, Fig. 4) are consistently ferroan and remarkably NiO-rich.

Feldspar occurs as grossly anhedral crystals that appear as scattered, amoeboid patches within the pigeonite oikocrysts (see orange in Fig. EA-1). These feldspar outcrops show optical continuity with one another over large subareas of the oikocrysts, generally several mm across, up to 10 mm. Generally (but there are many exceptions; e.g., Fig. EA-1) the feldspar optical continuity does not extend across boundaries between pigeonite oikocrysts. Although feldspar composition (Table 1, Fig. 5) is almost uniformly albite, it exhibits subtle location-linked diversity (discussed below).

A peculiar characteristic of NWA 6693 feldspar is the scarcity and vagueness of twinning. In most of the feldspar, especially in NWA 6926, although birefringence and optical continuity remain, only a nebulous, fuzzy hint of any sys-

Fig. 1. Low-magnification (width: 14 mm) crossed-nicols view of a fairly representative area of NWA 6693. For a more revealing color version of this image, see Fig. EA-1. The rock is dominated by pigeonite oikocrysts, a few of which are shown here almost in their entirety (one of these, in the upper right, is at extinction; i.e., it appears black). The irregular outlines of these oikocrysts, most conspicuously the two that dominate the right half of this view, suggest a corroded/embayed texture. The extremely anhedral feldspar appears mostly as various shades of light grey, although one relatively small grain (arrows, lower-central area, extending up into the largest visible medium-grey oikocryst) is at extinction. Larger arrow points to a suspected overgrown subgrain (or lobe) within the same large oikocryst.

Table 1
Representative electron microprobe analyses (in wt%) of individual phases in NWA 6693 and, as noted, NWA 6926.

<table>
<thead>
<tr>
<th>Description</th>
<th>Pyroxene</th>
<th>Olivine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Most ferroan</td>
<td>Most magnesian</td>
</tr>
<tr>
<td>SiO₂</td>
<td>52.15</td>
<td>51.97</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.10</td>
<td>0.06</td>
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<tr>
<td>FeO</td>
<td>0.23</td>
<td>0.16</td>
</tr>
<tr>
<td>MnO</td>
<td>25.64</td>
<td>24.48</td>
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<tr>
<td>MgO</td>
<td>19.73</td>
<td>20.76</td>
</tr>
<tr>
<td>NiO</td>
<td>0.07</td>
<td>0.08</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Sum</td>
<td>99.91</td>
<td>99.38</td>
</tr>
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</table>

Stoichiometry: cations on relevant number of oxygens (ideal pyroxene = 4 cations per 6 oxygens; olivine = 3 per 4 oxygens)

<table>
<thead>
<tr>
<th>Description</th>
<th>Feldspar</th>
<th>Glass</th>
<th>Cr-spinel</th>
<th>Merrilite</th>
<th>Metal (awaruite)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K-rich</td>
<td>End 1 NWA 6693</td>
<td>Olivine-rich enclave</td>
<td>All other NWA 6693</td>
<td>Cr-spinel in Cr-spinel</td>
</tr>
<tr>
<td>SiO₂</td>
<td>67.99</td>
<td>65.47</td>
<td>67.09</td>
<td>66.60</td>
<td>67.60</td>
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<tr>
<td>TiO₂</td>
<td>0.17</td>
<td>0.03</td>
<td>0.06</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17.95</td>
<td>20.66</td>
<td>20.01</td>
<td>20.09</td>
<td>18.94</td>
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<tr>
<td>Cr₂O₃</td>
<td>0.03</td>
<td>0.05</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.89</td>
<td>0.40</td>
<td>0.61</td>
<td>0.27</td>
<td>0.39</td>
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<tr>
<td>MnO</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>0.06</td>
<td>0.01</td>
<td>0.01</td>
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<tr>
<td>CaO</td>
<td>0.04</td>
<td>1.85</td>
<td>0.27</td>
<td>0.61</td>
<td>0.44</td>
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<td>Na₂O</td>
<td>6.25</td>
<td>10.67</td>
<td>10.96</td>
<td>10.69</td>
<td>11.14</td>
</tr>
<tr>
<td>K₂O</td>
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<td>0.02</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Sum</td>
<td>100.41</td>
<td>98.93</td>
<td>100.26</td>
<td>99.36</td>
<td>99.52</td>
</tr>
</tbody>
</table>

Stoichiometry: Total cations on relevant number of oxygens (ideal feldspar = 5 cations per 8 oxygens; spinel = 3 per 4 oxygens)

*aExcluding the olivine-oikocryst enclave.
**20-μm grain entirely mantled by olivine.

*All iron oxide calculated as FeO except in Cr-spinel, where proportionality between Fe-oxides is extrapolated based on ideal stoichiometry.

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tem of twin lamellae is discernible (Fig. EA-6); virtually no grains show sharp lamellae. In rare locations where pigeonites (mostly smaller grains) show twin lamellae, presumably shock-produced, they seem normally sharp. The scarce/fuzzy feldspar twinning is enigmatic. Among terrestrial plutonic rocks, untwinned plagioclase is about as rare, typically only 10–20%, among extremely Ca-poor varieties as for any other composition (Gorai, 1951). Probably the feldspars of NWA 6693 suffered degradation of crystal structure as an effect of shock metamorphism, akin to, but not so completely degenerative as, maskelynitization (Fritz et al., 2005).

Cr-spinel occurs mainly as equant, subhedral to euhedral grains, up to 0.4 mm across, in general widely scattered, but sometimes in small clusters of 2–3 small grains. Its composition, which appears rather uniform, is shown in Table 1. The largest merrillite observed is 0.2 × 0.1 mm. It, too, as far as can be measured by EPMA, shows a rather uniform composition (Table 1).

Scattered grains of metal (awaruite) are generally blocky but anhedral, and occur in all sizes up to 1.2 mm across; with one clump of millimeter-sized outcrops, possibly artificial subdivisions of a single connected, anhedral grain, spanning 2.5 mm. All of the analyzed metals are an extremely Ni-rich variety of awaruite (Table 1, Fig. 6). The trace of sulfide, found as mantles around small awaruite grains, includes two varieties, both Ni-rich. For the relatively Ni-poor sulfide (pentlandite, probably), our single analysis contains, by weight: 34.5% Ni, 33.2% S, 29.6% Fe, 2.6% Co and 0.15% Cr. The other sulfide (probably hazelwoodite; average of 3 analyses from 2 grains) contains, by weight: 71.9% Ni, 25.6% S, 2.6% Fe and 0.05% Cr.

3.2. Heterogeneities and other complexities

The general description above applies, except in detailed ways, for the vast majority of the volume of NWA 6693. However, our uncommonly extensive sampling has revealed that in both texture and mineralogy, the meteorite exhibits significant heterogeneity.

The original shape of the NWA 6693 stone was elongated, like a loaf of bread, with a maximum dimension (25 cm) about three times its dimensions in directions perpendicular to the long axis. Our studies began (Warren et al., 2011) with material from one end of the loaf, and “End 1” turned out to be atypical. In thin sections from End 1 (Fig. EA-7), pigeonite is not so preponderantly in the form of large oikocrysts. Most of the pigeonite is in the form of grains under 2 mm across. Although the largest is 5 mm across and contains olivine chadacrysts and amoeboid feldspar in optical continuity up to 2.5 mm, few other sampled pyroxenes in our two End 1 sections bear such clear resemblances to the typical oikocrysts elsewhere in the meteorite. The End 1 feldspar, in general, simply appears anhedral/interstitial. Its optical continuity rarely extends much beyond 1 mm. In places the feldspar wraps around lobes of mafic silicates (Fig. EA-8), a texture reminiscent of plagioclase “pincer” textures observed in impact-melted but essentially undifferentiated chondrites (Fig. 4 of Rubin and Jones, 2003).

The feldspar of End 1 is also subtly but consistently distinctive in composition, with Ca/K, in comparison to the feldspar typical of the rest of NWA 6693, enhanced by a factor of ~4 (Table 1). Perhaps not coincidentally, the only gross deviation from the typical albite NWA 6693 feldspar composition was also found in End 1: a single tiny grain of nearly CaO-free sanidine (An0.2Ab57.3Or42.5) composition (Fig. 5).

The Cr-spinel of End 1 is also distinctive, inasmuch as about half of the ~20 large (greater than ~100 μm) grains studied contain melt inclusions, typically voidy and about 10 μm in equivalent diameter. Cr-spinels from elsewhere in the meteorite contain similar inclusions (Fig. EA-8), but more commonly appear inclusion-free. In most cases, the melt inclusions consist purely or almost purely of felsic glass (Table 1). The compositions of these glasses, with their consistently very low MgO and generally high K2O (although K2O shows great scatter, from 0.15 to 4.6 wt%), indicate that the host spinels crystallized, i.e., the melt inclusions were trapped, at a late stage in the overall crystallization of NWA 6693; an inference also supported by the spatial distribution of the large Cr-spinels, mostly intergrown with feldspar and seldom surrounded by mafic silicates. The scenario is the opposite of the early trapping generally inferred for the melt inclusions in martian cumulates (e.g., Calvin and Rutherford, 2008).

One enclave of about 10 × 7 mm, found by Edwin Thompson on a sawn slab of NWA 6693 (Fig. EA-9), is highly distinctive in both mode and texture, although only subtly distinctive in terms of mineral compositions. The mode of this enclave, determined from BSE images of its interior (Fig. 7; cf. Figs. EA-10 and EA-11) is 53 vol% olivine, 37 vol% pyroxene, 10 vol% feldspar, with <1% of Cr-spinel and metal. Thus, its olivine/pyroxene ratio is over 6 times higher than that of NWA 6693 as a whole.

The interior of this enclave consists of 4–6 olivine oikocrysts, which enclose anhedral low-Ca pyroxene and feldspar. The appropriateness here of the term oikocryst might be debated; at any rate, these are olivine-dominated intergrowths of anhedral crystals. The exact count of separate olivine oikocrysts is unclear, because the largest 1–3 oikocrysts constitute a single domain, within which the angle of optical extinction of the olivine is nearly uniform, and yet at most rotations of the nicsols this single domain clearly divides into 3 similar-sized subareas with distinct interference colors. This subdivided structure may have originated as a single large oikocryst, constituting most of the volume of the enclave; and its subdivision may date from a disturbance, such as an impact, that marginally fragmented that oikocryst. In any case, the largest olivine oikocryst is 9 mm in maximum dimension. The enclave’s anhedral pyroxenes show optical continuity only up to 1 mm.

A distinctive aspect of the enclave’s texture (Fig. 7) is a tendency for the feldspars to feature linear/angular contacts with olivine, albeit these feldspars have grossly anhedral overall shapes, in optical continuity up to 3 mm. The feldspars thus show alignments that resemble runic writing, i.e., the “micrographic” texture characteristic of quartz-K-feldspar intergrowths in many terrestrial and a few lunar granitic rocks. The alignments, at least as best sampled...
within the enclave’s dominant olivine oikocryst (all 3 of its subareas), show parallelism in two directions angled roughly 100 degrees apart. The olivine-rich enclave’s olivine and Cr-spinel compositions are hardly distinguishable from ordinary NWA 6693 compositions (Table 1). The composition of the feldspar in the enclave is distinctively An-poor (Fig. 5), although the difference is only a matter of ~0.34 wt% CaO compared to typical NWA 6693 feldspar (Table 1). The enclave’s pyroxene compositions are also subtly distinctive, showing an odd juxtaposition of magnesian augite with ferroan pigeonite (Fig. 2). As will be discussed below, the olivine-feldspar intergrowth texture may help to constrain the composition of the enclave’s parent melt.

Elsewhere, constituting an extremely minor and widely scattered component of the overall rock, are local clusters of incongruously minute olivines. We subjected the exemplar of this type of cluster (Fig. 8; cf. Figs. EA-3 and EA-6) to detailed study. Clustered within a single feldspar outcrop of about 0.5 mm² (with some spill-over into nearby pyroxenes) are roughly 130 tiny, rounded olivines, mostly less than ~40 μm across; i.e., smaller than the predominant size of olivine elsewhere in the rock by an order of magnitude. Centered around the same feldspar outcrop is a cluster of even tinier merrillite grains (Fig. EA-3). Merrillite is fine-grained throughout the rock, but these grains are particularly fine. The olivine- and merrillite-studded feldspar outcrop is part of a large optically continuous anhedral

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grain within a pigeonite oikocryst, i.e., a typical NWA 6693 feldspar, except it is at the outer fringe of that feldspar, and of its host oikocryst (Fig. EA-6). Compositionally, the cluster-zone’s olivines and merrillites are hardly distinguishable from ordinary NWA 6693 compositions (Table 1).

Other aspects of heterogeneity appear to stem from the complex roles of impact, localized melt replenishment, and annealing (all possibly related) in the evolution of this material. Most of the rock’s constituent silicates appear at least slightly “cloudy” due to tiny, micrometer-scale inclusions. Most of the microinclusions are solids, and nearly all of those are oxides (spinel, presumably), although a few are metals. Some of the microinclusions are not solids but bubbles (Fig. 9; Figs. EA-12 and EA-13). We doubt that these bubbles are artifacts of lab fluids entering tiny cracks during the sample preparation process (Rudnick et al., 1985), because the bubbles are not concentrated near the margins but distributed across the full thickness of our sections, one of which is ~100 μm thick; and because in many instances the bubbles occur in closely spaced multiple parallel sets (e.g., Fig. EA-13), with no evident relationship to any system of shock-induced cracks.

Both types of microinclusions, solid and gaseous, largely occur in scattered arcuate “trains” of many inclusions in series, chaotically criss-crossing the material. Thus, these microinclusions appear to have been mobilized, at least, and perhaps also originally formed, as by-products of impact-shock shearing and injection. Other evidence of shock-mobilization and injection includes long, discontinuous veins of one silicate phase within another (Fig. 10). In pyroxene, these injection-veins often trend parallel with the dominant cleavages of the crystals (Figs. EA-14 and EA-15).

Fig. 4. NWA 6693 olivines are uniformly ferroan and have high Ni contents, here shown in comparison with GRA 06128 (Shearer et al., 2010a), diogenites (Shearer et al., 2010b), and lunar mare basalts and ferroan anorthosites (Borg et al., 2009).

Fig. 5. Feldspar major-element compositions shown on (two subareas of) the Ab–An–Or ternary. Red symbols represent the compositionally distinctive “End 1” area of NWA 6693. In the magnified (right) diagram, open-diamond symbols are feldspars from NWA 6926, and dark-filled circles represent the olivine-rich clast. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. Native metals in NWA 6693 are an extremely Ni-rich, low-Co/Ni variety of awaruite. Data acquired contemporaneously for awaruiites from two chondrites are shown for comparison.
Not all of the microinclusion alignments appear to have formed by injection. The dark ring seen within the large pigeonite oikocryst in the left-central portion of Fig. 1 (cf. color version, Fig. EA-1) consists of countless microinclusions of oxide. Note that this ring has the same shape as, and is centered within, a rounded-rectangular lobe within the oikocryst. Rather than injection, this distribution suggests some process involving diffusive reaction between the lobe core and a minor proportion of interstitial melt. Also, some of the more tightly clustered bubble inclusions show an unlikely outcome for shock-injection: clear alignment, both individually and collectively, with cleavages or twinning within the host crystals, including both pyroxene and (Fig. EA-13) feldspar.

At some point, a replenishment, or at least remobilization, of interstitial melt appears to have occurred. Mantling of olivine by pyroxene (Fig. 3, Figs. EA-4 and EA-5) is a common feature of mafic-igneous rocks. However, NWA 6693 also manifests instances of extensive pyroxene overgrowths onto pyroxene. The most clearly manifested pyroxene-on-pyroxene overgrowths are recognizable based on abrupt diminution in the abundance of microinclusions in the outer portions of the grains (Fig. 11), along with a stark contrast in interference colors, transitioning at approximately the same internal boundary within the grain (Fig. EA-16). Typically, although not always, the overgrowth mantles show crystallographic continuity (topotaxy) with the cores by going to optical extinction at the same, or virtually the same, angle of stage/nicsols rota-

Fig. 7. Backscattered-electron image of the unusual 10-mm enclave (cf. Figs. EA-7, EA-8 and EA-9) in which olivine (light grey) is the dominant, oikocryst phase. The other main phases are subequal proportions of pigeonite (medium grey) and feldspar (dark grey). Rare white grains are Cr-spinels (off-white) and awaruits (bright white). The feldspar manifests a “graphic” intergrowth texture, with crystal margins aligned dominantly at angles of about 70 and 330 degrees (clockwise) relative to vertical.

Fig. 8. Backscattered-electron (BSE) image of a region of anomalously fine, rounded olivine grains (light grey) associated with, although not entirely confined within, a single outcrop of feldspar (dark grey). The view’s width is 1.5 mm. For additional BSE and optical images of this area, see Figs. EA-3 and EA-6. Medium grey is virtually all pyroxene. Minor phases visible include an off-white grain of Cr-spinel in the upper left corner, and many tiny bright white grains of metal. Note rounded shapes of the fine olivines. Compositionally these olivines are indistinguishable from the coarsest olivines in NWA 6693.
tion. We studied internal compositional variations within four of these pyroxene-on-pyroxene overgrowth grains by acquiring a total of 119 analyses in a single EPMA session. Results are shown in Fig. 12. These analyses are all low-Ca. Although 3 of them have relatively high Wo (Wo 6–8), the effect of including or excluding these could hardly be discerned on the figure. In 3 of the 4 grains studied, the overgrowth zone shows a statistically significant albeit only very slight diminution in \( \text{mg} = \frac{\text{MgO}}{\text{MgO} + \text{FeO}} \) relative to the core. Also, although distinction of such small differences among analyses acquired over different EPMA sessions is an analytical challenge, those three compositionally distinct overgrowth zones have average \( \text{mg} \) of 56.7–57.1 mol%, lower than any other pyroxene among the diverse settings studied within NWA 6693, including the olivine-rich enclave (Fig. 2, Table 1). The episode of melt replenishment also may have been responsible for the embayed, corroded appearance shown by some of the large pigeonite oikocrysts (Fig. 1, Fig. EA-1). In the End 1 region, some of the olivines also have embayed shapes (Fig. EA-4). Scarcity of microinclusions, both solid and gaseous, in the overgrowths (Figs. 11, EA-16) suggests that the interstitial melt replenishment, or remobilization, occurred after an intense shock.

The complete history of the rock may have involved more than one significant shock, and available evidence hardly constrains whether bubbles (fluid inclusions) were already abundant in the initial igneous crystallization material. The textures of the overgrown pigeonite grains suggest that bubbles were abundant before the intense shock(s) that engendered the interstitial melt replenishment, while also, at least locally, altering the disposition of the bubbles. In any case, the rock eventually underwent annealing extensive enough to restore the mafic silicates to sharp optical extinction, i.e., S1 in the shock classification of Stöffler et al. (1991).

4. GEOCHEMISTRY

4.1. Oxygen isotopes

Oxygen isotopic compositions of NWA 6693 are listed in Table 2. The replicate analyses agree well and give an average of \( \delta^{18}O = 4.32\%_\text{O} \), \( \delta^{17}O = 1.19\%_\text{O} \), and \( \Delta^{17}O = -1.08\%_\text{O} \). Similar results have been reported for NWA 6693 by Jambon et al. (2012) and for NWA 6704 by Irving et al. (2011). Fig. 13 shows NWA 6693 plotted along with known groups of meteorites that have oxygen-isotopic compositions relatively close to it. There are no known ferroan differentiated meteorites with an oxygen-isotopic composition similar to NWA 6693. For example, the howardite–eucrite–diogenite clan, main group pallasites, and mesosiderites all have higher \( \Delta^{17}O \). NWA 6693 is also clearly different from the ungrouped FeO-rich achondrite GRA 06128/9, which plots close to the TF line (Shearer et al., 2010a; Day et al., 2009, 2012). Instead, NWA 6693 plots in the range of the acapulcoite-lodranite clan of magnesian primitive achondrites. Compared with chondrites, NWA 6693 has an oxygen-isotopic composition similar to two CH/CB chondrites, Isheyev (Ivanova et al., 2008) and NWA 2210 (Meteoritical Bulletin, number 90). Although NWA 6693 plots near the CR-mixing line (Schrader et al., 2011; Harju et al., submitted for publication), it has higher \( \Delta^{17}O \) than CH chondrites having similar \( \delta^{18}O \), especially compared with the CR data obtained by the CO2 laser-fluorination technique (Schrader et al., 2011; Harju et al., submitted for publication).


Fig. 9. Reflected-light, crossed nicols view of bubbles just below the surface of a polished plug sample of NWA 6693. The largest bubbles seen here form a tight cluster (center, below scale bar) that shows strong parallelism, albeit the arrangement is far from a “train”. The host phase is a feldspar. Near the right edge of the same feldspar is a cluster of much smaller objects, almost certainly bubbles, that do appear as a train. Even smaller objects visible elsewhere (especially in left-center grain) could be either bubbles or solids. For a lower-magnification context view, cf. Fig. EA-10.
Fig. 14, a plot of $\Delta^{17}$O versus olivine $mg$ for a comprehensive compilation of achondrites and also some chondrites, further illustrates the uniqueness of NWA 6693. The only achondrites with closely similar $\Delta^{17}$O are the acapulcoite–lodranites and LEW 88763. But the acapulcoite–lodranites are much more magnesian. LEW 88763 is not so decisively magnesian, but LEW 88763 has far lower $\delta^{18}$O than NWA 6693 (Fig. 13).

4.2. Other bulk composition results

Results from INAA and MFBA are shown in Table 3. Texturally and mineralogically NWA 6693 appears to be an igneous cumulate, i.e., a product of major crystal–liquid fractionation (cf. Irving et al., 2011; Jambon et al., 2012). Yet its bulk composition is for most elements remarkably unfractionated relative to chondrites. Concentration (weight) ratios relative to CI chondrites are shown for the weighted-mean composition in Table 3. If volatile and/or chalcophile elements (i.e., Zn, Ga, As, Se, Sb) are excluded, concentrations of the remaining thoroughly lithophile or thoroughly siderophile elements are consistently CI-like. The greatest positive deviation is for SiO$_2$ (2.25 × CI), and the most significant negative deviation is for Hf (0.40 × CI).

Incompatible elements are shown normalized to CI in Fig. 15. As noted, our results for this high-Co/REE material are unusually imprecise. The basic, negative-sloping REE pattern is apparent from the better-determined elements La, Sm, Yb and Lu. However, the extent of the neg-
Table 2
Whole-rock oxygen isotopic composition of NWA 6693.

<table>
<thead>
<tr>
<th>ID</th>
<th>Mass (mg)</th>
<th>(\delta^{18}O_{SMOW}(%o))</th>
<th>(\delta^{17}O_{SMOW}(%o))</th>
<th>(\Delta^{17}O(%o))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNU-159-1</td>
<td>3.42</td>
<td>4.32</td>
<td>1.17</td>
<td>-1.10</td>
</tr>
<tr>
<td>SNU-159-2</td>
<td>2.56</td>
<td>4.31</td>
<td>1.21</td>
<td>-1.06</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>4.32</td>
<td>1.19</td>
<td>-1.08</td>
</tr>
</tbody>
</table>

Fig. 12. Three out of four studied NWA 6693 pyroxene overgrowths (crosses) show mild but significant diminution in mg relative to the cores (filled squares) of these grains. The left half of Fig. 11 shows the “pointy” grain, and the right half shows the “C” grain (see also the crossed-nicols images in Fig. EA-12).

Fig. 13. Bulk oxygen-isotopic composition of NWA 6693. Literature data for meteorites that have similar oxygen-isotopic compositions and/or petrologic characteristics are shown for comparison. On this diagram, only data obtained with the CO\(_2\) laser-fluorination technique fall in the same area but with greater scatter. In terms of oxygen-isotopic composition, NWA 6693 shows resemblance to some primitive achondrites, including the acapulcoite-lodranite clan, and for \(\Delta^{17}O\) (but not \(\delta^{18}O\)) LEW 88763. Three reference lines are plotted: TF (terrestrial mass fractionation line), CCAM (carbonaceous chondrite anhydrous mineral line), and a line of \(\Delta^{17}O = -1.08\)‰ (average of NWA 6693).

Fig. 14. Olivine mg vs. bulk-rock \(\Delta^{17}O\) for NWA 6693, other achondrites (horizontal lines, except for ureilites) and selected chondrites (circular symbols). NWA 6693 is distinctly ferroan compared to most of the few materials with similar \(\Delta^{17}O\); i.e., among primitive achondrites, the acapulcoite–lodranites (“Ac–Lo”), ~F\(_{86}\) ureilites, and LEW 88763 (“LEW”); and among chondrites, Ishyaevo and NWA 2210. Tafassasset (“Ta”; Gardner-Vandy et al., 2012) is sometimes considered a primitive achondrite, but we show it with a circular symbol because it contains relict chondrules. Comparably ferroan materials mostly have \(\Delta^{17}O\) close to zero (i.e., the TF line), or else, in the case of NWA 011, distinctly lower than the \(\Delta^{17}O\) of NWA 6693. The ureilites are shown by a diagonal line, because unlike all other tightly linked classes of achondrites, ureilites feature diverse \(\Delta^{17}O\), with a diffuse but significant anticorrelation between \(\Delta^{17}O\) and olivine mg; the most ferroan olivine among ureilites is Fo\(_{83}\) (Warren, 2011, GCA). Although for simplicity the CR chondrites are shown by a single point, they contain minor ferroan olivine. Also, as suggested by the dotted line, CR chondrites show a range in \(\Delta^{17}O\), from –3.7 to –0.33‰ (Harju et al., submitted for publication). The \(\Delta^{17}O\) shown here is that of the CR mixing line (see Harju et al., submitted for publication) at the same \(\delta^{18}O\) as NWA 6693 (Fig. 13). The plotted achondrite groups (horizontal lines), in order of increasing \(\Delta^{17}O\), are: NWA 011, LEW 88763, acapulcoite–lodranites, pyroxene-grouped pallasites, winonaites, Diomoe, brachinites, mesosiderites, HED meteorites, GRO 06128/9, NWA 2968, main group pallasites, NWA 2293, NWA 4042, QUE 93148, Bunburra Rockhole, angrites, aubrites, NWA 5363, NWA 5400, lunar rocks (\(\Delta^{17}O\) = 0), NWA 4741, and Mars rocks. Additional data sources are too numerous to enumerate, but include Clayton and Mayeda (1996), Swindle et al. (1998), Yamaguchi et al. (2002), the review by Franchi (2008), Bland et al. (2009), and numerous recent entries in the Meteoritical Bulletin.
Bulk-rock compositional results for 5 separately powdered chips from NWA 6693.

| Mass (wt%) | Na2O | MgO | Al2O3 | CaO | FeO | MnO | TiO2 | H2O | P2O5 | Total Fe (as FeO) | SiO2 | Zn | Ga | Se | Ru | l | Zr | Nb | Cr | V | Mo | Nb | Y | La | Ce | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | Ta | W | Mo | Hf | Au | Gd | Ta | Ir | Os |
|------------|------|-----|-------|-----|-----|-----|------|-----|-----|-------|------|----|----|----|----|----|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| End 1a     | 350  | 1.00 | 18.7  | 1.95 | 50.5 | 1.43 | 0.24 | 24.4 | 0.44 | 0.31 | 4.1  | 0.58 | 63 | 2.99 | 530 | 13200 | <4 | 2.2  | 0.31 | <0.35 | <1000 | <11 | <15 | 0.20 | 0.4 | 0.125 | 0.057 | 0.020 | 0.036 | 0.101 | 0.012 | 0.050 | <0.05 | 540 | 410 | 117 | <0.04 |
| End 1b     | 387  | 1.07 | 18.6  | 2.10 | 50.1 | 1.51 | 0.25 | 24.6 | 0.37 | 0.36 | 4.0  | 0.54 | 61 | 3.02 | 470 | 6000  | <5 | 0.14 | <0.25 | <1000 | <13 | <40 | 0.43 | 0.8 | 0.20 | 0.06c | 0.03c | 0.038 | 0.106 | 0.011 | 0.043 | <0.04 | 180 | 140 | 36  | <0.04 |
| Center     | 568  | 1.04 | 18.2  | 1.84 | 50.7 | 1.44 | 0.24 | 24.7 | 0.44 | 0.40 | 4.0  | 0.27 | 2.85 | 470 | 8700  | <6 | 0.18 | <0.3 | <1000 | <25 | <23 | 0.20 | 0.4 | 0.117 | 0.036 | <0.03 | 0.077 | 0.012 | 0.050 | <0.05 | 280 | 220 | 63  | <0.04 |
| End 2      | 450  | 0.96 | 18.3  | 1.94 | 50.8 | 1.48 | 0.24 | 24.6 | 0.21 | 0.25 | 3.8  | 0.25 | 2.95 | 520 | 13400 | <4 | 0.39 | <0.4 | <10  | <30  | 0.17 | 0.6  | 0.111 | 0.065 | 0.022 | 0.046 | 0.077 | 0.012 | 0.050 | <0.05 | 4  | 20  | 320 | 115 | <0.04 |

Uncertainty (%): large

Cl-normalized: Cs/Cl = 1.54, Rb/Cl = 1.15, Th/Cl = 1.19, Zr/Cl = 2.25, Os/Cl = 1.14, Hf/Cl = 1.00, Rb/Cl = 1.05, Be/Cl = 0.37, Zn/Cl = 0.59, Eu/Cl = 0.69, Os/Cl = 0.91, Os/Cl = 1.11, Os/Cl = 1.13, Os/Cl = 1.00, Os/Cl = 0.97, Os/Cl = 0.005, Os/Cl = 0.22, Os/Cl = 0.14, Os/Cl = <0.015, Os/Cl = 0.3, Os/Cl = 0.84, Os/Cl = 0.07, Os/Cl = 9, Os/Cl = 0.84, Os/Cl = 0.85, Os/Cl = 0.81, Os/Cl = 0.93, Os/Cl = 0.59, Os/Cl = 0.74, Os/Cl = 0.57, Os/Cl = 0.56, Os/Cl = 0.40, Os/Cl = 3, Os/Cl = 0.97, Os/Cl = 0.55, Os/Cl = <5.

For highly incompatible elements in "End 1b" LEW 88763 data from Swindle et al. (1998).

Fig. 16 includes data for NWA 011, "primitive" achondrite LEW 88763, and two other meteorites that have been impact-melted but are still recognizably chondrites. Except for greater chalcophile/volatile depletions, the NWA 6693 pattern resembles LEW 88763 and one of the impact-melted chondrites. It does not resemble NWA 011.

We did not directly measure sulfur. However, a large fraction of the rock’s S presumably resides in sulfides, and as discussed above we find only about 0.001 vol% sulfur in our thin sections. The bulk-rock S content, assuming the average sulfide is 30 wt% S, is implied to be of order 10 μg/g, and confidently (assuming at least 10% of the S is represented in our modal sulfide result) less than 100 μg/g. Thus, S has been depleted to a level of order 0.0002 × CI, and confidently <0.002 × CI. Whether as a consequence of mutual volatility, or perhaps by partitioning into a lost S-rich phase or phases (melt?), the similar depletions shown by S and Zn, and to lesser extents As and Sb, are probably not coincidental.

Gallium is a useful element for probing relationships among differentiated planetary materials, for several reasons: Ga is primarily yet not completely lithophile; i.e., it is mildly siderophile and weakly chalcophile. Ga is mildly volatile, making for whole-parent-body diversity. Finally, during lithophile/igneous fractionation, Ga conveniently tracks closely with a major mineral-forming oxide, Al2O3 (i.e., feldspar), so that sample representativeness is seldom a problem for the ratio Ga/Al (e.g., Rubin et al., 2000).

Unfortunately, in our Ga analyses of NWA 6693, sensitivity and precision were impaired by the material’s extremely high Na (see Section 2). We only managed to detect Ga, barely (±30%, 1 − σ), in one of our 5 analyses (Table 3). However, upper limits from two other analyses are not much higher,
and Jambon et al. (2012) have provided a 1.4 times higher result using their sensitive ICP-MS technique.

Fig. 17 shows our results for Ga/Al, Na/Al, and Zn/Al in NWA 6693, along with literature data for a variety of other differentiated planetary materials. Compared to most of the basaltic achondrites (angrites, lunar basalts, HED eucrites, NWA 011, and even shergottites), NWA 6693 has an uncommonly high Na/Al. Its Na/Al is nearly matched by GRA 06128/9, however, and also by some primitive achondrites, including acapulcoite–lodranites and LEW 88763. The Ga/Al of NWA 6693 is similarly high, and yet in another sense, compared to its Na/Al and the overall trend of Na/Al vs. Ga/Al, the Ga/Al of NWA 6693 is distinctively low.

The overall pattern of Fig. 17b, which has Zn/Al substituted for Ga/Al, is a roughly similar diagonal trend. Although volatile fractionation was likely involved in producing the inter-parent-body variations in all three ratios (Na/Al, Ga/Al, Zn/Al), NWA 6693’s Zn/Al depletion is far more pronounced than its Ga/Al depletion. The only achondrite with a similar combination of high Na/Al and low Zn/Al is GRA 06128/9. This low Zn/Al, despite high Na/Al, is further evidence that chalcophile behavior, and...
not volatility alone, probably played a major role in the development of the Zn depletion (and the depletions of As, Se and Sb) in NWA 6693.

5. DISCUSSION

5.1. Initial igneous crystallization of NWA 6693 and origin of its textures

As mentioned above (and discussed in Section 5.3), after the main, initial phase of igneous crystallization, NWA 6693 appears to have been intensely shocked, resulting in scattered feldspar-selective melting, and possibly also infiltration of a small proportion of melt of nearby and compositionally similar derivation. However, in this section we focus on the initial crystallization, and what the materials and textures it produced suggest about the petrogenesis of NWA 6693, and in particular about the composition of its parent melt.

Coarse-poikilitic texture is common among igneous cumulates, i.e., rocks formed within layered intrusions (e.g., Hunter, 1996). However, some terrestrial mantle xenoliths are poikilitic (Downes et al., 1992). Brachinites and ureilites, both of which probably formed as asteroidal mantle restites, include poikilitic structures (Warren and Kallemeyn, 1989; Goodrich et al., 2004).

The bulk composition of NWA 6693 tends to confirm that it is a cumulate, not a restite. The bulk MgO/SiO2 is only about 0.5–0.6 times chondritic (Fig. 18), and would still be subchondritic even if the observed olivine/pyroxene ratio were atypically low compared to the original material. The major minerals of NWA 6693 have such MgO/SiO2 (wt ratio) that even if the “true” olivine/pyroxene ratio were >>10, the rock’s bulk composition would still have subchondritic MgO/SiO2. Subchondritic MgO/SiO2 has petrogenic significance, because in the low-pressure context of an asteroid, the low-MgO/SiO2 major minerals, pyroxene and feldspar, will always melt before the high-MgO/SiO2 mineral olivine. Thus, an asteroidal restite’s MgO/SiO2 must progressively increase as melt is removed; and any simple scenario of petrogenesis as an asteroidal restite should lead to a superchondritic MgO/SiO2. Barring some strange complication (diminishment of MgO/SiO2 due to near-liquidus or to 90°C below equilibrium?)), the subchondritic MgO/SiO2 implies that NWA 6693 was derived from an extracted partial melt, and is not a restite.

By conventional cumulate-genesis modeling (e.g., Hunter, 1996), olivine, as a chadacryst phase, probably accumulated as a saturated (liquidus) phase of the parent melt. The NWA 6693 parent melt was probably saturated in the oikocryst phase, pigeonite, as well. Hunter (1996, p. 92, p. 96) assumed that cumulate oikocrysts generally form when the parent melt, as the cumulus chadacrysts first accumulate, is not saturated in the oikocryst phase. But Hunter’s model, with its emphasis on pressure-driven compaction, may not be relevant for the environment of an asteroid, where simple chemical cementation probably dominates as mechanism for reduction of the early porosity (“densification”). Even on Earth, Barnes and Hill (1995) found conclusive evidence that cumulate oikocrysts may be “a...
gan (2012), various studies have suggested that graphic intergrowth texture tends to develop under conditions of undercooling. London and Morgan (2012) postulated that graphic texture is best developed if “the intergrowth includes all the major components in proportions close to those of the melt”. However, in the case of NWA 6693, including its olivine-rich enclave, this ideal scenario seems unlikely, because the two mafic silicates are solid solutions that normally have much higher mg than coexisting melts (e.g., Stolper, 1977; Jones, 1995).

Our interpretation implies that the NWA 6693 parent melt was multiply saturated, or virtually saturated, with all three major phases: pigeonite, olivine and albite. Saturation with feldspar is unsurprising in any basaltic magma not formed by melting so extensive that feldspar was exhausted in the source region. Cosaturation of both olivine and pigeonite is not so highly probable, but neither is it surprising. As discussed by Warren (1985), in highly FeO-rich systems the peritectic, “reaction” nature of the olivine–pigeonite phase boundary (Stolper, 1977) is offset by the fact that this boundary trends almost directly away from the composition of FeO-rich low-Ca pyroxene. Thus, as long as neither olivine nor low-Ca pyroxene is exhausted during melting in such an FeO-rich system, basalts will remain very close to pigeonite–olivine cosaturation. Even supposing pyroxene was exhausted in the source, fractional crystallization of olivine could have soon brought pigeonite back onto a layered-intrusive melt’s liquidus.

The areas of fine-grained olivine (Fig. 8) conceivably represent clusters (with detailed texture altered by later annealing) of fragments that spilled off normal-sized olivines during mild brecciation. However, the association with merrillite abundance (Fig. EA-3) suggests that these zones were among the last products of the original crystallization, with extensive fractionation of “trapped” liquid leading to P2O5 enrichment and thus the merrillite. The tiny olivines are not especially ferroan as expected from such a scenario, but that may be because during subsequent cooling, diffusion brought all of the rock’s olivines to a state of near-equilibrium; in which case small grains would have been among the most readily equilibrated.

In classical Wager and Brown (1967) cumulate modeling, cumulates rich in trapped liquid (orthocumulates) are supposedly identifiable based on mineral zoning. However, as reviewed by Hunter (1996), orthocumulates can have their original mineral-compositional heterogeneity erased by equilibration, as we infer happened with the fine-grained olivines. Also, the concentration of exsolution near the rims of the large pigeonites probably reflects a slight zonation in Ca content, increasing toward the rims, in the original crystals. The proportion of “trapped liquid” in NWA 6693 is hard to constrain, but the rock is probably not an adcumulate.

5.2. Oxybarometry

There is no guarantee that oxygen fugacity did not change during the episode of replenished interstitial melt, which, as mentioned above and further discussed in the next section, was likely impact-related. However, the observable effects of that late-stage melt are subtle enough to suggest that fO2 probably remained roughly consistent.

The distribution of nickel in NWA 6693 (Table 1) shows an uncommonly low ratio of metal/olivine partitioning (134), which suggests a high oxygen fugacity (cf. Ehlers et al., 1992, Fig. 9). Herd et al. (2009) found that fO2 has almost no influence on olivine/melt partitioning for Ni, but the low metal/olivine partitioning probably resulted indirectly from high partitioning (solubility) of NiO into the parent silicate melt. Borisov (2006) found that Ni solubility in silicate melt, as NiO, increases by nearly 2 orders of magnitude, from 0.2 wt% to ~13 wt%, as log fO2 increases from −9.5 to −6.0 (i.e., from the IW buffer to the QFM buffer) at 1430 °C. Dingwell et al. (1994) found that Ni solubility increases by a factor of 20, from 0.56 to 11.2 mg/g (reported in terms of Ni), as log fO2 increases from −10.8 to −8.2 (i.e., from IW to QFM − 1) at 1300 °C. Cobalt’s behavior is analogous, and our bulk-rock Co result (Table 3), compared with our data for the composition and abundance of awaruite, suggests that most of the rock’s Co is in its mafic silicates. However, other difficult-to-constrain factors, such as melt FeO, MgO and SiO2 contents, and the intensive variable of temperature, all significantly influence Ni and Co behavior, so it may not be possible, at this time, to derive any quantitative constraint on fO2 based on Ni and Co data.

Papike et al. (2004) proposed a method of oxybarometry based on vanadium content in spinel. Comparing the average atomic V/(Al + Cr) ratio of the NWA 6933 spinels (0.75, Table 1) to Fig. 5b of Papike et al. (2004), the implied fO2 is IW + 2.2 log units.

The olivine–pyroxene–spinel oxybarometer of Wood (1991) may be applicable to NWA 6693, with two caveats. First, the pyroxene of NWA 6693 is Wo3 pigeonite, not orthopyroxene. Second, we constrain the ferric iron content of the spinel only indirectly, by stoichiometry (Table 1). Wood (1991) cautioned that serious errors can result if the spinel FeO4 component is not directly measured. However, in the case of NWA 6693, the FeO4 content may be high enough that the final error is not vastly larger than that inherent in most oxybarometers. The result, based on the data in Table 1, most notably the overall average of 2.14 wt% FeO4 in spinel, is QFM −3.5 log units; i.e., at roughly 900 °C, IW +0.7.

By small-parent-body standards, IW +0.7 would be a high fO2, and IW +2.2 very high. As reviewed by Wadhwa (2008), for the best-constrained small bodies, the aubrite asteroid, the HED parent body, the Moon, and the angrite parent body, typical/representative oxygen fugacities are IW −5, −1, −1, and +1, respectively.

5.3. Later evolution of NWA 6693

As a cumulate (cf. Irving et al., 2011; Jambon et al., 2012), NWA 6693 does not retain the bulk composition of its parent melt. However, the thermodynamic MELTS model of Ghiorso and Sack (1995) can help to place limits on a possible parent melt’s liquidus T. For the weighted mean bulk composition (Table 3), assuming fO2 ~ IW + 1,
MELTS finds a $T_{\text{liquidus}}$ of 1470 °C. The parent melt may have been lower in MgO and richer in plagiophile oxides. If the composition is modified to have MgO reduced to 5.5 wt% (implying a melt mg of 28 mol%), and the balance is modeled by addition of average Table 1 feldspar (raising the contents of Na2O, Al2O3, SiO2 and K2O to 2.6, 4.8, 60 and 1.6 wt%, respectively), MELTS finds a $T_{\text{liquidus}}$ of 1300 °C. MELTS experiments of this general type suggest that even if the parent’s mg was far lower, and/or it was greatly enriched in plagiophile oxides compared to its observed bulk-rock product, the parent’s $T_{\text{liquidus}}$ was probably not greatly different from the typical liquidi of per, 1977; Longhi, 1992).

The initial assemblage formed by igneous aggregation of coarse pyroxene oikocrysts (or locally, olivine oikocrysts), enclosing smaller subhedral olivine chadacrysts and interstitial feldspar, along with much smaller Cr-spinel and metal grains. At some point, probably while still hot, the material was subjected to a severe shock (or shocks), the heterogeneous effects of which included millimeter-scale mobilization of minute opaque debris, along with fluids that included shock-melted major silicates as well as the more volatile fluids that left the widespread bubbles. Most of the feldspar, with its low shock imperviousness, was transparently melted, but crystallinity survived, or recovered, enough for it to still show, in fuzzy, difficult to discern form, twinning. Most of the bubbles probably did not exist in their final forms before the shock, because even mild shock metamorphism tends to destroy (decrepitate) fluid inclusions (Madden et al., 2004), and some of the observed bubbles occur in feldspar with the typical NWA 6693 scarcity of clear twinning.

Probably as a result of heterogeneous shock melting, a minor proportion of additional, late melt appears to have percolated within the igneous-intrusive body. Pyroxene overgrowths (Fig. 11) grew from the new generation of interstitial melt. The basic framework of coarse pyroxene oikocrysts was not destroyed, but minor, localized displacements marred the final optical continuities of these large crystals, and the embedded margins of some of the oikocrysts (Fig. 1) probably developed as a result of reaction with the impact-melt. The impact’s structural dislocation and melting effects were probably most intense in the End 1 portion of the rock (Figs. EA-8 and EA-9).

Final cooling was slow enough for the mafic silicates to anneal all the way back to S1 shock-stage classification. For derivation of final phase-equilibration temperatures, $T_{eq}$, a complication is that not all of our pyroxene analyses fully resolved low-Ca pyroxene from minute blebs and lamellae of augite. Taking $\text{En}_{9.3}\text{Wo}_{3.2}$ and $\text{En}_{9.3}\text{Wo}_{3.3}$ as representative of clean low-Ca and high-Ca pyroxene, respectively (Table 1), the 2-pyroxene method (Lindsley, 1983) implies a $T_{eq}$ of 985 °C. The average olivine composition (0.063 wt% CaO; including data from NWA 6926), applied in the method of Kohler and Brey (1990), implies a $T_{eq}$ of 955 °C (Fig. EA-17). The average Cr-spinel and olivine compositions (Table 1) together imply 873 °C by the formula of Wlotzka (2005), or slightly lower, 873 °C, by the method of Sack and Ghiors (1991). These equilibration temperatures indicate a moderate final cooling rate; fast in comparison to some achondrites, such as Divnec and some HED diogenites ($T_{eq\text{ olivine Ca} < 800 \degree \text{C}}$), yet slow compared to LEW 88763 and most brachinites (which have $T_{eq}$ by this method > 1000 °C), and the remarkably fast-cooled ureilites (~1200 °C) (Warren and Rubin, 2012).

5.4. NWA 6693 as a new type of planetary material

The observed bulk-rock mg of 57 mol% (Table 3) represents mainly compositionally cumulus crystals considerably more magnesian than the parent melt. Cumulus framework matter probably accounted for at least 50 vol% of the initial assemblage, and further crystallization-growth (and also possibly compaction) occurred before chemical interaction with the main mass of melt became occluded. Enhancement in mg for crystals relative to parent melt is governed by

$$K_D = \frac{(\text{FeO})_c/(\text{FeO})_l)}{(\text{MgO})_c/(\text{MgO})_l)}$$

where the concentrations are all molar and the subscripts C and L denote crystals and liquid, respectively. The value of $K_D$ is constrained, for low-pressure, low-Ti systems, by countless experiments (e.g., Stolper, 1977) to be close to 0.30 for both low-Ca pyroxene and olivine. With the further assumption that the FeO content of the pigeonite-dominated mix of cumulus matter is roughly the same as in the parent melt (i.e., $D_{\text{FeO}}$ is ~1) (Stolper, 1977; Bartels and Grove, 1991; Jones, 1995), the implied mg of the parent melt ranges from 38 mol% for the extreme assumption of 50% trapped liquid, to 30 mol% assuming 10% trapped liquid. NWA 011, which appears to be a simple basalt, not a cumulate (Yamaguchi et al., 2002; Floss et al., 2005), has a bulk mg of 36 mol% (Yamaguchi et al., 2002; Isa et al., 2008). The original parent melt of NWA 6693 was similarly, if not more, ferroan.

The high, near-chondritic siderophile element contents in NWA 6693 (Fig. 16) place important constraints on the significance of this sample as a representative of its parent body. Yamaguchi et al. (2002) suggested that the comparatively low siderophile contents of NWA 011 (for Ir 0.06× the NWA 6693 level, for Ni 0.016×; Fig. 14) are too high to be explained “in terms of igneous processes” and that NWA 011, which is a recrystallized breccia, represents a mixture “contaminated by projectile materials.” Floss et al. (2005) invoked extensive fractional crystallization to account for the low mg of NWA 011. Thus, in principle, the ultimate parent magma of NWA 6693 might have started with a relatively high mg (conceivably in the range of acapulcoites and lodranites), before undergoing (1) major fractional crystallization, and then, before NWA 6693 accumulated yet too late for much igneous fractionation of siderophile elements, (2) a massive siderophile contamination. However, any simple contamination model seems unlikely. The high, near-chondritic siderophile levels in NWA 6693 imply that the contamination component, surely much less than 50 wt% of the rock, could not possibly be any known type of chondrite. Even among iron meteorites (Wasson, 1985), those with near-chondritic Ni/Ir seldom have Ir much higher than 10× CI (i.e., 10× the NWA 6693 level); yet obviously, NWA 6693 is not 10% Fe-metal. Thus, the siderophile evidence suggests that Fe-
metal, with its enormous tendency to sequester siderophile elements and to fractionate HSE from less ideally siderophile elements, played no major role in the differentiation of the NWA 6693 parent material.

The near-chondritic pattern of ratios among the siderophile elements in NWA 6693 (Fig. 14: Co, Ni, Os, Ir and Au) also seems an unlikely outcome from extensive pure-silicate fractional crystallization. Even in the absence of metal, these elements have highly diverse partitioning behaviors vis-a-vis olivine, spinel and silicate melt (Righter et al., 2004). Thus, for example, olivine fractionation would deplete Ni (Gaetani and Grove, 1997; Li et al., 2003) and Ir (Brenan et al., 2005) relative to Au (Righter et al., 2004).

Lithophile elements, including Cr and Sc, which are compatible with pyroxene, also show little evidence of fractionation (Table 3; cf. Jambon et al., 2012). The simplest interpretation of the trace-element evidence is that the NWA 6693 parent magma was never extensively fractionated; i.e., high FeO and low mg were already properties of a primary magma produced by melting of an extremely oxidized (FeO-rich) variety of primitive material.

Dale et al. (2012) have noted that in a general way, both oxygen fugacity and mantle (or more generally, noncore) concentrations of highly siderophile elements correlate with parent-body mass, including planets Mars and Earth. The correlation between /O2 and noncore HSE content presumably arises because low /O2 leads to pervasive metal, the carrier phase for sequestration of HSE into the core. It is also reasonable to suppose that oxygen, which forms volatile species with the light elements H and C, tends to be generally most abundant in the largest of the differentiated bodies. However, these correlations are far from perfect. Mercurian meteorites have not yet been found, but MESSNER constraints suggest that very low /O2 prevails in Mercury’s FeO-poor crust (McCubbin et al., 2012). Angrites, which presumably come from an asteroid no larger than Vesta, features still fractionated (Table 3; cf. Jambon et al., 2012). The simplest interpretation of the trace-element evidence is that the NWA 6693 parent magma was never extensively fractionated; i.e., high FeO and low mg were already properties of a primary magma produced by melting of an extremely oxidized (FeO-rich) variety of primitive material.

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9. The limited fractionation among nonchalcophile, non-volatile elements, including even the siderophile elements, suggests that the parent melt was not produced by extensive fractional crystallization. Thus, the high FeO and low Mg# of NWA 6693 were probably in large measure already properties of the original primary magma, produced from an extremely oxidized (FeO-rich) variety of primitive material. NWA 6693 indicates that high oxygen fugacity inherited from oxidized-chondritic building blocks may persist within small bodies, despite melting extensive enough to engender igneous cumulates.

ACKNOWLEDGMENTS

We thank two anonymous colleagues for helpful, constructive reviews, and Edwin Thompson for his very generous donations of multiple large samples of NWA 6693. This work was supported by NASA grants NNG06GE86G (P.H.W.), NNG06GF95G (A.E.R.) and Korean Government Grant NRF-MEST 2009-0086316 (B.-G.C.)

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2012.12.025.

REFERENCES


Associate editor: Christian Koeberl