（2018 年度報告）

2019 年 3 月

課題名：（日本語）C 型小惑星サンプルリターンに向けた隕石を用いた分析プロトコルの構築

（英文）Construction of analytical protocol towards Hayabusa2 sample return mission for C-type asteroid.

Noboru Nakamura

（担当教員）: Eizo Nakamura

We can expect carbonaceous meteorite-like materials for the Hayabusa2 samples which might be returned from C-type asteroid, “Ryugu”. In order to establish the best analytical protocol applicable to these samples, it is important to examine;

1st, Reference materials (typical of CI-chondrites) for comparison with and evaluation of the Hayabusa2 samples.

2nd, Evaluation and improvement (if necessary) of current analytical tools, such as ICP-MS, at IPM, Okayama Univ.,

Current Status of evaluation of Cosmic elemental abundances; focused on REE

Past few decades, cosmic elemental abundances have been repeatedly presented by many authors, based mainly on CI chondrite elemental abundances, indicating that so-called “cosmic elemental abundances have not been sufficiently established until today. Nevertheless, relatively limited numbers of data sets of CI-chondrites have commonly been cited. The most commonly cited CI-data sets are from Anders & Ebihara, (1982), Wasson & Kallemyn 1988, Palme et al 1988, McDonogh & Sun 1985; Evenson et al, 1978; Lodders 1999; Nakamura, 1974). Among them, the mean CI-chondrite values evaluated by Anders & Grevesse (1989) are the most widely accepted and used as reference values for the CI-normalization (Korotev, 2010). Because of unique cosmic/planetary information, we have focused on abundances of trace elements, typically rare earth elements (REE), in CI-chondrites and reference materials, such as the Allende reference sample and terrestrial standard rocks such as JB-2, BCR-1 etc.We would like to show here the summary of our results of REE examination.

As discussed by Boynton (1998), REE chondrite-normalization values have been adopted basically from analytical results by neutron activation (NA) and isotope dilution (ID) techniques for CI and/or ordinary chondrites. Although the ID values are much more precise than NA values in general, application of this technique is limited to REE with poly stable isotopes, i.e. ten REEs. The typical precision of available REE ID data for chondrites are 1~3％ (Nakamura, 1974; Evensen et al., 1978), though those for NA analyses are ~10-20%. Then, the mono-isotope REE data for chondrites have been solely depend on the NA analyses until recent, ~1995, when the Inductively-coupled mass spectrometry (ICP-MS) have been applied to analysis of silicate rocks including meteorites.

Because the ICP-MS technique is applicable to analysis of all 14 REEs (except for extinct element; Promethium) for silicate rock samples, and thus have much potential to examine the detailed REE patterns for planetary materials, we are much interesting to know current status of REE data sets for meteorites, particularly for CI-chondrites. Nevertheless, CI-REE data obtained by ICP-MS are quite limited (i.e. Makishima & Nakamura 2006; Barrat et al., 2012; Poulmand et al., 2012). One of the most hard problems of ICP-MS is overwhelming matrix to trace elements, which has been overcome partially by extreme dilution (Makishima and Nakamura 1997) and reasonable correction of oxide effects.

As pointed out by Korotev (2010), the general data quality is evaluated by “smoothness” of REE pattern when normalized to the CI-values. He also noted that they have obtained the most smooth REE patterns when normalized to the mean CI-REE data set presented by Anders & Grevesse (1989), and then recommended these authors’ CI-REE data set as best men CI-values. We have accepted their suggestion for many years until today, i.e. their CI-REE data are well consistent with those obtained by the isotope dilution technique (Nakamura 1974; Evensen et al. 1978). This is well understandable, because their 10 CI-REE data have been estimated originally from ID data when available.

On the other hand, however, when compared with other commonly cited CI-data sets, the

REE patterns (normalized to Anders & Grevesse 1989) indicate systematic irregularities at Tb, -1.8±0.6%, Ho, -2.7±1.3% and Tm ＋3.0±0.6% (see Table 1).

As shown in Table 1, Similar heavy REE zigzag patterns are noted for standard rocks, typically, JB2 and several meteorites including Chaleyabinsk meteorite bulk samples (Nakamura et al 2019) and bulk ordinary chondrites (Shinotsuka et al. 1995).

From our search for detailed REE patterns of commonly cited CI-chodnrites, we concluded that the long-standing CI-REE values by Anders & Grevesse (!989) may not be reasonable as CI-reference. We, therefore, carried out statistical data treatment using CI-REE data which have been commonly cited reference CI and/or recommended CI-data sets. Starting from the commonly cited 12 CI-data sets including Anders & Grevesse (1989), 6 CI-data sets are selected as least standard deviations (±1σ ≲1.0%) for the mutually normalized REE patterns. The best 6 CIs are from

Palme et al. (2014), Pourmand et al. (2012), Palme (1988), McDonough & Sun (1995), Wasson & Kallemeyn (1988), Evensen et al. (1978).

The relative variability to mean 6 CI-chondrites is shown in Figs. 1 and 2.

Note that all the 6 CIs indicate flat REE pattern relative to the mean CIs. It is noted that absolute abundances are range from +3% to -3%. On the other hand, general REE pattern from Anders & Grevesse (1989) (±1σ=1.4%) shows relatively flut but indicate depletion of Pr and Tm but positive at Tb and Ho. Barrat et al (2012) analyzed 6 Orgueil (CI) samples by ICP-MS technique and obtained 5 consistent REE date sets only one sample deviate significantly from other 5 samples and and presented the mean five samples as best CI-chondrites. It is thus quite surprising that their mean Orgueil pattern shows relatively large overall deviations (±1σ=2.2%) including light REE depletion but heavy REE indicate relatively flut but Lu depletion (by 2.2%).

As shown in Table 1, it is interesting to note that REE data sets obtained by IPM group indicate more or less similar depletion at Tb, a little more depletion at Ho and significantly larger depletion (~5%) at Tm for JB2. In the same way, three Chaleyabinsk (LL5) meteorite bulk samples are found to indicate 2~5% more depletion at Tb, Ho and Tm compared with CI-data from other groups. Although the quantity of these depletion is marge of analytical precision, the systematic deviations seems to be partly due to the reference CI-chondrite REE data but may more likely to ICP-MS analytical problems. In order to clarify detailed REE abundance patterns and exemplify specific abundance anomalies of REE patterns of planetary materials such as chondritic materials, as well as potential Hayabusa 2 samples, the analytical details must be urgently revised

From above discussion, we concluded that the mean 6 CI-REE values calculated in this work is recommended as a reference normalization data set. This conclusion, however, need further substantiation in future by more advanced ICP-MS technique such as MC-ICP-MS (Baker et al.,(2002) including chemical separation using ion exchange columns (Pourmand et al. 2012).

References

Anders E. & Ebihara M. (1982); Geochim Cosmochim Acta **46**, 2363-2380.

Anders E. and Grevesse N. (1989); Geochim Cosmochim Acta **53**, 197-214

Baker J., Waight T., Ulfbeck D. (2002); Geochim Cosmochim Acta **66**, 3635-3646.

Barrat A.A., Keller E., Amosse J, Taylor R., Nesbitt and HirataT. (1996); Geostandards Newsletter **20**, 133-139.

Evensen N.M., Hamiltpn P.J., Onions R. K. (1978); Geochim. Cosmochim Acta **42**, 1199-1212

Kent A.J.R., Jacobsen B., Peate D.W., Waight T.E., Baker J.A. (2004); Geostandards and Geoanalytical Research **38**, 413-429.

Korotev R.L (2010); J. Radioanal. Chem. **1**, 337-348.

Lodders K. (2003); Astrophysical Jounal **591**, 1220-1247.

Lodders, K., Palme H., Gail H.-P (2009); In: Truper JE (ed) Landolt Bornstein, New Series, **VI/48**, pp560-598, Berlin Springer

Makishima, A. and Nakamura, E (1997); Geostandards Newsletters, The Journal of Geostandards and Geoanalysis **21**, 307-319.

Makishima, A. and Nakamura, E (2006); Geostandards and Geoanalytical Research **30**, 245-271.

Mcdonough W.F. and Sun S.-S. (1995); Chem Geol **120**, 223-253.

Nakamura E., Kunihiro T., Ota T., Sakaguchi C., Tanaka,R., Kitagawa H., Kobayashi K., Yamanaka M., Shimaki Y. Bebout G.E., Miura H., Yamamoto T. Malkovets V., Grokhvsky V.,Koroleva O.and Konsta (2019), Proc. Japan Acadmy, Ser. B (in press):

Nakamura N. (1974) Geochim Cosmochim Acata **38**, 757-775.

Palme H. (1988); Reviews in Modern Astronomy (G. Klare, editor) Springer, Berlin pp. 28-51.

Palme H., Lodders K. and Jones A. (2014) In: Asteroid, Comets and the Solar System, Vol. 2 of Treatise on Geochemistry (2nd ed) (ed. A.M. David) pp.15-36.

Pourmand A., Dauphas N. and Ireland T. J. (2012); Chemical Geology **291**, 38-54.

Shinotsuka K, Hidaka H. and Ebihara M. (1995); Meteoritics **30**, 694-699.

Wasson J.T. ang Kallemeyn G.W. (1988). Phylos. Trans. R. Soc. London. Ser A. **325**,535-544.

Yokoyama T., Nagai Y., Hinohara Y. and Mori T. (2016); Geostandards and Geoanalytical Research **41**, 221-242.

Table 1 Mono-isotope HREE のジグザグ（Tr, Ho, Tm 変動）（まとめ）

⑴ グループごとの CI データ：Anders ＆ Grevesse (1989)の CI 平均値で規格化した場合、

Barrat et al (2012): ICP-MS	Tb＝-1.4%	Ho= -2.7%	Tm=+4.2%
Wasson & Kallemyn (1988): NAA	Tb= -2.7%	Ho= -2.4%	Tm=+2.9%
Palme (1988): NAA	Tb= -2.3%	Ho= -2.0%	Tm= +2.9%
Boynton (1985): NAA	Tb= -1.2%	Ho= -2.5%	Tm= +2.7%
McDonough & Sun (1995):（選択平均）	Tb= -1.9%	Ho= -2.8%	Tm= +2.2%
Pourmond et al (2012) ICP-MS	Tb= -2.1%	Ho=-5.6%	Tm= +3.2%
Lodder (2003)（選択平均）	Tb = -1.3%	Ho= -1.3%	Tm= -3.2%*
Palme et al (2014)（選択平均）	Tb = -0.7%	Ho= -3.1%	Tm= +3.7%
Evensen et al (1978): ID+NAA 平均	Tb= -1.1%	Ho= -2.5%	Tm= +2.7%

n= 8 mean　Tb= -1.6±0.7, Ho= -2.8±1.2% Tm=＋3.1±0.6% (*excluded)

⑵ JB2 (Anders & Grevesse (1989) normerized)

Makishima & Nakamura (2006):	Tb= -2.7%(-0.2)	Ho= -4.7%(-2.5)	Tm= -1.4 %
Yokoyama et al (2017):	Tb= -2.9%(-0.4)	Ho= -5.4%(-3.2)	Tm= -1.5 %
Yamanaka (2018)	Tb= -0.8%(+1.5)	Ho= -3.7%(-1.5)	Tm= -1.5 %
Barrat et al (2012):	Tb= -0.7% (+1.5)	Ho= -2.6%(~-0.5)	-----

⑶ Cheleyabinsk bulk meteorite (Nakamura E et al, 2019) (Anders & Grevesse (1989)-norm)

(SRC):	Tb= -3.4% (-0.9)	Ho= -5.4% (-3.2)	Tm= -3.4%
(MLT):	Tb= -5.2% (-2.7)	Ho= -4.5% (-2.3)	Tm= -2.1%
(MIX):	Tb= --3.1% (-0.6)	Ho= -6.2% (-4.0)	Tm= +0.4%
(Mean3)	Tb= -3.9± 1.1%	Ho= -5.4± 0.9%	Tm= -1.7%

仮に Anders & Grevesse (1989) 以外の CI（Wasson & Kallemyn 1988 and/or Palme 1988）で規格化しても以下の変動が見られる；

Tb= -1.2%, Ho= -3.1%, Tm= -4.7%のズレが生じる。

⑷ その他 Chondrites (都立大グループ Shinotsuka et al 1995：

Jilin (H5):	Tb= -5.6%	Ho= -6.3%	Tm= -4.9 %	
St Severin (LL6):	Tb= --5.7%	Ho= -6.2%	Tm= -2.1 %	
Modoc (L6):	Tb= -4.7%	Ho= -4.9%	Tm= -4.6 %	
Atlanta (EL6):	Tb= -4.0%	Ho= -6.0%	Tm= -6.0 %	Mean 4 chon＝-5.1± 0.5%
R-chondrites (15Mean)	Tb= -0.2%	Ho= -0.6%	Tm= +1.0%	ジグザグ無し
Y-980459(Mar)(Shirai2004)	Tb= +5.4%	Ho= -1.6%	Tm= -0.3 %	(分析精度悪い？)

●ICP-MS のデータ（Barrat et al, 2012）や Pourmand et al (2012)のみならず、放射化分析（NAA）のデータにも重希土（HREE）のジグザグが見られる。