

Analysis of the Elemental Composition of Chondrites

By

Masako SHIMA

Department of physical Sciences, National Science Museum, Tokyo.

I. Introduction

The bulk composition of the chondrite has been analyzed by many workers using various methods. However, because of difficulties of complete decomposition of chondrites and necessity of separation of three states of iron, analytical data by only a few workers have been employed for further discussion, though these must be the most important basic data for all kinds of researches of chondrites.

In 1968, Bernas proposed a new decomposition method for silicates. Since then the method has been applied to the analysis of many kind of inorganic siliceous materials such as granites, diabases (Bernas, 1968; Langmyhr *et al.*, 1968), tektites (Bernas, 1968), meteorites (Nava *et al.*, 1971), lunar soils (Schnetzler *et al.*, 1971) and lunar rocks (Nakamura *et al.*, 1973).

In this paper, the above method was employed to the systematic analyses of major component elements in Japanese chondrites and data obtained were compared with those by former methods (Shima *et al.*, 1967; Shima, 1974; Murayama *et al.*, 1978).

The recommended methods combined with the new decomposition method including a part of former procedures are proposed for the complete determination of major elements in chondrites.

II. Experimental

A. *Decomposition of chondrites*

1. Method of Bernas. About 50~80 mg of pulverized chondrite sample was weighed and transferred into a teflon decomposition vessel. About 0.5 ml of aqua regia and 3 ml of 48% HF were added to the sample and the vessel was covered with a teflon sealing disk then closed by hand tightening the screw cap. The vessel was placed into a drying oven at $110 \pm 10^\circ\text{C}$. Because some chromite grains in chondrite are hard to dissolve in HF, the time of decomposition in the oven was set to 8, 6 and 1.3 hours for chondrites Nogata, Duwun and Ogi respectively. This decomposition resulted in 100%, 65% and 15% of the total Cr in Nogata, Duwun and Ogi being recovered. Of course, depending on chondrites, hardness of chromite is different, but it seems necessary to keep sample in oven more than 8 hrs.

After the sample was cooled to room temperature, the cap was unscrewed and

the decomposed sample solution was transferred completely into a 50 ml teflon beaker with the aid of about 5 ml of redistilled water. About 2.8 g of boric acid was added to the solution, the solution was stirred well with a teflon rod, then diluted with about 40 ml of water. To obtain a clear solution, it took more than 1 hour. The solution was transferred into a polyethylene bottle which was first weighed, with about 50 ml of redistilled water, and the weight again measured. The concentration of each element was expressed in μg element/g. solution (ppm), and was determined by atomic absorption spectrometry without dilution or, if necessary, the solution was diluted with a weighed quantity of water. After atomic absorption spectrometry was performed, the rest of the solution was weighed and used for the determination of P and S by colorimetry and gravimetry, respectively.

2. *Other methods.* The conventional acid decomposition by $\text{HF}+\text{HClO}_4$, alkaline fusion by Na_2CO_3 and fractional dissolution methods were used for the decomposition of chondrite sample for the comparison. The procedure were described in the former papers (Shima *et al.*, 1967; Shima, 1974).

B. *Determination of elements*

Mg, Fe, Al, Ca, Na, K, Cr, Mn, Ti, Ni, and Co have been determined by atomic absorption spectrometry using a Shimadzu AA-640-12 spectrometer. Si obtained by the new decomposition method was also measured by atomic absorption but Si from alkaline fusion and fractional dissolution was analyzed gravimetrically. Details are described below:

1. Mg and Fe. Mg and Fe contents in chondrite are so high, that an aliquot of the original solution containing 50~80 mg of decomposed sample in about 100 g solution must be diluted 1000 fold and 100 fold for Mg and Fe respectively. Using these dilute solutions there are no problems in analysis with Ne filled hollow cathode lamps in 2852 Å and 2483 Å in air-acetylene flame.

2. Mn and Ni. These elements can be analyzed by Ne filled hollow cathode lamps using the lines of 2794.8 Å and 2320.03 Å respectively in air-acetylene flame without any disturbance of co-existing elements in sample solution. An aliquot of the original solution above was diluted to 5 times.

3. Na and K. These elements can be measured in air-acetylene flame, but the sample solution from the new decomposition method contains HF and a large amount of H_3BO_3 which makes absorbance lower, as is shown in Figs. 1 and 2.

For Na and K, instead of the most sensitive lines, 5889.9 Å (Na) and 7664.9 Å (K), the lines 3302.3 and 3303.0 Å (Na) and 7699.0 Å (K) were used for analyses. Because, these elements are the commonest on the earth and moreover, too sensitive in atomic absorption measurements, this results in higher values than the real contents in chondrite due to laboratory contamination etc.

4. Co. The excess amount of HF and H_3BO_3 in the examined solution makes absorbance of 2407.27 Å Co in air-acetylene flame higher as indicated in Fig. 3. It is necessary to make the standard solution with the appropriate amount of the HF

and H_3BO_3 for measurement of Co in the solution obtained by the new decomposition method.

5. Al. Al was determined in N_2O -acetylene flame with a Ne filled hollow cathode lamp using the line, 3092.7 \AA . The high concentration of H_3BO_3 in the sample solution makes absorbance lower as seen in Fig. 4. It is necessary to draw the calibration

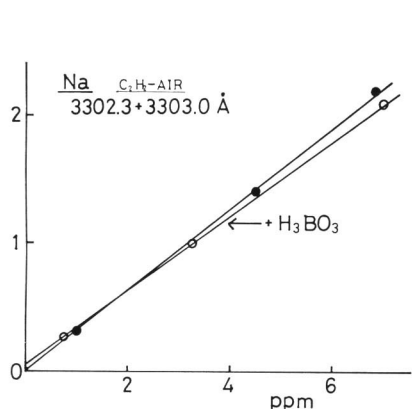


Fig. 1. The calibration curve for Na. When $HF+H_3BO_3$ (in figure the line indicated $\leftarrow +H_3BO_3$) was added, absorbance become apparently lower. The number of the vertical axis is proportional to the absorbance and number "2" corresponds to the absorbance "0.1".

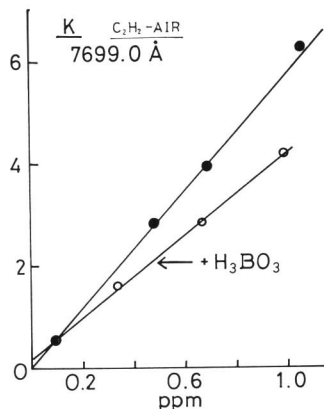


Fig. 2. The calibration curve for K. Details are same as Fig. 1.

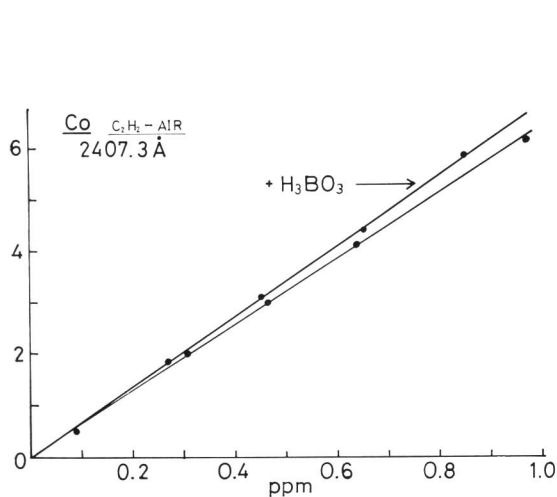


Fig. 3. The calibration curve for Co. Details are same as Fig. 1.

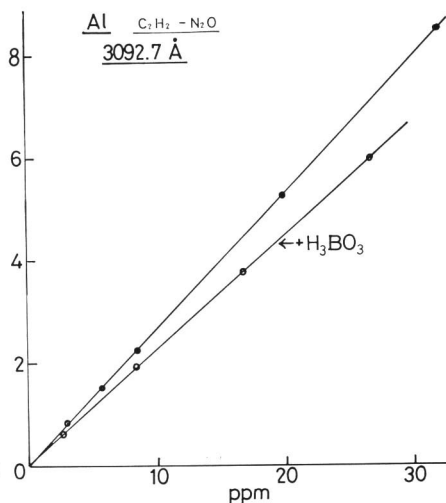


Fig. 4. The calibration curve for Al. Details are same as Fig. 1.

curve with the standard solution containing the appropriate amount of H_3BO_3 .

6. Ca. Although accurate measurement of Ca using atomic absorption presents a few problems, we could say that it is still the most simple, sensitive and accurate method of Ca determination, with a little care.

The air-acetylene flame could be used for Ca determination without any problem in most cases. But when the sample solution contains many cations and anions like decomposed meteorite solution with acids and alkalis, sometimes it gives unknown effects. These are not simple as is described in many texts or literatures. To avoid such effects, N_2O -acetylene flame is recommended for the determination of Ca in chondrites. In this case, excess of HF and H_3BO_3 do not affect the measurement of Ca. The decomposed chondrite solution, however, contains many readily ionizable cations in rather high concentrations. For the actual determination of Ca in 50–80 mg chondrite sample in about 100 g solution, the solution was diluted to 5 times with water and KCl solution to make the concentration of KCl in it about 1 mg K per g of solution. The standard solutions for the calibration curve contain also KCl in similar concentration to the sample solution. The calibration curves for Ca determination are shown in Fig. 5. A Ne filled hollow cathode lamp with 4227 Å absorbing line was used for Ca determination.

7. Cr. Cr could be analysed in both air-acetylene and N_2O -acetylene flame in 3578.69 Å, without any disturbance in most cases 5-fold diluted solution. Only for the test solutions containing rather high amounts of Fe like $2\text{KCl}\cdot\text{CuCl}_2$ solution by the fractional dissolution of chondrite, a N_2O -acetylene flame is recommended.

8. Ti. Ti was determined in N_2O -acetylene flame with a Ne filled hollow cathode lamp using the 3642.68 Å absorption line with a 10 times expansion scale. Excess of H_3BO_3 and HF, and the presence of Fe^{+++} gives the lower absorption curve

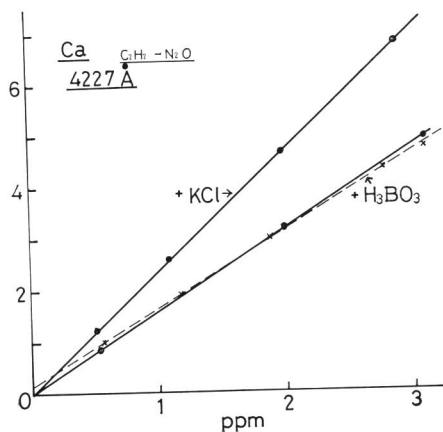


Fig. 5. The calibration curve for Ca. The presence of H_3BO_3 does not disturb the curve while KCl gives higher value due to ionization.

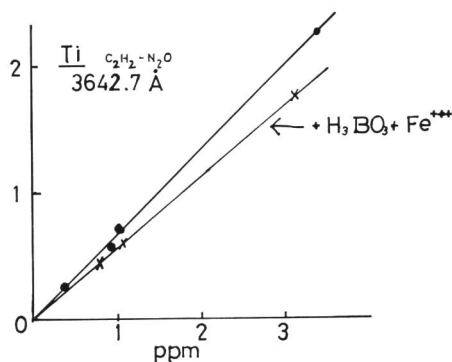


Fig. 6. The calibration curve for Ti. Addition of H_3BO_3 and Fe^{+++} gives apparent effect.

as indicated in Fig. 6. The effect of Fe^{+++} in solutions with large excesses of alkaline elements such as the solution containing Na_2CO_3 fusion sample was negligible, while for acid decomposition samples, it could not be neglected.

9. Si. The Si standard solution was prepared with 0.24 g of 99.99% SiO_2 , Brazil quartz powder, dissolved in the mixture of 4 ml of redistilled H_2O , 3 ml of 4% HF and 2.8 g of H_3BO_3 . After complete dissolution, which takes about a week, the solution was diluted with redistilled water to about 100 g, and was weighed. The concentration of the solution is about 1 mg Si/g.

The calibration curve for the atomic absorption using N_2O -acetylene flame, 2516.7 Å absorption line with Ne filled hollow cathode lamp was made by diluting this standard solution. No difficulty arises for the Si determination in chondrites by the atomic absorption method.

Si in alkaline fusion sample and in the residue of the fractional dissolution sample was determined gravimetrically by the conventional method.

10. P. About 10–20 g aliquots of the original solution, containing 50–80 mg decomposed chondrite sample were taken for the colorimetric determination of P.

Using the method proposed by Ikeda (1951), P could be measured without any separation procedure from other coexisting elements, but better color development is obtained after the separation of Fe^{+++} .

Passing the sample in 6N-HCl solution through about 5 ml of anion exchange resin, Dowex-1, X-8, 100–200 mesh, treated by 6N-HCl, P was eluted in the first step, and Fe^{+++} remains in the resin. 1.4 ml of 3.6 N- H_2SO_4 was added to the solution eluted from the resin column and HCl was evaporated completely. The resulting solution was used for the colorimetry of P.

11. S. The rest of the solution after all above elements were determined, was used for the determination of S. The majority of S should be in the sulphate form, but to make sure, S was oxidized with Br_2 in acidic solution. After excess of Br_2 was evaporated from the slightly acidic solution SO_4^{--} was precipitated by adding excess of 10% BaCl_2 solution, as BaSO_4 . The BaSO_4 precipitate must be well washed with redistilled water for taking out any coprecipitant.

For accurate determination of S, it is desirable to take more than 100 mg of chondrite samples.

III. Results

Results obtained by four kinds of decomposition methods applied to the chondrite Nogata are shown in Table 1. Data in this table obtained by four different method of decomposition agree very well with each other.

Using the new decomposition method, all elements can be measured simply with atomic absorption spectrometry. However, among three or sometimes more states of Fe, troilite Fe, FeS, can be calculated as the equimolar amount of S, but other states, mainly metallic Fe and silicate Fe with valency 2, and magnetite- and hematite-Fe,

Table 1. Results of major elements in chondrite Nogata using four different decomposition methods.

	New decomp.	Acid	Alkali	Fractional diss.	
				1	2
Sample taken (g)	0.08261	0.5128	0.2823	0.2830	0.4070
SiO ₂	40.618	—	40.950	40.611	40.265
MgO	26.259	25.584	25.617	25.481	25.758
Al ₂ O ₃	2.026	2.252	2.098	2.023	2.083
CaO	1.764	1.769	1.872	1.824	1.796
Na ₂ O	0.945	0.987	—	—	—
K ₂ O	0.102	0.102	—	—	—
Cr ₂ O ₃	0.434	(0.144)	0.435	0.598*	0.595*
MnO	0.340	0.339	0.334	0.333	0.327
TiO ₂	0.098	(0.153)	0.092	0.116	0.117
P ₂ O ₅	0.236	0.269	0.234	0.203	0.228
FeO	14.691**	14.504**	14.210**	15.397	15.398
FeS	6.301	—	6.526	5.736	5.909
Fe	4.028**	3.960**	3.968**	3.930	4.258
Ni	1.555	1.522	1.449	1.415	1.544
Co	0.070	0.062	0.071	0.069	0.073
H ₂ O***	0.209	0.209	0.209	0.209	0.209
Total Fe	19.451	19.121	19.160	19.542	19.981
Sum	99.676	—	—	—	—

* These higher values may be caused by contamination of reagents.

** Calculated by using the ratios obtained by fractional dissolution.

*** Dried the pulverized sample in silica gel desiccator before each sample was taken.

can not be separated by this method only.

The conventional acid decomposition and alkaline fusion method present the same problem, and moreover by acid decomposition Si and S, and very often Cr can not be determined, while by alkaline fusion, determination of Na and K are hindered by fusing reagent Na₂CO₃.

On the other hand, careful application of the fractional dissolution method gives a clear solution for Fe states experimentally. In Table 1, metallic Fe and silicate Fe were calculated by using the ratio obtained by the fractional dissolution method.

IV. Recommended method for the analysis of the chondrite

The new decomposition method of Bernas *et al.* (1968) with minor modification is simple and adequate for the decomposition of chondrite. The modification is the decomposition period which must be much longer than originally proposed for the decomposition of terrestrial rocks, that is, more than 8 hours is necessary. For the accurate determination of S, more than 0.1 g of the pulverized sample should be used. Details of the determination methods of major elements by atomic absorption are

Table 2. Summary of the determination of major elements in chondrites by atomic absorption spectrometry using Ne filled hollow cathode lamps.

Element	Dilution*	Reagent** added	Concn. range (ppm)	Flame (oxidiz. agent)	Wave length (Å)	Expansion****
Si	5	none	6-100	N ₂ O	2517	2.00
Mg	1000	none	0.01-0.3	air	2852	1.00
Al	1	HF+H ₃ BO ₃	1-30	N ₂ O	3093	2.00
Ca	1	KCl***	0.1-3	N ₂ O	4227	0.50
Na	1	HF+H ₃ BO ₃	1-10	air	{ 3302 3303	1.00
K	1	HF+H ₃ BO ₃	0.1-1	air	7699	1.00
Cr	5	none	0.1-3	{air N ₂ O	3579	{2.00 5.00
Mn	5	none	0.1-3	air	2795	1.00
Ti	1	HF+H ₃ BO ₃	1-10	N ₂ O	3643	10.00
Fe	100	none	0.3-3	air	2483	1.00
Ni	5	none	0.3-5	air	2320	1.00
Co	1	HF+H ₃ BO ₃	0.3-1	air	2407	1.00

* For example dilution number "1" is without dilution and "5" means diluted solution to 5 times by weight.

** Reagent added to the standard solution to measure element obtained by new decomposition method.

*** KCl added. Also added to sample solution to make the concentration 1 mg K/g for measuring the Ca obtained by other than new decomposition method.

**** When expansion is 1.00, vertical axis "2" in Figs. 1-6, corresponds to absorbance "0.1", and 2.00 is simply twice this.

summarized in Table 2. Phosphorus can be measured colorimetrically while sulphur is determined gravimetrically as BaSO₄.

Besides the new decomposition method, the fractional dissolution method must be applied to about 0.3-0.5 g of the pulverized sample for determining three or more states of Fe in chondrite, that is, metallic Fe, troilite Fe, and silicate Fe with valency 2 and with the stoichiometrical mixtures of valency 2 and 3. By application of the fractional dissolution method, fayalite and ferrosilite ratios in olivine and pyroxene can also be determined.

When these two methods are employed, we could analyze chondrites accurately with ~0.5 g samples. However, depending on the chondrite, some have quite large crystals or inclusions, or dark parts and light parts in a large area. With such heterogeneous samples, it is necessary to use 10 g or more to obtain the average concentration of major elements in chondrite. Even in such cases, when as a first step 10-30 g sample were pulverized, only 0.5 g of it was used for analysis and the rest of it could be stored for other research purposes.

References

- BERNAS, B., 1968. A New method for decomposition and comprehensive analysis of silicates by atomic absorption spectrometry. *Anal. Chem.*, **40**: 1682–1686.
- IKEDA, N., 1951. New colorimetric method for phosphate ion using sodium thiosulphate. *J. Chem. Soc. Japan. Pure Ed.*, **72**: 23–26. (in Japanese).
- LANGMYHR, F. J. and P. E. PAUS, 1968. The analysis of inorganic siliceous materials by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique Part I. The analysis of silicate rocks. *Anal. Chim. Acta*, **43**: 397–408.
- MURAYAMA, S., Masako SHIMA and A. OKADA, 1978. The chemical composition, petrography and mineralogy of the Japanese chondrite Nagai. *Bull. Nat. Sci. Mus. Ser. E.*, **1**: 19–29.
- NAKAMURA, N., A. MASUDA, T. TANAKA and H. KURASAWA, 1973. Chemical compositions and rare-earth features of four Apollo 16 samples. *Proceed. 4th Lunar Sci. Conf.*, **2**: 1407–1414.
- NAVA, D. F., L. S. WALTER and A. S. DOAN, Jr., 1971. Chemistry and mineralogy of the Lost City meteorite. *J. Geophys. Res.*, **76**: 4067–4071.
- SCHNETZLER, C. C. and D. F. NAVA, 1971. Chemical composition of Apollo 14 soils 14163 and 14259. *Earth Planet. Sci. Letts.*, **11**: 345–350.
- SHIMA, Masako and M. HONDA, 1967. Distribution of alkali, alkaline earth and rare earth elements in component minerals of chondrites. *Geochim. Cosmochim. Acta*, **31**: 1995–2006.
- SHIMA, Masako, 1974. The chemical compositions of the stone meteorites Yamato (a), (b), (c) and (d), and Numakai. *Meteoritics*, **9**: 123–135.