Chemie der Erde 76 (2016) 111–116

Contents lists available at ScienceDirect

Chemie der Erde

journal homepage: www.elsevier.de/chemer

Petrography and classification of NWA 7402: A new sulfide-rich unequilibrated ordinary chondrite

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ARTICLE INFO

Article history:
Received 26 January 2015
Received in revised form 1 September 2015
Accepted 4 January 2016
Editorial handling - K. Keil

Keywords:
Meteorite classification
Unequilibrated ordinary chondrites
Meteoritics
Cosmochemistry
Early solar system
Petrography

ABSTRACT

We classify a new chondritic find Northwest Africa (NWA) 7402. This meteorite is highly unequilibrated, and is therefore potentially significant for the study of primitive Solar System materials. Mineralogy, mineral chemistry, and modal abundances of minerals indicate that NWA 7402 is most likely an L chondrite. However, the specimen contains a higher abundance of sulfide than commonly seen in ordinary chondrites. The structural order of organic matter in the matrix and the chromium content of Fe-rich olivine grains indicate a petrologic type of 3.1. NWA 7402 largely escaped thermal metamorphism, and secondary phases formed by aqueous alteration are rare to absent. Minor planar fractures and undulatory extinction of olivine grains suggest that NWA 7402 experienced shock up to stage 2 or 3. Terrestrial weathering is heterogeneous in the specimen; much of the stone's exterior shows substantial Fe oxidation (weathering grade 2), while some parts of the interior remain relatively fresh (weathering grade 1). NWA 7402 has some unusual features that should be investigated further. The sulfide abundance is higher than reported sulfide contents for other L chondrites, and the chromium content of the olivines does not fall on the trend established for unequilibrated ordinary chondrites by Grossman and Brearley (2005).

1. Introduction

A new chondritic meteorite find Northwest Africa (NWA) 7402 displays rare features suggesting that it could be highly primitive, warranting detailed study for classification purposes. NWA 7402 is a 4013.4 g individual stone, purchased on August 26, 2010 by Eric Twelker of the Meteorite Market from a meteorite trader in Morocco (Fig. 1). Its history – including finder and location – remain unknown, as is the case with many NWA meteorites. Samples of NWA 7402 were supplied to the University of Hawai'i at Mānoa for classification purposes, and a mass of 25.5 g was sent to the University of New Mexico repository as the type sample. We have employed optical microscopy, scanning electron microscopy (SEM), electron microprobe analysis (EPMA), and Raman spectroscopy to determine the chemical group, petrologic type, stage of shock, and terrestrial weathering grade. During the classification process, some unusual features were noted that potentially deserve further study.

2. Analytical techniques

Primary petrographic characterization of NWA 7402 was conducted with optical microscopy. To evaluate terrestrial weathering, the degree of oxidation of metal grains was assessed, following Wlotzka (1993). The modal abundances of Fe-bearing phases (metal, sulfides, and weathering products) were determined by point counting using the reflected-light method of Boeck et al. (2009). The optical microscopy methods and criteria proposed by Stöffler et al. (1991) were used to assess the degree of shock in NWA 7402.

The thin and thick sections were subsequently carbon-coated for the SEM and EPMA. Qualitative mineral identification was done with energy-dispersive X-ray spectroscopy (EDS) on the SEM. The modal abundance of components (including chondrules, fine-grained matrix and rims, opaque assemblages, and isolated silicate grains) were counted in the NWA 7402 thick section using a grid and a backscattered electron (BSE) map of dimensions 3 mm × 2.5 mm.

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http://dx.doi.org/10.1016/j.chemer.2016.01.001
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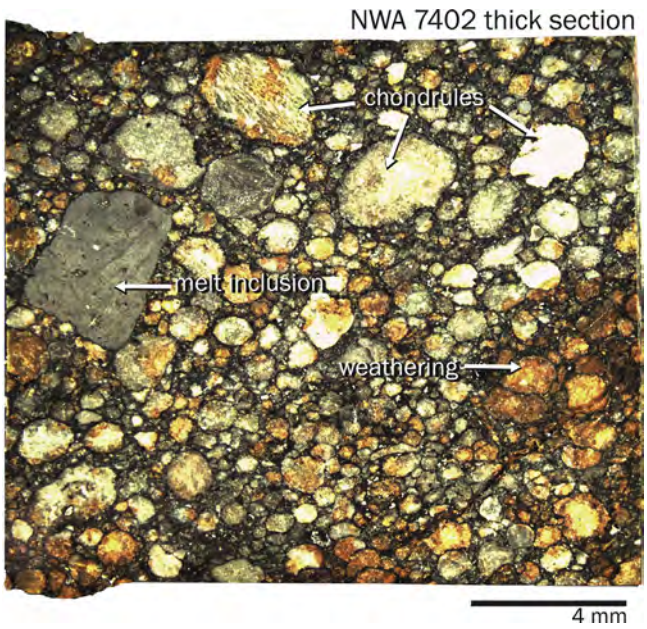

Fig. 1. Optical image of the NWA 7402 thick section. Chondrules vary in size from <200 μm to >3 mm. Heterogeneous terrestrial weathering is apparent as rust-colored regions in the sample.

Multi-element X-ray maps were taken using the JEOL Hyperprobe JXA-8500F Electron Microprobe at the University of Hawaii. X-ray maps were taken at 20 keV, 50 nA with a 5 μm beam diameter, and 25 ms dwell time.

Quantitative elemental analyses were conducted with EPMA to determine the chondrite group for NWA 7402, using the methods of Van Schmus and Wood (1967). Over the course of two sessions, a total of 261 chondrule silicates were chosen at random and measured for Al, Ti, Na, Fe, K, Si, Cr, Mg, Mn, and Ca. Standards included San Carlos olivine, sphene glass, Amelia albite, orthoclase, Verma garnet, and USNM 117075 chromite. The Fe contents of the silicates are also reported in terms of the fayalite (Fa) content for olivine and the ferrosilite (Fs) content for pyroxene, expressed in mol%.

The Cr_2O_3 contents of Fe-bearing olivines were used to determine the petrologic type, following Grossman and Brearley (2005). Of the NWA 7402 olivine grains measured by EPMA, 140 had FeO > 2 wt%, suitable for petrologic-type determination. To assess the accuracy of the analyses, 56 chondrule olivine grains in Semarkona (LL3.00) and 43 in Bishunpur (LL3.15) were also measured for Cr_2O_3 under the same analytical setup. The measurement points were selected from regions not visibly affected by the fusion crust, as entry heating could have altered the Cr_2O_3 composition of exposed olivine.

To further constrain petrologic type, Raman spectroscopy measurements were conducted at Laboratoire de Géologie de Lyon (Université Claude Bernard – Ecole Normale Supérieure de Lyon, France). Following Quirico et al. (2003) and Bonal et al. (2006, 2007), matrix material was separated (<50 mg) and measured via Raman spectroscopy. For type 3 chondrites, the most sensitive spectral parameters to thermal metamorphism are the width and intensities of the so-called D and G bands. Spectral parameters for the D and G bands were fit with Lorentzian and Breit–Wigner Fano mathematical profiles, respectively. Petrologic type can be assigned by comparing these parameters to those of reference samples.

3. Results

3.1. Petrographic observations of NWA 7402

NWA 7402 is a chondritic breccia, with occasional lithic clasts of impact melt present (Fig. 1). Rust-colored, apparently weathered areas with orange-brown chondrules surround less-weathered regions containing light yellow-gray chondrules set within a darker gray groundmass (Fig. 1). The less-altered regions on the interior of the meteorite show minor oxide veins (Fig. 2) and alteration of Fe-rich phases, consistent with weathering classification of W1 (Wlotzka, 1993). However, the more weathered portions show at least moderate oxidation of metal with about 20–60% being affected, consistent with a W2 grade (Wlotzka, 1993).

The meteorite contains a high abundance of chondrules embedded in a clastic, sulfide-rich matrix (Figs. 1 and 2). Opaque assemblages composed of metal, Ni-poor sulfide (either as troilite or pyrrhotite), and magnetite are common. Apparent chondrule diameters range from ~0.2 to 3 mm; this distribution may differ from the true sizes due to sectioning effects (Hughes, 1978; Eisenhour, 1996). A melt inclusion of approximately 4 mm in length is present in the thick section (Fig. 1), and an anomalously large barred-olivine chondrule of 8 mm in diameter exists in one thin section. Chondrule types include porphyritic olivine and/or pyroxene, barred olivine, radial pyroxene, and cryptocrystalline. Many chondrule mesostases retain a glassy and/or quenched texture, apparently unaffected by pre-terrestrial aqueous alteration (Fig. 2).

Most olivine grains show undulatory extinction and irregular fractures, though a few instances of planar fractures exist (Fig. 3). According to the shock classification scheme for ordinary chondrites (Stöffler et al., 1991), undulatory extinction in olivine is ubiquitous in chondrites of shock stage S2 (very weakly shocked), and planar fractures occur at stage S3 (weakly shocked).

The modal abundances of the chondritic components determined from the NWA 7402 thick section by point counting (Table 1) are consistent with those of ordinary chondrites (e.g., Brearley and Jones, 1998; Weisberg et al., 2006). No Ca–Al-rich inclusions were found in the sections studied, although one aluminous chondrule was identified. The fine-grained silicate rims that surround some chondrules are typically FeO-rich and embedded with micron-sized Fe sulfides. Large opaque assemblages (~300 μm in diameter) contain kamacite, taenite, Fe sulfides, and Fe oxides. The sulfides

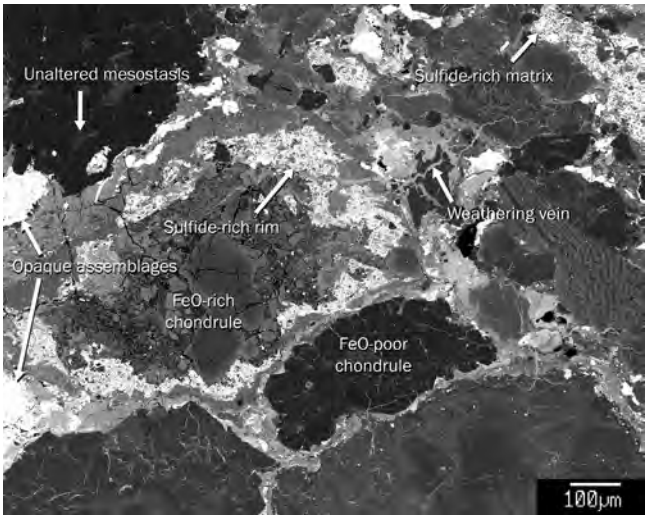

Fig. 2. BSE image of NWA 7402 showing a variety of chondrule types embedded in a fragmented matrix. Much of the fine-grained material is sulfide-rich, and multiple opaque assemblages are apparent.

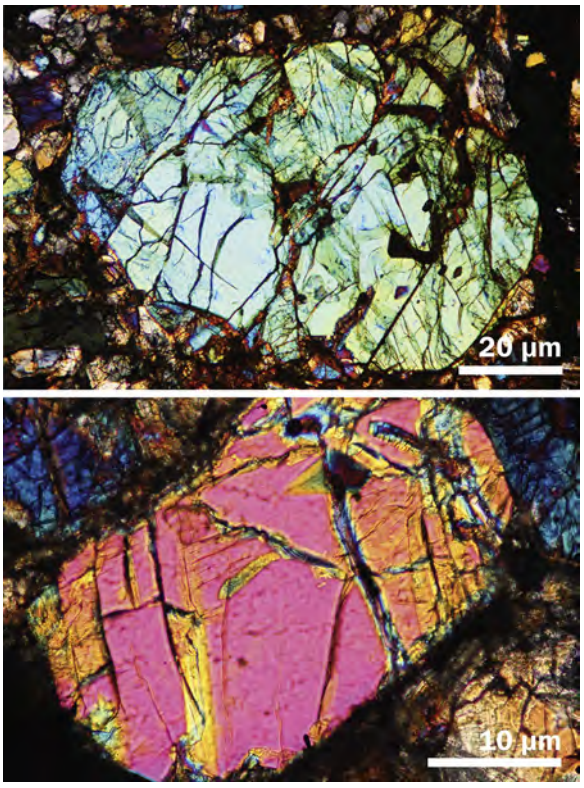

Fig. 3. Cross-polarized optical photomicrographs of weakly shocked olivine grains in NWA 7402, indicating a shock stage of S2 to S3. Some planar fractures are evident in both crystals.

Table 1
Modal abundances of components in NWA 7402.

Component	Point count	Volume %
Chondrules	489	69.9
Fine-grained matrix and rims	121	17.2
Opaque assemblages	70	10.0
Isolated silicates	23	3.3
Total	703	100

are primarily Ni-poor, existing as either troilite or pyrrhotite (as determined by EDS). Some Fe oxides appear in veins and as halos surrounding metal, and are likely products of terrestrial weathering.

The modal abundances of Fe-bearing phases in NWA 7402 are given in Table 2, as identified under optical reflected light. These abundances were converted into weight percent using the methods of Keil (1962) and Boeck et al. (2009), assuming all sulfides to be stoichiometric troilite (FeS) and weathering products to be goethite (FeOOH). This analysis yields an Fe,Ni content of 7.8 wt%. However, if the weathering products formed largely from the oxidation of primary Fe,Ni metal, then the pre-weathering metal abundance could have been up to 9.6 wt%. These values would place NWA 7402 into the L-chondrite range of 4.4–11.7 wt% Fe,Ni as defined

Table 2
Modal abundances of Fe-bearing phases in NWA 7402, expressed in vol% and wt%.

Phase	Point Count	Volume %	Weight %
Sulfide	98	14.4	18.1
Fe,Ni	26	3.8	7.8
Weathering	19	2.8	2.9
Silicates	539	79.0	71.2
Total	682	100.0	100.0

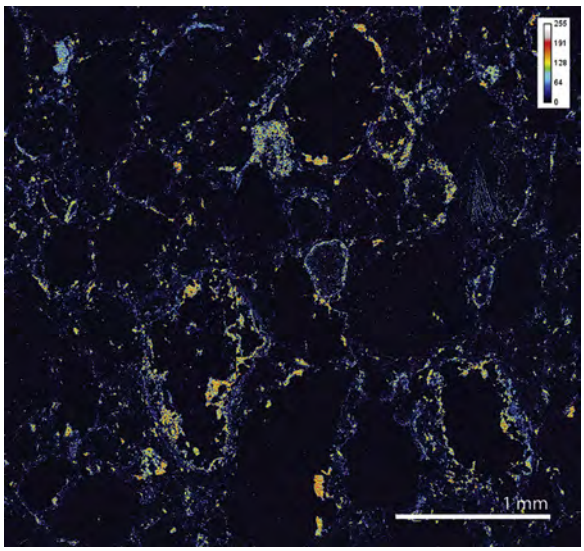

Fig. 4. Sulfur X-ray map of a 4 mm × 4 mm section of NWA 7402. Color bar calibrated such that pure FeS regions are orange-red. The volume fraction of sulfide is approximately 9.5 vol%, as determined using ImageJ software.

for equilibrated ordinary chondrites (Keil, 1962; Gomes and Keil, 1980; Weisberg et al., 2006).

The abundance of sulfides determined by point counting is 14.4 vol% (Table 2), likely representing an upper limit as most sulfide-rich fine-grained materials were counted as sulfide due to their appearance under reflected optical light. Sulfur x-ray maps were therefore taken (Fig. 4) and analyzed for volume fraction using ImageJ software for a more accurate sulfide abundance, yielding 9.5 vol% (or ~12 wt%) sulfides.

3.2. Electron microprobe analyses of chondrule silicates

Elemental oxide compositions measured from chondrule silicates are reported in Table 3 (the full dataset is available as supplementary material). The Fa content of chondrule olivine in NWA 7402 is highly variable, ranging from <1 to ~36 mol% (Fig. 5). The average Fa content of chondrule olivine grains is 12.4 ± 7.9 mol%, and the pyroxene analyses yield an average Fs content of 9.1 ± 8.2 mol%. The Fa distribution for olivine in NWA 7402 is consistent with Fa distributions for petrologic type 3 UOCs, and the 61% percent mean deviation (PMD; defined by Dodd et al., 1967) of

Table 3
Average elemental abundances (wt%) for NWA 7402 chondrule (a) olivines and (b) pyroxenes.

(a) Average olivine analyses			(b) Average pyroxene analyses		
Oxide	wt%	1σ	Oxide	wt%	1σ
SiO_2	39.6	±1.5	SiO_2	58.1	±2.4
Al_2O_3	0.05	±0.05	Al_2O_3	0.53	±0.63
FeO	11.6	±7.0	FeO	6.1	±5.3
MgO	47.3	±6.8	MgO	34.5	±5.0
CaO	0.18	±0.10	CaO	0.75	±1.56
K_2O	bdl	bdl	K_2O	bdl	bdl
Na_2O	0.01	±0.02	Na_2O	0.03	±0.03
TiO_2	0.02	±0.02	TiO_2	0.07	±0.07
MnO	0.29	±0.17	MnO	0.30	±0.20
Cr_2O_3	0.39	±0.13	Cr_2O_3	0.68	±0.23
Total	99.4	±1.4	Total	101.2	±1.5
Fa [Avg.][a]	12.4	±7.9	Fs [Avg.][a]	9.1	±8.2
PMD	61%		PMD	85%	

[a] Fayalite and ferrosilite contents are reported in mol%.

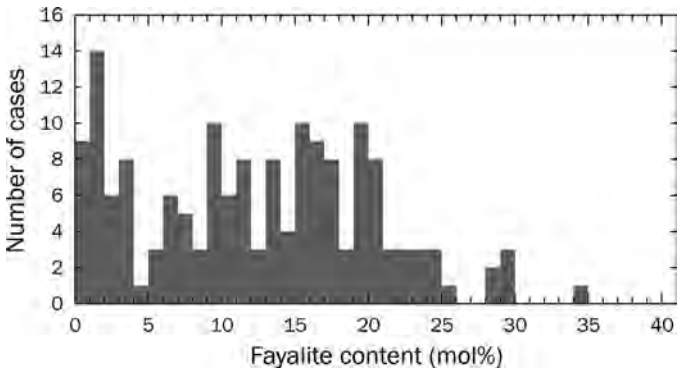

Fig. 5. Histogram for the fayalite content of chondrule olivine grains in NWA 7402. The percent mean deviation (PMD) for this distribution is 66.9%.

the FeO content indicates a petrologic type <3.4 (Van Schmus and Wood, 1967; Huss et al., 2006).

The Cr_2O_3 content of Fe-rich chondrule olivine ranges from 0.2 to 0.7 wt%, with an average of 0.41 ± 0.13 wt% (Fig. 6). The range of Cr_2O_3 abundances in NWA 7402 is comparable to the Cr_2O_3 distributions for type 3.0/3.1 UOCs from literature (Grossman and Brearley, 2005). However, on a plot of the standard deviation of Cr_2O_3 versus mean Cr_2O_3 content (Fig. 7), NWA 7402 falls off of the general trend defined for typical UOCs (Grossman and Brearley, 2005). The analyses of the control specimens, Semarkona and Bishunpur, generally agree with the literature values (Grossman and Brearley, 2005), falling within 0.05 wt% of the mean Cr_2O_3 values and within 0.006 wt% of σ-Cr_2O_3 (Fig. 7).

3.3. Raman spectroscopy of NWA 7402 matrix separates

Matrix separates in NWA 7402 were measured with Raman spectroscopy to determine the width and intensities of the D and G spectral bands (Quirico et al., 2003; Bonal et al., 2006, 2007). The full width at half-max (FWHM) of the D band is plotted against the ratio of the peak intensities (I) for the D and G bands in Fig. 8, which compares data for NWA 7402 (black symbols) to reference analyses for Semarkona (LL3.00), Bishunpur (LL3.15), Chainpur (LL3.4), and Axtell (CV > 3.4), shown in gray. The average of the NWA 7402 analyses (large point with error bars) is in excellent agreement with the Bishunpur data, and is resolved from Semarkona analyses (Fig. 8).

4. Discussion

The type 3 UOC NWA 7402 has experienced little thermal metamorphism and aqueous alteration, making it a valuable meteorite for studying early Solar System processes. Petrographically, NWA 7402 is most similar to an unequilibrated ordinary chondrite (UOC).

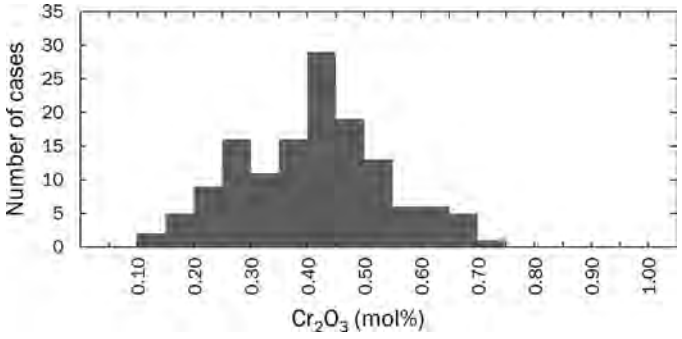

Fig. 6. Histogram for the chromium content of chondrule olivine grains with FeO > 2 wt% in NWA 7402. The mean value is 0.41 ± 0.13.

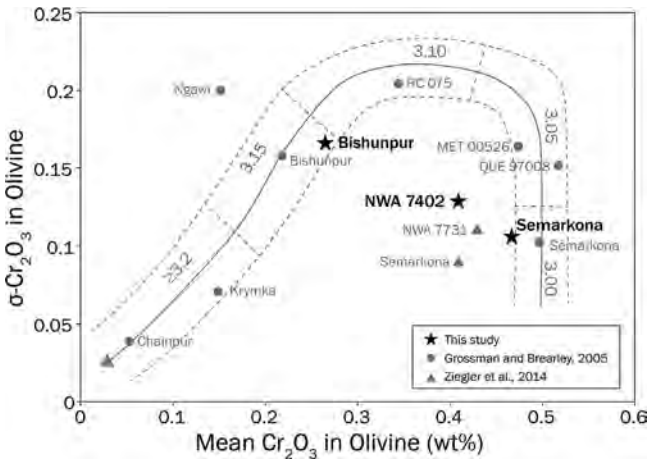

Fig. 7. A plot of the standard deviation versus the mean of the Cr_2O_3 content of ferroan olivine (FeO > 2 wt%) for NWA 7402. Semarkona and Bishunpur ordinary chondrites were also measured to determine relative accuracy. The data in study are shown as bold stars. Previously measured UOCs from Grossman and Brearley (gray circles; 2005) and Ziegler et al. (gray triangles; 2014) are plotted for reference. The solid gray line represents the approximate UOC trend, while the dashed lines represent the approximate spread for UOC samples (Grossman and Brearley, 2005). NWA 7402 plots away from the typical UOC trend (see text).

However, NWA 7402 also displays attributes that are unusual for UOCs. The elevated sulfide abundance and anomalous chromium content of olivines suggests that NWA 7402 may have an anomalous origin.

4.1. Classification of NWA 7402

The ordinary chondrites are characterized by chondrule abundances between 60 and 80 vol%, matrix abundances of 10–15 vol.%, and chondrules of all textural type (e.g., Brearley and Jones, 1998; Weisberg et al., 2006). The high abundance of chondrules (70 vol%) and the variation in chondrule sizes and types are clear indications that NWA 7402 is an ordinary chondrite. Chondrule olivine compositions in NWA 7402 range from FeO < 1 wt% to ~36 wt%, with variable Cr_2O_3 abundances (0.41 ± 0.13 wt%) characteristic of

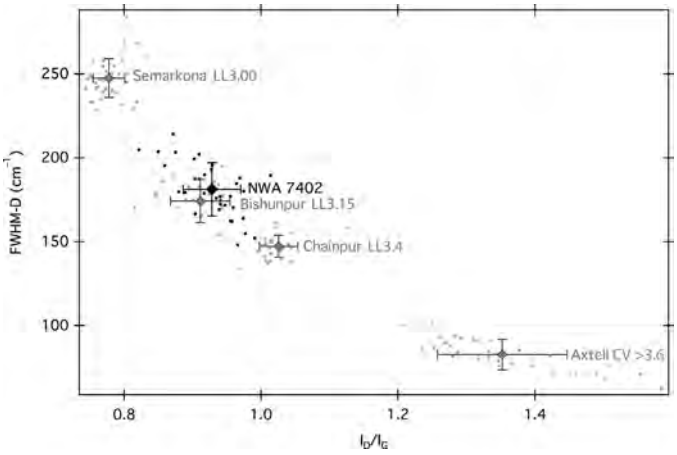

Fig. 8. To characterize the maturity of the matrix carbonaceous material in NWA 7402, we compare Raman spectral parameters. Plotted are the FWHM of the Raman D band (cm^{-1}) versus the ratio of peak intensities for the D and G bands, ID/IG. Small dots represent the individual data points, while the large points with error bars represent the weighted averages of all measurements and 2σ standard deviation. The point in black is NWA 7402, plotting close to Bishunpur (LL3.15) shown in gray. Gray points are well-known petrologic type 3 chondrites. Lower petrologic types trend toward the upper left of the diagram; down and to the right are higher metamorphic grade type 3's.

a petrologic type <3.2 (Grossman and Brearley, 2005; Huss et al., 2006). However, on a plot of variation in Cr_2O_3 content versus the average Cr_2O_3 value, NWA7402 olivine falls off of the petrologic type trend defined for UOCs, making it difficult to quantify (Fig. 6). The Raman analyses can help constrain the petrologic type (Fig. 7), suggesting that NWA 7402 has undergone a similar thermal history to Bishunpur (near type 3.15).

While equilibrated ordinary chondrite subgroups are characterized by the average Fa content of chondrule olivines (in mol%: H 16–20; L 23–26; LL 27–32; Weisberg et al., 2006), chondrule olivines in UOCs do not necessarily follow these trends since the FeO is dispersed (>5% mean deviation in FeO content; Van Schmus and Wood, 1967; Huss et al., 2006; Weisberg et al., 2006). Therefore, the olivine composition is not a reliable indicator of group for the unequilibrated NWA 7402. The abundance of Fe,Ni metal for NWA 7402 (between 7.8 and 9.6 wt%) was instead used to identify the meteorite as an L chondrite (Keil, 1962; Gomes and Keil, 1980). Additional isotopic and elemental studies may be worthwhile in future studies to confirm this group.

4.2. Sulfide abundances in ordinary chondrites

The high abundance of sulfides (~12 wt%) in NWA 7402 is beyond the norm for equilibrated ordinary chondrites, which typically have 5–7 wt% sulfides (e.g., Gomes and Keil, 1980). However, elevated sulfide abundances of ~9 wt% have been reported in low petrologic type ordinary chondrites (e.g., McCoy et al., 1994), and some equilibrated L chondrites contain up to 10.3 wt% (Dunn et al., 2010). Although these samples are not as sulfide-rich as NWA 7402, there appears to be more variability in ordinary chondrite sulfide abundances than is generally appreciated.

Most of the sulfides observed in NWA 7402 occur in fine-grained chondrule rims and matrices, or in metal-sulfide assemblages. S-rich matrices are characteristic of primitive type 3 ordinary chondrites, where the bulk S content in decreases with increasing petrologic type (Allen et al., 1980; Nagahara, 1984; Lauretta et al., 1997; Grossman and Brearley, 2005; Agee et al., 2013). The S-rich fine-grained lithology in NWA 7402 likely reflects the low-metamorphic grade and primitive nature of the sample, possibly being formed under S-enriched conditions.

The metal-sulfide assemblages in NWA 7402 are similar to the kamacite–taenite–troilite assemblages common in UOCs such as Bishunpur (e.g., Rubin et al., 1999). These assemblages may represent the unaltered precursors of carbide-magnetite and Ni-rich-sulfide assemblages described in aqueously altered type 3 UOCs, such as Semarkona (Krot et al., 1997; Brearley and Jones, 1998; Rubin et al., 1999; Huss et al., 2006). No such secondary assemblages were found in NWA 7402. The retention of the primary Ni-poor sulfide features support the idea that NWA 7402 has largely escaped parent body processing, and may help to explain the high sulfide abundance.

4.3. Anomalous chromium composition of Fe-bearing olivines

The Cr_2O_3 composition of NWA 7402 olivine does not follow established trends for UOCs (Fig. 7). Another new African find, NWA 7731, seems to be very similar to NWA 7402 (Agee et al., 2013; Ziegler et al., 2014; Ziegler and Agee, 2014). Both contain abundant S-rich opaque matrix, are highly primitive, and NWA 7731 plots within 0.02 wt% Cr_2O_3 of NWA 7402 in Fig. 7. While the Cr content may suggest that these two stones are related, we note that the mean Cr_2O_3 value obtained for Semarkona in the Ziegler et al. (2014) study is shifted by nearly 0.1 wt% to the low side of the trend defined by Grossman and Brearley (2005) (Fig. 7). If this shift indicates a systematic calibration issue for EPMA analyses, then the NWA 7731 data would also be affected, and may not be in proximity to NWA 7402 after all. In that case, NWA 7402 would be truly anomalous with Cr_2O_3 characteristics unlike other UOCs, making the sample an intriguing object for future studies.

5. Conclusion

We utilized a variety of micro-analytical methods for classification of NWA 7402. The abundance and variety of components suggests that NWA 7402 is an unequilibrated ordinary chondrite, and the modal metal abundance (7.8–9.6 wt% Fe,Ni metal) suggests that NWA 7402 is an L chondrite. The FeO contents of olivine and pyroxene revealed the highly unequilibrated nature of the sample. Raman spectroscopy of organic matter in the fine-grained matrix indicates that the sample has undergone little thermal metamorphism, and is of similar petrologic type to Bishunpur (3.15). The range of chromium abundances in olivine generally support that NWA 7402 lies between types 3.00 and 3.15, but falls off the trend for typical UOCs. Such anomalous chromium content in olivine complicates the petrologic type classification, and therefore NWA 7402 remains an L3.1 until additional observations can justify a more accurate petrologic type. Optical microscopy reveals that the sample has experienced moderate shock and weathering, corresponding to maximum stages S3 and W2, respectively. The largest inconsistency with this classification is the elevated sulfide abundance in NWA 7402 (~12 wt%), which may be a reflection of the minimal parent body processing. We therefore suggest that the meteorite is categorized as a sulfide-rich L3.1 UOC, weathering grade W1/W2, and shock stage S3. In addition, the unusual chromium and sulfide abundances suggests that there may be more to its history than meets the eye, making it a good target for further study.

Acknowledgements

The authors would like to thank E. Hellebrand for his assistance with EPMA, and to E.R.D. Scott and G.J. Taylor for their helpful comments. This work was supported by NASA Headquarters under the NASA Earth and Space Science Fellowship Program – Grant NNX14AO29H, as well as NASA cosmochemistry grant NNX11AG78G (G.R. Huss, PI), and NAI cooperative agreement NNA04CC08A (K. Meech, PI). This manuscript is HIGP publication #2174 and SOEST publication #9491.

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.chemer.2016.01.001.

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