コンドリュール形成時における内部鉱物の累帯構造に関する理論的研究 Numerical study on chemical zoning of olivines at chondrule formation

*武田 康佑¹、三浦 均¹ *Kosuke Takeda¹, Hitoshi Miura¹

1.名古屋市立大学 システム自然科学研究科
1.Graduate School of Natural Sciences, Nagoya City University

地球に落下する隕石はその多くがコンドライトと呼ばれる種類の隕石である。コンドライト内にはコンド リュールと呼ばれるミリメートルサイズの球状のケイ酸塩組織が含まれている。コンドリュールは、46億年昔 の初期太陽系において、コンドリュールの前駆体である星間ダストが何らかの原因により溶融し、その後急冷 凝固して形成したと考えられている。コンドリュールに含まれるオリビンなどのケイ酸塩結晶には累帯構造 (化学組成の不均一性)が観察され、これは結晶が成長した際の周囲の環境変化を反映している。しかし、コ ンドリュールが経験したであろう熱履歴からどのような累帯構造が生じるのかは、よく分かっていない。 本研究では、溶融したコンドリュール内におけるオリビン結晶の融解・成長過程の数値計算を実施し、結晶内 に記録される累帯構造を検討した。成長する結晶の組成はコンドリュールの平均組成とは異なるため、結晶の 成長とともに結晶に取り込まれない成分が液相側に吐き出される(元素分配)。数値計算では、固液界面での 元素分配に加え、固体内および液相内での元素拡散を考慮した。計算手法として、合金の分野で用いられてい るフェーズフィールド法に、 Mg-Fe オリビンの理想溶体モデルを組み合わせたモデルを用いた。 コンドリュールが経験した熱履歴を、加熱(昇温速度一定)、温度維持、冷却(冷却速度一定)の三段階に分 けた計算では、加熱・温度維持期においてオリビンの融解が進行した。その後の冷却期においてオリビンは成 長に転じるとともに、累帯構造が形成した。累帯構造は、昇温速度やピーク温度継続時間にはほとんど依存せ ず、冷却速度によって大きく変化することが分かった。また、オリビンが成長に転じた位置において鉄濃度が 局所的に小さくなる一種の逆累帯構造が確認できた。次に、より現実的な状況として、典型的なコンド リュール形成モデルである衝撃波加熱モデルに基づいた熱履歴を用いて計算を行った。この場合も、累帯構造

の主要な特徴は主に冷却期の熱履歴によって決まり、その組成勾配は冷却のみを考慮した累帯構造モデル[1] と整合的であることが分かった。

以上の結果から、コンドリュール形成時におけるオリビン結晶の累帯構造は、主に冷却期の環境を記録してい るといえる。

参考文献: [1] H. Miura and T. Yamamoto (2014), The Astronomical Journal 147, 54 (9pp).

キーワード:コンドリュール、累帯構造 Keywords: chondrule, chemical zoning 複合コンドリュールの形成過程:過冷却液滴の衝突による結晶化 Formation Process of Compound Chondrules: Collision-Induced Crystallization of Supercooled Droplets

*荒川 創太¹、中本 泰史¹ *Sota ARAKAWA¹, Taishi NAKAMOTO¹

1.東京工業大学大学院理工学研究科
1.Tokyo institute of technology

Some chondrules are composed of two (or more) chondrules fused together. They are called compound chondrules. Compound chondrules have several remarkable features. In this study, we focus on three features; (1) textural types, (2) the size ratio between two components, and (3) the fraction of compound chondrules. In previous studies, these three features are remained to explain. Textural types of chondrules originate from their thermal histories. Non-porphyritic chondrules (e.g., barred olivine, radial pyroxene, and cryptocrystalline) are formed from completely molten precursors, while porphyritic chondrules are formed from partially molten precursors. As for single chondrules, the majority is porphyritic type (84%) and non-porphyritic ones are rare (16%). In contrast, more than 80% of all the compound chondrules have non-porphyritic textures. This significant feature suggests that compound chondrules are crystallized from completely molten precursors.

Experimental studies revealed that floating completely molten precursors turn into supercooled droplets without crystallization, and non-porphyritic chondrules are produced by crystallization of supercooled droplets triggered by contact with something. In addition, theoretical studies suggest that the duration of supercooling can be long.

Here, we propose a new model for the compound chondrule formation: compound chondrules are formed by collision-induced crystallization of supercooled droplets. This model is based on the feature (1) and experimental facts. Additionally, we can obtain the feature (2) that larger ones of compound chondrules keep round shapes while smaller ones are deformed. This feature is explained by the reason that larger ones are likely to be collided more than smaller ones.

We also estimate the product of the number density of precursors n and the duration of supercooling t for reproducing the fraction of compound chondrules. Then the product of the number density and the duration is $n \ t = 0.1 \ \text{cm}^{-3}$ s. Thanks to the supercooling, we can explain the fraction of compound chondrules with large t and low n.

キーワード: 複合コンドリュール、過冷却、結晶化、衝突 Keywords: compound chondrule, supercooling, crystallization, collision Nogoya CMコンドライトに含まれるカルサイトの酸素・炭素同位体比 Oxygen and carbon isotopic ratios of calcite in the Nogoya CM chondrite

*藤谷 渉¹、福田 航平²、小池 みずほ³、石田 章純³、佐野 有司³ *Wataru Fujiya¹, Kohei Fukuda², Mizuho Koike³, Akizumi Ishida³, Yuji Sano³

1.茨城大学、2.東京大学、3.東京大学、大気海洋研究所

1. Ibaraki University, 2. University of Tokyo, 3. Atmosphere and Ocean Research Institute, University of Tokyo

CM chondrites exhibit evidence for aqueous alteration to variable degrees. Carbonate is a secondary mineral of aqueous alteration. Detailed petrological and mineralogical observations along with O-isotope measurements have been carried out by previous studies. These studies have suggested that carbonates in CM chondrites did not form in a single event but formed intermittently (Tyra et al., 2012; Lee et al., 2013). In this study, we conducted in-situ O- and C-isotope measurements on calcite grains in the Nogoya CM 2.2-2.3 chondrite. Isotope measurement on carbonates in multiple "generations" could shed light on the evolution of O and C isotopic compositions during aqueous alteration.

We found many calcite grains by SEM observation. As reported in the previous studies (e.g., Lee et al., 2014), two types of calcite grains with distinct mineralogical characteristics were found. Following the definition by Lee et al. (2014), we describe these calcite grains as type 1 and 2 grains. Most type 1 grains are single crystals and have serpentine/tochilinite rims. On the other hand, type 2 grains are polycrystalline and microporous, and do not have rims.

Oxygen isotopic compositions are highly different between type 1 and 2 grains, but similar within each type ($d^{18}O = 34.7$ %(type 1) and 19.3 %(type 2) on average). The average $D^{17}O$ values are -2.5 % (type 1) and -5.4 %(type 2). The $d^{18}O$ and $D^{17}O$ values indicate that type 2 calcite formed later than type 1 calcite, because progressive alteration led to 0-isotope exchange between water and anhydrous silicate with lower $d^{18}O$ and $D^{17}O$ values than water. Carbon isotopic ratios of type 1 grains are similar ($d^{13}C = 31.8$ %on average), whereas type 2 grains have variable $d^{13}C$ values ranging from 28.8 to 61.2 %. These observations indicate an increase in $d^{13}C$ values in later stages of aqueous alteration.

It has been suggested that the Rayleigh-type isotopic fractionation driven by the escape of ¹³ C-poor CH_4 could have led to ¹³C enrichments of the dissolved inorganic C (Guo and Eiler, 2007). The observed d¹³C increase of ~30 &can be explained if ~28 % of the dissolved C was reduced to produce CH_4 and was lost at 28 °C. If true, aqueous alteration in CM chondrites would have occurred in an open system at least in later stages.

キーワード:カルサイト、酸素同位体、炭素同位体、CMコンドライト Keywords: calcite, oxygen-isotope, carbon-isotope, CM chondrite CI、CMコンドライト隕石の鉱物学および希ガス同位体組成に基づく

含水小惑星の脱水過程の解明

Dehydration process of hydrous asteroids inferred from mineralogy and noble gas signatures of dehydrated CI and CM chondrites

*菊池 知紀¹、中村 智樹²、中嶋 大輔²、長尾 敬介³、今栄 直也⁴、山口 亮⁴、小島 秀康⁴ *Kazuki Kikuchi¹, Tomoki Nakamura², Daisuke Nakashima², Keisuke Nagao³, Naoya Imae⁴, Akira Yamaguchi⁴ , Hideyasu Kojima⁴

1.東北大学理学部地球惑星物質科学科、2.東北大学理学研究科地学専攻、3.韓国国立極地研究所、4.国立極地 研究所

1.Department of Earth and Planetary Materials Sciences, FacultyGraduate School of Science, Tohoku University, 2.Department of Earth and Planetary Materials Sciences, Faculty of Science, Tohoku University, 3.Korea Polar Research Institute, 4.National Institute of Polar Research

CI and CM carbonaceous chondrites are the most primitive materials in the solar system in terms of their unfractionated chemical compositions. But they have experienced aqueous alteration to various degrees and thus retain little or no primordial mineralogy. Their parent bodies are believed to be hydrous C-type asteroids based on the similarity of reflectance spectra between the meteorites and the asteroids [1]. However, reflectance spectra of a subset of hydrous C-type asteroids are similar to those of hydrous carbonaceous chondrites that experienced heating and dehydration [2] and thus it was suggested that dehydration has occurred in hydrated asteroids. Since more than 20 meteorites showing evidence of dehydration have been found, dehydration is a common process of primitive hydrous asteroids. However, dehydration process especially for CI chondrites and the heat source for dehydration remain unknown. The purpose of this study is to evaluate the degrees of heating and to constrain the heating temperatures based on mineralogical properties and noble gas signatures of the two meteorites. In this study, we used two samples; Yamato (Y)-982086 and Y-980115, which are classified as CM and CI chondrites, respectively.

The two meteorites were analyzed using an optical microscope, a field-emission scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometry (EDS), an electron probe micro-analyzer (EPMA) and synchrotron X-ray diffraction (S-XRD) for petrology and mineralogy. Y-980115 was analyzed for noble gas isotopes.

Petrologic observation indicates that Y-982086 has experienced a moderate degree of aqueous alteration and is classified to CM 2.3 based on the classification scheme [3]. S-XRD shows that matrix phyllosilicate exhibits no 001 basal reflection, but remains prism reflections and secondary olivine is not identified, suggesting that phyllosilicate starts to decompose to be poorly crystalline. Based on (1) the presence of pentlandite and pyrrhotite with pentlandite lamellae and (2) the mean and standard deviation of Cr_2O_3 contents in FeO-rich olivine [4], it is suggested that the meteorites was heated at a temperature of 400 to 450 °C, which corresponds to the heating stage II [5].

Y-980115 contains coarser phyllosilicates and higher abundance of Fe sulfide than the Orgueil CI chondrite, suggesting that Y-980115 has not experienced advanced aqueous alteration compared with Orgueil, because it is known that phyllosilicate becomes smaller and Fe sulfide becomes less abundant with progressive aqueous alteration of CI chondrites [6]. Very weak 001 reflection of matrix phyllosilicate suggests that phyllosilicate is poorly crystalline, like Y-982086. Coexistence of carbonate and carbonate-decomposed product, periclase, suggests a heating temperature of 520 to 550 °C, which corresponds to the heating stage II to III [5]. This is consistent with similarity of noble gas release patterns of Y-980115 to those of CM chondrites of

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heating stage II [7]. Cosmic-ray exposure age estimated from cosmogenic 3 He (0.16 Ma) is shorter than that from cosmogenic 21 Ne (0.48 Ma). We argue that thermal dehydration occurred along with diffusive loss of cosmogenic 3 He not on its parent asteroid but during transit to the Earth by solar heating.

References

[1] Gaffey M.J. et al. (1989) Asteroid II, edited by R. P. Binzel,T. Gehrels, and M. S. Matthews, 98-127.

[2] Hiroi T. et al. (1993) Science, 261, 1016-1018.

[3] Rubin A.E. et al. (2007) Geochim. Cosmochim. Acta, 71, 2361–2382.

[4] Grossman J.N. and Brearly A.J. (2005) Meteorit. Planet. Sci., 40, 87-122.

[5] Nakamura T. (2005) J. Mineral. Petrol. Sci., 10, 260-272.

[6] Tomeoka K. et al. (1989) Antarct. Meteorite Res., 2, 36–54.

[7] Nakamura T. et al. (2015) Meteorit. Planet. Sci., 50, #5147 (abstr.).

キーワード:含水炭素質コンドライト、水質変成、熱変成

Keywords: hydrous carbonaceous chondrite, aqueous alteration, thermal metamorphism

COおよびCHコンドライト中難揮発性包有物のBe-Bシステマティクス Be-B systematics of refractory inclusions in CO and CH chondrites

*福田 航平¹、藤谷 渉²、比屋根 肇¹、杉浦 直治¹、高畑 直人³、佐野 有司³ *Kohei Fukuda¹, Wataru Fujiya², Hajime Hiyagon¹, Naoji Sugiura¹, Naoto Takahata³, Yuji Sano³

1.東京大学大学院理学系研究科地球惑星科学専攻、2.茨城大学理学部、3.東京大学大気海洋研究所
1.Department of Earth and Planetary Science, Graduate School of Science, University of Tokyo,
2.College of Science, Ibaraki University, 3.Atmosphere and Ocean Research Institute (AORI),
University of Tokyo

Observations of solar-type Young Stellar Objects (YSOs) have shown enhanced and frequent X-ray flares accompanied by intense flux of accelerated particles [1]. The powerful X-ray activity around newborn stars suggests that intense irradiation from the proto-Sun has also occurred in the early solar nebula. Be-B systematics of refractory inclusions, the first solids in our solar system [2, 3], can potentially shed light on irradiation processes in the early solar system.

Previous studies have demonstrated that a short-lived radionuclide ¹⁰Be, which decays to ¹⁰B with a half-life of 1.4Myr [4], was present in the early solar system with initial ¹⁰Be/⁹Be ratios ranging from 10⁻⁴ to 10⁻² [5-13]. However, most of the data come from refractory inclusions in CV3 chondrites. To further investigate the distribution of ¹⁰Be and irradiation conditions in the early solar system, we conducted Be-B isotopic measurements using a NanoSIMS 50 (at AORI, Univ. of Tokyo) on compact melilite-rich CAIs in primitive chondrites, Y81020 (C03.05) and SaU290 (CH3).

The melilite-rich CAI in Y81020 yields an isochron with the initial ¹⁰Be/⁹Be ratio comparable to those of CV CAIs within uncertainties. The results suggest that CO CAIs have also experienced irradiation processes similar to CV CAIs. In contrast, a melilite-rich CAI in SaU290 shows no resolvable excesses in ¹⁰B from the terrestrial value. Previous studies have demonstrated that hibonite-rich inclusions in CMs and FUN inclusions in CVs typically show lower ¹⁰Be/⁹Be ratios than those of most normal CAIs [7, 9, 12, 13]. In addition, these inclusions are known to have low ²⁶Al abundances, which is interpreted as their formation prior to the injection of ²⁶Al into the solar system [e.g., 14]. These observations may suggest that FUN-like inclusions record irradiation history in the protosolar molecular cloud [9, 15] and/or heterogeneous distribution of ¹⁰Be in the early solar system [12, 13]. A substantial fraction of CH CAIs also has little ²⁶Al [16], suggesting possible relevance to FUN-like inclusions. The low ¹⁰Be/⁹Be ratio of the CH CAI observed in this study could, therefore, support the above hypothesis. References

[1] Feigelson E. D. and Garmire G. P. (2002) The Astrophysical Journal, 572, 335-349. [2] Bouvier A. and Wadhwa M. (2010) Nature Geoscience, 3, 637-641. [3] Connelly J. N. et al. (2012) Science, 338, 651-655. [4] Korschinek A. et al. (2010) Nuclear Instruments and Methods in Physics Research B, 268, 187-191. [5] McKeegan K. D. et al. (2000) Science, 289, 1334-1337. [6] Sugiura N. et al. (2001) Meteoritics & Planetary Science, 36, 1397-1408. [7] MacPherson G. J. et al. (2002) Geochimica et Cosmochimica Acta, 67, 3165-3179. [8] Chaussidon M. et al. (2006) Geochimica et Cosmochimica Acta, 70, 224-245. [9] Wielandt D. et al. (2012) The Astrophysical Journal Letters, 748, L25 (7pp). [10] Gounelle M. et al (2013) The Astrophysical Journal Letters, 763, L33 (5pp). [11] Srinivasan G. and Chaussidon M. (2013) Earth and Planetary Science Letters, 374, 11-23. [12] Liu M. C. et al. (2009) Geochimica et Cosmochimica Acta, 71, 5051-5079. [13] Liu M. C. et al. (2010) The Astrophysical Journal Letters, 719, L99-L103. [14] Sahijpal S. and Goswami J. N. (1998) The Astrophysical Journal, 509, L137-L140. [15] Desch S. J. et al. (2004) The Astrophysical Journal, 602, 528-542. [16] Krot A. N. et al. (2008) The Astrophysical Journal, 672, 713-721.

キーワード:初期太陽系、宇宙線照射過程、Be-B同位体 Keywords: early solar system, irradiation processes, Be-B isotopes 実験的に加熱したTagish Lake隕石の反射スペクトル、鉱物学、化学組成 Reflectance spectra, mineralogy, and chemistry of experimentally heated Tagish Lake carbonaceous chondrite

*茂木 郁¹、中村 智樹¹、山下 小百合¹、松岡 萌¹、佐藤 勇大¹、古川 善博¹、奥村 聡¹、中嶋 大輔¹ *Kaoru Mogi¹, Tomoki Nakamura¹, Sayuri Yamashita¹, Moe Matsuoka¹, Yudai Sato¹, Yoshihiro Furukawa¹, Satoshi Okumura¹, Daisuke Nakashima¹

1. 東北大学大学院理学研究科地学専攻

1.Department of Earth and Planetary Materials Science, Graduate School of Science, Tohoku University

C-, P-, and D-type asteroids, orbiting at the outer asteroid belt, are important objects for understanding of the evolution of outer solar nebula. A subset of these asteroids shows evidence of thermal evolution such as dehydration (Jones et al., 1990), though the thermal effects on reflectance spectra, mineralogy, and chemistry are not fully understood. The purpose of this study is to reproduce the spectral, mineralogical, and chemical changes of D-type asteroids caused by heating events, using the experimentally heated samples from Tagish Lake meteorite which is believed to have derived from a D-type asteroid (e.g., Hiroi et al., 2001). Besides, this study was performed to identify constituent minerals of Martian moons, Phobos and Deimos. The spectra of Phobos and Deimos are similar to that of D- and T-type asteroids (e.g., Rivkin et al., 2002). However the 3.0-µm absorption band is shallower than these asteroids, suggesting that they are heated D-type objects.

The Tagish Lake carbonaceous chondrite fragments were experimentally heated in a vacuum at temperatures of 400, 600, and 900°C for 50 hours. Unheated and heated samples were analyzed using the powder and synchrotron X-ray diffraction (XRD) methods for bulk mineralogy, field-emission scanning electron micro scope (FE-SEM) for texture, elemental analyzer for C, N, S contents, mass spectrometer for carbon isotope ratios, and FT-IR for reflectance spectra.

XRD patterns and FE-SEM observation showed that the unheated Tagish Lake sample consists of saponite, Mg-Fe carbonate, pyrrhotite, olivine and magnetite. Saponite was replaced by olivine, and recrystallization of secondary olivine was proceeded from 600°C to 900°C. Similarly, by heating at 600°C, Mg-Fe carbonate was decomposed into magnesiowüstite, which was reduced into taenite by heating at 900°C.

Carbon content and isotope ratio (δ^{13} C values) start decreasing from the temperature of 600°C. Decomposition of carbonate, which has δ^{13} C value of ~+67% (Grady et al., 2002), is responsible for the decrease of carbon content and δ^{13} C value up to 600°C. Meanwhile, from 600 to 900°C, carbon content and δ^{13} C value decreased due to gasification of organic carbons (δ^{13} C of ~-9%; Grady et al., 2002) by thermal cracking and oxidation taken place during heating at 900°C.

The 3.0-µm absorption band in a reflectance spectrum is responsible for interlayer and structural water of saponite and absorbed water. The 3.0-µm band of the unheated sample was deep and broad, which becomes shallower and shaper with increasing heating temperatures. Interlayer water was dehydrated up to 600°C, and structural water was dehydrated up to 900°C. In contrast, structural water of serpentine in the Murchison carbonaceous chondrite, which is derived from a C-type asteroid, was dehydrated at lower temperature of 600°C (Yamashita et al., 2015). Therefore, it may be possible that C- and D-type asteroids have different water content when they are heated at the same temperature.

Mineralogical, chemical, and spectral changes of Tagish Lake proceed with increasing heating temperatures; (1) saponite is dehydrated and recrystallized into olivine, (2) interlayer and

structural water of saponite are dehydrated step by step, (3) Mg-Fe carbonate is replaced by magnesiowüstite and finally reduced into taenite, and (4) volatile elements including carbon, nitrogen, and sulfur are gasified and C isotope ratios are changed accordingly.

Comparison to Phobos and Deimos spectra suggests that 400°C and 600°C heated samples of Tagish Lake matches better. But 0.65-µm absorption band that is characteristic absorption of the Phobos red areas was not reproduced. Therefore, the reproduction of 0.65-µm absorption requires additional conditions, if Phobos was originally D-type asteroids.

キーワード: Tagish Lake隕石、脱水 Keywords: Tagish Lake, dehydration 始源的CV3.1-3.2コンドライト、NWA 8613 A primitive chondrite, NWA 8613 chondrite, CV3.1-3.2

佐藤 亮太¹、*木村 眞¹、藤谷 渉¹ Ryota Sato¹, *Makoto Kimura¹, Wataru Fujiya¹

1.茨城大学理学部

1.Faculty of Science, Ibaraki University

Carbonaceous chondrites are primitive meteorites, and they give important information about the early processes in the solar system. Especially one of them, CV chondrites are characterized by the occurrence of large refractory inclusions and chondrules. They are classified into three subgroups: two oxidized groups, CV_{oxA} and CV_{oxB} , and a reduced group, CV_{red} [1]. Oxidized CVs were subjected to the secondary metasomatic reactions and partly aqueous alteration. On the other hand, CV_{red} chondrites preserve their primitive nature, although most of them partly experienced the secondary reactions [2]. Here we present our petrographic results on a new CV chondrite.

We studied NWA 8613. This is a newly classified CV chondrite. The shock stage is S1, and the weathering grade is W3. It consists of large chondrules (0.84 mm on average diameter, and 38 vol.% in modal composition), refractory inclusions (13 vol.%), and matrix (41 vol.%). Magnetite and phyllosilicate are not encountered, but kamacite is abundant. All these features indicate that the NWA 8613 is classified as CV_{red}.

Chondrules in NWA 8613 do not show preferred orientation, and are mostly porphyritic olivine and olivine-pyroxene type (89%). Mesostasis phases are mainly anorthitic plagioclase often with diopside. Olivine phenocrysts are mostly magnesian ($Fa_{2.1}$ on average). The width of ferroan rims of olivine gains is below 1 μ m in general. Low-Ca pyroxenes are also magnesian ($Fs_{1.7}$). Chondrules contain kamacite and troilite.

Type A CAI and AOA are most common refractory inclusions. Melilite is the most abundant mineral, and gehlenitic (Geh_{72-93}). Magnesian spinel (mostly <0.3 wt.% FeO) is abundant in many inclusions. A few CAIs contain ultrarefractory metal nuggets. Olivines in AOAs hardly show chemical zoning, and the width of ferroan rims is smaller than 1 μ m. Matrix comprises fine-grained minerals, mainly ferroan olivine with spinel, metal and sulfides. Matrix contains Ni-rich metal, troilite, and pentlandite.

Kimura and Ikeda [2] showed that even chondrules in CV_{red} chondrites experienced the secondary reactions, such as replacement of low-Ca pyroxene by ferroan olivine, secondary zoning of olivine, and exchange of Ca-Na to produce nepheline and sodalite. Chondrules in NWA 8613 hardly show the evidence for all these reactions. Only very thin nepheline lamellae (<0.5µm in width) and narrow ferroan rims of olivine grains are noticed in chondrules.

Metamorphic degree (petrologic subtype) can be estimated for CO and partly CV chondrites by several methods. One of them is the grain size of matrix olivine [3]. That of NWA 8613 is <0.9 µm on average. The width of ferroan olivine rims in AOAs is also a key for the classification [4], and is <1 µm in NWA 8613. Although Fe-Ni metals in chondrules do not show typical plessitic texture in Semarkona (type 3.01) [5], tiny Ni-rich metals are encountered within host kamacite. All these features indicate that NWA 8613 is classified as type 3.1-3.2.

We conclude that NWA 8613 hardly experienced shock metamorphism, thermal metamorphism, and metasomatism. This is one of the most primitive CV chondrites so far. Therefore, NWA 8613 is a significant sample to classify CV chondrites, and to clarify the processes in the early solar system.

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References: [1] Weisberg et al. (2006) Meteorites and the Early Solar System II, 19-52. [2] Kimura and Ikeda (1997) Antarctic Meteorite Research, 10, 191-202. [3] Komatsu et al. (2015) Meteoritics & Planetary Science, 50, 1271-1294. [4] Chizmadia et al. (2002) Meteoritics & Planetary Science, 37, 1781–1796. [5] Kimura et al. (2008) Meteoritics & Planetary Science, 43, 1161-1177.

キーワード:炭素質コンドライト、岩石学的タイプ Keywords: Carbonaceous chondrite, Petrologic type X線回折測定によるCO3炭素質コンドライトのサブタイプの特徴 The differences among CO3 chondrites from the X-ray diffraction

*今栄 直也^{1,2}、中牟田 義博³ *Naoya Imae^{1,2}, Yoshihiro Nakamuta³

1.情報・システム研究機構 国立極地研究所、2.総合研究大学院大学、3.九州大学 1.Antarctic Meteorite Research Center, National Institute of Polar Research, 2.SOKENDAI, 3.Kyushu University

1. はじめに

非平衡コンドライトの変成過程や初期状態などの微弱な差異を調べる手段としてバルクサンプルのX線回折測定 は最適な研究手法の一つである。非平衡コンドライトのX線から、サブミクロンからなるマトリックス組織を含 めた構成鉱物の大局的なバルクの特徴や鉱物相に関して知見が得られる。炭素質コンドライトの1グループを構 成するCOの岩石学的タイプは3のみで、3.0-3.9のサブタイプに区分されている。本研究では、CO3の薄片試料か ら粉末X線回折パターンを取得し、サブタイプ間の差異についての新たな知見を得たので報告する。

2. 実験

国立極地研究所に2014年に導入したX線回折装置(SmartLab, RIGAKU)を用いた。試料台には自動試料交換台 (ASC10)を用いた。試料は25mmの石英ガラス円板に貼り付けて作成した石質隕石の研磨薄片を用いた。9個の C03隕石の薄片(Y-81020 CO3.0, ALH-77307 CO3.0, Colony CO3.0, Y-791717 CO3.3, Lance CO3.5, ALH-77003 CO3.6, Isna CO3.8, A-882094, Y983589)を用いた。X線源にはCu管球を用い、Kβ線はNiフィルターにより除去 した。管電圧・管電流は、それぞれ、40kV・30mAで行った。0.4度/分の走査速度、10mm のX線照射入射 幅、100rpmの試料面内回転、の測定条件で行った。この測定法は、Imae (2015)で行った粉末X線回折と整合的 な回折線を得ることをあらかじめ確認した。ピークの半値幅と強度の解析にはVisual Basic 6.0ランタイムに よるピーク分離プログラムを用いた。

3. 結果・議論

かんらん石の(130)の回折線は、高い非平衡(3.5以下)ではピークがスプリットする。これらは、鉄成分に富む マトリックス(低角側)とマグネシウム成分に富むI型コンドリュール(高角側)の回折線に相当する。3.6以上の サブタイプではシングルピークである。この差異をより詳しく見る(図1)と、(130)の高角側回折線は、サブタ イプが3.0から3.5上昇すると、半値幅が増大し、回折線は低角へシフトする(鉄成分に富む)が、3.6以上では ピークは消失する。 (130)の低角側は、Fa~35-45の鉄に富むかんらん石で、マトリックス構成かんらん石に相 当し、3.0から3.8へとサブタイプの上昇とともに半値幅が減少し、ピーク強度が増す。こうした変化は、微弱 な熱変成で顕著なことを意味し、かんらん石のマグネシウムと鉄との元素拡散が構成単位のコンドリュールの サイズ以上の単一鉱物を超えたスケールで生じていることを意味する。また、こうした元素拡散は岩石学的タ ィプ3の変成過程で大規模に生じると解釈できる。

単斜エンスタタイトの(22-1)の回折線はサブタイプによらず認められ、直方エンスタタイトの(321)の回折線が サブタイプによらず認められた(図2)。高いサブタイプの直方エンスタタイトは低温型であってもよいが、低い サブタイプの直方エンスタタイトはコンドリュール形成時に形成した高温相由来と考えられる。一方、同様に X線測定した、非平衡普通コンドライトからは低いサブタイプから高温型直方エンスタタイトは検出されず、単 斜相のみであった。このことからCO3のコンドリュールは普通コンドライトのコンドリュールと異なった温度履 歴であった考えられる。この結果はImae et al. (2013)のEPMA測定の結果と整合的である。

4. 謝辞

単斜エンスタタイトの回折線に関してご教示いただいた滋賀大の大井修吾さんに感謝致します。 5. 文献

Imae N. et al. (2013) Geochim. et Cosmochim. Acta 100, 116-157.

Imae N. (2015) NIPR Symposium on Antarctic Meteorites.

キーワード:X線回折、CO3 コンドライト、かんらん石、輝石 Keywords: X-ray diffraction, CO3 chondrite, olivine, pyroxene





Fig. 2. The ratios of orthoenstatite (oen) to two phases of enstatites (opx+cpx) for various subtypes of the CO3 chondrites. Cen=clinoenstatite.

炭素質コンドライト中のネフェリン形成過程: 再現実験によるアプローチ Formation process of nepheline in carbonaceous chondrites: Reproductive experimetal approach

市村 隼¹、*瀬戸 雄介¹、留岡 和重¹ Shun Ichimura¹, *Yusuke Seto¹, Kazushige Tomeoka¹

1.神戸大学大学院理学研究科
1.Graduate School of Science, Kobe University

In CO/CV chondrites, nepheline is widely distributed in the Ca, Al-rich inclusions (CAIs), the chondrule mesostases and the matrices. Recent petrographic studies have shown abundant evidence suggesting that the nepheline is secondary phases altered from melilite and/or plagioclase by a chemical reaction with Na-rich fluids, and the reaction (Na-metasomatism) occurred in the chondrite parent bodies. Because of the high volatility and mobility, Na is potentially a powerful indicator reflecting aqueous environments of the parent bodies. While many petrographic studies of natural meteorites had made considerable progress on revealing behaviors of Na-metasomatism, quantitative uncertainty for the aqueous condition still remains. In the present study, we performed a number of hydrothermal experiments using melilite and plagioclase as starting materials, and made crystal identifications, micro-textural observations, chemical analyses and thermal analyses for run products. The purpose of this study is constraint of environment in carbonaceous chondrite parent bodies by revealing process of nephelinization.

We used i) synthetic melilite $(Ca_2Al_2SiO_7) + SiO_2$, and ii) natural plagioclase $(Na_{a_5}Ca_{a_5}Al_{1_5}Si_{2_5}O_8)$ as starting materials. The reaction solution of 1N (mol/l)-HCl (pH 0), H₂O (pH 7), 0.1N-NaOH (pH 13) and 1N-NaOH (pH 14) were prepared for the hydrothermal experiments with different water/rock ratios (4.67, 46.7 and 467 ml/g). Na⁺ concentration in all solutions is maintained at 1 mol/l by addition of NaCl. Hydrothermal alteration experiments were performed with a PTFE reaction vessel loaded into steel autoclave at 200 °C and 1.5 MPa for run duration time of 168 hours. The recovered samples from the hydrothermal and thermal experiments were analyzed by XRD, SEM, TEM, and TG-DTA. The experiments using melilite without SiO2 under the conditions of WR 46.7 and pH 7-14 showed that hydro-grossular $(Ca_{3}Al_{2}[SiO_{4}]_{1,5}[OH]_{6})$ forms as a secondary altered phase. Under the same WR and pH conditions, as the proportion of SiO2 in increases, various Na-rich zeolitic materials were observed in the run products including analcime (Anl, NaAlSi₂O₆H₂O), nepheline-hydrate (NephH, NaAlSi0₄[H₂0]) and hydroxy-cancrinite (Canc, Na₂Al₆Si₆O₂₄[OH]₂[H₂O]₂). At the high W/R (=467) condition, no secondary phase was observed, while Anl and Canc occur at the low W/R (=4.65) under pH 14. In the experiments using plagioclase with high W/R ratios and pH 0-7 solutions, no secondary phases formed. Anl and NephH formed under pH 13-14 conditions. At low W/R ratios, secondary phases were identified as Anl, and NephH.

The TG-DTA and XRD analyses for nepheline hydrate showed that NephH is transform to nepheline at 796-841 °C at the heating rate ranging of 1-14 °C/min. From the analyses of the reaction kinetics, we estimated that NephH alter to nepheline for $\sim 10^5$ years at 515 °C. Although we failed to analyze the reaction kinetics for Canc and Anl because of their complicated DTA curves, thermostatic experiments suggested that both material also change to nepheline at 760 °C (Canc) and 800 °C (Anl).

The present results suggest that melilite and plagioclase are easily altered into zeolitic materials in Na⁺-rich high alkali solutions. The present experimental condition demonstrated in the present study seems to be comparable to actual carbonaceous chondrite parent body. Thus, we infer that nepheline in carbonaceous chondrite formed initially as zeolitic materials during aqueous

alteration, and they were subsequently dehydrated to nepheline.

キーワード:ネフェリン、コンドライト、水質変成 Keywords: nepheline, chondrite, aqueous alteration 炭素質コンドライト中の六角板状をした方解石負晶および抜け殻結晶様空隙について Negative crystals of calcite and empty crystals in the shape of hexagonal plate in carbonaceous chondrites.

*北山 晃¹、土山 明¹、中村 隆太¹、三宅 亮¹、中野 司²、上杉 健太朗³、竹内 晃久³、伊神 洋平¹、高山 亜紀 子¹、瀬戸 雄介⁴、伊藤 正一¹、ゾレンスキー マイケル⁵

*Akira Kitayama¹, Akira Tsuchiyama¹, Ryuta Nakamura¹, Akira Miyake¹, Tsukasa Nakano², Kentaro Uesugi³, Akihisa Takeuchi³, Yohei Igami¹, Akiko Takayama¹, Yusuke Seto⁴, Shoichi Itoh¹, Michael Zolensky⁵

 京都大学大学院理学研究科地球惑星科学専攻、2.産業技術総合研究所 地質情報研究部門、3.SPring-8 高輝 度光科学研究センター、4.神戸大学大学院理学研究科、5.NASA ジョンソン宇宙センター
Division of Earth and Planetary Sciences, Kyoto University, 2.Geological Survey of Japan, AIST,
SPring-8/Japan Synchrotron Radiation Research Institute, 4.Graduate School of Science, Kobe
University, 5.ARES, NASA Johnson Space Center

CI、CM、CRコンドライトなどの水質変成を受けた炭素質コンドライト中には、水質変成作用により生じた方解 石などの炭酸塩鉱物が見られる。FIB(集束イオンビーム)装置と放射光X線マイクロCTを組み合わせることによ り、このような鉱物中から流体包有物を見出そうとする研究が行われている[1]。このような研究において、外 形が不定形の方解石中に六角板状の形状をもつ負晶や、マトリクスの物質中に六角板状の抜け殻結晶様の空隙 が見出された。方解石は多様な結晶形状をもつことが知られており、六角板状の形状を示すものは比較的稀で ある。方解石の結晶形状は生成時の温度やCO₂の分圧を反映すると考えられ[2]、負晶などの形状から水質変成 の環境を知る手がかりとなる可能性がある。本研究では、このような六角板状を示す負晶や抜け殻結晶様空隙 について、結晶学的な考察をもとにした形状についての詳細な研究を行うとともに、比較のため六角板状など の結晶外形をもつ地球上の方解石中の負晶形状についても調べた。

炭素質コンドライトとしてSutter's Mill隕石(CM)およびIvuna隕石(CI)を、また比較のため神岡鉱山産の六角 板状(約40x20 mm、厚さ約5 mm)および鋲頭状(約20x20 mm、厚さ約5 mm)の方解石単結晶を試料として用い た。Sutter's Mill隕石中の方解石結晶(約40 mm)、Ivuna隕石中のマトリクス中のNa, Mg, Si, S, Oに富む不定 形物質(約40 mm)を、方解石単結晶についてはc軸に平行な薄片において光学顕微鏡で流体包有物を含む部分を 選んだ。薄片からFIBにより箱型または円筒形にサンプル(約20~30 mm)を切り出し、SPring-8のBL47XUにおい て結像型吸収X線CT装置を用いて、約150 nmの実効空間分解能において3次元CT像を得た。これらのCT像か ら、2値化により空隙や流体包有物を画像解析により抽出した。得られた3次元形状は、表面をポリゴンで近似 し、その法線ベクトルのステレオ投影を行い結晶面の同定を試みた。また、方解石単結晶サンプルについては SEM/EBSDにより結晶学的方位を求め、流体包有物外形と比較した。

Sutter's Mill隕石の方解石粒子は放射光X線回折から単結晶であることがわかった。この中に、ファセットを もつ2つの空隙すなわち負晶(約2 mm)が見られた。そのひとつは六角板状の形状をもち、最も発達した六角形の 面を(001)面と仮定して指数付けしたところ、天然で見られる六角板状の結晶((001)および(104)面からなる)と は異なる結晶面組み合わせをもつことが分かった。また、もうひとつの負晶は六角板状には見えないが、六角 板状のものと類似した結晶面組み合わせをもつことが分かった。一方、この方解石粒子内には微細な包有物 (<1mm)が多数みられ、(001)と推定した面に平行にバンド状に分布している。従って、母結晶が(001)面を成長 面として包有物を取り込みながら成長し、微細な包有物分布による累帯構造をつくるとともに、(001)面の発達 した比較的大きな負晶をつくったと考えれる。

Ivuna隕石のNa, Mg, Si, S, 0に富む不定形物質中には、複数の六角板状の空隙(約3 mm)が見出された。これ についても、最も発達した六角形の面を(001)面と仮定して指数付けしたところ、Sutter's Mill隕石の方解石 負晶とは異なり、(001)面と(100)面の組み合わせで説明できることが分かった。また、その形状から6回回転対 称または3回回反対称の区別はできず、方解石構造をもつ炭酸塩だけでなく、磁硫鉄鉱のような鉱物の抜け殻結 晶である可能性も否定できなかった。

神岡鉱山産方解石中の負晶は様々な方向の面状に分布していることからヒールドクラックであると考えられる。その形状は母結晶の形状(六角板状および鋲頭状)とは異なっていた。六角板状の結晶は、(001)面と

(104)面の組み合わせからなるが、その負晶(約20 mm)では(104)面のみが発達し、(001)面は見られな かった。一方、鋲頭状の結晶は(018)面からなるが、その負晶(約5 mm)では(1-12)面が発達していた。ヒールド クラック内の負晶は、その発達過程において溶解・再結晶作用により長時間経過すると表面自由エネルギーの 小さな結晶面が発達するようになる。六角板状結晶中の負晶では表面自由エネルギーの高い(001)面は、一度出 現しても消滅したかあるいは最初から存在していなかったと考えらえる。一方、Sutter's Mill隕石の方解石負 晶は、結晶成長時に生成されてから溶解・再結晶作用による形状変化をほとんど受けてなかったものと考えら れる。

[1] Tsuchiyama et al. 2014, *MAPS*, 49: A404. [2] Krasnova & Petrov 1997, Genesis of mineral individuals and aggregates. Nevsky kuryer, St.-Petersburg.

キーワード:炭素質コンドライト、方解石、負晶 Keywords: carbonaceous chondrite, calcite, negative crystal X線顕微鏡を用いたAllende隕石マトリクス中有機物のin-situ分析-その分布と起源解明をめざして-*In-situ* obsevation of organic matter in the Allende meteorite matrix using X-ray microscopy

*菅 大暉¹、武市 泰男²、宮本 千尋³、宮原 正明¹、間瀬 一彦²、小野 寛太²、高橋 嘉夫³ *Hiroki Suga¹, Yasuo Takeichi², Chihiro Miyamoto³, Masaaki Miyahara¹, Kazuhiko Mase², Kanta Ono², Yoshio Takahashi³

1.広島大学大学院理学研究科、2.高エネルギー加速器研究機構、3.東京大学大学院理学系研究科 1.Graduate School of Science, Hiroshima University, 2.High-Energy Accelerator Research Organization, 3.Graduate School of Science, The University of Tokyo

Previous studies have reported that many kinds of carbon components are included in Allende CV3. The carbon components might be modified because they were extracted through acid treatments in the previous studies. Although the carbon components are mainly contained in the matrix of Allende CV3, their natures and occurrences have not been described in detail. *In-situ* sample extraction protocol without any chemical treatments should be applied for the characterization of the carbon components. In this study, we applied a scanning transmission X-ray microscopy (STXM) analysis combined with a focused ion beam (FIB) technique for functional group analysis and speciation. First, Allende CV3 chip sample was cut by ISOMET under non-water and non-oil conditions. The cross section of the chip sample was coated with gold for a SEM observation. The matrix portion of the Allende CV3 was observed by a SEM. Several portions of interest selected through SEM observations were processed to ultra-thin foils using a FIB. The foils were attached to a Mo-grid. STXM analyses were conducted using STXMs at BL-13A, Photon Factory and BL-4U, UVSOR. After STXM observation, TEM observations were also conducted for textural observations.

The carbon components were found along with the grain-boundaries of fine-grained olivine crystals (diffusional). Several dense carbon components were also found in the diffusional carbon components (particulate). The constituent rates of particulate and diffusional carbons are approximately fifty-fifty. Based on C K-edge NEXAFS, the particulate carbon (aromatic-rich and carboxylic-poor) appears to be insoluble organic matter of Allende CV3 [1]. The diffusional carbon portion, on the other hand, mainly consists of aromatic-poor and carboxylic-rich carbon components. Fe L- and O K-edge NEXAFS spectra and TEM observations showed that spinel and chromite crystals are embedded in the particulate carbon. These minerals might be the fragments of CAIs, because such high temperature condensation minerals are not formed thorough thermal metamorphism occurred on the Allende parent-body. Our FIB-STXM analyses depict the existences of different two type carbon components in the Allende CV3. Based on the assumption that each carbon components had different origins, the following tow hypothesis is made. (i) The particulate carbon component might correspond to nano-globules included in carbonaceous chondrites. In some cases, silicate-minerals are surrounded by the nano-globules [2]. As same to this case, the particulate carbon component might had formed on the spinel and chromite crystals in the solar nebula, and accreted into the Allende parent-body. (ii) On the other hand, diffusional carbon component is similar to diffuse organic matter in the Orgueil and Murchison [3], except for the carbonate peak in the NEXAFS spectra. It is possible that the diffusional carbon component formed through aqueous alteration occurred on the Allende parent-body.

References

[1] Cody G., Ade H., Alexander M., Araki T., Butterworth A., Fleckenstein H., Flynn G., Gilles M., Jacobsen C., Kilcoyne A., Messenger K., Sandford S., Tyliszczak T., Westphal A., Wirick S. and Yabuta H. Quantitative organic and light-element analysis of comet 81P/Wild 2 particles using C-, N-, and O-µ-XANES. Metorit Planet Sci 43, 353-365. (2008)

[2] Le Guillou C., Bernard S., Brearley A. J. and Remusat L. Evolution of organic matter in Orgueil, Murchison and Renazzo during parent body aqueous alteration: In situ investigations. *Geochim Cosmochim Acta* 131, 368–392. (2014)

[3] Nakamura-Messenger K., Keller L. P., Messenger S., Clemett S. J., Nguyen A. N. and Frank D. Coordinated analysis of diverse components in whole stardust cometary tracks. *43rd Lunar and Planetary Science Conference*, #2551. (2012)

キーワード:アエンデ隕石、炭素成分、走査型透過X線顕微鏡、収束イオンビーム、吸収端近傍微X線吸収細構 造、放射光

Keywords: Allende meteorite, Carbon component, Scanning Transmission X-ray Microscopy (STXM), Focused Ion Beam (FIB), NEXAFS, Synchrotron radiation 太陽系小天体におけるアミノ酸前駆体の形成へのガンマ線の影響の評価 Evaluation of gamma-ray effects for formation of amino acid precursors in the Solar System small bodies

*三澤 柊介¹、癸生川 陽子¹、依田 功²、吉田 聡³、橘 省吾⁴、小林 憲正¹ *Shusuke Misawa¹, Yoko Kebukawa¹, Isao Yoda², Satoshi Yoshida³, Shogo Tachibana⁴, Kensei Kobayashi¹

 1.横浜国立大学、2.東京工業大学、3.放射線医学総合研究所、4.北海道大学
1.Yokohama National University, 2.Tokyo Institute of Technology, 3.National Institute of Radiological Sciences, 4.Hokkaido University

地球上における生命の誕生にはアミノ酸等の有機物が必要である。そのアミノ酸の供給源の一つとして、隕石 などの地球外物質が考えられている。このような隕石の多くは小惑星を起源としているため、小惑星中の有機 物の起源を考える必要がある。太陽系形成初期に、塵、氷、分子雲由来の低分子有機物を含む小惑星では、²⁶ Alの放射性崩壊による熱により氷が溶けて水質変質が起こった。隕石中に存在する複雑な高分子有機物(不溶性 有機物)は、このような液体の水(0~150℃程度)が存在する環境下で形成された可能性が指摘されている [1]。この説を基に小惑星での水熱変成を模擬した実験で、ホルムアルデヒド、アンモニア、水を加熱すると隕 石有機物のような高分子有機物が形成されることがわかった[2]。本研究では、水質変質過程において²⁶Alの放 射性崩壊により発生するガンマ線が有機物生成にどれだけ影響するか調べることを目的とした。

出発物質として超純水200µLに対し、モル比が水:ホルムアルデヒド:アンモニア=100:5:5になるように試験 管に加え、試験管内を真空にして封緘したものに、東京工業大学の⁶⁰Co線源を用いてガンマ線を様々な線量率 と時間で照射した。比較のため、放医研のHIMAC重粒子線加速器を用いて重粒子線(C線:290 MeV/u)を照射した サンプルや、オーブンで加熱(150℃及び80℃,24時間)をしたサンプルも作成した。またホルムアルデヒドから 糖を形成するホルモース反応の触媒となるCa(OH)₂を入れた系も用意した。照射あるいは加熱後の試料はまず遠 心分離により不溶性物質を回収し、CaF₂プレートにのせ乾燥させた後、顕微FT-IRを用いて分析を行った。 遠心分離したサンプルの上澄みは酸加水分解をして、その前後について陽イオン交換HPLCを用いてアミノ酸分 析を行ったCa(OH)₂を含む系はAG 50-X8を用いて脱塩してから陽イオン交換HPLCで分析した。

酸加水分解を行ったサンプルのほとんどから、グリシン、アラニン、β-アラニンなどのアミノ酸が検出された。加水分解を行わないサンプルからはアミノ酸は検出されないか、比較的少量だった。

Ca(OH)₂を含む系のアミノ酸生成量は、加熱サンプルの方がガンマ線照射サンプルよりも多かったのに対し、含まない系のアミノ酸生成量はガンマ線照射サンプルの方が加熱サンプルよりも多くなった。このことから、Ca(OH)₂は熱によるアミノ酸生成に触媒効果があるが、ガンマ線によるアミノ酸の生成にはあまり影響しな

いと考えられる。

また、加熱サンプルはグリシンに対するアラニンの量が比較的少ないのに対し、照射サンプルはグリシンに対 するアラニンの生成量が比較的多かった。これは熱と放射線による反応経路の違いによると考えられる。 また線種としてはガンマ線より重粒子線の方がアミノ酸生成量は多くなった。

出発物質にCa(OH)₂を含み、150℃、24時間加熱したサンプルのみ、遠心分離後に不溶性物質が確認できた。顕 微FT-IRの分析結果から、水溶性物質は不溶性物質よりも多くのアミド結合を有した構造をしていることがわ かった。

[1] G.D.Cody et al., PNAS, 108, 19171-19176 (2011).

[2] Y.Kebukawa et al., Astrophysical J., 771, 19 (2013)

キーワード:隕石、小惑星、有機物、ガンマ線 Keywords: Meteorites, Asteroids, Organic matter, Gamma ray

小天体内部水熱反応による有機物合成実験

Soluble organic molecules formed under hydrothermal conditions in small bodies

*磯野 雄生¹、橘 省吾²、Piani Laurette²、癸生川 陽子³ *Yuki Isono ¹, Shogo Tachibana², Laurette Piani², Yoko Kebukawa³

1.北海道大学 理学部 地球惑星科学科、2.北海道大学 理学院 自然史科学専攻 システム科学分野、3.横浜国立 大学 大学院工学研究院 機能の創成部門

1.Department of Science, Earth and Planetary Science, Hokkaido University, 2.Department of Natural History Science, Hokkaido University, 3.Faculity of Engineering, Yokohama National University

Extraterrestrial organic materials found in chondrites, micrometeorites, and IDPs record the processes in the Sun's parent molecular cloud, the protosolar disk, and parent bodies. Organic materials could be newly synthesized from simple molecules such as formaldehyde and ammonia (Cody et al., 2009) and/or altered by hydrothermal processes within parent bodies (Herd et al., 2011). The correlation between the L-enantiomeric excess of amino acids and the degree of alteration also indicates that organic materials evolved in parent bodies (Glavin and Dworkin., 2009). Recent studies on soluble organic matter in the Murchison meteorite (Schmitt-Kopplin et al., 2010; Yamashita and Naraoka, 2014) have shown that a large variety of soluble organic molecules are present in the aqueously altered Murchison, some of which could have been synthesized by parent body alteration processes.

In order to understand the formation of soluble organic molecules under hydrothermal conditions in Solar-System small bodies, we conducted hydrothermal experiments following the experimental procedure of Kebukawa et al. (2013). Paraformaldehyde, glycolaldehyde, calcium hydroxide, and ammonium water (8 wt%, NH₃) were put into pyrex glass tube with ultrapure water. The N/C atomic ratio of the starting material was set at 0.1. The glass tube enclosing the starting materials was sealed in the air, and the sealed glass tubes were heated at 90 degree C for 72 hours. We also made experiments without ammonia and only with ultrapure water for comparison.

The liquid phase changed its color from transparent to brownish after the heating, and solid organic components were found in the tube. The liquid phase was diluted by a factor of 100 with a water-methanol mixture (1:1), and was analyzed with Orbitrap Elite LC-MS (Thermo Fisher Scientific). A 10uL of the solution was first injected to a liquid chromatograph EASY-nLC 1000 (Thermo Fisher Scientific). The molecules separated through the LC depending on their polarities, were introduced to an electrospray ionization (ESI) source, and positively-charged ions were detected in the range of m/z=50-750 with a mass resolution of 240,000 at m/z=400. The solutions from the heated samples both with and without ammonia contained molecules showing a broad peak at the retention time of 15-25 min on chromatogram. The averaged mass spectra at the retention time of 19-20 min were averaged and analyzed with the "mMass"-software. Most of the molecules show a successive increase of CH₂O, suggesting that they were formed by the formose reaction (polymerization of formaldehyde). The solution with ammonia contained molecules with an odd number of molecular weights, while that without ammonia did not. These molecules with an odd number of molecular weights should contain an odd number of nitrogen.

キーワード:地球外有機物、水熱実験、LC/MS

Keywords: Extraterrestrial organic matter, Hydrothermal experiments, LC/MS

Evolution of three distinct water reservoirs through the history of Mars Evolution of three distinct water reservoirs through the history of Mars

*臼井 寛裕¹ *Tomohiro Usui¹

1. 東京工業大学地球惑星科学科

1. Department of Earth and Planetary Sciences, Tokyo Institute of Technology

The surface geology and geomorphology of Mars indicate that it was once warm enough to maintain a large body of liquid water on its surface, though such a warm environment might have been transient. The transition to the present cold and dry Mars is closely linked to the history of surface water, yet the evolution of surficial water is poorly constrained. This study identifies three distinct Martian water reservoirs based on the analyses of Martian meteorites, telescopic observations, and Curiosity measurements. One is mantle-derived water that has a D/H ratio similar to those seen in planetary building blocks (i.e., chondrites) and in the Earth's ocean water. The second reservoir is atmospheric water with a mean D/H ratio of ~6 times the terrestrial value. The third, subsurface-ice reservoir, has been recently detected based on analyses of Martian near-surface materials. This reservoir has a relatively restricted range of D/H ratios (2-3 times Earth's ocean water), which is distinct from the low-D/H primordial and the high-D/H atmospheric water reservoirs. This subsurface-ice reservoir could have possibly acquired its intermediate-D/H composition from the ancient surface water before the rise of the atmospheric D/H ratio to the present level. During ancient times, the atmosphere and hydrosphere could have approached isotopic equilibrium due to the high water activity relative to the recent dry Mars.

キーワード:火星、水、水素同位体 Keywords: Mars, water, hydrogen isotope NWA 7397レールゾライトシャーゴッタイトの岩石 · 鉱物学的記載 Petrology and mineralogy of Northwest Africa 7397 lherzolitic shergottite

*吉田 壮志¹、宮原 正明¹、境 毅²、大藤 弘明²、山口 亮³ *Masashi Yoshida¹, Masaaki Miyahara¹, Takeshi Sakai², Hiroaki Ohfuji², Akira Yamaguchi³

1.広島大学理学研究科地球惑星システム学専攻、2.愛媛大学地球深部ダイナミクス研究センター、3.極地研究 所

1.Department of Earth and Planetary Systems Science, Graduate School of Science, Hiroshima University, 2.GRC, Ehime University, 3.NIPR

Martian meteorites are important samples in order to understand geologic process on Mars. Shergottite, which is the largest group among Martian meteorites, is divided into three groups based on their petrologic and mineralogical features; i.e., basaltic shergottite, olivine-phyric shergottite, and lherzolitic shergottite. The petrologic and mineralogical features of lherzolitic shergottites are similar each other. In addition, their crystallization and exposure ages are also identical each other. Accordingly, it is widely accepted that lherzolitic shergottites share the same original source on Mars, and were probably ejected by the same impact event, and finally fell on the Earth as separate falls [1]. The major object of this study is to describing the detail petrographic and mineralogical characteristics of a newly found lherzolitic shergottite, Northwest Africa 7397 (NWA 7397).

A polished thin section of NWA 7397 was prepared for this study. A field-emission scanning electron microscope (FE-SEM) was employed for detailed textual observations. The chemical compositions of individual minerals were determined with an electron probe micro-analyzer (EPMA). Phase identification of the minerals was conducted using a laser micro-Raman spectrometer.

Our FE-SEM observations and EPMA analyses reveal that the petrologic and mineralogical features of NWA 7397 are similar with other lherzolitic shergottites. NWA 7397 shows two areas with poikilitic and non-poikilitic. In the poikilitic area, coarse-grained pyroxene oikocrysts enclose olivine (< ~500 µm) and chromite (< ~150 µm) grains. In the non-poikilitic area, the major constituents are olivine, pyroxene, and plagioclase (now maskelynite), with minor chromite, ilmenite, alkali feldspar, Ca-phosphate, and Fe-sulfide. Pyroxenes in the poikilitic area are chemically zoned from core $(En_{71}Fs_{25}Wo_4)$ to rim $(En_{65}Fs_{25}Wo_{10})$. Most pyroxenes in the non-poikilitic basaltic area are pigeonite with small amount of augite. Olivine in the non-poikilitic area (Fa₃₈₋₄₀) is more Fe-rich than that in the poikilitic area (Fa_{29-37}). NWA 7397 may have originally been located at a shallower level within the lherzolitic shergottite igneous block because Fe contents in the olivine are higher than those in other lherzolitic shergottites. Several melt-pockets were observed in the non-poikilitic area. The existences of maskelynite and melt-pockets are obvious evidences for an impact event occurred on Mars. Some plagioclase entrained in the melt-pockets dissociate into CAS + stishovite. This is the first report of CAS and stishovite from lherzolitic shergottites. Based on the phase diagram of basaltic composition [2], the pressure and temperature conditions recorded in the melt-pocket are estimated to be ~25 GPa and 2300-2500 °C. Olivine around the melt-pockets probably dissociated into bridgmanite + magnesiowüstite. The bridgmanite would have back-transformed to glass due to residual heat during adiabatic decompression.

References

[1] Mikouchi T. and Kurihara T. 2008. Mineralogy and petrology of paired lherzolitic shergottites Yamato 000027, Yamato 000047, and Yamato 000097: Another fragment from a Martian ''lherzolite'' block, Polar Science 2:175–194 [2] Beck P., Gillet P., Gautron L., Daniel I., and El Goresy A. 2004. A new natural high-pressure (Na,Ca)-hexaluminosilicate $[(Ca_xNa_{1-x})Al_{3+x}Si_{3-x}0_{11}]$ in shocked Martian meteorites. Earth and Planetary Science Letters 219:1–12.

 $\pm - \nabla - \kappa$: lherzolitic shergottite, shock metamorphism, High-pressure polymorph Keywords: lherzolitic shergottite, shock metamorphism, High-pressure polymorph

火星の角礫岩隕石NWA 7034についての岩石学的記載と形成過程の研究 Petrography and formation process of Martian breccia meteorite NWA 7034

野津 佳¹、*小澤 信²、大谷 栄治² Kei Nozu¹, *Shin Ozawa², Eiji Ohtani²

1. 東北大学理学部地球惑星物質科学科、2. 東北大学大学院理学研究科地学専攻

Department of Earth and Planetary Materials Science, School of Science, Tohoku University,
Department of Earth and Planetary Materials Science, Graduate School of Science, Tohoku
University

NWA 7034とそのペア隕石は火星の表土角礫岩であるとされている。これらの隕石に含まれる鉱物にはSNC隕石や ローバーミッションなどで分析された火星の土壌に似た化学組成を持つものもある。NWA 7034を調べることに よって、SNC隕石よりも直接的に火星表面の情報を得ることができると期待される。そこで我々は、この角礫岩 についてFE-SEM-EDS、EPMAをもちいて組織観察・化学組成分析を行い、その形成過程を考察した。

NWA 7034は多様なクラスト(岩石片・鉱物片)とその間を埋める細粒のマトリックスから成るポリミクトな角礫 岩である。観察の結果から、特定したクラストをモノミネラリッククラスト、火成岩クラスト、角礫岩クラス ト、Group Xクラスト、Group Yクラスト、メルトクラストの6つのグループに分類した。

I) モノミネラリッククラストは単一の鉱物から成る鉱物片である。観察された鉱物は長石、輝石、アパタイト、マグネタイト、イルメナイトであり、~100 μm程度の大きさのものが多い。特に斜長石(Ab₄₄₋₈₉An₅₋₅₅Or₁₋₆)、輝石(En₂₀₋₈₅Fs₁₂₋₅₄Wo₂₋₄₄)は様々な組成をもち、離溶が見られるものと見られないものがある。このことから、様々な起源をもつ鉱物片が本試料中に含まれていることが分かる。また、化学組成の類似性によれば、他のグループのクラストを構成する鉱物の破片であるものを含んでいる。

II) 火成岩クラストは輝石、斜長石、マグネタイト、イルメナイトなど複数の鉱物から成り、粒状組織やオ フィティック組織といった、火成岩によく似た組織を示す。クラストの長辺は40 µm~1 mmと多様であり、各構 成鉱物は10 µm~50 µmの大きさのものがほとんどである。また輝石の組成についてはSNC隕石の輝石とよく似た 傾向を示す。これらの結果から、火成岩クラストは火星の火成活動によって形成されたと考えられる。

III) 角礫岩クラストは自形から半自形の鉱物(~100 µm程度)と、その間を埋める針状の細粒鉱物(1 µm以下)から構成されている。粗粒と細粒組織の構成鉱物はどちらも主に斜長石、輝石、マグネタイトである。見られたクラスト全体の長辺は340 µm~1.8 mmである。その組織から、NWA 7034角礫岩形成以前に存在していた角礫岩が衝突などの熱により部分溶融・急冷・角礫化したものであると考えられる。

IV) Group Xとしたクラストは2 ~ 3個の鉱物結晶から成り、火成岩クラストのように入り組んだ組織は持たない。クラスト全体の長辺は40 µm~1mmであった。構成鉱物は斜長石、輝石、アパタイト、マグネタイト、イルメ ナイトである。構成鉱物や組織から火成岩クラストの一部であると考えられる。

V) Group Yクラストは細粒の輝石(10 μm以下)の集合体の周りに斜長石から成るリムが見られるものである。ク ラスト全体の長辺は70 μm~580 μmであり、形状はアメーバ状や球状など多様である。また、内部にマグネタイ トを含むものも見られた。このクラストと同様のものは角礫岩クラストにも含まれている。

VI) メルトクラストは直径約3 mmの球状のクラストである。クラスト本体はカンラン石の樹枝状結晶(デンドラ イト)を含んでいる。本試料中でカンラン石が見られたのはこのクラストのみである。カンラン石の樹枝状結晶 の長さはクラスト中心部では1 mm程度であり、外側では150~200 µmであった。このクラストで特徴的なの は、クラスト本体の周りに約3層のリムを伴うことである。一番内側のリムには長さ50~150 µmの輝石の針状結 晶が含まれている。この輝石はクラスト本体のカンラン石結晶よりもマグネシウムに富むという特徴を持 つ。その外側のリムには輝石と同じ大きさの針状の斜長石結晶が含まれており、ナトリウムに富むという特徴 を持っている。クラスト本体のカンラン石結晶とリムの輝石・斜長石結晶が、一つの針状結晶としてつな がっている部分も見られる。また、一番外側のリムは1 µm以下の輝石、斜長石、鉄酸化物から成っている。カ ンラン石の樹枝状結晶を含んでいることやクラストが球状であることはコンドリュールの特徴と共通してお り、メルトが急冷して形成したことが推測される。また針状結晶を含むリムは、このクラストが二次的な熱の 影響を受けた際に形成した可能性が考えられる。 VII) マトリックスはクラストの間を埋めており、数~10 µmの破片状の鉱物と1 µm以下の細粒の鉱物から成る。構成鉱物は斜長石、輝石、アパタイト、マグネタイトである。

以上の分析結果より、NWA 7034は主にSNC隕石を構成する火星起源の火成岩の粉砕・角礫化・溶融により形成した多様なクラストを含む角礫岩隕石であることがわかった。また、各クラストの形成時期や形成環境は異なり、少なくとも2回以上の角礫岩化作用を受けたものと考えられる。

キーワード:火星隕石、表土角礫岩、メルト小球体 Keywords: Martian meteorite, regolith breccia, melt spherule 危難の海から回収されたルナ24号レゴリス試料のキャラクタリゼーション Characterization of LUNA 24 regolith for deciphering the magmatism history on Mare Crisium

寺田 健太郎¹、*橋口 友実¹、河井 洋輔¹、宮原 正明² Kentaro Terada¹, *Hashiguchi Minori¹, Yosuke Kawai¹, Masaaki Miyahara²

1.大阪大学大学院理学研究科、2.広島大学大学院理学研究科

1. Graduate School of Science, Osaka University, 2. Graduate School of Science, Hiroshima University

Lunar regolith is the mixture of fine grains/powders found on the surface of the Moon, and is considered to be the result of mechanical disintegration of basaltic and anorthositic rocks, caused by continuous meteoric bombardment over billions of years. Since LUNA 24 samples classified into Very-Low-Ti (VLT) basalt were dated as the youngest lunar rocks/soils of 2.9 Ga [1], it has been generally considered that VLT basalt magmatism is the most prolonged magmatism on the Moon (about 1.4 billion years from the oldest age of 4.35 Ga of monomict breccia, Kalahari 009 [2], to the youngest age of 2.9 Ga). However, in the chronology of regolith, it should be taken into account that individual grains have a different origin. Moreover, late impact events might have disturbed the radiometric age, making the age younger apparently. Therefore, comprehensive studies on both elaborating mineralogical description and the high-spacial resolution dating are required to decipher the precise history of VLT magmatism. Here, we report the characterization of LUNA 24 regolith collected from Mare Crisium at the depth of 130-132 cm and the future-plan of in-situ U-Pb dating.

キーワード:月レゴリス Keywords: Lunar regolith A high-pressure polymorph inventory in shocked L type ordinary chondrites A high-pressure polymorph inventory in shocked L type ordinary chondrites

*宮原 正明¹、山口 亮²、大谷 栄治³、齋藤 優人^{1,4} *Masaaki Miyahara¹, Akira Yamaguchi², Eiji Ohtani³, Masato Saitoh^{1,4}

広島大学理学研究科、2.極地研究所、3.東北大学理学研究科、4.東北大学工学研究科
Graduate School of Science, Hiroshima University, 2.NIPR, 3.Graduate School of Science, Tohoku
University, 4.Graduate School of Engineering, Tohoku University

Planetary collision phenomenon is one of fundamental process for planet evolution. So, shock metamorphism is recorded in many meteorites. The existence of high-pressure polymorphs is one of distinct evidences for the planetary collision phenomenon. Many colleagues have worked on high-pressure polymorphs in shocked ordinary chondrites. We could constrain shock pressure conditions, impact velocities and their parent-body sizes using the high-pressure polymorph assemblages in the shocked ordinary chondrites and their kinetics, which will give clues for how the ordinary chondrite parent-bodies were destroyed. Radio-isotope measurements along with such high-pressure mineralogical investigations could date when the parent-body destroys occur in the solar nebula. Ordinary chondrite is classified into H, L and LL based on metallic iron content. Individual ordinary chondrite is further divided into petrologic type 3, 4, 5 and 6 (and 7) based on the differences on thermal metamorphism degree. Most previous investigations working on high-pressure polymorphs have just focused on type 6, especially L6 ordinary chondrite. Few systematic investigations about a high-pressure polymorph in other type ordinary chondrites have not been conducted up to now. A parent-body of an ordinary chondrite is expected to have an onion shell-like structure. The inventories of high-pressure polymorphs included in all type ordinary chondrites are required to depict the destroy process of an ordinary chondrite parent-body. Accordingly, in this study, we described high-pressure polymorphs included in L3, L4 and L5 type ordinary chondrite through a fine textural observation by a FEG-SEM and mineral identification by a laser micro-Raman spectroscopy. Twenty-one Antarctica and one non-Antarctica L-type ordinary chondrite thin sections were used for this study.

Four L3 type ordinary chondrites including shock-induced melting textures were selected through optical microscopic observations. Most chondrules are slightly flattened. The boundaries between the flattened chondrules and surrounding matrices are distinct. Several isolated melting textures (hereafter, a melt-pocket) are observed around the boundaries. High-pressure polymorphs were not identified in and around the melt-pockets although several plagioclase grains become maskelynite. In case of L4 type ordinary chondrites (ten specimens), the boundaries between chondrules and matrices are not so clear compared with L3. The grain-sizes of constituents in the matrices are coarser than L3. Melt-pockets occur around the boundaries like L3. A shock-melt vein occurs only in one specimen. Jadeite was identified in plagioclase grains entrained in and around the melt-pockets or shock-melt veins. Maskelynite was also identified. In case of L5 type ordinary chondrites (five specimens), the boundaries between chondrules and matrices are indistinct. All melting textures occur as a shock-melt vein. Jadeite occurs in plagioclase grains entrained in or around the shock-melt vein partly transforms into wadsleyite.

Our investigations reveal that shock-induced melting occur in L3, L4 and L5 besides L6 ordinary chondrites. Most shock-induced melting occur as a melt-vein in L6 and L5, whereas as a melt-pocket in L3 and L4. Ringwoodite, wadsleyite, akimotoite, majorite, bridgmanite, jadeite, lingunite and tuite occur in and around the shock-melt veins of L6. Only jadeite occurs ubiquitously in and

around the shock-melt veins and melt-pockets of L4 and L5. The shock pressure condition can be estimated based on a high-pressure polymorph phase equilibrium diagram deduced from static high-pressure synthetic experiments. The estimated shock pressure conditions are as follows; about from 13 to 24 GPa for L6, about from 2.5 to 12 GPa for L4 and L5, and less than about 2.5 GPa for L3.

 $\pm - \nabla - \aleph$: High-pressure polymorph, Ordinary chondrite, Shock-induced melting Keywords: High-pressure polymorph, Ordinary chondrite, Shock-induced melting

局所U-Pb年代分析に向けたポストレーザーイオン化SNMSの開発 Development of Laser Post-Ionization Secondary Neutral Mass Spectrometer for in-situ U-Pb chronology

*河井 洋輔¹、松田 貴博¹、宮 晃平¹、薮田 ひかる¹、青木 順¹、本堂 敏信²、石原 盛男¹、豊田 岐聡¹、中村 亮介³、寺田 健太郎¹

*Yosuke Kawai¹, Matsuda Takahiro¹, Kohei Miya¹, Hikaru Yabuta¹, Jun Aoki¹, Toshinobu Hondo², Morio Ishihara¹, Michisato Toyoda¹, Ryosuke Nakamura³, Kentaro Terada¹

1.大阪大学大学院理学研究科、2.大阪大学大学院工学研究科、3.大阪大学産学連携本部

1.Graduate School of Science, Osaka University, 2.Graduate School of Engineering, Osaka University, 3.Office for University-Industry Collaboration, Osaka University

In space and planetary sciences, Secondary Ion Mass Spectrometers (SIMS) with an ion micro-beam has been widely used for in-situ isotopic analyses of micron scale samples [1]. In the SIMS analysis, the surface of the sample is irradiated by a primary ion beam, and among the sputtered materials, secondary ions are introduced into the mass spectrometer. One of the disadvantage of the SIMS is that the secondary ion yield is low (less than a few %), and a large fraction of the sputtered samples are lost as neutrals without being analyzed, which makes it difficult to carry out trace element analyses with a sub-micron spatial resolution due to the severely low ion counting statistics.

In order to improve this disadvantage, we have carried out the post-ionization of the secondary neutrals with a femtosecond laser [2]. By irradiating the high power laser above 10¹⁵ W/cm², 100% of the sputtered atoms and molecules can be ionized. In addition, in the high electromagnetic fields, all kinds of species are ionized, regardless of ionization potential, through the non-resonant ionization regime and can be analyzed simultaneously by using the time of flight (ToF) mass spectrometer.

The multi-turn time of flight secondary neutral mass spectrometer (MULTUM-SNMS) has been developed in Osaka University [3]. This instrument consists of a focused ion beam with a liquid metal gallium ion source, a femtosecond laser and multi-turn ToF mass spectrometer. The sample is sputtered with a 30 keV Ga⁺ ion beam which can be focused to a spot diameter of 40 nm and maximum current density is 30 A/cm². The ejected neutrals are irradiated with the femtosecond laser, and the post-ionized ions are introduced into the multi-turn ToF analyzer (MULTUM), the ion optical system of which achieves an ultra high mass resolving power of 250000 [4].

The performance evaluation of MULTUM-SNMS has conducted with a lead plate sample. It was demonstrated that the post-ionization with the femtosecond laser can make the Pb+ secondary yield about 10000 times higher. In addition, a mass resolution greater than 12000 is achieved utilizing MULTUM ion optics. Toward the application to U-Pb chronology, 91500 zircons which contain around 100 ppm uranium and used as a standard specimen of zircon U-Pb chronology was measured using MULTUM-SNMS. From a sputtered area of around 1 um in diameter, U^+ , $U0^+$ and $U0_2^+$ signal peaks were detected. In this presentation, we will also report the lead isotope ratio of the same specimen and discuss the feasibility of sub-micron scale in-situ U-Pb chronology with MULTUM-SNMS.

[1] Terada K. and Sano Y. (2012) Mass Spectrometry, 1, A0011.

[2] Ishihara M., et al. (2010) Surf. Interface Anal., 42, 1598-1602.

[3] Wucher A. (2013) In *ToF-SIMS: Surface Analysis by Mass Spectrometry*, (J. C. Vickerman and D. Briggs, eds.), pp. 217–246. IM Publications and Surface Spectra Limited.

 $\begin{bmatrix} 4 \end{bmatrix} \text{ Toyoda } M \quad \text{of } al \quad (2012) \quad \end{bmatrix} \quad \text{Mass Snastrom Soc. Jun. } 60 \quad 07 \quad 102$

[4] Toyoda M., et al. (2012) J. Mass Spectrom. Soc. Jpn., 60, 87-102.

キーワード:U-Pb年代分析、SIMS、SNMS Keywords: U-Pb dating, SIMS, SNMS