NWA 16813 (CK6) Records One of the Highest Oxygen Fugacities in Meteorites (Postprint)

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Full Text

Preamble

NWA 16813 (CK6) Records Among the Highest Oxygen Fugacity in Meteorites

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Abstract

Magnetite-ilmenite pairs in meteorites serve as reliable thermometers and oxygen fugacity (fO_2) indicators for constraining both nebular conditions and thermal metamorphic histories. While CK and CV chondrites exhibit nearly identical petrological characteristics and oxygen isotope compositions, our analysis of NWA 16813 reveals it records the highest fO_2 yet measured among these meteorites (log $fO_2 = -20.51$ at 589.34°C to log $fO_2 = -14.21$ at 608.63°C). This finding provides critical evidence that CK and CV chondrites experienced fundamentally different redox conditions during their formation. The fO_2 data from NWA 16813, combined with its distinct petrological and mineralogical features, strongly suggest that CK and CV chondrites originated from chemically separate reservoirs in the protoplanetary disk despite their apparent similarities.

Key words: meteorites, meteors, meteoroids -Planetary Systems -minor planets, asteroids: general

1. Introduction

Despite the growing availability of extraterrestrial returned samples, meteorites continue to serve as crucial materials for investigating both nebular and planetary processes. The accurate classification of meteorites constitutes a fundamental yet challenging task in meteoritical research. Among these, carbonaceous chondrites hold particular significance for deciphering the early evolution of the solar system. However, the classification relationship between CV and CK chondrites remains controversial, as they exhibit remarkably similar petrographic characteristics, overlapping oxygen isotopic compositions, comparable cosmic-ray exposure age distributions, and consistent reflectance spectral features—despite having undergone distinctly different thermal histories (Righter & Neff 2007; Greenwood et al. 2010; Chaumard & Devouard 2016).

Several studies have proposed that CV and CK carbonaceous chondrites originated from the same parent body, with CK chondrites representing thermally equilibrated CV chondrites (Greenwood et al. 2003; Greenwood et al. 2004). The metamorphic progression appears continuous between CV and CK chondrites, with peak metamorphic temperatures ranging from <850 K for CVs, 850-920 K for CK3, and 920-1140 K for CK4-6 (Chaumard & Devouard 2016). Indeed, ordinary, enstatite, and carbonaceous chondrite groups represent distinct compositional regimes in the solar nebula, spanning from highly reduced (with all Fe present as metal) to fully oxidized (where Fe is entirely incorporated into silicates and oxides), with only rare exceptions deviating from this trend (Righter & Neff 2007). The oxidation conditions of CV and CK chondrites appear continuous or very similar, with the oxidized CV subgroup showing the closest affinity to CK chondrites. The data from the NWA 16813 CK6 chondrite presented in this study further support Righter & Neff (2007)' s interpretation, which contrasts markedly with the previous hypothesis.

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2. Material and Methods

The NWA 16813 sample was prepared as a one-inch epoxy mount. Petrographic analysis was carried out using a JEOL JSM-IT500 tungsten filament scanning electron microscope at the State Key Laboratory of Lunar and Planetary Sciences, Macau University of Science and Technology. The microscope is equipped with an Oxford energy dispersive spectrometer (EDS), which was used for both point analysis and mapping analysis.

The major (more than 1.0 wt.%) and minor (less than 1.0 wt.%) element concentrations of olivine, pyroxene, plagioclase, magnetite, ilmenite, and pentlandite were analyzed using a JEOL JXA-iSP100 electron probe microanalyzer (EPMA) also at the State Key Laboratory of Lunar and Planetary Sciences, Macau University of Science and Technology. The conditions for EPMA analysis were as follows: an acceleration voltage of 15 kV, a probe current of 20 nA, a peak counting time of 30 s, and a background counting time of 15 s. The elemental data were calibrated using a series of natural minerals and synthetic materials. Based on analysis of internal laboratory standards, the precision for major elements (more than 1.0 wt.%) and minor elements (less than 1.0 wt.%) is better than 1.5% and 5.0%, respectively.

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3. Results

3.1. Petrography

3.1.1. Overall Texture and Modal Abundance NWA 16813 shows a typical chondritic texture, consisting mainly of chondrules, isolated silicates, and opaque minerals set in a fine-grained matrix [Figure 1: see original paper]. The modal abundances of NWA 16813 were calculated using ImageJ software based on EDS mapping data. Olivine is the most abundant mineral at 55 vol.%, followed by plagioclase at 20 vol.%, pyroxene at 13 vol.%, magnetite at 5 vol.%, and sulphides and other phases at 7 vol.%. Secondary plagioclase is present in both chondrules and matrix, with grain sizes ranging from 50 to 600 m.

3.1.2. Chondrules The chondrule boundaries in NWA 16813 are diffuse [FIGURE:1(a)-(c)]. Based on EDS mapping data, we identified 20 chondrules with an average diameter of 0.72 mm, consistent with the typical chondrule size (0.8 mm) reported for CK chondrites (Scott & Krot 2003). Only porphyritic olivine (PO) chondrules were observed. Chondrules consist primarily of olivine, plagioclase, pyroxene, magnetite, ilmenite, pentlandite, and apatite. The olivine and pyroxene grains within the chondrules do not exhibit secondary diffusional zoning. One unusual chondrule was discovered where the olivine is extensively filled with plagioclase [FIGURE:1(c)].

3.1.3. Matrix The matrix of NWA 16813 is composed of fine-grained olivine, plagioclase, opaque minerals (mainly magnetite and rare sulphides), and pyroxene.

3.2. Mineralogy

3.2.1. Olivine Representative EPMA analysis results for olivine are presented in . Olivine occurs most commonly in chondrules and matrix. The mean Fo value of olivine is 67.36, with a corresponding percent mean deviation (PMD) of 1.67. The range of Fo values is .

3.2.2. Pyroxene Representative EPMA analysis results for pyroxene are presented in . Pyroxene is divided into low-Ca (<0.15 atomic Ca/(Ca+Mg+Fe)) and high-Ca pyroxene (or Ca-pyroxene). The mean Fs of low-Ca pyroxene is 30.12, with a range of 28.82–32.99 and PMD of 4.52; the mean Wo of low-Ca pyroxene is 0.79, with a range of 0.44–1.91 and PMD of 60.50. The mean Fs of Ca-pyroxene is 12.18, with a range of 10.64–14.08 and PMD of 11.94; the mean Wo of Ca-pyroxene is 45.14, with a range of 41.09–46.72 and PMD of 6.00.

3.2.3. Plagioclase Representative EPMA analysis results for plagioclase are presented in . Plagioclase compositions are heterogeneous, with An values ranging from 18.41 to 46.49.

3.2.4. Magnetite Magnetite occurs in chondrules, at chondrule edges, and in the matrix [FIGURE:1(a), (f)]. Magnetite grain sizes range from 5 to 300 m. Ilmenite exsolution is commonly observed within magnetite grains [FIGURE:1(d), (e)], and some apatite can also be found in magnetite grains [FIGURE:1(f)]. Representative EPMA results for magnetite are shown in . The results indicate that magnetite in NWA 16813 is chromium-rich, with Cr_2O_3 content of 3.48–4.87 wt.%, Al_2O_3 content of 0.31–1.91 wt.%, MgO content of 0.06–0.19 wt.%, and Fe_2O_3 content of 58.85–63.48 wt.%.

3.2.5. Pentlandite Pentlandite is the only sulphide found in NWA 16813, with grain sizes ranging from 5 to 35 m. Some pentlandite coexists with Fe-Ti oxides [FIGURE:1(d)]. Representative EPMA analysis results for pentlandite are presented in , showing that the atomic ratio of metal to sulfur in all analyzed pentlandites is close to 1.1, which is almost identical to the composition of pentlandite ($(Fe, Ni)_9S_8$) and distinctly different from that of Fe-rich monosulphide solid solution (MSS). MSS ($(Fe, Co, Ni)_1$ S) has also been reported in CK chondrites (Geiger & Bischoff 1995), where it coexists with pentlandite in the same phase region at around 600°C.

4. Discussion

4.1. Classification Based on Petrographic Characteristics

NWA 16813 has a high abundance of magnetite (approximately 5 vol.%), which falls within the range observed in CK chondrites (1–8 vol.%, with an average of 4 vol.%) (Geiger & Bischoff 1995). No iron-nickel metal was found, consistent with the highly oxidized nature of CK chondrites. The average diameter of identified chondrules is 0.72 mm, similar to that of CK4-6 chondrites (0.5–1.1 mm, with an average of 0.6 mm) (Chaumard & Devouard 2016). The proportion of identified chondrules in NWA 16813 (approximately 9 vol.%) is significantly lower than in CK3 and CV3 chondrites (CV3: 18.5–55.7 vol.%; CK3: 17.1–25.7 vol.%). The size range of secondary plagioclase grains (50–600 m diameter) is consistent with CK6 chondrites (CK5: 4 m < D < 50 m; CK6: D > 50 m) (Kallemeyn et al. 1991). Based on these petrographic characteristics, NWA 16813 is classified as a CK6 carbonaceous chondrite.

4.2. Classification Based on Mineralogical Characteristics

The main mineralogical classification criteria for the CK group can be summarized as follows (Geiger & Bischoff 1991): (1) presence of equilibrated olivines with mean Fa contents between 28 and 33 mol%, NiO content of ~0.5 wt.%, and CaO content <0.1 wt.%; (2) occurrence of two different pyroxenes: low-Ca pyroxene ($Fs_{24\ 28}$) and augitic pyroxenes ($Fs_{8\ 12}$); (3) presence of heterogeneous plagioclase varying compositionally between An_{20} and An_{75} (with some CK chondrites showing bimodal distributions) (Keller 1993; Noguchi 1993); and (4) occurrence of several opaque phases: (a) abundant magnetite (commonly containing exsolution lamellae of spinel and ilmenite), (b) various Fe- and Ni-rich sulphides (including pentlandite, pyrite, pyrrhotite, and Fe-rich MSS), and (c) sulphides, tellurides, and arsenides rich in refractory siderophile elements (Pt, Os, Ir, Ru) and in Au and Ag.

The average Fa value of olivine in NWA 16813 is 32.64, falling within the 28–33 mol% range; the average NiO content is 0.67 wt.%, close to the expected ~0.5 wt.%; and the CaO content is 0.04 wt.%, which is far less than 0.1 wt.%. The average Fs value of low-Ca pyroxene is 30.12, close to the reported range of 24–28, while the average Fs value of Ca-pyroxene is 12.18, very close to the range for augitic pyroxene ($Fs_{8\ 12}$) reported in previous studies. The An value range of 18.41–46.49 indicates wide variation, with almost all plagioclase grains falling within the An_{20}–An_{75} range.

Magnetite in carbonaceous chondrites is generally considered a product of low-temperature aqueous alteration of metal (Choi et al. 2000). Since magnetite is relatively resistant to terrestrial weathering, we can assume that terrestrial alteration has little effect on its composition. However, the chemical composition of magnetite may have been altered by later thermal metamorphism on the parent body. Therefore, magnetite chemistry can be used to effectively distinguish between CV, CK3, and CK4-6 chondrites (Dunn et al. 2016). The major element composition (Fe_2O_3) and minor element composition (MgO, Cr_2O_3, TiO_2, and Al_2O_3) of magnetite in NWA 16813 are compared with previous studies of CK3 (Dunn et al. 2016), CK4-6 (Geiger & Bischoff 1995; Greenwood et al. 2010; Rubin 1993; Chaumard et al. 2014; Davidson et al. 2014), and CV (Haggerty & Mcmahon 1979; Rubin 1991; Murakami & Ikeda 1994; Greenwood et al. 2010) chondrites in [Figure 2: see original paper]. The results indicate that, except for one titanium-poor magnetite and one low-Fe_2O_3 magnetite, most magnetite compositions in NWA 16813 fall within the range of CK4-6 chondrites.

4.3. Temperature and Oxygen Fugacity

4.3.1. Temperature Iron-titanium oxides in igneous and metamorphic rocks are widely used to calculate and constrain the physicochemical conditions during magma crystallization or metamorphism, particularly for determining equilibrium temperature and oxygen fugacity. A series of iron-titanium oxide thermometers and oxygen fugacity meters have been established (Yavuz 2021). WinMlgob is a software tool that compiles and directly executes these calculation methods (Yavuz 2021). In this study, WinMlgob was used to perform temperature and oxygen fugacity calculations using the methods of Carmichael (1966), Anderson (1968), Lindsley & Spencer (1982), and Stormer (1983), based on the calibrations of Andersen & Lindsley (1985).

The temperature and oxygen fugacity of NWA 16813 were calculated based on 14 magnetite-ilmenite pairs, with results shown in . The calculated temperature range is 564.68–616.22°C, with an average temperature of 587.32°C, which falls within the 300–658°C range reported for CK chondrites by Righter & Neff (2007). This lower temperature is further supported by the presence of pentlandite [FIGURE:1(d); FIGURE:3], which is not stable at temperatures greater than 883 K (610°C) and is distinguished from MSS based on the atomic ratio of metal to sulfur. The phase diagram for pentlandite in this study shows more concentrated compositions than those of Righter & Neff (2007).

Re-equilibration temperatures calculated for the CK6 chondrite NWA 16813 are compared with temperatures for CK and R chondrites from Righter & Neff (2007) and ordinary chondrites in [Figure 4: see original paper] (Kessel et al. 2004; Slater-Reynolds & Mcsween 2005). The temperatures calculated for NWA 16813 rank among the highest reported by Righter & Neff (2007) but are much lower than those calculated for type 6 ordinary chondrites by Kessel et al. (2004) based on olivine-spinel equilibrium and by Slater-Reynolds & Mcsween (2005) based on two-pyroxene thermometry. Although some discrepancy may be attributed to differences in thermometers used, it may also indicate that CK chondrites record lower metamorphic re-equilibration temperatures than type 6 oxidized chondrites. Furthermore, the re-equilibration temperature of NWA 16813 is close to the lower limit of the peak metamorphic temperature range of 920–1140 K (645°C–865.85°C) calculated by Chaumard & Devouard (2016).

4.3.2. Oxygen Fugacity Petrologic evidence for oxidized formation of CK chondrites includes the absence of Fe-Ni metal and the abundance of magnetite (Geiger & Bischoff 1995). CV chondrites contain Fe-Ni metal in both reduced and oxidized subgroups (Krot et al. 2004), and even the oxidized CVs are more reduced than CK chondrites since they contain metal. Oxygen fugacities recorded by coexisting magnetite-ilmenite pairs in the CK chondrites studied here range from log $fO_2 = -20.51$ (589.34°C) to -14.21 (608.63°C). The CK temperature and oxygen fugacity plot forms a linear trend [Figure 5: see original paper], suggesting they equilibrated across a small temperature range but parallel to an oxygen buffer.

4.4. The Relationship Between CV and CK

The CV and CK carbonaceous chondrite groups have often been compared due to their petrographic similarities, overlapping oxygen isotopic ratios, similar cosmic-ray exposure age distributions, and consistent reflectance spectral characteristics. Some researchers have suggested that these two groups formed from the same parent body and that CKs are equilibrated CVs (Greenwood et al. 2003; Greenwood et al. 2004). The oxidized CVs have been most closely related to CKs, and the continuous peak metamorphic temperatures between CV and CK3, CK4-6 chondrites appear to support this viewpoint. However, the oxygen fugacity reported in this study does not support this hypothesis.

Oxygen fugacities calculated for CK chondrites in this study and from Righter & Neff (2007), Noguchi (1993), and Geiger & Bischoff (1995) are consistently higher than those for CVs, by as much as 4 log fO_2 units. This suggests that if CKs were derived from CVs, the metamorphic conditions or fluids must have been highly oxidizing. Furthermore, relative oxygen fugacity and olivine composition (Fo) show that CKs are depleted in metal compared to CVs, not simply because CK chondrites are more oxidized than CV chondrites [Figure 6: see original paper].

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5. Future Plan

CK chondrites are the most oxidized chondrites, yet the mechanism behind their oxidation has not been studied in detail, warranting further investigation.

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Note: Figure translations are in progress. See original paper for figures.