論文の内容の要旨 (Dissertation Abstract)

論文題目 (Title): Compiling a new database of meteorites: Analyses on bulk elemental abundances of meteorites and their implications to future space resources
(隕石組成データベースの構築：隕石の全岩組成と資源的価値に関する検討)

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Asteroids are small solar system bodies composed of ice, rocks and/or metals, whose sizes range from more than 1000 km down to the size of pebbles. While their origins and evolutionary histories are still not fully understood, they are generally considered as materials left over from the formation of the solar system; some are likely shattered remnants of planetesimals on their ways to form proto-planets, while others may experience long-term interactions with dusts and debris. Various dynamical groups of asteroids have been found including those in the main asteroid belt, Trojans asteroids, and Near-Earth asteroids (NEAs), whose closest trajectories (perihelion) to the sun are less than 1.3 AU[1, 2]. Among them, NEAs are of particular interests because much of our understanding of asteroids comes from examining fragments of meteorites, most of which are known to be sourced from NEAs[3][4]. In this way, meteorites are useful for obtaining a better understanding of the stages of solar system evolution from condensation of primordial solids through to aggregation, differentiation, alteration, and brecciation.

Asteroidal meteorites vary from undifferentiated chondritic meteorites with primitive compositions, which have provided most insight into pre-planetary processes, to those highly differentiated formed by planetary differentiation and core formation processes. Even for the latter, meteorites are generally known as highly heterogeneous in terms of their chemistries and structures. Thus, analyses of meteorite require highly precise measurement techniques for discrete components to unravel specific process of its formation histories. For this reason, majority of researches on meteorites report results of their analyses on chemical fractions or isotopes of a very small part of a meteorite. In contrast, bulk analyses of meteorite compositions can provide complementary datasets that hold information on complex meteorite histories. In other words, for recognition of a parent body of an individual meteorite, there are merits for studying the bulk chemistry of meteorites.
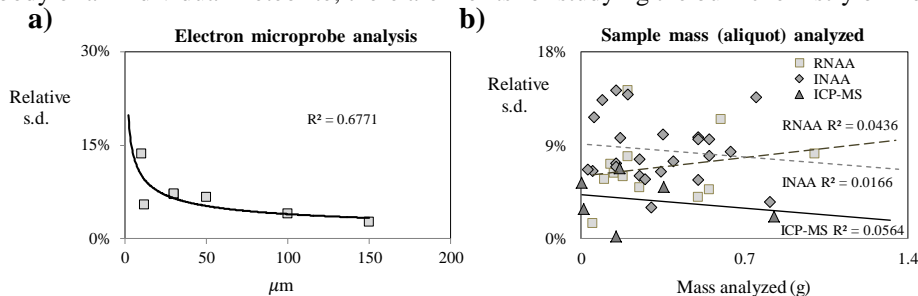

Figure 1: (a) Size of sample (slice width in μm) v.s. relative standard deviation of reported chemical abundances in our meteorite database analyzed only by electron microprobes. Slice widths of less than ~10 microns can lead to higher error readings **(b)** Mass of sample v.s. relative standard deviation of reported chemical abundances in our meteorite database by different measurement instruments such as inductively coupled plasma mass spectrometry (ICP-MS) and instrumental /radiochemical neutron-activation (INAA/RNAA). Note that the deviations of measurements depend largely on instruments but not on the mass of sample.

Several meteorite databases have been compiled previously [5-8]. However, because most of them are for the purpose of classifying meteorites, their elemental coverage is somewhat incomplete. Also, the numbers of meteorites and of classified groups are limited, which is natural because they rely heavily on pre-1970's chemical measurements [8]. Furthermore, statistical studies based on these databases sometimes suffer differences in accuracy of measurements, which confuses the treatments of various kinds of errors. We consider that this issue may be minimized by assuming that newer measurements have higher accuracy. Therefore, in this work, we develop a new meteorite chemical database based on this idea by sourcing published chemical abundances from peer-reviewed journals. Our new database currently contains 28,961 analyses of bulk chemical abundances for 1,187 meteorites. Input errors and miss-classifications common in such databases are minimized by thorough checks.
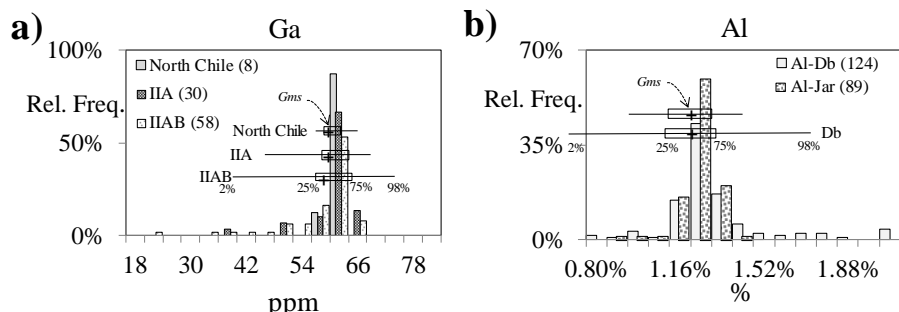
Figure 2: **(a)** Relative frequency histogram of concentrations of Ga (ppm) for a particular Iron meteorite (8 samples of North Chile), 30 samples of its subgroup (IIA), and 58 samples of its group (IIAB). The error bars are for 2%, 98% confidence limits, plus 25 and 75 quartiles. Note that regardless of number of samples, subgroups and larger sized groups tend to show similar distributions (symmetry/ peakedness around the same central tendency and geometric means); **(b)** Relative frequency histogram of Al (%) for L-chondrite for different numbers of samples in different databases (124 and 89 for ours and Jarosewich 1990, respectively). Note the similar distribution shapes regardless of the difference in number of samples.
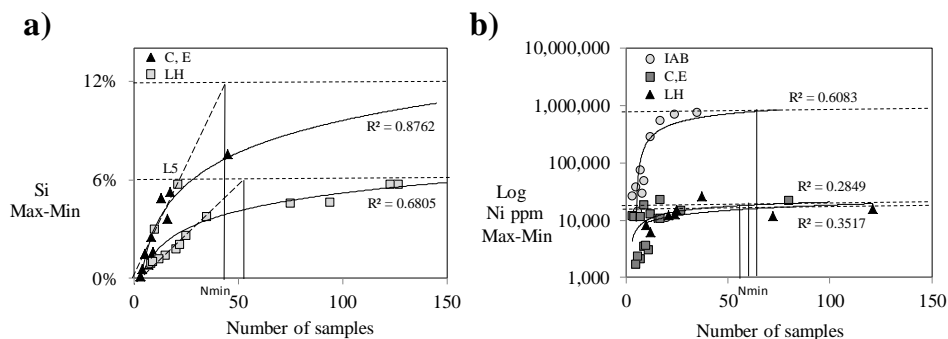

Figure 3: The number of samples versus the range of reported values (difference between maximum and minimum values) for different meteorite subgroups. **(a)** The range of Si for LH, C, and E chondrites; **(b)** The range of Ni in log scale for LH, C and E, chondrites and IAB iron meteorites. In both figures, plots of meteorite subgroups are fitted by 2nd-order polynomial curves. The curves tend to flatten out where we roughly define the possible maxima of chemistry range (sill; dotted line). We assume that the regression of the first part of the plots follows a 1st-order curve (linear line; dash line) and where this intersects with the sill it may indicate the minimum number of samples (Nmin) for roughly estimating the maximum range of the values. Note that the calculated Nmins are generally around 40~60 regardless of the distributional patterns of chemical abundances.

       As a nature of bulk chemistry measurements, data of elemental abundances should intrinsically deviate due to precision errors of instruments as well as effects of metamorphism, weathering or other processes. In fact, most meteorites are heterogeneous even at the scale of thin sections, which often casts doubt of the usefulness of bulk chemistry measurements. However, our new database based on our new method has low standard deviations of chemical abundances with a weighted-average value of the entire elements less than 6%, which indicates that the assumptions we made are reasonable to minimize statistical errors. Our assumption includes the premise that the precision is automatically better for newer measurements regardless of the way the sample is processed. This might be problematic as electron microprobes slice widths of less than ~10 microns can cause higher error readings (Fig. 1a). However, we find this assumption does not generally cause additional errors because relative standard-deviations of reported chemical abundances in our database are not a function of the size (mass) of the sample analyzed (Fig. 1b). Furthermore, distributions of chemical abundances in our new database tend to show statistical resemblances with those previously reported in terms of geometric means and distributional shapes (Fig. 2) [6, 7, 9]. The same meteorites are often repeatedly measured by different researchers. Thus, we plot the reported values of each element for each subgroup to understand whether the distributional shape is impacted. Contrary to our expectation, we find that ~40% of distributions are not Gaussian. We thus develop a terrestrial rock database in the same way as

meteorites to evaluate if this is a result of biases. Interestingly, we find similar results even for terrestrial rocks; for example, only ~88 % of terrestrial rocks show Gaussian distributions for O to P, Ga- Ge, and most REE, compared with ~86% for meteorite types for these same elements. We also find that, in more than 85% of the case when the elemental distributions do not show Gaussian distributions, the distributions do not become Gaussian even with an increased number of samples; contrary, skewness and kurtosis do not change regardless of the number of samples. However, chemistry range and standard deviation appear to increase with number of samples to account for increased heterogeneity in chemistry and petrology, while it seems that thermal metamorphism, aqueous alteration, and/or other processes might possibly effect asymmetry and peakedness such that Gaussian distributions are not necessary always attained for all elements in nature. Overall, we consider the above tests generally confirm that the meteorite database is reliable.

Legend:
- Anomalous in chondrites & nickel-iron meteorites
- Exceed terrestrial mining cut-off levels in chondrite and nickel-iron meteorites
- Anomalous in a few chondrite & nickel-iron meteorites
- Anomalous in HED and Ni-Fe poor achondrites
- Ni — Anomalous in lunar samples
- ± May be in sufficient concentrations for processing credits

Selected annotated elements:
- 12 Mg — Ureilite
- 21 Sc — ±SNC
- 22 Ti — ±HED; 23 V — ±HED; 24 Cr — ±HED
- 25 Mn — ±Pal, Mes, SNC
- 26 Fe — Only EH
- 27 Co — Only Iron, E, H, Lod
- 28 Ni — All chond
- 29 Cu — Only H6
- 30 Zn — ±CI, EH, C
- 31 Ga — ±IAB
- 32 Ge — IAB±Pal, Mes
- 34 Se
- 38 Sr; 39 Y; 40 Zr; 42 Mo — SNC
- 44 Ru — All chon; 45 Rh — Only Iron; 46 Pd — Not E; 47 Ag — Only CO3 ±CM2; 48 Cd — ±CI
- 49 In — ±CI, EH, CM2
- 74 W — ±HED
- 75 Re — Only Iron; 76 Os — All chon; 77 Ir — All chon; 78 Pt — All chond; 79 Au — All Chon
- 80 Hg — ±LL4
- 81 Tl — ±CI, CM2; 82 Pb — None; 83 Bi — ±CI
- 57 La; 58 Ce; 60 Nd; 63 Eu; 64 Gd; 67 Ho; 68 Er; 70 Yb; 71 Lu
- 90 Th

Figure 4: The Periodic table highlights relationships between anomalous values of geometric means (*Gms*) of atomic elements in our meteorite database compared to terrestrial values from 114 terrestrial mines and exploration deposits. Pal, Mes, SNC, and HED represent pallasite, mesosiderite, Martian meteorites, and meteorites from 4-Vesta. The blue font (All chon) indicates that the *Gms* for all chondrite types exceed terrestrial cut-off grades for that atomic element. For Pd 'Not E' means all chondrite types except E-chondrites contain Pd in excess of terrestrial cut-off grades. 'Ge, IAB ±Pal, Mes' means that Ge is above the terrestrial cut-off for IAB meteorites, and high enough for processing credits to be obtained from pallasite and mesosiderite meteorites. Over 34% of atomic elements are at anomalous levels in chondrite meteorites compared to upper and lower continental crust, or with terrestrial exploration and mining projects. C- and E-chondrites contain up to 24 anomalous elements. HED (from 4-Vesta) and silicate-rich achondrites contain anomalies of alkali metals (group I), alkali earth metals (group II) and transitional metals (Group 3-6); whereas, the only viable exploration target for most REE is the moon.

One of our purposes for compiling the meteorite database is to analyze the number of anomalous metals in meteorites (and ultimately, asteroids). Prior to that analysis, we compare elemental anomalies in meteorites with minimum mining concentrations, which are compiled from over 114 mineral exploration prospects and mines to ascertain current values for each. Importantly, only a few classes of meteorites/rocks (such as those from the moon, Mars, and 4-Vesta) are barren for base and precious metals. Contrary, C, E, and

LH-chondrites, and iron-rich meteorites have higher anomalies in up to 34% of periodic table elements as compared to material in the upper and lower continental crust of Earth [10, 11]. Some have anomalies even higher than those found in current mines. E-, C- and LH-chondrites can contain as many as 10 metals above terrestrial cut-off levels and 24 anomalous major, minor, and trace elements. We also find that the L5-6, H5-6 chondrites tend to have higher overall metal contents than lower petrologic types; generally, anomalies of Co, Cu, Pd, Ir, Mn, Ni, As, Fe, and Mg tend to increase with increasing petrologic type in L and H chondrites, while Cr, Si, Ru, In, Mo, Bi, and Sn decrease.

Many meteorites are considered as sourced from NEAs based on orbital parameters and spectral similarities. Our database confirms this as well; LH-chondrites account for 67.4% of the meteorite *falls*, which coincides with the proportions reported for S and Q-type NEAs (~65%) [4]. This supports the idea that proportions of meteorites collected from observed *falls* reflect the 'least biased estimate' of the composition of asteroid fragments that are most likely to hit the Earth [4]. While the exact proportions of subgroups in asteroids is not yet fully understood, meteorite *falls* provide a fairly robust approximation for calculation of metals in an average asteroid of any class.

There was still a concern as to whether we could make the assumption that a sufficient number of meteorites of any class exists to cover the chemistry range of asteroids. During our database validation process, we noted that the standard deviation correlates with the number of samples and the range of distributions (maximum-minimum value). However, as we show in Fig. 3, the range appears to achieve a maxima when we fit distributions using 2nd-order polynomial curves. The maxima is roughly (95%) attained by a certain number of samples, defined as the minimum number of samples (Nmin) required to cover the chemistry maxima. We find Nmin is likely about 40 for meteorites, which indicates that about 40 samples are required to cover 95% of the range of elemental distributions of meteorites/asteroids, providing a theoretical basis for using meteorites to analyze asteroids (Fig. 3).

Using the above approach we show that, on average, 98% of N#-type (nickel-rich), 95% of K-type, 80% of M-type, and 50% of S (or Q) -type NEA PGE + Au concentrations may exceed minimum terrestrial mining levels. In contrast, the asteroid 4-Vesta [12] is almost barren in PGEs, and most base-metals. It seems that moon may be a far better target for Al_2O_3, TiO_2 and for REE than asteroids, while Mars may be a better target for Mo, Bi, and Sn. We note that it is currently not technically possible to mine or process asteroid materials in space; but substantially lower capital and operating costs make it cheaper and more functional for material to be processed on Earth using existing processing facilities. Asteroid capture and sample return costs must be less than the sales revenue from refined metals minus terrestrial processing costs; thus, LEO (low Earth Orbit) space-transportation costs need to be fall substantially for asteroid mining to be viable.

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