Precise determination of chlorine concentrations and stable isotopic compositions of silicate materials and its applications to primitive meteorites

Fujitani, Tatsuya

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Precise Determination of Chlorine Concentrations and Stable Isotopic Compositions of Silicate materials and Its Applications to Primitive Meteorites

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神戸大学大学院自然研究科

藤谷達也（Tatsuya Fujitani）

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Precise Determination of Chlorine Concentrations and Stable Isotopic Compositions of Silicate materials and Its Applications to Primitive Meteorites

（珪酸塩物質中の塩素濃度及び塩素安定同位体組成の
精密測定と始原的隕石への応用）

平成18年2月

神戸大学大学院自然研究科

藤谷達也　(Tatsuya Fujitani)

Abstract

The precise determinations of chlorine concentrations and stable isotopic compositions in silicate materials have been developed. The techniques were applied to analyze the primitive meteorites and some new findings were obtained.

A procedure for isotope dilution technique (ID) using negative thermal ionization mass spectrometry (N-TIMS) of chlorine is described. Silicate samples of about 10 mg were spiked and decomposed with hydrofluoric acid, and chlorine was isolated by precipitation of silver chloride after neutralization with $Ca(OH)_2$. The ammonical solution of AgCl was then subjected to N-TIMS. Replicate analyses of standard rocks, typical of JB-1, JR-1, demonstrated the high quality of the analyses (accuracies for Cl are ± 1-2 per cent). The most precise data sets of chlorine concentrations in nine igneous standard rocks, three basalts (JB-1, JB-2, JB-3), two andesites (JA-3, AGV-1), two rhyolites (JR-1, JR-2), and two granodiorites (JG-3, GSP-1) are presented. The chlorine concentration ranges from 152 ppm in AGV-1 to 1008 ppm in JR-1. The results presented here are partly in agreement but not necessarily with recommended values, if they are available. The N-TIMS ID can thus be used as a mean of high-precision analyses of small silicate materials with low chlorine contents.

An analytical technique applicable to precise determination of chlorine isotopic compositions for a few hundred-milligrams sizes of silicate samples, typical of nine igneous standard rocks, by thermal ionization mass

spectrometry (TIMS) has been developed. About 50 μg of chlorine was extracted from each sample (sizes about a few hundred milligrams) by hydrofluoric acid leaching. Chlorine was recovered as AgCl and converted to CsCl with Cs-form ion exchange resin. The sample was loaded as CsCl form containing 2 μg Cl on a Ta filament together with graphite powder. The TIMS measurement of isotopic ratio was performed as Cs_2Cl^+ ions.

Replicate analyses of laboratory standard (CsCl reagent), seawater and a NIST Cl isotope standard, as well as standard rock demonstrated of the high quality of the analyses. The internal standard error (2 σ m) associated with the mean ($^{37}Cl/^{35}Cl$) ratio of each run (400 ratios) was 0.1-0.2‰ for the most samples. The Cl isotopic composition represented by per-mil deviation relative to the standard mean ocean chloride ($\delta^{37}Cl_{SMOC}$) of nine igneous standard rocks including three basalts (JB-1, JB-2, JB-3), two andesites (JA-3, AGV-1), two rhyolites (JR-1, JR-2) and two granodiorites (JG-3, GSP-1) show relatively small variations, ranging from +0.25±0.26‰ for JR1 to +4.30±0.30‰ for AGV-1, but the $\delta^{37}Cl$ values are clearly resolvable from sample to sample. It is pointed out that all igneous rock samples shift to positive $\delta^{37}Cl$ values but no systematic differences in $\delta^{37}Cl$ values are observed among different rock types.

The chlorine concentrations and isotopic compositions of one CI, two CM, one CV, three CK, three Enstatite, and eight Ordinary chondrites have been examined. Several grains of chondrules in Allende (CV3) were also investigated. The chlorine concentrations were determined precisely by isotope dilution method using N-TIMS. Cl contents in the carbonaceous

chondrites ranged from 760 to 282 ppm. Three enstatite chondrites ranged from 824 to 217 ppm. Eight ordinary chondrites ranged from 412 to 44.3 ppm.

The chlorine isotopic compositions of 20 samples in 17 chondrites were determined by positive thermal ionization mass spectrometry (P-TIMS). In chlorine extraction procedure, the chemical yields ranged from 89% for Hedjaz to 52% for Indarch and the average of all analysis is 76%. All the chondrite groups other than the L-chondrites were almost showing enriched in ^{37}Cl relative to SMOC ($\delta^{37}\mathrm{Cl}_{\mathrm{SMOC}}=-0.56\sim7.99‰$) as well as the values of terrestrial igneous rocks. On the contrary, four L-type ordinary chondrites indicated to be deplete in ^{37}Cl relative to SMOC ranging from −4.60‰ to −0.74‰.

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Chapter 1 General Introduction

Chlorine is the element with atomic number 17 and belongs to the halogens, which are five non-metallic elements found in group 17 of the periodic table. All halogens have 7 electrons in their outer shells, giving them an oxidation number of −1.

In nature, chlorine is found only as the chloride ion. Chlorides make up much of the salt dissolved in the Earth's oceans. In the atmosphere, very trace chlorides exist in volcanic gas and aerosol. In the lithosphere, higher concentrations of chloride are dissolved in underground brine deposits. Average chloride abundance in the crust was about 180ppm (Taylor, 1964) fixed e.g., in halide minerals as halite, sylvite and carnallite, phosphate minerals as apatite, and lattice substitution for hydrous silicate minerals. In the solar system, chlorine abundance in C1 chondrite was reported to be 704ppm (Anders and Grevesse, 1989). Chlorine is ubiquitous and the behavior of chlorine in various geological settings can indicate useful information (Ito et al., 1983; Jambon et al., 1995). Also, chlorine in meteorite is drawing attention for cosmochemists because of its mobility in aqueous environment.

There are two stable isotopes of chlorine, of mass 35 and 37, respectively. Natural abundances are 75.78% for ^{35}Cl and 24.22% for ^{37}Cl. Other six radioactive isotopes have been known, though only ^{36}Cl occurs in nature as well as stable ones. ^{36}Cl is produced in the atmosphere by spallation of ^{36}Ar by interactions with cosmic ray protons. For the origin of the stable isotopes, explosive nucleosynthesis was responsible for ^{35}Cl and carbon burning, s-process and explosive nucleosynthesis were for ^{37}Cl (Anders and Grevesse, 1989).

Generally, the chemical nature of the stable isotopes of the certain element is almost the same. However, the isotope fractionation through various physic-chemical processes could be caused due to their relatively large mass differences for light elements (e.g., H, B, C, N, O and S). The use of stable isotope ratios of these elements is well established to solve various kind of geochemical and cosmochemical problems (Faure, 1986). Two chlorine stable isotopes as ^{35}Cl and ^{37}Cl have a relative mass difference of 5.7%. Due to such a mass difference, significant natural variations in ^{35}Cl/^{37}Cl ratio is expected and can be used for useful tracer during geo and cosmochemical processes.

In the early works, chlorine isotopic compositions have been investigated by CH_3Cl-gas mass spectrometry (Kaufmann et al., 1984) and Cl^- thermal ionization mass spectrometry (N-TIMS) (Vengosh et al., 1989; Taylor and Grimsrud, 1696). The precision measurements by CH_3Cl-gas mass spectrometry revealed the variations of chlorine isotope ratio in groundwater (Desaulniers et al., 1986), fluid inclusion in ore deposits (Eastoe and Guilbert, 1992), and evaporates (Eggenkamp et al., 1995; Eastoe et al., 1999). Kaufmann et al. (1984) reported analytical results for seawater samples that the ^{35}Cl/^{37}Cl ratio of modern seawater is analytically homogeneous. Recent development of analytical technique of chlorine isotopes using Cs_2Cl^+ thermal ionization mass spectrometry (P-TIMS) could satisfy both precision and sensitivity (Xiao and Zhang, 1992; Numata et al., 2001). This technique allows only several micro-grams Cl for the analysis and could yield precision better than 0.25‰ (Magenheim et al., 1994). However, due to analytical difficulties including troublesome chlorine extraction procedures, the isotopic analyses of silicate materials with low chlorine contents, such as volcanic rocks as well as meteorites, are quite limited yet. This is the same even if the measurement of chlorine concentration in silicate materials is concerned.

In the Chapter 2, a procedure for isotope dilution technique (ID) using negative thermal ionization mass spectrometry (N-TIMS) of chlorine in igneous rocks was described. Replicate analyses of JB1 and JR1 showed good precisions about or less than 1%. The usefulness of the N-TIMS ID that can be used as a mean of high-precision analyses of small silicate materials with low chlorine contents was presented. Results of other standard rocks were also described.

In the Chapter 3, an analytical technique applicable to precise determination of chlorine isotopic compositions for a few hundred-milligrams sizes of silicate samples, typical of nine igneous standard rocks, by thermal ionization mass spectrometry (TIMS) was described. Chlorine extraction from the silicate materials using hydrofluoric acid leaching was examined. Replicate analyses of laboratory standard (CsCl reagent) and seawater, as well as standard rocks demonstrated that the high quality of the analyses. It was pointed out that all igneous rock samples shift positive δ^{37}Cl values but no systematic differences in δ^{37}Cl values are observed among different rock types.

Finally, new data sets of chlorine concentration and isotopic composition of 18 primitive meteorites were presented in Chapter 4. Analytical procedures were already described in Chapter 2 and 3. All the chondrite groups other than the L-chondrites were almost showing enriched in ^{37}Cl relative to SMOC as well as the values of terrestrial igneous rocks. On the contrary, four L-type ordinary chondrites indicated to be deplete in ^{37}Cl relative to SMOC.

Chapter 2 Determination of chlorine in nine standard rocks by isotope dilution mass spectrometry

Introduction

Recent investigations have revealed the importance of the role of fluid on the evolution of mantle, especially in relation to the subduction zones. (e.g., Tatsumi et al. 1986; Schmidt and Poli 1998; Scambelluri and Philippot 2001). Because the halogens, including chlorine are one of the most mobile elements having affinities with fluids, they can be useful indicators to investigate on various geochemical processes (Ito et al. 1983; Jambon et al. 1995; Straub and Layen 2003). The distributions of chlorine in geological samples are thus most interesting geochemically.

Analyses of chlorine in geological samples have been carried out by several techniques such as photometric method (Terashima 1974), X-ray fluorescence spectrometry (Terashima 1976), ion-selective electrode method (Aruscavage and Campbell 1983), instrumental or radiochemical neutron activation analysis (Unni and Schilling 1978; Shinonaga et al. 1994), ion chromatography (Wilson and Gent 1983, Blackwell et al. 1997) and isotope dilution mass spectrometry (IDMS) (Shinonaga et al. 1994). Among them, IDMS may be considered as one of the most accurate analytical methods.

Determination of chlorine isotopic composition has been carried by CH_3Cl^+ gas mass spectrometry (Kaufmann et al. 1984), Cs_2Cl^+ thermal ionization mass spectrometry (P-TIMS) (Xiao and Zhang, 1992; Numata et al. 2001), and negative thermal ionization mass spectrometry (N-TIMS)

(Taylor and Grimsrud 1969; Vengosh et al. 1989). The former two methods are expected to have high analytical precisions (normally 0.1 ~ 0.2‰ in $^{37}Cl/^{35}Cl$ ratio) but required much greater amounts of sample compared to N-TIMS. The N-TIMS technique provides much (in the order of 10^3) higher sensitivity of chlorine relative to P-TIMS, though its isotopic precisions (normally better than a few ‰) are much worse than these of the two methods. However, the application of N-TIMS technique to isotope dilution (ID) can provide a quite useful tool for chlorine concentration determination allowable of a few % precision, normally required for precision analyses for silicate samples with relatively low Cl concentrations.

As part of our systematic search for chlorine concentration and isotope distributions in standard rocks and meteorites, we developed a N-TIMS technique for high-precision ID of chlorine and present here new chlorine concentration data sets for nine igneous standard rocks issued by Geological Survey of Japan (GSJ) and/or US Geological Survey (USGS).

Experimental

Calibration of Cl Spike

The ^{37}Cl-enriched spike (^{37}Cl 98.21%) was obtained from Oak Ridge National Laboratory. The aqueous spike solution (Cl: 2.5g/kg) was prepared and stored (as frozen in a bottle when it was not used). For calibration of spike solution, a standard solution (0.05012g-Cl/kg) was prepared from a commercial grade NaCl reagent (99.99%). We prepared nine spike/standard mixed solutions with different mixing ratios. The chlorine isotopic ratios of the mixed solutions were determined by N-TIMS technique as described in detail later.

In order to confirm our calibration, we obtained a NIST SRM 3182 chloride anion standard solution and a NIST SRM 975a chlorine isotopic standard, which have been provided with certified values of Cl concentration and isotopic composition, respectively. We measured isotopic compositions of Cl in both standards by P-TIMS as well as N-TIMS.

Chemical procedures

Rock samples were decomposed with hydrofluoric acid and excess amounts of F^- were precipitated and removed as CaF_2 by neutralizing with $Ca(OH)_2$, and chlorine was isolated as silver chloride (Musashi et al. 1998). The rock powder sample with about 10mg in weight (see Tables 2-2 and 2-3) was weighed carefully using a semi-micro balance (precision of 0.02mg) and transferred into a Teflon vessel with a cup. An about 100mg ^{37}Cl-enriched spike solution and an about 50μL high purity hydrofluoric acid (HF: 22M) were added to the sample (HF had been purified by bottle to bottle distillation in our laboratory). The vessel was closed tightly and then shaken continuously for 24 hours at room temperature to leach Cl from the sample and to achieve the isotopic equilibration between the sample and spike. The total HF contents in the acid solution used here correspond (stoichiomerically) to about two times of total cations in samples, implying that the Cl-bearing minerals such as chlorapatite can be easily reacted.

After one-day acid leaching, the calcium hydroxide slurry (200g-$Ca(OH)_2$ /L-water; $Ca(OH)_2$: Merk, 95%) was added to the sample solution to convert free F^- ions into CaF_2 precipitate. To ensure complete removal of F^- ions, the slurry solution was added until pH of the supernatant reached to 9 or higher. About 45~50mg $Ca(OH)_2$ was necessary for the total procedure. The solution was centrifuged, and the supernatant was removed from the ingredient precipitates using a pipette. Chlorine in the supernatant was precipitated and separated as silver chloride by adding 0.03 M $AgNO_3$ solution. The AgCl precipitate was dissolved with aqueous ammonium solution. A part of the solution was then subjected to N-TIMS procedures as mentioned bellow. Water used in this study was 18MΩ deionised water using a Mill-RX 12 Plus and a Milli-Q systems. Overall chemical procedures are illustrated in Fig. 2-1.

Mass spectrometry

In this work, we employed negative thermal ionization technique (N-TIMS) for measurements of chlorine isotopes using a thermal ionization mass spectrometer, Finnigan MAT Model 262 (equipped with 5-Faraday cups and a secondary electron multiplier), which has been converted to negative ionization mode. The conditions of mass spectrometry are shown in Table 2-1. A Re-Re double filament mode (Heumann 1988) was employed in this work using Zone-refined Re ribbons (0.025×0.75mm; purity: 99.999%; H. CROSS CO.). About 1μL sample solution containing less than 500ng of chlorine as AgCl ammonical solution was deposited onto a degassed flat Re filament and evaporated to dryness slowly at low filament current (0.7A). To avoid distillation of chlorine, a care was taken not to overheating. It was then loaded into the mass spectrometer for isotopic measurement. An accelerating voltage was set to -10kV (resistor: $10^{11}\Omega$/each cup) and the sample filament (Ev) was fixed to zero currents and only the ionization filament current (Io) was increased automatically up to about 1.8A and then manually to 2.0A, which corresponds to the filament temperature about 1,300℃. In order to suppress isotopic fractionations of chlorine during the measurements, we controlled the intensities of $^{35}Cl^-$ and/or $^{37}Cl^-$ signals to be ten to twenty mV. Data were acquired in static mode setting as the #2 cup for $^{37}Cl^-$ (m/z=37) and the #6 cup for $^{35}Cl^-$ (m/z=35). The 100 ($^{37}Cl/^{35}Cl$) ratios for 5 blocks (20 cycles each block) were collected for one run that takes about 20 minutes.

Rock samples

The seven igneous standard rocks issued by The Geological Survey of Japan (GSJ) and two USGS were analyzed in this work (see Table 2-3). All the samples had been already powdered. Standard rocks in this study include major igneous rock types such as basalts (JB-1, JB-2, and JB-3), andesites (JA-3 and AGV-1), rhyolites (JR-1 and JR-2), and granodiorites (JG-3 and GSP-1). The volcanic rocks from GSJ are all Quaternary formed on Japan island arc settings. Chlorine contents of JB-1, JB-2, JR-1, AGV-1 and GSP-1 were reported as the recommended values, but chlorine contents of the rest samples have not been established yet (Imai et al. 1995; Gladney et al. 1992).

In the early part of this work, we had carried out four replicate analyses for JR-1 and single analyses for the rest samples. After refinement of the analytical procedures, replicate analyses were carried out for JB-1 and JR-1 samples, and the rest of samples were analyzed once again for each.

Results and Discussion

Isotope fractionation effect

Because of relatively large mass difference in Cl isotopes, it is possible that a significant mass fractionation occurs during the measurement of $^{37}Cl/^{35}Cl$ ratio. In order to evaluate the extent of mass fractionation, a typical example of Cl isotopic measurement for rock samples is shown in Fig. 2-2. It was found that within the experimental errors no systematic variations of $^{37}Cl/^{35}Cl$ ratio occurred until five to six blocks at about 1320 ~ 1330℃ for about twenty minutes but the ratio increases gradually with increasing of block and/or filament temperature. It is apparent that significant mass fractionation took place at temperature above 1340℃ (or over the 6th block) . This result suggests that the isotopic fractionations in the first 5 blocks (at the temperature about 1320℃) are quite limited, well within the experimental errors. We, therefore, normally employed the mean $^{37}Cl/^{35}Cl$ ratios of the first 5 blocks (100 ratios) obtained at about this temperature. Nevertheless, in view of possible isotopic fractionations due to unexpected changes of run conditions, we always examined chlorine isotopic ratios if the isotopic fractionations occurred significantly or not during the data acquisition. The internal errors ($2\sigma_m$) of the mean $^{37}Cl/^{35}Cl$ ratios of 5 blocks (100 ratios) are normally smaller than 1‰ (0.1%), which corresponds to uncertainties of about 0.1-0.15% in Cl concentrations; error magnification factors are calculated to be 1.001-1.0015 in our experimental conditions.

Another possible mass fractionations may be possible if the chemical recovery yield of chlorine from samples is very low. Beside this work, we have examined a possible Cl isotopic fractionations (by P-TIMS) for larger samples (~100mg) and confirmed that no isotopic fractionations (within 0.2~0.3‰) occurred in the same chemical procedures as employed in this work (recovery yields of 70-90%). We, therefore, speculate that significant mass fractionations over at least 1‰, which is typical precision of chlorine isotopic analyses in present work, did not occur during chemical procedures of much smaller samples used in this work.

Spike calibration and NIST standards

We have carried out isotopic measurements of chloride for the NIST isotope standard SRM 975a and the ^{37}Cl-enriched spike used in this study. Isotopic measurements were performed by two different methods, one is the measurement of Cs_2Cl^+ by P-TIMS (Xiao and Zhang, 1992; Numata et al., 2001), and another is by N-TIMS. The ^{35}Cl/^{37}Cl ratio measured for the isotopic standard SRM 975a was 3.1239±0.0004 (2 σ m) by P-TIMS and 3.1225±0.0023 (2 σ m) by N-TIMS. Both isotopic compositions agree well with each other and are also in good agreement with the NIST certified absolute abundance ratio of 3.1279±0.0047. The ^{37}Cl abundance in SRM 975a was calculated to be 24.25%. The ^{37}Cl/^{35}Cl isotopic ratio of the ^{37}Cl-enriched spike used in this study was determined to be 49.297±0.032 (2 σ m) and thus the ^{37}Cl abundance was calculated to be 98.01%, Which was in agreement within 0.2% with the value given by Oak Ridge National Laboratory

For spike calibration, we have carried out the N-TIMS isotopic measurement for 9 NaCl-standard/spike mixed solutions. In-run precisions

(2 σ m) of $^{35}Cl/^{37}Cl$ ratio for individual runs are less than 0.1%. The mean concentration of Cl in the spike solution was calculated to be 48.21 ±0.17 (2 σ m) ppm. In order to confirm our spike calibration, the NIST SRM 3182 Cl anion standard were also analyzed by N-TIMS ID using the same spike solution as mentioned above. We prepared 6 mixed solutions of SRM 3182/spike with different mixing ratios and carried out isotopic measurements. Results are shown in Table 2-2. The concentration of Cl in SRM 3182 standard determined in this work was 997.3±2.3ppm, that is in complete agreement with the certified value of 997±5ppm.

Blanks

It is pointed out that the IDMS technique requires isotopic equilibration between sample and spike and chemical yields during analytical processes should have no direct effect on analytical precision. One of the most important factors influencing on the analytical precision is, however, blanks in the chemical processes, particularly in the case of small samples and/or the low contents of elements to be determined. The quantity of rock sample used in our analysis is only about ten mg; we can then decrease the quantities of reagents (HF and $Ca(OH)_2$) according to sample sizes for chemical processes.

For chemical processes of rock samples, most abundant reagents used in this work were hydrofluoric acid and $Ca(OH)_2$ powder. The reagent of $Ca(OH)_2$ (purity 95%, Merk) was found to contain several ppm chlorine. In order to remove chlorine contaminants which might stick significantly on the surface of $Ca(OH)_2$ particles, the $Ca(OH)_2$ powder was washed with water by shaking and centrifuged repeatedly (10 times). Blank Cl in $Ca(OH)_2$ could be decreased to 1/10 or less by this procedure. Because of technical difficulty, the blank in hydrofluoric acid were not directly determined but estimated to be negligibly small compared to $Ca(OH)_2$ from the total procedural blanks determined in this work. The total procedural blanks, which corresponds to the blanks including 50 μL-hydrofluoric acid and 50mg-$Ca(OH)_2$ were 0.014 and 0.023 μg for 10mg-size samples. This result implies that the blank in the chemical procedure was derived mostly from $Ca(OH)_2$.

As mentioned above, we used two reagent solutions ($AgNO_3$ and NH_3) during the Cl collection procedures from samples. The same solutions were also used for isotopic measurements of Cl spike, which means that the blanks of the solutions reflected on the isotopic compositions of the spike. Nevertheless, We measured the Cl blanks in the same reagent ($AgNO_3$+NH_3) mixed solution, which was used for isotopic compositions of samples and the spike. The blank value obtained by N-TIMS was 0.0076 μg, which corresponding to 0.11% or less. This observation is consistent with the fact that isotopic compositions of Cl spike obtained in this work are in well agreement with those given from Oak Ridge National Laboratory, which will be mentioned later.

Cl concentrations in the standard rocks

Results for nine standard rocks obtained after refinement of our IDMS are presented in Tables 2-2 and 2-3. Concentrations were obtained after corrections for the total procedural blank (0.018±0.005 μg). The procedural blanks observed here correspond to 0.2-0.9% of Cl contents in the most samples, which have higher concentrations (Cl>260ppm: Table 2-3) but 1.2 % for one of the smallest sample, JB-1, with the lower Cl concentration (166.4ppm: Table 2-2). It is pointed out that the concentration (165.5ppm) obtained after blank correction for one of the smallest sample of JB-1 (8.67mg) is in agreement within 0.9% with the mean value, suggesting that blank correction is approximately valid (within about 0.6%). To elucidate real precisions in our analyses for such small samples, replicate analyses of two standard rocks with the lowest and the highest chlorine concentrations were carried out and the results are shown in Table 2-2. The errors (1SD) associated with five independent analyses were 0.9 % for JB-1 and 0.7% for JR-1, respectively.

The precision attained here was much improved compared to our earlier analyses for JR-1 (1000±32 (1S.D.) ppm by four replicate analyses), which agrees within 1 % with our new result (1007.7 ±6.9; Table 2-2). The newly obtained value of JB-1 (166.4 ±1.5; Table 2-2) is also in agreement within 1% with that (166ppm) of our earlier single analysis. Our preliminary results of the rest samples (JB-2: 263; JB-3: 261; JA-3: 363; JR-2: 683; JG-3: 156; AGV-1: 152; GSP-1: 283 in ppm) are also generally consistent with new results. Only for three samples, JA-3, AGV-1 and GSP-1, our old results differ by+4.4% for JA-3, -2.6% for AGV-1, +3.5% for GSP-1 from the new results shown in Table 2-3. The reasons of such large deviations of these samples are not clear, but misleading errors may have occurred at the early stage of this work, which will be discussed bellow. The above consideration indicates that the accuracies of our new results for nine standard rocks (shown in Table 2-3) are 1 –2%.

As mentioned above, the precision of concentration determination associated with isotopic measurement is 0.1-1.5%, which is about 1/10 times smaller than the accuracies (1-2%) as inferred from the concentration data sets shown Tables 2-2 and 2-3. The unexpectedly large uncertainties in concentration determination need careful consideration to evaluate quality of our N-TIMS ID data. Because of too small samples (up to several milligrams in weight) handled in this work, the weighing errors (0.02mg) of a semi-micron balance used in this work may also affect the analytical precisions. The weighing error may be smaller than 0.2% for larger (>10mg) samples but could be 0.3-0.5% for smaller (<10mg) samples. From the above consideration, we suggest that the observed precisions of our ID data shown in Table 2-3 are governed mainly by uncertainties of procedural blanks and partly by uncertainties of weighing errors. This conclusion has been reached at the later stage of the present work and thus some our preliminary results obtained without serious consideration about these problems might have contained misleading errors, as mentioned above.

In Table 2-3, the present results for nine standard rocks are compared with those of previous works. GSJ reported the recommended values of Cl concentrations in the three standard rock samples such as JB-1, JB-2, and JR-1, together with their analytical methods (Imai et al., 1995). The results obtained for these three samples in this study are in good agreement with the recommended values (see Table 2-2 and 2-3). Our value (1007.7 ± 6.9ppm) of JR-1 is in agreement within analytical errors but appears to be sufficiently higher than the recommended one (920±81ppm). Among the eight compiled values of JR-1 by GSJ, only one value was obtained by IDMS and its value was 972 ppm (Shinonaga et al. 1994), which agree well with our results. USGS also reported the recommended values of AGV-1 and GSP-1 (Gladney et al. 1992). Our result (156.1 ppm) for AGV-1 is significantly higher than recommended value (119 ±24ppm) and our result (273.3 ppm) for GSP-1 is also significantly lower than the recommended value (330 ±24ppm) . The recommended value of AGV-1 was from the compiled 25 analyzed data with various kinds of analytical methods. Wilson and Gent (1983) reported Cl concentration (160ppm) in AGV-1 obtained by ion chromatography, which agrees well with our result.

Regarding other four samples, JB-3, JA-3, JR-2, and JG-3, no recommended values are reported yet. From the comparison of our results to the available recommended values as mentioned above and in view of our precisions envisioned above, we strongly suggest that our results of JB-3, JA-3, JR-2, and JG-3 as well as other five standard rocks would also be reliable within the precisions of 1-2%.

Several analytical techniques have been applied to determine chlorine in the standard rocks. Table 2-3 shows the results in this work together with the data from previous works analyzed by wet-chemical methods, except INAA and XRF. Because of the difficulty in extraction of chlorine from rock samples, the quantity of the sample needed for analysis has increased and even the blank value becomes relatively high along with it. More than 0.25g of samples were used in alkaline fusion for ion chromatography (Blackwell et al. 1997) and Shinonaga et al. (1994) decomposed 0.5g of samples by HF for IDMS. We could obtain good precision (~1%) of analysis by N-TIMS ID using less than 1/50 of the sample quantity of traditional methods.

After refinement of our earlier procedures, we have now established the N-TIMS ID technique for precise determination of chlorine for silicate samples as small as about 10mg in routine work bases. For example, under the present laboratory conditions, the analyses of 10-20 powdered samples can be accomplished in three days: two days for sample preparation-HF-leaching and chemical treatment, one day for mass spectrometry. In this work, the sample-sizes are limited to about several mg mainly due to blanks of $Ca(OH)_2$ and weighing errors as well as other handling problems in chemical separation processes. If we use a microbalance and more high quality $Ca(OH)_2$ reagent, the sample-sizes can be significantly reduced. It is also advisable that the separation of AgCl precipitation could be more easily performed in miniaturized experimental procedures. The about 10mg-sample used for ID analyses contains chlorine about 2 μg or larger, which is about five times of chlorine enable us to analyze by N-TIMS. This mean that if these problems are solved, the N-TIMS ID established here could be applied to even much smaller samples such as a few mg or less.

Conclusions

Silicate samples of about 10 mg were spiked and decomposed with hydrofluoric acid, and chlorine was isolated by precipitation of silver chloride after neutralization with $Ca(OH)_2$. The ammonical solution of AgCl was then subjected to N-TIMS. Replicate analyses of standard rocks, typical of JB-1, JR-1, demonstrated the high quality of the analyses (accuracies for Cl are ±1-2 per cent).

Table 1. Conditions of mass spectrometry

Sample loading	
AgCl ammonical solution ($[Ag(NH_3)_2Cl]$)	Cl < 500ng
Mass spectrometry	
Double filaments	Re-ionization filament (Io) Re-evaporation filament (Ev)
Static mode: Faraday cup setting	Cup#6: $^{35}Cl^-$ (m/z=35) Cup#2: $^{37}Cl^-$ (m/z=37)
Accelerating voltage	-10kV (Resistor: $10^{11}\Omega$)
	Filament currents:
Preheating (Auto: 0.18A/min.)	Io = 0 → 1.8A (Ev = 0 A)
Data acquisition (20 cycles, 5 blocks)	Io = 2.0A (Ev = 0 A)

Table 2. Results of replicate analyses of Cl for NIST SRM 3182 standard, JB-1 and JR-1, compared with certified or recommended values.

	Sample weight (mg) a)	Concentration (ppm)	Literature data (ppm)
SRM 3182 (NIST)	499.2	997.8	997 ± 5 c)
	498.0	995.0	
	499.1	999.7	
	499.3	999.7	
	500.9	993.5	
	500.0	998.4	
	(Average)	997.3 ± 2.3 b)	
JB-1	47.70	165.5	176 ± 18 (N = 9) d)
	24.07	164.7	
	22.17	167.7	
	24.95	168.6	
	8.67	165.5	
	(Average)	166.4 ± 1.5 b)	
JR-1	6.38	1004.0	920 ± 81 (N = 8) d)
	9.61	1018.2	
	12.80	1012.6	
	17.60	998.6	
	20.55	1005.0	
	(Average)	1007.7 ± 6.9 b)	

a) Weight (in mg) of sample used for analysis.

b) Errors are represented by 1 SD.

c) Data are from National Institute of Standards and Technology (NIST), Certificate of Standard Reference Material R 3182, Chloride Anion Standard Solution Lot No. 990506.

d) Data are from Imai et al. (1994); N refers to the number of compiled data.

Table 3. Results of N-TIMS isotope dilution analyses of Cl for standard rocks, compared with those from previous studies

Sample	Rock type	Present work		Previous works						
		Weight (mg) a)	Concentration (ppm)	Recommend (ppm) c)	Method d)					
					Color	XRF	IC	INAA	RNAA	IDMS
JB-1	Basalt	8.67-47.7	166.8 ± 1.5 b)	176 ± 18	167	170	151	172	186	159
JB-2	Basalt	10.23	266.3	281 ± 58	267	360	247	345, 240	321	297
JB-3	Basalt	11.35	260.8					220	336	
JA-3	Andesite	10.90	347.8					340		
JR-1	Rhyolite	6.40-20.6	1007.7 ± 6.9 b)	920 ± 81	817	1030	891	940, 850	999	972
JR-2	Rhyolite	12.14	691.3			730		700	1000	
JG-3	Granodiorite	12.70	156.6					200		
AGV-1	Andesite	11.88	156.1	119 ± 24			170			
GSP-1	Granodiorite	8.85	273.3				330			

a) Weght of sample used for analyses. b) Average of replicate analyses (see Table 2). c) Recommended values from Imai et al.,(1994); Glandney et al., (1992). d) Methods of previous works (abbreviated name): Color=Colorimetry, XRF=X-ray Fluorescence, IC=Ion Chromatography, INAA=Instrumental Neutron Activation Analysis, RNAA=Radiochemical Neutron Activation Analysis, IDMS=Isotope Dilution Mass Spectrometry. References: Terashima (1974); Terashima (1976); Unni and Schilling (1978); Evans and Moore (1980); Wilson and Gent (1983); Bower et al. (1985); Sims et al. (1988); Shinonaga et al. (1994); Blacwell et al. (1997)

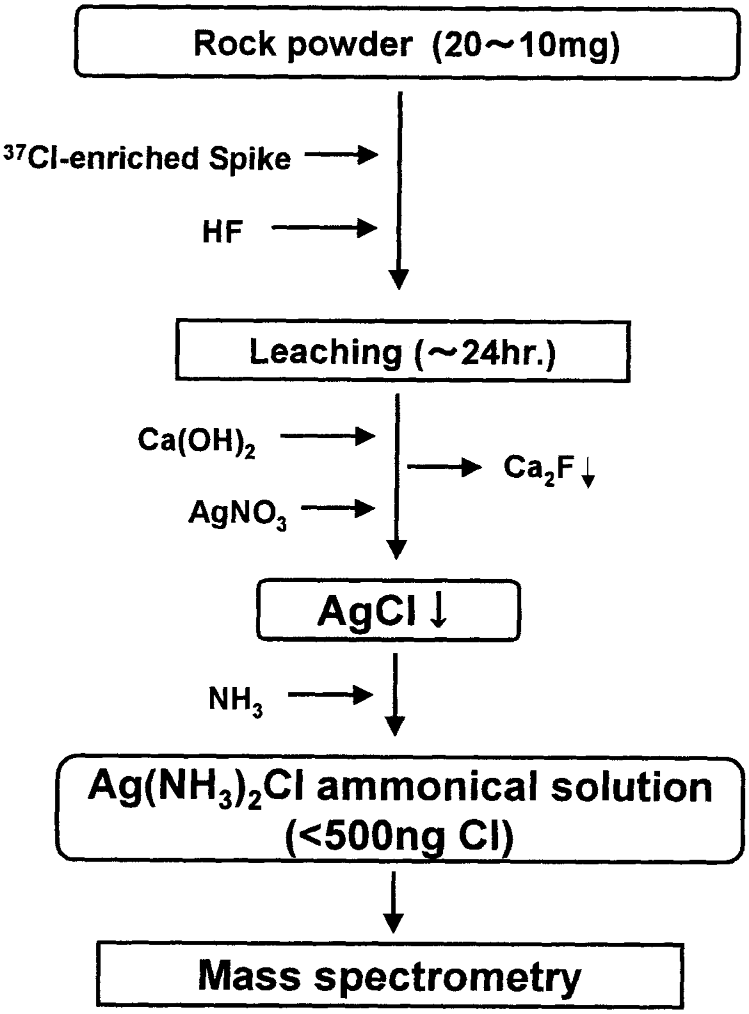

Figure 2-1. Schematic illustration of chemical procedures employed in this study.

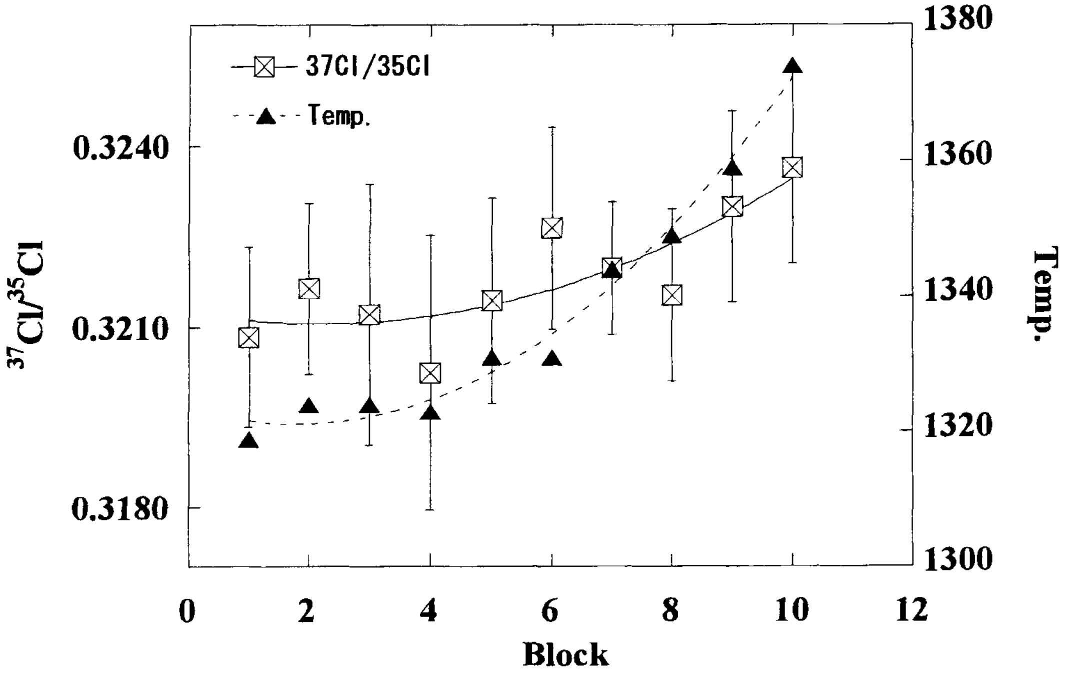

Figure 2-2.

The plot of ^{37}Cl/^{35}Cl and the filament temperature against the block number of one run. Each block consists of 20 cycles (twenty ratios). Error bars represent 1SD. During the first 5 blocks which takes about 20 minutes, the current/temperature of the filament was controlled at about 2.20A (or 1320℃) and monitor signals of ^{35}Cl$^-$ and/or ^{37}Cl$^-$ were controlled to be 10-20 mV. Then mass fractionation was suppressed as minimum and thus never exceeds the experimental errors. The mass fractionation occurred in accordance with the filament temperature raised above 1340℃

Chapter 3 Precise determination of chlorine isotope compositions of igneous standard rocks by thermal ionization mass spectrometry

Introduction

Stable isotope compositions of some light elements such as hydrogen, oxygen, carbon, and sulfur have been investigated in cosmo- and geochemistry, and a great deal of fruitful results were obtained (Faure, 1986). Chlorine has two stable isotopes ^{35}Cl and ^{37}Cl, with relative abundances as 75.5% and 25.5%, respectively (Shields et al., 1962). Chlorine is one of the representative volatile elements and easily removable from solid to vapor and/or aqueous phases, and behaves effectively as one of the important components of fluid during geochemical processes (Ito et al., 1983; Michael and Schilling, 1989; Jambon et al., 1995; Straub and Layen, 2003). Therefore, its isotope compositions can play potentially an important role as a tracer through material cycle among mantle, crust, hydrosphere, and atmosphere (Kaufman et al., 1984; Desaulniers et al., 1986; Volpe and Spivack, 1994; Magenheim et al., 1995). Recently chlorine isotopic composition began to be used as a tool for investigation of environmental problems in related with chlorinated hydrocarbons (Holt et al., 1997; Jendrzejewski et al., 2001; Numata et al., 2002).

In the early works, chlorine isotopic compositions have been investigated by CH_3Cl-gas mass spectrometry (Kaufmann et al., 1984) and Cl^- thermal ionization mass spectrometry (N-TIMS) (Vengosh et al., 1989;

Taylor and Grimsrud, 1696). The precision measurements by CH_3Cl-gas mass spectrometry revealed the variations of chlorine isotope ratio in groundwater (Desaulniers et al., 1986), fluid inclusion in ore deposits (Eastoe and Guilbert, 1992), evaporates (Eggenkamp et al., 1995; Eastoe et al., 1999), and Cl-bearing silicate minerals (Long et al., 1993). The CH_3Cl method displayed high precision of better than 0.1‰ (Long et al., 1993). This technique, however, requires relatively large quantities of chlorine (> 1mg Cl), which correspond to more than several ten grams of sample. On the other hand, the negative thermal ionization mass spectrometry (N-TIMS) has relatively high sensitivity, in which less than 1 μ g of chlorine was required for analysis but was not precise enough for most geological samples (Vengosh et al., 1989).

Recent development of analytical technique of chlorine isotopes using Cs_2Cl^+ thermal ionization mass spectrometry (P-TIMS) could satisfy both precision and sensitivity (Xiao and Zhang, 1992). This technique allows only several micro-grams Cl for the analysis and could yield precision better than 0.25‰ (Magenheim et al., 1994). However, due to analytical difficulties including troublesome chlorine extraction procedures, the isotopic analyses of silicate materials with low chlorine contents, such as volcanic rocks as well as meteorites, are quite limited yet.

In this study, we have developed an analytical technique applicable to precise determination of chlorine isotopic compositions for various types of igneous standard rocks, and demonstrated that the P-TIMS technique established here was successfully applied to a few hundred-milligrams sizes of nine igneous standard rocks, in a routine bases.

Experimental

Extraction of chlorine

In general, extractions of chlorine from the rock samples have been performed by an alkali fusion method (Eggenkamp et al., 1995) or a pyrohydrolysis one (Dreibus et al., 1979) both of which required large amount of dilution of the Cl-bearing solution (Magenheim et al., 1994; Willmore et al., 2002). Musashi et al., (1998) proposed a new Cl extraction method that combined hydrofluoric acid leaching and Cl concentration using anion-exchange chromatography for isotope ratio mass spectrometry (IRMS). Compared with alkali fusion method, this method has an advantage because only a fewer chemicals are used through its chemical separation procedure. In this work, we employed a hydrofluoric acid leaching for sample decomposition in the similar way to that of Musashi et al. (1998). Overall chemical procedures are illustrated in Fig. 3-1.

As mentioned later, about 2 μ g of chlorine was used to determine isotopic compositions for each thermal ionization mass spectrometric run (TIMS) and then chlorine of ca. 50 μ g was collected from the whole rock sample powder for repeated TIMS. Chlorine contents of samples studied range from 119 ppm (AGV1) to 920 ppm (JR1) (Imai et al., 1995; Gladney et al., 1992). For example, if we analyze a rock sample that contains 250 ppm Cl, about 125mg of the sample is necessary. The sample containing 50 μ g Cl was weighted precisely using a small Teflon® vessel (15ml in volume). The sample was first wet with 125 μ l of water and then hydrofluoric acid of four times volume of water volume (500 μ l) was added drop by drop to avoid heating up, which might release chlorine gas. We used purified hydrofluoric acid obtained by bottle-to-bottle distillation. The sample vessel was closed tightly and shaken continuously for about one day at room temperature. After one-day slow reaction, the sample became a paste and the solution became colorless, as described by Musashi et al., (1998). The sample solution including the paste was centrifuged and the paste was washed with water twice. Water used in this study was purified using a Milli-RX12Plus and a Milli-Q SP system. As expected, the quantities of the remained paste tend to be more abundant for basic rocks than for acidic ones. The resultant solution after centrifuge was transferred into a 15ml polypropylene centrifuge tube. The HF solution recovered was then neutralized with $Ca(OH)_2$ slurry solution to remove fluorine from the solution as precipitation of CaF_2. The $Ca(OH)_2$ reagent (Merk, 95%) was purified by heavy shaking with water ten times to remove chlorine absorbed on the surface of the reagent particles. The slurry solution containing 200mg/ml-$Ca(OH)_2$ was added drop-by-drop to the tube which had been cooled by water. CaF_2 precipitation was observed immediately after each drop but the slurry were added until pH of the supernatant became more than 9. About 450mg $Ca(OH)_2$ was necessary for this process After over night setting, the solution was centrifuged. The volume of the precipitate came to nearly 1.5ml. The precipitate was washed with the same volume of water and the suppernant was separated by centrifugation. This procedure was repeated four times. All the supernatant was collected in a Teflon® beaker and evaporated for concentration until its volume was ca. one ml using a hot plate. After concentration, the solution was transferred into a 1.5ml polypropylene centrifuge tube.

Purification of chlorine

Chloride ions dissolved in the solution was precipitated as AgCl with 0.03M $AgNO_3$ (HNO_3 acidic) solution and the solution including precipitates was left aging for two hours at room temperature in a darkroom. The solution was then centrifuged and the supernatant was discarded. The precipitate of AgCl was washed with 50 μl of 0.03M HNO_3 twice and 50 μl of water once. After washing, the AgCl was dissolved with 100 μl of 1M NH_3. In order to remove Ag^+ ion, Mg powder (ca. 1mg) was added to the solution and stood for one hour. The solution was centrifuged and the supernatant was recovered in a 1.5ml Teflon vessel. The precipitate was washed with 50 μl water twice. All supernatant were evaporated to dryness on hot plate (120℃). Excess NH_3 were evaporated and NH_4Cl and MgCl residue was remained. The residue was dissolved in 50 μl water and loaded on a column (i.d. 2mm) that contained 0.1ml of Cs-form cation exchange resin (DOWEX 50W×8, 200-400mesh) for lower part of the column and 20 μl of Ca-form cation exchange resin. The latter resin was to catch the fluorine anions that might remain in the sample solution. The column was washed with 300 μl of water. Generally, organic contaminants in the sample often interfere with isotope determination (Xio and Zhang, 1992). Willmore et al. (2002) added H_2O_2 to the CsCl solution to oxidize any organic carbon. In this work, the fluent was collected in the 1.5ml-centrifuged tube together with activated charcoal powder to remove the organic contaminants from the sample solution

(Magenheim et al., 1994). The activated charcoal powder (1mg, GL Sciences GX-60) was previously washed with water to remove possible contaminant of Cl^-. After 30 min., the solution was centrifuged to separate the activated charcoals. Finally CsCl solution was obtained. In order to obtain the total yield of chlorine during the chemical processes, a part of the solution was subjected to concentration measurement using an ion chromatography (Numata et al., 2001). The major part of the solution was then carefully evaporated to dryness on a hot-plate. The dried CsCl residue was dissolved in a few drops of water for later use of the mass spectrometry.

Mass spectrometry

Measurements of isotopic composition were performed using a Finnigan MAT Model 262 thermal ionization mass spectrometer. Filament used was flat undegassed Ta ribbons (purity: 99.95%; 0.025 × 1.5 mm, Nilaco) for single filament mode.

Sample loading on the filament was performed in the same way of Numata et al. (2001), which was modified method of Xiao and Zhang (1992), Magenheim et al. (1994), and Xiao et al. (1995). Two micro-grams of chlorine as CsCl aqueous solution mixed with approximately 50 μ g of graphite powder as a slurry in 80% ethanol were deposited on the center of the filament and then dried carefully at a filament current of 1.5A. The sample filament was loaded as a single filament mode on the mass spectrometer. The filament current was raised automatically up to 1.2A in 10 min and then increased manually to about 1.4A (Temperature was too low to be measured using an optical pyrometer) at which Cs_2Cl^+ signals start increasing. When the Cs_2Cl^+ signals was stabilized at approximately 2×10^{-13}A, the isotopic measurement was started.

Data were acquired in static (multi-Faraday cup) mode setting by Faraday cups #6 for $Cs_2{}^{35}Cl^+$ (m/z=301) and #4 for $Cs_2{}^{37}Cl^+$ (m/z=303) at an accelerating voltage set to 8kV. The Cs^+ and Cs_2F^+ signals were also monitored before and during the analyses. Normally, the intensity of Cs^+ ion beam was almost the same as that of $Cs_2{}^{35}Cl^+$ beam current. The Cs_2F^+ signals were not normally observed but even when observed its intensity was very weak. The 20 ratios of $Cs_2{}^{37}Cl^+$ C/$Cs_2{}^{35}Cl^+$ (mass ratio of 303/301) were measured in one block and the 400 ratios (20 blocks) were obtained each run. Two or three runs were repeated for one sample loading and more than several runs were carried out for each sample (see Tables 3-1 and 3-2). Particularly, repeated runs of CsCl laboratory standard as well as seawater were carried out before, between and after the analyses of standard rocks (see Table 3-1 and Figure 3-2).

Samples

We have examined chlorine isotopic compositions for nine igneous standard rocks issued by The Geological Survey of Japan (GSJ) and USGS that are listed in Table 3-2. All the samples were already powdered. These standard rocks included main types of igneous rocks such as three basalts (JB1, JB2, and JB3), two andesites (JA3 and AGV1), two rhyolites (JR1and JR2) and two granodiorites (JG3 and GSP1). The volcanic rocks issued from GSJ are all the Quaternary ones originated on Japan island arc settings (Sugimura and Uyeda, 1973). Chlorine contents of JB1, JB2, JR1, AGV1 and

GSP1 were reported from each GS as the recommended values, and Cl contents of the rest samples were available as the preferable values (Imai et al., 1995; Gladney et al., 1992). The replicate Cl extraction processes were carried out for JB1 (triplicate), JR1, JR2 and AGV-1 (later three: duplicate each). Cl extractions of other samples were carried out only one time.

Results and Discussion

Blank values through the chemical separation processes

The measurements of blank values of chlorine through the chemical separation processes were carried out by the isotope dilution technique (ID) of negative (Cl^-) thermal ioniztion mass spectrometry (N-TIMS) (Heumann, 1988; Shinonaga et al., 1994). The N-TIMS shows much higher sensitivity compared with positive thermal ionization mass spectrometry (P-TIMS) but poor precision (Taylor and Grimsrud, 1969; Vengosh et al., 1989). Because of too small quantity (only a few ten nanograms chlorine) of sample available for blank analyses, the N-TIMS technique was employed for the ID analyses of blank. The precision (about one ‰) of the measurement would be enough for isotope dilution technique (Fujitani and Nakamura, 2005). We prepared the spike solution enriched in ^{37}Cl (^{37}Cl abundance was 98.01%). In the Cl^- mass spectrometry, Re double filaments were used and loading form of the sample was AgCl ammonical solution. Acceleration voltage was set at 10kV. The $^{35}Cl^-/^{37}Cl^-$ data sets were collected by static mode.

During the course of chemical separation process of rock samples, most abundant reagents were the hydrofluoric acid and $Ca(OH)_2$ powder. The hydrofluoric acid used was purified in a Teflon distillation apparatus under relatively low temperature. $Ca(OH)_2$ used was purity 95% (Merk) and it might be contaminated with several ppm of chlorine. Thus, $Ca(OH)_2$ could be considered the most influential reagent in the blank value. The influences of other reagents such as $AgNO_3$ and HNO_3 were not checked individually but the final solution obtained through the chemical separation process of blank material equivalent with the reagents used for extraction of 250mg rock sample was checked by ID method. The contaminants in $Ca(OH)_2$ was also checked by ID. To remove chlorine contaminants, $Ca(OH)_2$ powder was rinsed by water and centrifuged. Chlorine content in $Ca(OH)_2$ which was not rinsed yet was more than 2.0ppm by ID. On the contrary, after ten times of rinse by water, Cl content in Ca(OH)2 slurry was detected of only 0.2ppm by ID. Chlorine content in the final solution of blank materials was 0.12 μ g. This is corresponding to 0.24% in the final solution that contained ca. 50 μ g Cl extracted from the rock sample. It can be considered that the blank value of this study could not affect the measurement of chlorine isotope ratio.

Cl-recovery yield in chemical procedure

Cl-recovery yields were calculated from the concentration of Cl^- in the final solution, which was determined by the ion chromatography. Analysis was performed on a Hitachi Ion Chromatograph L-7000 (Numata et al., 2001). Chemical yields of the samples range from 57 to 89%, averaging of 78% (see Table 3-2). Assuming that Cl contents given in literatures are correct, significant amounts (mean of about 20%) are found to have been lost during the chemical processes. One of the most possibilities of Cl loss could be considered that a part of chloride ions were removed by co-precipitation with CaF_2 precipitates. If this is the case, it may be possible that the occluded chloride ions were not easily washed out with diluted HNO_3 solution, as mentioned above. Another possible process of chlorine loss may be the separation of AgCl precipitate from their solvent. Because the quantity of the precipitate was very small as ca. 50 μ g in the 1.5 ml centrifuged-tube, even a few loss of Cl could affect large influence of chemical yield. It should be noticed that the Cl concentrations used for the yield calculation were not only the recommended values but also the preferable ones and thus have not necessarily been established yet.

Seawater as a standard material

The chlorine isotopic ratio of each sample is expressed as per-mil deviation ($\delta^{37}Cl$) relative to Standard Mean Ocean Chloride (Kaufmann et al., 1984);

$$\delta^{37}Cl_{SMOC} = (R_{sample} / R_{SMOC} - 1) \times 10^3 \qquad R = {}^{37}Cl/{}^{35}Cl$$

However, currently there exists no common Cl-isotope ocean water standard (Xiao et al., 2002). Different laboratories use seawaters from different locations for calibration. In our laboratory, the seawater sample was taken from the Pacific Ocean (8° 39.5' N, 153° 56.6' E, depth: 0m) during the cruse KH-98-1 (03/04/1998) (Numata et al., 2001). The chloride ion in the seawater was isolated as AgCl and was converted into CsCl. The measured Cl isotopic compositions of the seawater sample are sown in Table 3-1 and Fig. 3-2. In each run, about 400 sets of ${}^{303}Cs_2Cl^+/{}^{301}Cs_2Cl^+$ were measured and the internal precision for the individual runs shows $2\sigma_m$ (σ_m: standard error). In-run precision ranged from 0.15‰ to 0.28‰. External error for the average of 8 Runs shows $1\sigma_{SD}$. In this case, external error was 0.31‰. The average value of the seawater sample was used for the calculations of $\delta^{37}Cl_{SMOC}$ of the CsCl laboratory standard which has most frequently been analyzed together with standard rocks.

CsCl reagent as a laboratory standard material

While isotopic measurement was carried, discharge or other electric troubles took place in the instrument by accident. Owing to the change of instrument condition, the value of isotope ratio of the same material may drift slightly (Magenheim et al., 1994). In order to check the day-to-day isotope drift, a sample and the standard seawater should be measured alternately. This study employed CsCl reagent for the secondary standard reference instead of seawater to avoid troublesome in the chemical procedure. We used the Nacalai Tesuque CsCl reagent (>99%)(Numata et al., 2001). Thus it was convenient that CsCl solution was directly loaded on the filament, it could be possible to measure a sample and CsCl reagent alternately. Table 3-1 shows the result of the measured Cl isotopic ratio of CsCl reagent analyzed from April to June 2003. The averaged δ^{37}Cl value of 12 analyses was –2.47‰ and their external reproducibility was 0.22 (1 σ SD). It is clear that δ^{37}Cl of CsCl reagent in this study corresponded almost perfectly to the result of Numata et al. (2001) within the range of error. Then, we could use the CsCl reagent as a secondary standard instead of the seawater.

Analytical results of chlorine isotope composition of standard rocks

Analytical results of chlorine isotope composition of nine standard rock samples together with CsCl reagent are shown in Table 3-2. All of the samples show enrichment in ^{37}Cl relative to seawater as δ^{37}Cl were from +0.25‰ to +4.30‰. Errors are the external reproducibility represented by 1 standard deviation of all analysis. JB1, JR1, JR2, and AGV-1 samples were performed replicate Cl extractions, and the results of other samples were obtained from one Cl extraction. We could check the difference of the isotopic ratios among the replicate Cl extraction splits of the same sample.

Thus JR1 refers to the rhyolite whose Cl content is highest such as 920ppm (Imai et al, 1995) in this study; it is suitable as one of the reference samples of igneous rocks. JR1 was carried out duplicate Cl extractions. The former split was performed isotopic measurement eight times and the latter' one was six times. Figure 3-3 shows the result of Cl isotopic composition of JR1, in which Run' number of one to eight refer to the first extraction and nine to fourteen refer to the second one. The former average was 0.21‰ ± 0.21 and the later average was 0.29‰ ± 0.31. It is clear that there is no difference between the two splits within their errors. The average of all the data was 0.25‰ and $1\sigma_{SD}$ was 0.26‰. Although Magenheim et al. (1994) shows higher precision of rock samples than this study, the number of the same sample analysis was only from four to two and the variation of their seawater standard measurements indicate the external reproducibility of 0.25‰ (79 analyses of 32 individual sample extractions). Precision that we obtained from the CsCl reagent analyses was little less than one of JR1 such as 0.22‰.

JB1 was carried out triplicate Cl extractions and 14 analyses were performed. The first analyses were carried on from the end of July to the beginning of August 2003, and the latter two analyses were on January 2004. We have performed CsCl reagent analyses together with sample measurements, and their values of daily variation were available. The results of CsCl reagent isotopic ratio from April 2003 to April 2005 are shown in Fig. 3-4. The isotopic ratios of the period between August and October 2003 were clearly lower than other period's measurements. The average of isotopic ratio from April to June 2003 was perfectly coincident with the average from November 2003 to April 2004. The difference between their two parts refers to 0.63‰. The reason of the drift of isotopic ratio like this was not clear but some change of the instrumental condition such as the electrical discharge may influence to measure (Magenheim et al., 1994). In addition, we could obtain the external reproducibility of all measurements (47 analyses) of CsCl reagent as 0.19‰ took into the consideration of their drift.

Figure 3-5(a) shows the result of Cl isotopic composition of JB1. The isotopic composition of the first Cl extraction was 0.31914 and the average of latter two Cl extractions was 0.31930. There exists clear discrepancy between the former analyses and the latter two ones. The difference corresponded to about 0.50‰. The first offset in the mean isotopic ratio occurred on the end of July 2003 and the first measurement of JB1 was carried out just after this offset. The second JB1 measurement was performed after second offset of CsCl measurements. Discrepancy of the JB1 results can be considered to be the drift owing to change the instrumental condition. Recalculation δ^{37}Cl of JB1 under the correction in related with the drift shows that δ^{37}Cl of the former refers to 0.38‰±0.14 and the latter one refers to 0.56‰±0.18 and they are fairly well consistent with each other within their errors. The average δ^{37}Cl of JB1 (14 analyses) can be obtained good precision such as 0.44‰ ± 0.17 (Fig.3-5(b)). On the triplicate Cl extractions of JB1, chemical yields were calculated respectively (cf. Table

3-1). The yields of the former two chemical extractions could be obtained around 80%. On the other hand, the yield of the last chemical procedure showed fairly low (57%) though the reason of the poor yield was not clear. It should be noticed that there were relatively no differences between the isotopic compositions from the high yield chemical separation and from the low one.

The result of isotopic composition of JR2 was also obtained from 14 analyses in the duplicate Cl extractions. The results of isotopic composition of the rest six samples were from one chemical extraction procedure. The external errors of all of the samples represented by 1 σ SD were ranged from 0.17 ‰ to 0.37 ‰. It is pointed out that these errors were almost corresponding to the reproducibility of the measurements of CsCl reagent.

Characteristics of Cl isotopic composition of igneous standard rocks

The results of δ^{37}Cl for the standard rocks studied were shown in Fig. 3-6. All the samples are enriched in ^{37}Cl relative to the seawater. We have investigated all the type of igneous rocks from basalts to rhyolites and plutonic rocks. We could not recognize the difference in δ^{37}Cl values in relation to their rock types and the Cl concentrations of the rocks. Although there are sparse of the terrestrial rocks' δ^{37}Cl values, available δ^{37}Cl data for MORB and their related minerals show +0.2 to +7.2 (Magenheim et al., 1994), the same rage as the data of this study. On the contrary, subduction-zone pore waters in Nankai trough show considerably light ^{37}Cl relative to seawater such as around −7 (Ransom et al., 1995). GSJ standard rocks investigated in this study are the Quaternary volcanic rocks in relation to island arc settings. It is very interesting that island arc related magmas have relatively heavy ^{37}Cl to seawater but there under subduction zone pore waters show strictly light ones. Further study on chlorine isotopic composition would reveal the relationship between island arc magma and subduction related fluid. The results imply that the Cl extraction method for relatively small quantities of rock samples in this study and its related mass spectrometry could warrant obtaining good precision almost the same as the one for CsCl reagent.

Conclusions

The Cl isotopic compositions of nine igneous standard rock samples were analyzed by thermal ionization mass spectrometry. About 50 μg Cl was extracted from each sample weighed only a few hundred- milligrams by hydrofluoric acid leaching. Final loading quantity on the filament was 2 μg Cl as CsCl form. We confirmed using isotope dilution method that there were little influence of contaminants from the chemical reagents through sample preparation. External reproducibility of 47 analyses for CsCl reagent used as a secondary standard material could be obtained within 0.19‰. More than fine analyses were performed in each rock sample and their external reproducibility ranged from 0.17‰ to 0.37‰. The external reproducibility of isotopic determination for the rock samples with multiple analyses could almost coincide with the one for the analyses of the CsCl reagent.

All the igneous standard rocks studied shift to positive δ^{37}Cl values but no systematic differences in δ^{37}Cl values are observed among different rock types.

Table 3-1. Results of replicate measurements of chlorine isotopic compositions for the sea water samples and the CsCl reagent (laboratory standard)

Seawater[a]			CsCl standard[b]		
Run No	^{37}Cl/^{35}Cl[c]	δ^{37}Cl (‰)$_{\mathrm{SMOC}}$[c]	Run No	^{37}Cl/^{35}Cl[c]	δ^{37}Cl (‰)$_{\mathrm{SMOC}}$[c]
1	0.319083 ±0.000054	-0.08 ±0.17	1	0.318301 ±0.000072	-2.53 ±0.23
2	0.319239 ±0.000073	0.41 ±0.23	2	0.318399 ±0.000071	-2.22 ±0.22
3	0.318942 ±0.000066	-0.52 ±0.21	3	0.318353 ±0.000068	-2.36 ±0.21
4	0.319204 ±0.000087	0.30 ±0.27	4	0.318279 ±0.000069	-2.59 ±0.22
5	0.318992 ±0.000090	-0.36 ±0.28	5	0.318424 ±0.000082	-2.14 ±0.26
6	0.319142 ±0.000078	0.11 ±0.24	6	0.318459 ±0.000067	-2.03 ±0.20
7	0.319110 ±0.000083	0.01 ±0.26	7	0.318252 ±0.000080	-2.68 ±0.25
8	0.319144 ±0.000075	0.12 ±0.24	8	0.318263 ±0.000067	-2.65 ±0.21
	—		9	0.318298 ±0.000059	-2.54 ±0.19
	—		10	0.318287 ±0.000073	-2.57 ±0.23
	—		11	0.318284 ±0.000061	-2.58 ±0.19
	—		12	0.318245 ±0.000064	-2.70 ±0.20
(Average)	0.319107 ±0.000100[d]	0 ±0.31[d]		0.318320±0.000071[d]	-2.47 ±0.22[d]
				Numata et al. (2001)	-2.49 ±0.22[d]

a) Seawater samples were collected from the Pacific Ocean (Location: 8°39.5'N, 153°56.6'E; depth: 0 m) during the cruse KH-98-1(03/04/1998).

b) Laboratory standard reagent measured during the course of this work.

c) Error for the individual runs is 2SE.

d) Error for the average value is 1SD.

Table 3-2. Results of chlorine isotopic analyses for nine standard rocks, a CsCl labaratory standard and a NIST Cl isotope standard.

Sample		Cl content (ppm)		Weight (mg)$^{a)}$	Yield (%)$^{b)}$	n$^{c)}$	^{37}Cl/^{35}Cl$^{d)}$	^{37}Cl/^{35}Cl (Mean)$^{d)}$	δ^{37}Cl$_{SMOC}$ (‰)
	Rock type		#1	321.2	82	4	0.31919 ±0.00006		
JB1	Basalt	176$^{e)}$	#2	345.0	81	5	0.31928 ±0.00010	0.31925 ±0.00008	0.44 ±0.17
			#3	340.5	57	6	0.31931 ±0.00005		
JB2	Basalt	281$^{e)}$		193.5	81	11		0.31946 ±0.00009	1.50 ±0.31
JB3	Basalt	259$^{f)}$		201.3	82	5		0.32004 ±0.00006	3.31 ±0.22
JA3	Andesite	274$^{f)}$		145.8	82	6		0.31934 ±0.00007	1.12 ±0.25
JR1	Rhyolite	920$^{e)}$	#1	68.8	79	9	0.31923 ±0.00008	0.31925 ±0.00007	0.25 ±0.26
			#2	72.5	89	5	0.31926 ±0.00007		
JR2	Rhyolite	736$^{f)}$	#1	82.3	80	5	0.32001 ±0.00012	0.32004 ±0.00010	2.86 ±0.37
			#2	91.6	74	8	0.32006 ±0.00009		
JG3	Granodiorite	156$^{f)}$		330.0	65	6		0.32000 ±0.00009	3.20 ±0.33
AGV1	Andesite	119$^{e)}$		498.0	86	5		0.32054 ±0.00009	4.30 ±0.30
GSP1	Granodiorite	330$^{e)}$		204.0	70	6		0.31935 ±0.00006	0.66 ±0.33
		CsCl laboratory standard				47		0.31834 ±0.00006	-2.49 ± 0.19
		NIST SRM 975a Cl satndard				5		0.319431 ±0.000044	0.91 ±0.14

a) Weight (in mg) of sample dissolved. b) Recovery yields (in percents) relative to literature Cl contents (Imai et al., 1995; Gladney et al., 1992). c) n refers to the run number of individual analysis. d) Errors is 2SE for individual runs and 1S.D. for the average values, respectively.e) Recommended value (Imai et al., 1995; Gladney et al., 1992). f) Preferable value (Imai et al., 1995).

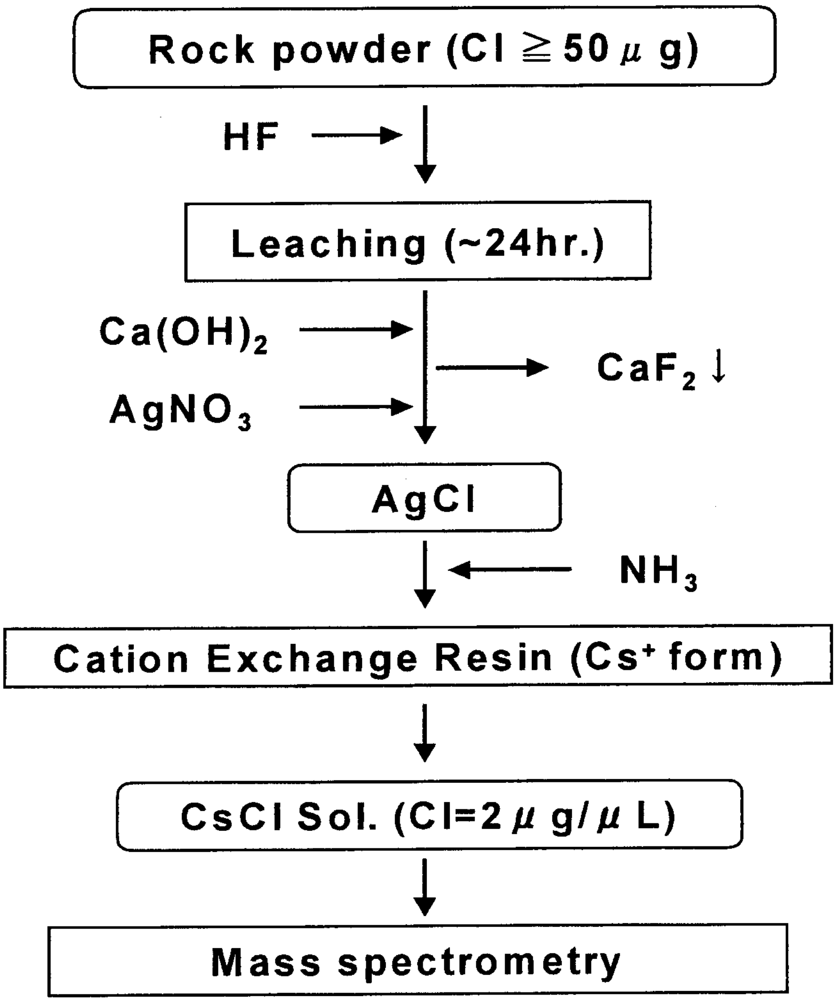

Figure 3-1. Schematic illustration of chemical procedures employed in this work. (modified after Musashi et al., 1998)

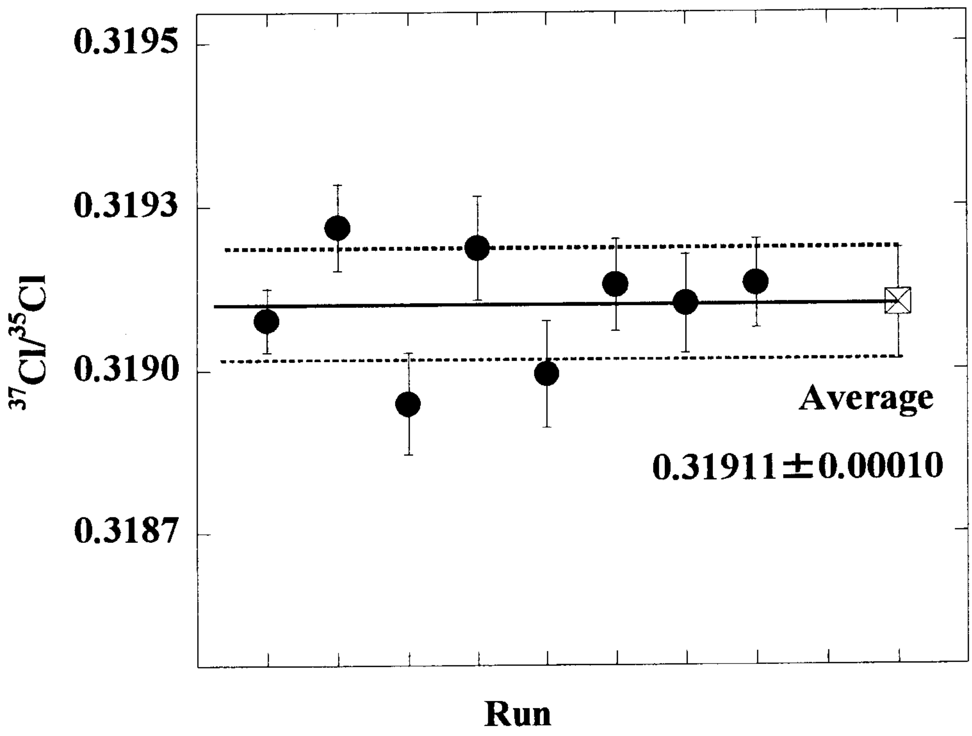

Figure 3-2. Results of replicate analyses of chlorine isotopes in a seawater sample collected from the Pacific Ocean (8° 39.5' N, 153° 56.6' E, depth: 0m) during the cruse KH-98-1 (03/04/1998).

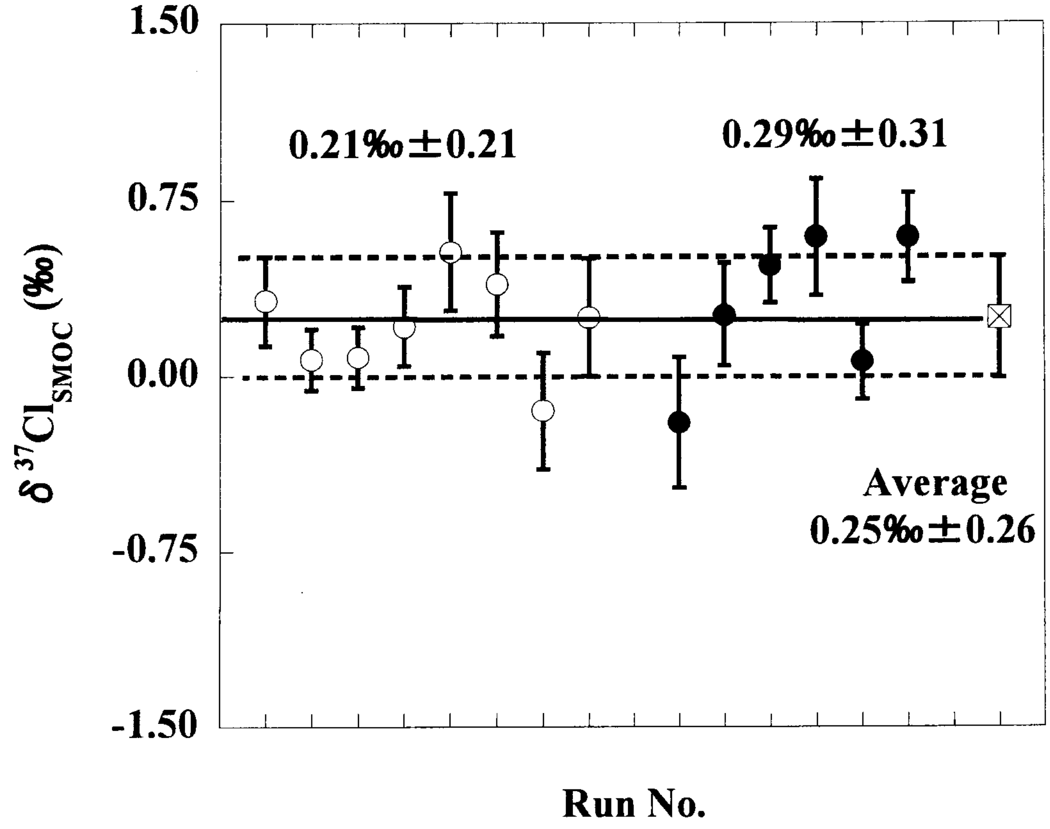

Figure 3-3. Results of replicate analyses of chlorine isotopes for two separate samples extracted from JR-1 standard rock. The $\delta^{37}Cl_{SMOC}$(‰) is defined as relative variations of $^{37}Cl/^{35}Cl$ ratio measured for JR1 to seawater (see text). Open circles refer to the first extraction and the individual isotopic analyses are eight times with error bar of internal standard error ($2\sigma_m$). Solid circles refer to the second one and analyses are six times with error bar. Cross square refers to the average of all data. Error bar of the average represents the external standard deviation ($1\sigma_{SD}$).

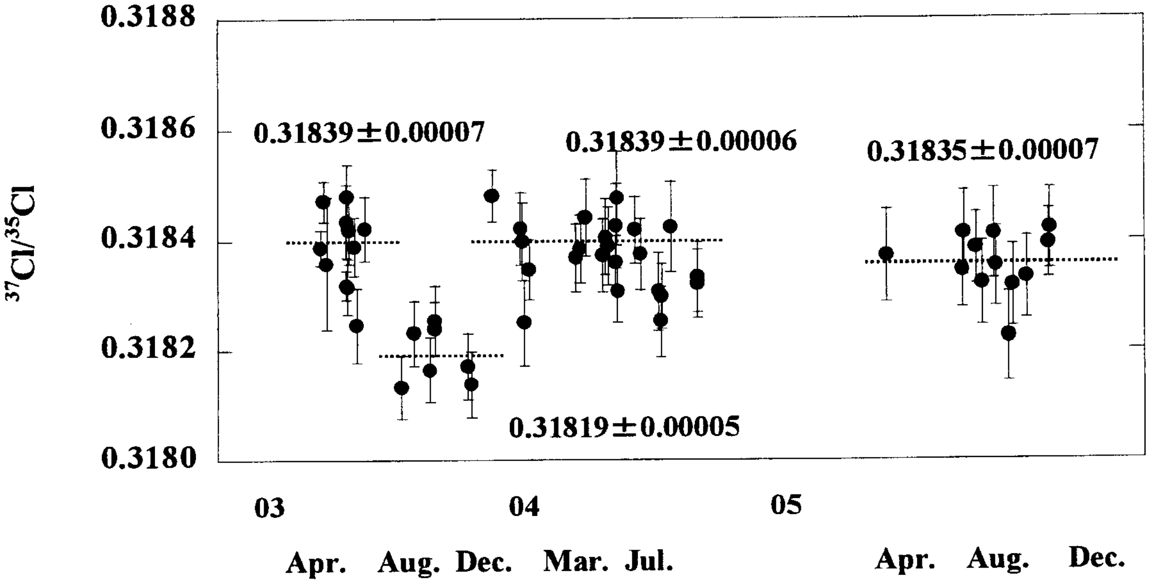

Figure 3-4. Chlorine isotopic compositions of a CsCl reagent used as a laboratory standard for the period between April 2003 and November 2005. There were clear offsets that one is between July and August 2003 and another is between November and December 2003. The difference between two parts is 0.63‰.

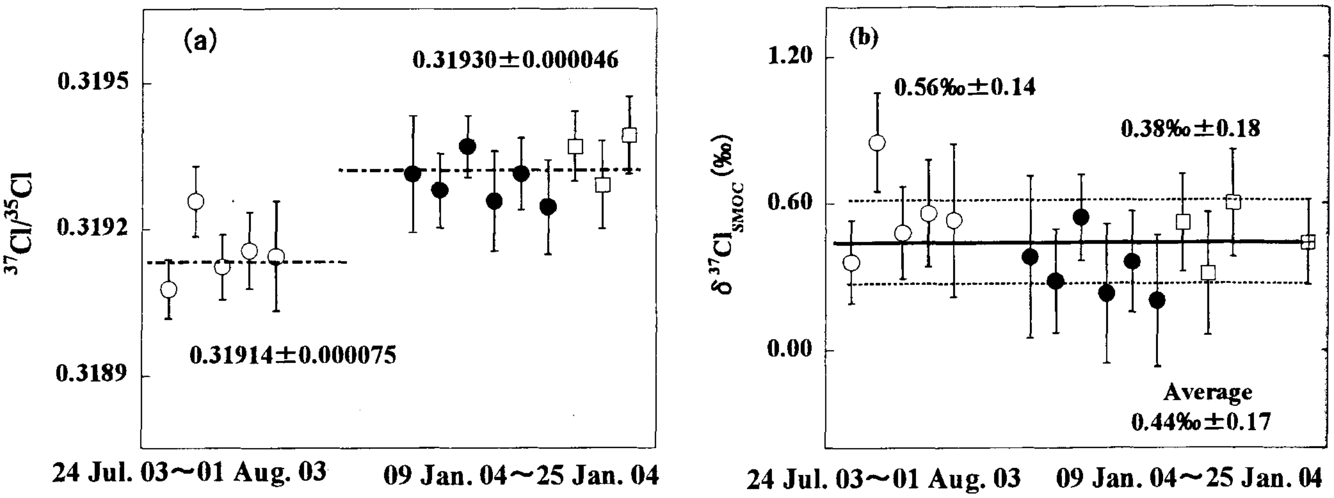

Figure 3-5. (a) Variations of ^{37}Cl/^{35}Cl in JB1 triplicate Cl extractions. Open circles refer to the isotope analyses of the first Cl extraction. Solid circles refer to the second one and open squares are the last. Error bars show the internal standard errors ($2\sigma_m$). The difference between the first set of analyses and the second and third ones is 0.50‰.
(b) Variations of $\delta^{37}Cl_{SMOC}$(‰) in JB1 triplicate Cl extractions with recalculation under the correction in related with the drift. Symbols are as same as (a).

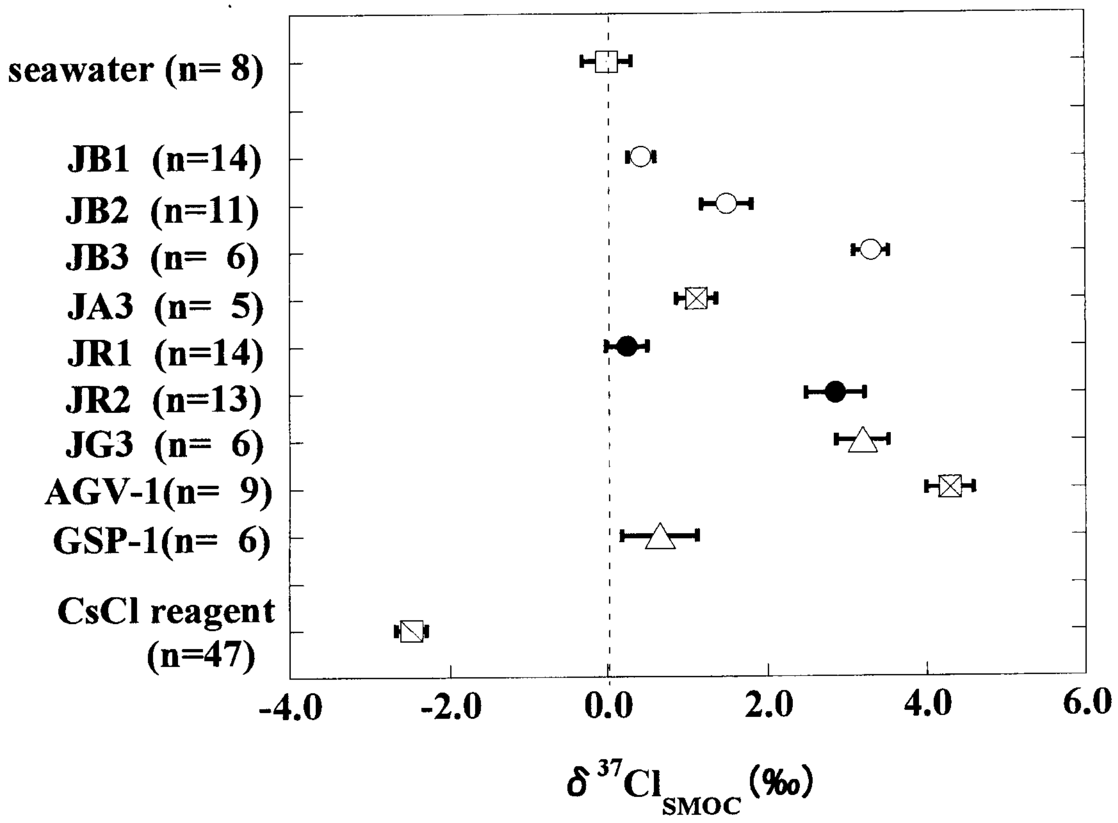

Figure 3-6. δ $^{37}Cl_{SMOC}$ of chlorine isotope measurements of nine standard rocks, seawater and CsCl reagent (n: number of separate runs). Error bars are 1 σ . The same symbols imply the same rock type samples.

Chapter 4 Chlorine isotope compositions in primitive meteorites

Introduction

Chlorine is one of the light and mobile elements, and highly diffusive among vapor, fluids and solid during geochemical processes. Thus, the behavior of chlorine in various geological settings can afford useful information (Ito et al., 1983; Jambon et al., 1995). Also, chlorine in meteorite is drawing attention for cosmochemists because of its mobility in aqueous environment but the precise measurements of chlorine concentration in meteorites were sparse (Dreibus et al., 1979; Garrison et al., 2000).

In meteorite, the chondrites have chemical compositions that closely resemble that of the volatile-free Sun. They are, therefore, regarded as chemically primitive, in contrast to other meteorites (Hutchison, 2004). Chondrites are subdivided into three groups such as carbonaceous, ordinary and enstatite. Carbonaceous chondrites have been considered the most primitive that formed from primitive, nebular material that accumulated into planetesimals in the earliest stages of solar system formation. Carbonaceous chondrites contained phyllosilicates (Rubin, 1997) that indicates the evidence for aqueous alteration (Tomeoka and Buseck, 1990). In carbonaceous chondrites, chlorine is considered to occur in the phyllosilicates as lattice substitutions. In addition, aqueous alteration could bring the formation of serpentine and/or sodarite from anhydrous minerals in the carbonaceous chondrites (Kojia and Tomeoka, 1996). Recently, chlorine minerals such as halite and sylvite were found in H5 chondrite and fluid inclusions existed in the halite (Zolensky et al., 1999, Whitby et al., 2000). To obtain the accurate chlorine concentration in chondrites is significant to monitor the behavior of chlorine and to understand the process of aqueous alteration of chondrites and/or other weathering.

On the other hand, chlorine has two stable isotopes such as ^{35}Cl and ^{37}Cl. Similar to the chlorine stable isotopes, other light stable isotope sets (e.g., H, C, N, O) were already well established in the study of geo and cosmochemistry. Especially, oxygen isotope cosmochemistry (Clayton, 1993) was the most successful example. The chondrite groups and classes are essentially defined by their chemical compositions, but oxygen isotope compositions in chondrites can clearly distinguish their groups and classes.

Chondrites could be considered the most primitive materials that now we can obtain, thus it is very important to know their chlorine isotope ratios. However, the data of chlorine isotope ratio in chondrites we can obtained now are only three such as Orgueil, Allende and Murchison (Magenheim, 1995; Magenheim et al., 1994) for bulk analysis. Magenheim et al. (1995) argued Earth's mantle evolution using the Orgueil chlorine isotope ratio to represent the bulk Earth. In their calculations, approximately 40% of the Cl originally in the degassed mantle now resides in Earth's surface.

In this work, twenty data sets of precisely determined chlorine concentrations and isotopic compositions in eighteen primitive meteorites by mass spectrometry are presented. The goals of this work were to determine the chlorine isotopic composition in various types of chondrite, and to reveal the isotopic characteristics among the different chondrite groups.

Experimental

Chondrite samples

The primitive meteorites examined in this study were eighteen chondites. In details, they are one CI, two CM, one CV, three CK, three Enstatite, and eight Ordinary chondrites (Table 4-1). Several grains of chondrules in Allende (CV3) were also investigated. In the Ordinary ones, each three chondrites belong the L and the H groups and one meteorite belongs to the LL group. Only three chondrites such as Maralinga (CK4), Y-74191 (L3) and Brownfield (H3) were "finds" and the rest were all "falls". Each samples were 1.58~0.44 g of pieces which volumes are about 8mm×8mm×8mm except one samples. The photographs of all the sample pieces are available (Fig. A-1, -2 and -3 in the Appendix). The piece of the sample was washed by ultra sonic waves in distillated n-hexane three times. After dryness, the piece was crushed and the obvious dirt and rust etc. on the surface were removed by hand picking. The fragments were powdered in the agate mortar for the analyses of Cl concentration and isotopic composition. The records of sample pulverization and consumption for analyses are arranged in the flowcharts (Fig. A-4 to A-23 in the Appendix).

The measurements of Cl concentration by isotope dilution method

Chlorine analyses in silicate materials like meteorites have been applied by several methods such as photometric (Terasima, 1974), X-ray fluorescence spectrometry (Terasima, 1976), ion-selective electrode (Aruscavage and

Campbell, 1983), instrumental or radiochemical neutron activation (Sinonaga et al., 1994), ion chromatography (Blackwell et al., 1997). For chlorine analyses in meteorites, Dreibus et al. (1979) and Garrison et al. (2000) employed neutron activation technique.

In our study, we employed isotope dilution technique (ID) using negative thermal ionization mass spectrometry (N-TIMS) to determine chlorine concentration in meteorites precisely. Powdered samples about 5~25mg were spiked and decomposed with hydrofluoric acid, and chlorine was isolated by precipitations of silver chloride after neutralization with $Ca(OH)_2$ (Musashi et al., 1998). The ammonical solution of AgCl was then subjected to N-TIMS. The ^{37}Cl-enriched spike (^{37}Cl abundance: 98.01%) was used in this study. $^{37}Cl^-/^{35}Cl^-$ was measured by negative thermal ionization technique using a thermal ionization mass spectrometer, Finnigan MAT Model 262. A Re-Re double filament mode was employed using Re ribbons (0.025 × 0.75mm; purity: 99.999%). From the isotope ratio of spike mixed sample, we can obtain the precise chlorine concentration in the sample. The precision of analysis by this method could be obtained about 1%.

The measurements of chlorine isotopic compositions

Isotopic compositions were determined by positive-ion thermal ionization mass spectrometry of $CsCl^+$ (Xiao and Zhang, 1992; Numata et al., 2001). Sample preparations and instrumental conditions were as same fashion as in Chapter 2. and summarized briefly below.

Sample decomposition for the chlorine extraction were employed a hydrofluoric acid leaching in the similar way to that of Musashi et al. (1998).

Samples about 1,000~100mg were decomposed to recover ~50 μ g Cl from the samples. The chlorine in the decomposed solution was isolated by precipitations of silver chloride after neutralization with $Ca(OH)_2$. The ammonical solution of AgCl was converted to CsCl solution by elution through AC50-X8 resin in the cesium form. The final form for chlorine isotope measurements was CsCl solution containing 2 μ g of Cl.

Measurements of chlorine isotopic composition as $Cs_2{}^{37}Cl^+/Cs_2{}^{35}Cl^+$ were performed using a Finnigan MAT Model 262 thermal ionization mass spectrometer. Filament used was flat undegassed Ta ribbon (0.025 × 1.5mm; purity: 99.95%, Nilaco) for single filament mode. Sample loading on the filament was performed in the same way of Numata et al. (2001). CsCl aqueous solution containing 2 μ g of Cl was mixed with approximately 50 μ g of graphite powder as a slurry in 80% ethanol to enhance ionization was deposited on the center of the filament. The 20 ratios of $Cs_2{}^{37}Cl^+/Cs_2{}^{35}Cl^+$ (mass ratio of 303/301) were measured in one block and 200~400 ratios (10~20blocks) were obtained each run. In-run precision ranged from 0.15‰ to 0.28‰. Particularly, repeated runs of CsCl laboratory standard as well as seawater were carried out before, between and after the analyses of the meteorite samples.

Results and Discussion

Analytical error with respect to isotope dilution method

It is pointed out that the IDMS technique requires isotope equilibration between sample and spike and chemical yields during analytical processes should have no direct effect on analytical precision. One of the most important factors influencing on the analytical precision is blanks in the chemical processes. For chemical processes of the Cl extraction from the meteorite samples, most abundant reagents used in this study were hydrofluoric acid and $Ca(OH)_2$ powder. Small quantities of other two reagent solutions of $AgNO_3$ and NH_3 were also used. In this study, total procedural blanks , which corresponds to the quantity of reagents using about 25mg sample decomposition were 0.014 and 0.023μg Cl determined by N-IDMS (see Chapter 2). This blank value corresponds to ~0.5% of Cl contents in the most samples.

Isotope fractionation effects during the measurements of $^{37}Cl^{-}/^{35}Cl^{-}$ of sample spike mixed solution are normally smaller than 0.1%. Such a fractionation is small compared to other uncertainties in the analysis. However, when the quantity of the spike differs extremely from the quantity of the sample, large error in concentration can cause even if the accuracy of isotopic measurement is good. The approximation equation for the standard deviation of Ns (Ns refers to the number of atoms in the sample) by the laws of propagation of errors is as follows (Heumann, 1988).

$$SD^2(Ns) \fallingdotseq SD^2(Nsp) + f^2(R)\,SD^2(R)$$

where SD is the standard deviation, Nsp is the number of atoms in the spike, R is isotope ratio and f (R) is the error multiplication factor for the R value. If the amount f (R) becomes minimum, the optimum value of R is reached. In this study, we used ^{37}Cl-enriched spike that the ^{37}Cl abundance was 98.01%. The isotope ratio R of all sample spike mixed solutions determined shows range from 1.11 to 8.98 and we can calculate the error multiplication factor f as 1.001-1.0015 in our experimental conditions. Under similar condition, our previous work reached ~1% precision of Cl analysis by N-TIMS ID (see Chapter 2).

The concentration of chlorine in the primitive chondrites

Results for 18 chondrites and Allende chondrules of Cl concentrations are presented in Table 4-2 with some previous works' values. Figure 4-1 shows the chlorine concentration in various types of chondrite. We can obtain good precision of Cl analysis by N-TIMS ID compared to other analytical technique. However, chlorine is ubiquitous in the hydrosphere, lithosphere and atmosphere of the Earth as major anion, so we pay close attention for the terrestrial contamination to analyze the extraterrestrial materials as the meteorites samples. Garrison et al. (2000) analyzed Cl contents in about one hundred meteorite samples determined by neutron activation analysis using nuclear reaction $^{37}\mathrm{Cl}\ (n, \gamma)\ ^{38}\mathrm{Ar}$. They utilized the stepwise heating technique, and succeeded in dividing into high-temperature released Cl and low-temperature released Cl. They considered the latter Cl was derived from terrestrial contamination. Many meteorites of "finds" show relatively large low-temperature Cl compared to the meteorites of "falls". The samples investigated in this study are almost "falls" except three samples. Their analytical results of Abee (EH4), Indarch (EH4) and Hvittis (EL6) show few terrestrial contamination and the results of Abee and Hvittis are good consistent with this study. Our result of Indarch is rather larger than the result of Garrison et al. (2000). This discrepancy is argued later.

The highest value of Cl is 824ppm in the enstatite chondrite as Indarch (EH4), and the lowest one is 44.3ppm in the ordinary chondrite as Allegan (H5). Cl contents in the carbonaceous chondrites range from 760 to 282ppm. Three enstatite chondrites range from 824 to 217ppm. Eight ordinary chondrites range from 412 to 44.3ppm. Figure 4-2 shows the relationship between the chondrite groups and their Cl concentrations. The most primitive CI and CM2 chondrites show relatively high content of Cl. We analyzed three samples of Allende (CV3). Allende A refers to the bulk analysis, and B refers to 0.35 mg of small chip analysis. Several Allende chondrules were also analyzed. Allende A and B show good agreement each other. On the contrary, Allende chondrules have relatively higher content of Cl than in the bulk sample. CV chondrites including Allende were abundantly subjected to secondary alteration (Krot et al., 1995). Especially, there existed secondary altered minerals such as nepheline and sodalite in Allende chondrules (Ikeda and Kimura, 1995; Shimoda et al., 2005). Excess of Cl in the chondrules seems to reflect the occurrence of altered minerals. Enstatite chondrite groups also have substantially high Cl content compared to that of the ordinary ones, which seems to be related to the differences in trace mineralogy (Garrison et al., 2000; Rubin, 1997). Garrison et al. (2000) concluded that there are no difference between H and L ordinary chondrites groups. In our results, relatively high concentrations of Cl in L condrites group rather than H ones are observed.

Precise determination of chlorine isotopic composition in primitive chondrites

The isotopic compositions of chlorine are represented in per mil (‰) deviation from those of the Standard Mean Ocean Chloride (Kaufman et al., 1984), and a reagent grade CsCl (Nacalai Tesuque) was utilized as a routine laboratory standard of Cl isotopic composition during the course of this study (Numata et al., 2001: see Chapter 3).

$$\delta\,^{37}\mathrm{Cl}_{\mathrm{SMOC}} = (\mathrm{R}_{\mathrm{sample}} / \mathrm{R}_{\mathrm{SMOC}} - 1) \times 10^3 \qquad \mathrm{R}={}^{37}\mathrm{Cl}/{}^{35}\mathrm{Cl}$$

We have performed CsCl reagent analyses together with sample measurements, and their values of daily variation were available. The results of CsCl reagent isotopic ratio from April 2005 to December 2005 were shown in Fig. 4-2. In the course of this study, the mean value of the CsCl reagent isotopic compositions was 0.318357 and its standard deviation was ±0.000055, which refers to 0.17‰ (see Table 4-3). We calculated the $\delta\,^{37}\mathrm{Cl}_{\mathrm{SMOC}}$ value of the sample from this secondary laboratory standard (see Chapter 3).

The analytical results of isotopic compositions for 20 samples in 17 chondrites were shown in Table 4-4. Table 4-4 also represents the chemical recovery yields (in percent) thorough the sample preparation based on the Cl concentrations determined in this study. The chemical yields ranged from

89% for Hedjaz to 52% for Indarch and the average of all analysis is 76%. In Chapter 3, the average chemical yield for 13 standard rocks was 77%. However, the yield for Indarch was too low in comparison with the value of other meteorites. Cl content in Indarch by our analysis was 824 ppm, though the value from Garrison et al. (2000) was 400 ppm. It implies one possibility that there is some heterogeneity in Indarch and the portion for ID used had incidentally high Cl concentration.

Replicate isotope analyses were performed for 3～10 times each sample. Analytical errors were displayed as 1SD and their values were ranged from 0.20‰ to 0.41‰ and fifteen in 20 analyses displayed their errors better than 0.30‰. Figure 4-3 shows the variations of the replicate isotopic analyses of Allende A (CV3) and Allende chondrules. Their $\delta^{37}Cl_{SMOC}$ values are agreeing narrowly in the range of the error. Figure 4-4, -5, and -6 show the variations of replicate isotopic analyses of the enstatite group chondrites as Hvittis (EL6) and Abee (EH4), H-ordinary group ones as Brownfiled (H3) and Tahara (H5) and L-ordinary group ones as Homestead (L5) and Y074191 (L3). $\delta^{37}Cl_{SMOC}$ values of all samples were shown in Fig. 4-7. It should be noticed that the isotopic compositions of each chondrite group seems to have certain characteristic values. In particular, EH4 enstatite chondrites as Abee and Indarch have almost identical values as 3.05‰ and 3.10‰ and clearly differ from the value of EL chondrite (see Fig. 4-4). The isotope compositions of CK group was 0.54‰ (Ningqiang CK3) to −0.56‰ (Kobe CK4). CM2 group (Murchison and Boriskino) and CV3 (Allende) were clearly different from CK group. Previous works reported Murchison and Allende values as 3.4‰ (Magenheim et al., 1994) and 4‰

(Magenheim, 1995), respectively. These values are fairly consistent with our results.

In our result, all the chondrite groups other than the L-chondrites were almost enriched in ^{37}Cl relative to SMOC. The $\delta\,^{37}\mathrm{Cl}_{\mathrm{SMOC}}$ values of the terrestrial igneous rocks ranged from +0.25‰ to +5.64‰ (see Chapter 3). Other terrestrial igneous and metamorphic rocks and minerals reported also showed enrichment in ^{37}Cl relative to SMOC (Magenheim et al., 1994; Magenheim et al., 1995; Boudreau et al., 1997; Willmore et al., 2002). On the contrary, four L-type ordinary chondrites indicated depletion in ^{37}Cl relative to SMOC ranging from −4.60‰ to −0.74‰ (see Fig. 4-6). Y-74191 (L3) ($\delta\,^{37}\mathrm{Cl}_{\mathrm{SMOC}} = -4.60$‰) and Hedjaz (L3-6) ($\delta\,^{37}\mathrm{Cl}_{\mathrm{SMOC}} = -3.42$) were relatively large depletion and about 5~6‰ lighter than the carbonaceous chondrite values. Such a large depletion relative to SMOC has not been reported about terrestrial silicate samples and it is difficult to explain the mineralogical fractionation from enriched ^{37}Cl materials. Recently, water-bearing halite crystals were reported in two H-chondrites such as Zag and Monahans (Zolensky et al., 1999; Whitby et al., 2000; Rubin et al, 2002). Bridges et al. (2004) measured the isotopic composition of water-soluble halogen from Zag halites. The $\delta\,^{37}\mathrm{Cl}_{\mathrm{SMOC}}$ of two halites were −1.9 and −1.4, respectively. They also measured the water-soluble halogen from bulk samples of Zag and Plains (H5) ordinary chondrites and Murchison (CM2). Zag and Plains water-soluble halogen showed −2.9 and −2.8‰ of $\delta\,^{37}\mathrm{Cl}_{\mathrm{SMOC}}$. However, the water-soluble Cl concentrations of two condrites were 0.418 and 0.627 ppm, respectively and that of Murchison was 0.627ppm. The Cl content in bulk sample of Murcison was 430ppm in this study, so water-soluble Cl was only

1/100 of Cl in the bulk meteorite. In our result, the H-type ordinary chondrites indicated to rather enriched ^{37}Cl relative to SMOC, and we could not observe the influence of such depleted ^{37}Cl materials. However, L-type chondrites might be much influenced by the deplete ^{37}Cl materials which suggests a more extensive light Cl isotopic reservoir (Bridges et al., 2004).

Conclusions

The chlorine concentrations of twenty samples of 18 primitive meteorites were analyzed by isotope dilution method using N-TIMS. Carbonaceous and enstatite chondrites show relatively high concentration of chlorine. The chlorine in H-and LL-type chondrites indicated low contents. The chlorine isotopic compositions of twenty samples of 18 primitive meteorites were also analyzed by P-TIMS. All the chondrite groups other than the L-chondrites were almost showing enriched in ^{37}Cl relative to SMOC. It should be noted that four L-type ordinary chondrites indicated to be deplete in ^{37}Cl relative to SMOC ranging from −4.60‰ to −0.74‰.

Table 4-1

Sample names and their weight pulverized using this study.

Sample	Group and Class	Fall or Find	Weight (g)[a)]
Orgueil	CI	Fell 1864, May 14	0.061
Murchison	CM2	Fell 1969, Sep. 28	0.420
Boriskino	CM2	Fell 1930, Apr. 20	0.182
Allende A	CV3	Fell 1969, Feb. 8	15.2
Allende B			0.313
Allende chondrules			0.380
Ningqiang	CK3	Fell 1983, June 25	0.510
Kobe	CK4	Fell 1999, Sep. 26	0.452
Maralinga	CK4	Found 1974	0.732
Abee	EH4	Fell 1952, June 10	0.728
Indarch	EH4	Fell 1891, Apr. 7	0.521
Hvittis	EL6	Fell 1901, Oct. 21	0.521
Y-74191	L3	Found 1994	1.34
Hedjaz	L3-6	Fell 1910, in the spring	0.678
Homestead	L5	Fell 1875, Feb. 12	0.930
Fukutomi	L5	Fell 1882, Mar. 30	0.725
Brownfield	H3	Found 1937	0.865
Allegan	H5	Fell 1899, Jul. 10	1.425
Tahara	H5	Fall on Mar. 26, 1991	1.266
Dhurumsala	LL6	Fell 1860, Jul. 14	0.934

a) Weight (in g) of sample which was pulverized.

Table 4-2
Chlorine concentration (ppm) in primitive meteorites analysed by isotope dilution method.

Sample	Group and Class	Weight (mg)[a]	Cl concentration (ppm)	Literature
Orgueil	CI	4.61	760	678[b]
Murchison	CM2	22.6	430	180[b]
Boriskino	CM2	9.85	632	
Allende A	CV3	27.6	337	237[b], 372[c]
Allende B		27.1	306	
All. chondrules		23.6	472	
Ningqiang	CK3	19.2	369	
Kobe	CK4	25.0	282	263[c]
Maralinga	CK4	26.5	404	
Abee	EH4	23.1	450	560[b], 507[d]
Indarch	EH4	18.7	824	400[d]
Hvittis	EL6	19.1	217	297[d]
Y-74191	L3	25.7	278	235[e]
Hedjaz	L3-6	19.8	172	
Homestead	L5	22.0	147	
Fukutomi	L5	22.4	412	
Brownfield	H3	26.1	260	
Allegan	H5	24.9	44.3	
Tahara	H5	26.6	62.4	
Dhurmsala	LL6	26.3	64.3	

[a] Weight (in mg) of sample dissolved. b) Dreibus et al. (1979); c) Oura et al. (2002); d) Garrison et al. (2000); e) Shinonaga et al. (1994)

Table 4-3.
Measured Cl isotopic compositions of the CsCl reagent (the secondary standard)

Run	$^{37}Cl/^{35}Cl$	$\delta^{37}Cl_{SMOC}$(‰)
1	0.318371±0.000084[a)]	-2.31±0.26[a)]
2	0.318345±0.000068	-2.39±0.21
3	0.318412±0.000077	-2.18±0.24
4	0.318385±0.000065	-2.26±0.20
5	0.318321±0.000077	-2.46±0.24
6	0.318411±0.000082	-2.18±0.26
7	0.318352±0.000072	-2.37±0.23
8	0.318225±0.000081	-2.76±0.25
9	0.318317±0.000075	-2.48±0.24
10	0.318332±0.000074	-2.43±0.23
11	0.318393±0.000062	-2.24±0.19
12	0.318420±0.000073	-2.15±0.23
average	0.318357±0.000055[b)]	-2.35±017[b)]
Numata et al. (2001)	0.318953±.000069	-2.49±0.22

a)Error for the individual runs is 2SE
b)Error for the average value is $1\sigma_{SD}$.

Table 4-4

Results of chlorine isotopic analyses for 17 primitive meteorites.

Sample	Group and Class	Weight (mg)[a]	Yield (%)[b]	n[c]	$\delta^{37}\mathrm{Cl}_{\mathrm{SMOC}}$ (‰)[d]
Murchison	CM2	170	74	9	7.99±0.23
Murchison-2	CM2	101	87	3	2.27±0.22
Boriskino	CM2	121	81	6	4.43±0.25
Allende A	CV3	255	69	10	2.26±0.30
Allende B		175	71	8	0.87±0.34
Allende chondrules		160	82	7	1.77±0.21
Ningqiang	CK3	98	77	5	0.54±0.27
Kobe	CK4	153	74	6	-0.56±0.22
Maralinga	CK4	149	80	8	0.47±0.27
Abee	EH4	180	79	8	3.05±0.28
Indarch	EH4	198	52	4	3.10±0.26
Hvittis	EL6	200	81	4	5.22±0.31
Y-74191	L3	250	75	9	-4.60±0.28
Hedjaz	L3-6	273	89	8	-3.42±0.20
Homestead	L5	276	79	6	-0.74±0.27
Fukutomi	L5	140	76	8	-2.23±0.20
Brownfield	H3	251	75	4	3.78±0.36
Allegan	H5	1,317	69	4	5.02±0.41
Tahara	H5	858	71	4	-0.57±0.26
Dhurumsala	LL6	901	78	7	0.76±0.21

a) Weight (in mg) of sample dissolved. b) Recovery yields (in percents). c)n refers to the run number of individual analysis. d) Error is 1S.D.

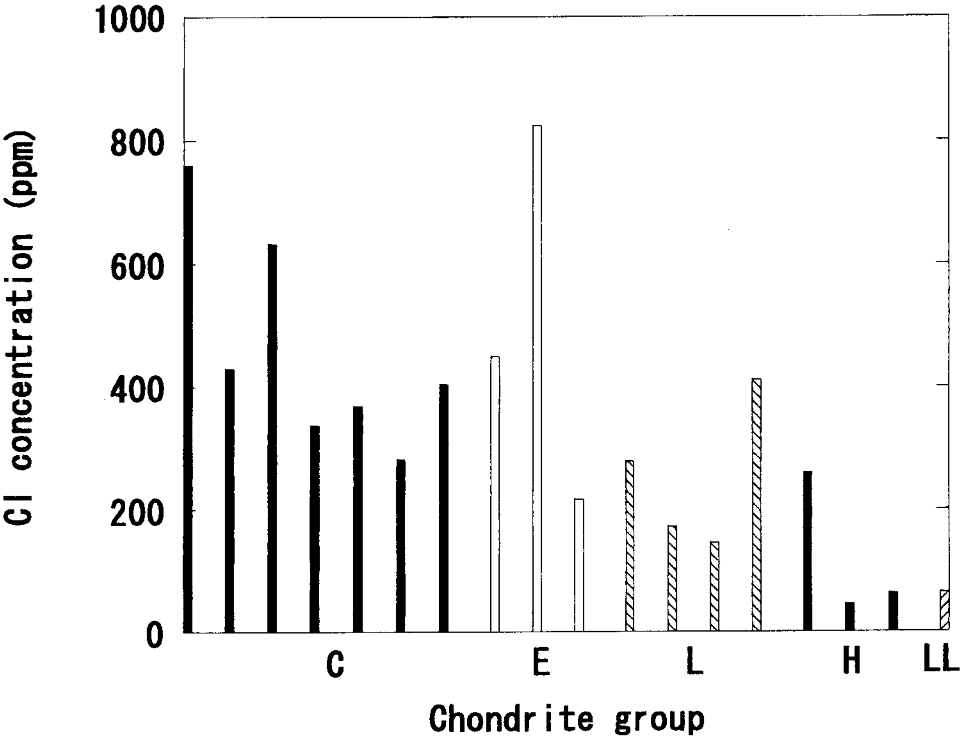

Fig. 4-1. Chlorine concentration (ppm) in chondrite groups. C refers to the carbonaceous chondrites, E refers to enstatite ones, L refers to L-ordinary ones, H refers to H-ordinary ones and LL refers to LL-ordinary one.

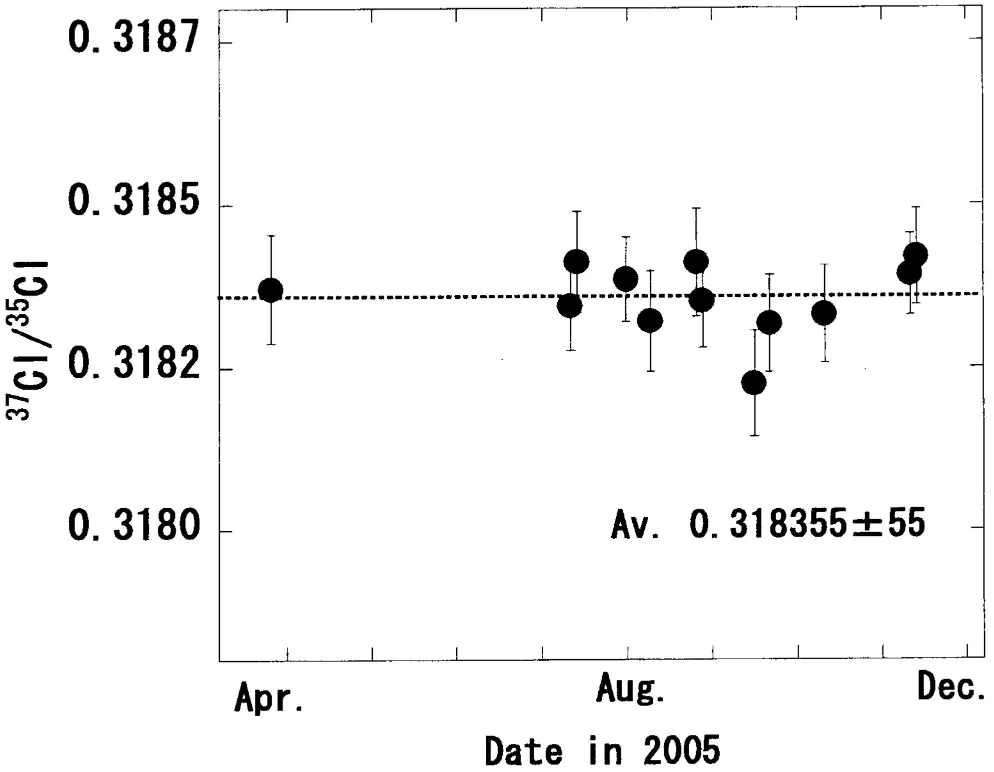

Fig. 4-2. Chlorine isotopic compositions of a CsCl reagent used as a laboratory standard for the period between April and December 2005.

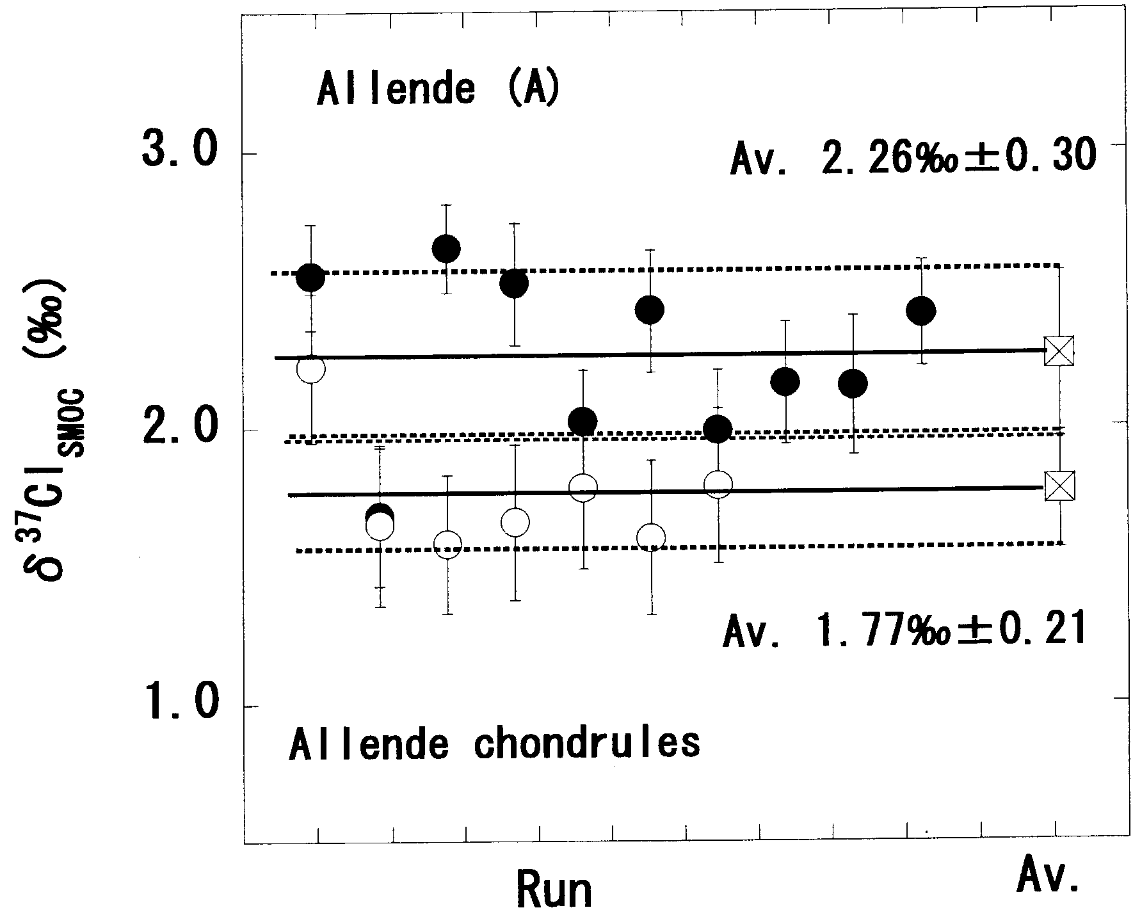

Fig. 4-3. Variations of $\delta^{37}Cl_{SMOC}$ of replicate analyses in Allende A (solid circles) and Allende chondrules (open circles). Error bars with their symbols represent the internal standard error (2 σ m). Cross squares refer to the average of all data. Error bars of the average represent the external standard deviation (1SD).

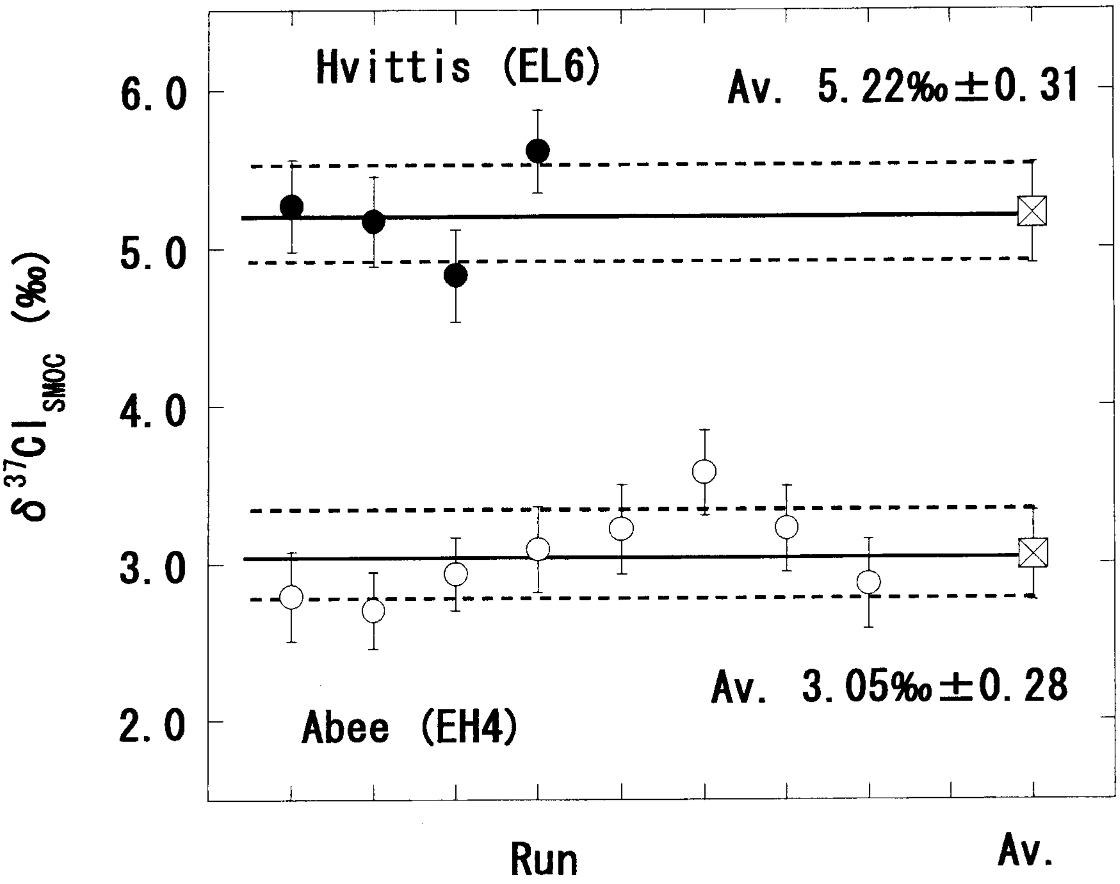

Fig. 4-4. Variations of δ $^{37}Cl_{SMOC}$ of replicate analyses in Enstatite chondrites as Havittis (solid circles) and Abee (open circles). Error bars with their symbols represent the internal standard error (2 σ m). Cross squares refer to the average of all data. Error bars of the average represent the external standard deviation (1SD).

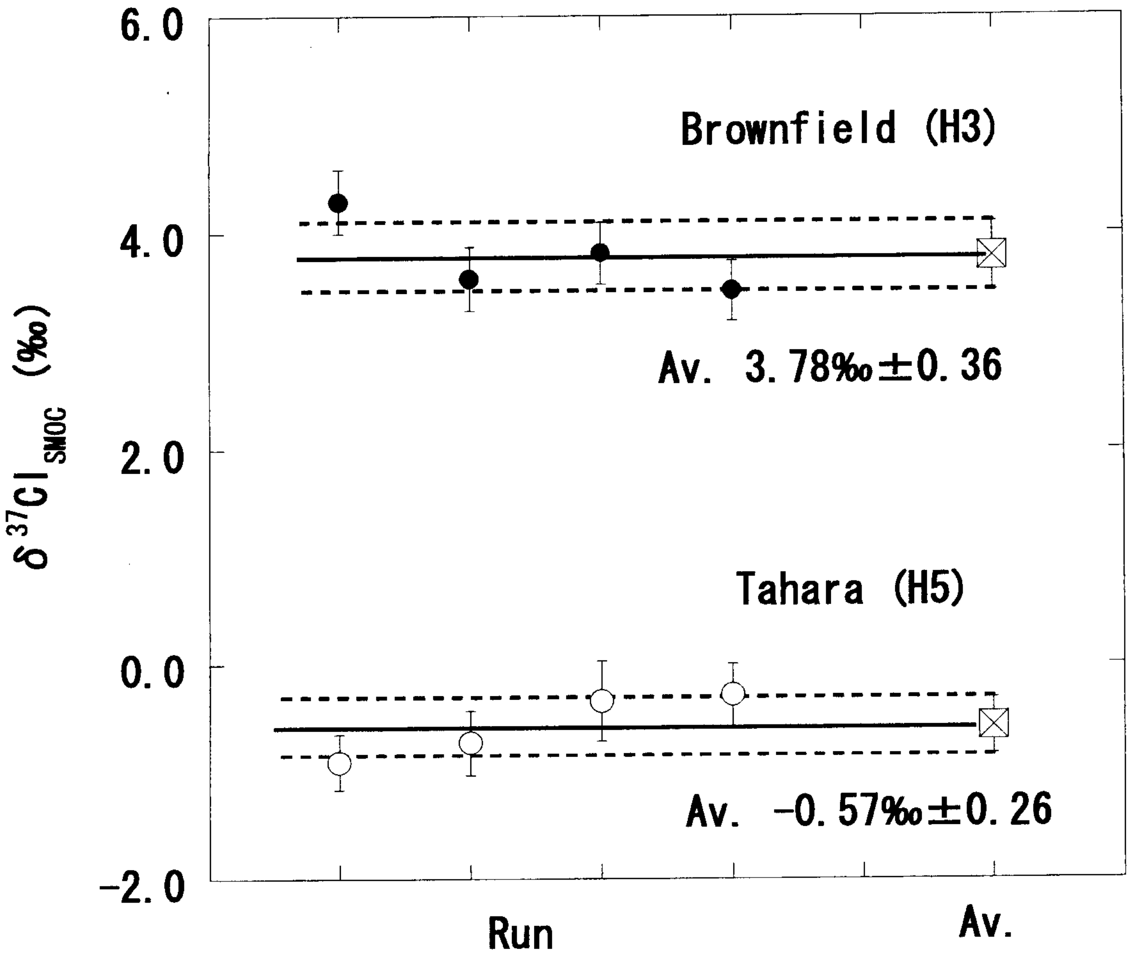

Figure 4-5. Variations of $\delta^{37}Cl_{SMOC}$ of replicate analyses in H ordinary chondrites as Brownfield (solid circles) and Tahara (open circles). Error bars with their symbols represent the internal standard error (2 σ m). Cross squares refer to the average of all data. Error bars of the average represent the external standard deviation (1SD).

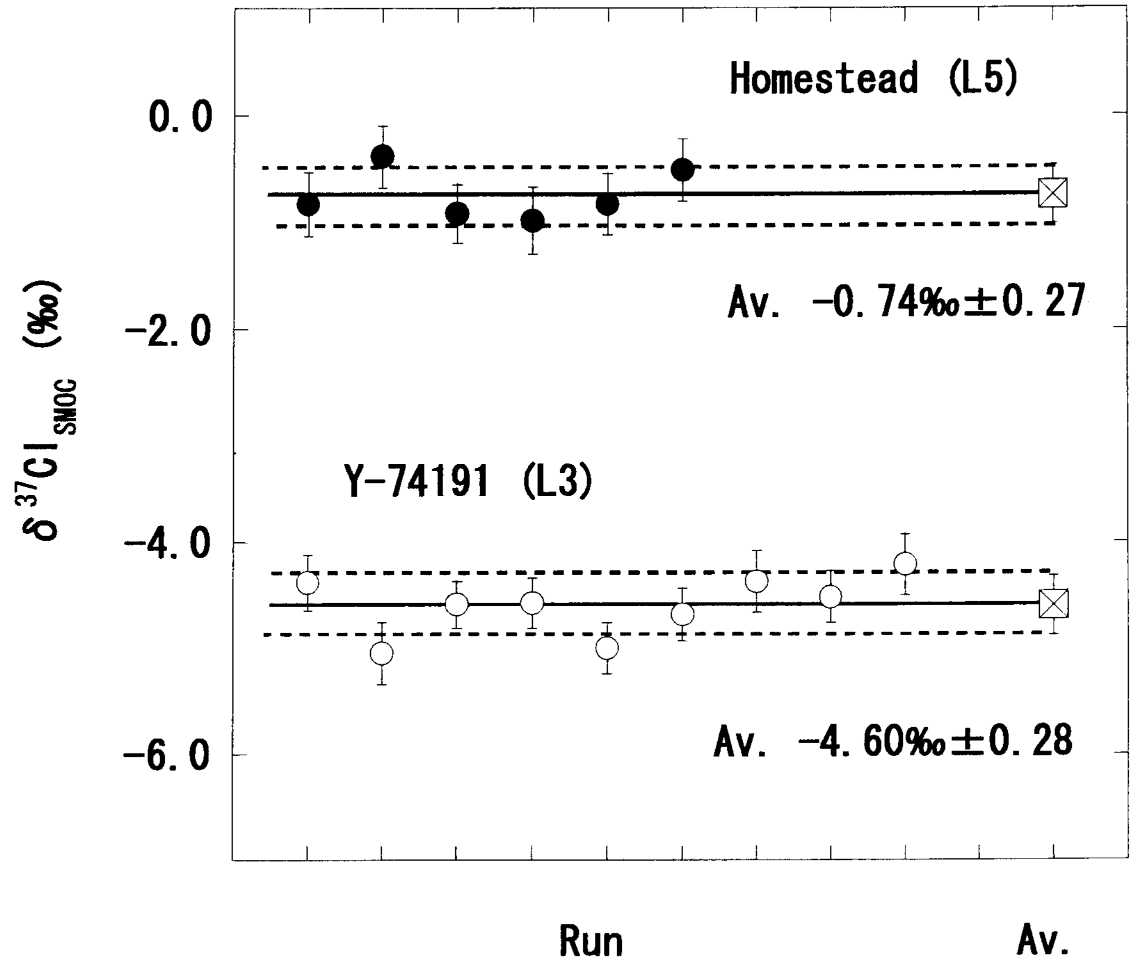

Figure 4-6. Variations of $\delta^{37}Cl_{SMOC}$ of replicate analyses in L ordinary chondrites as Homestead (solid circles) and Y-74191 (open circles). Error bars with their symbols represent the internal standard error (2 σ m). Cross squares refer to the average of all data. Error bars of the average represent the external standard deviation (1SD).

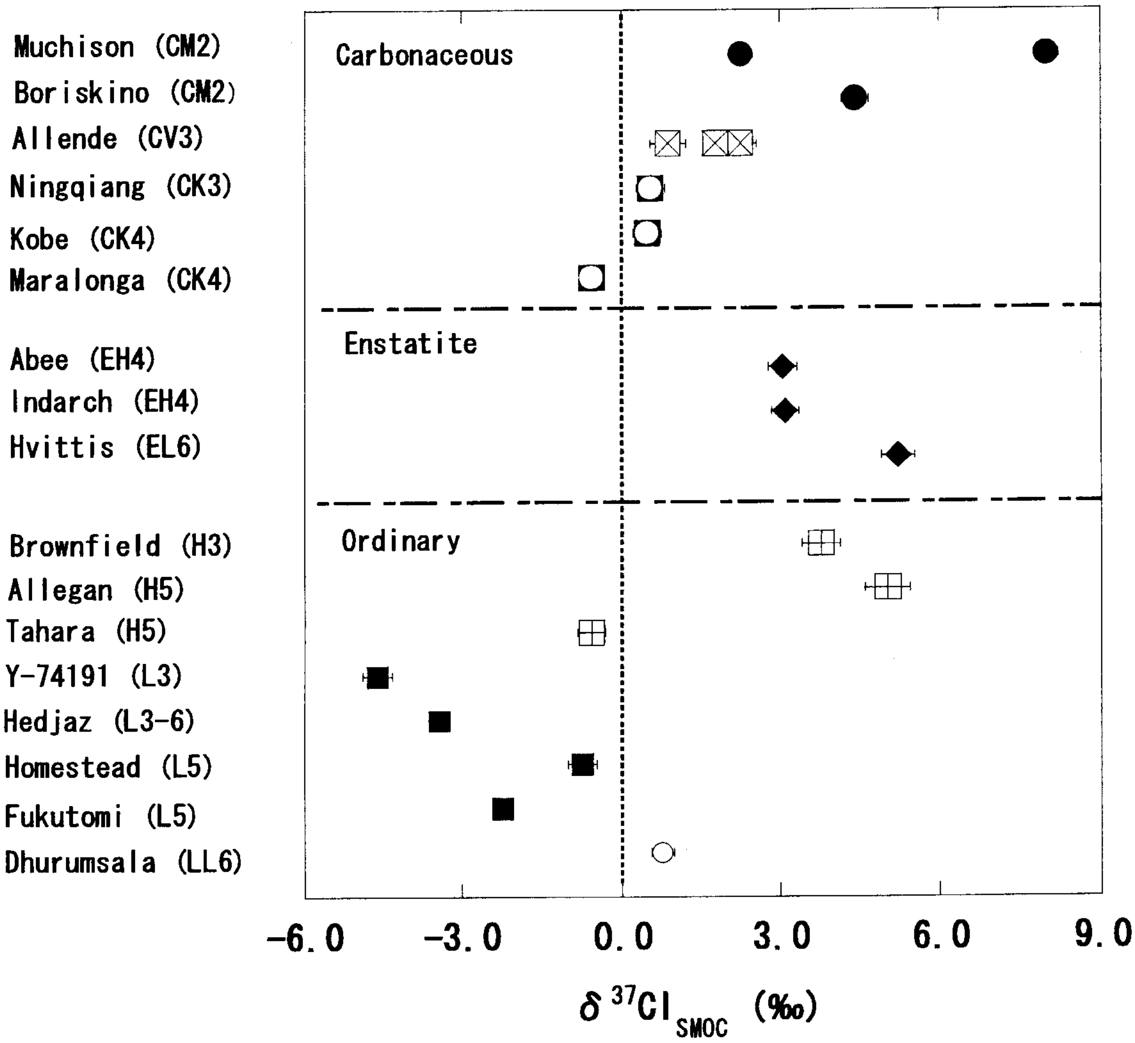

Fig. 4-7. $\delta^{37}Cl_{SMOC}$ of chlorine isotope measurements of 17 chondrites and Allende chondrules. Error bars are 1SD. The same symbols imply the same chondrite group.

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Appendix

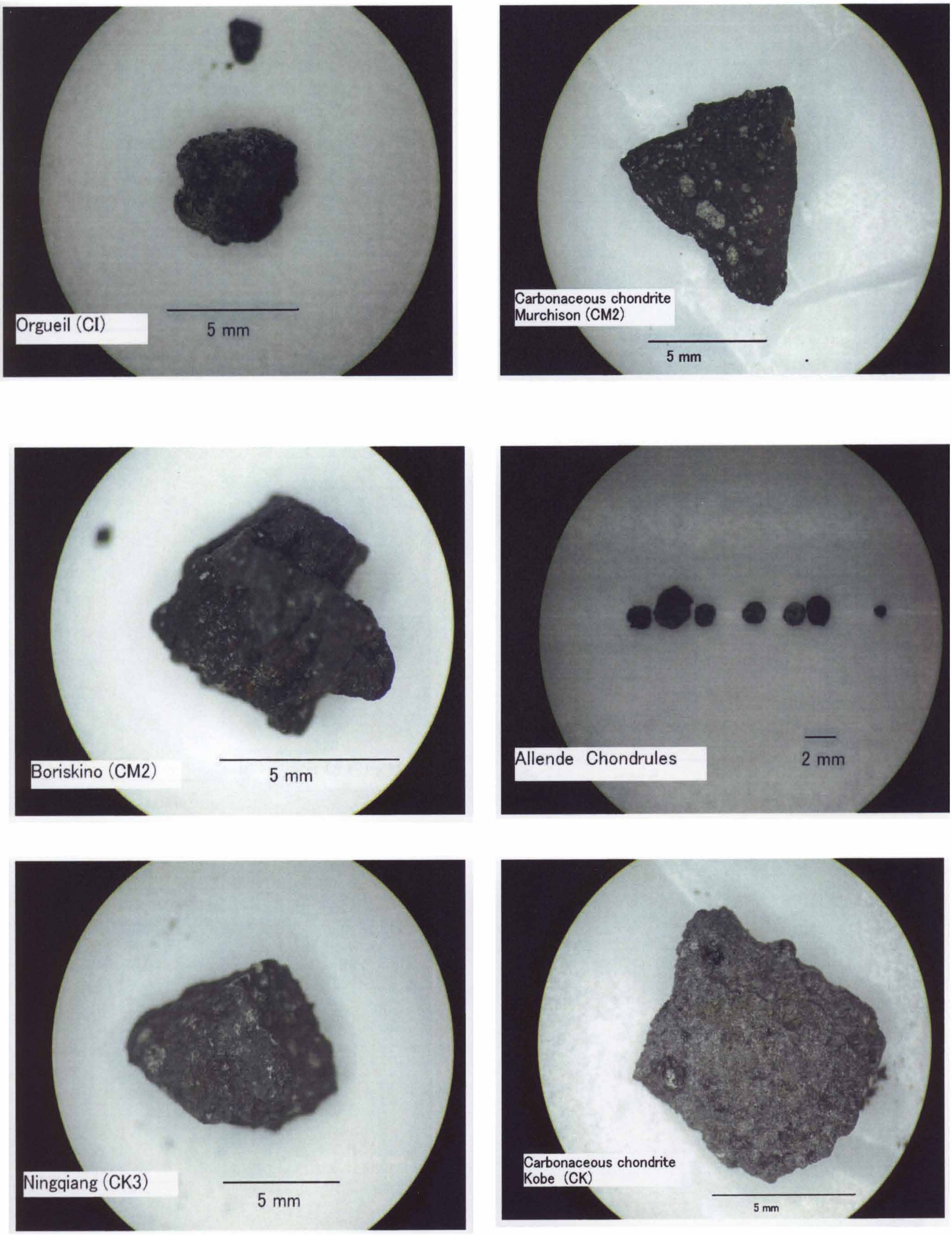


Figure A-1. Photograph of Orguil, Murchison, Boriskino, Ningqiang and Kobe chondrites and Allende chondrules.

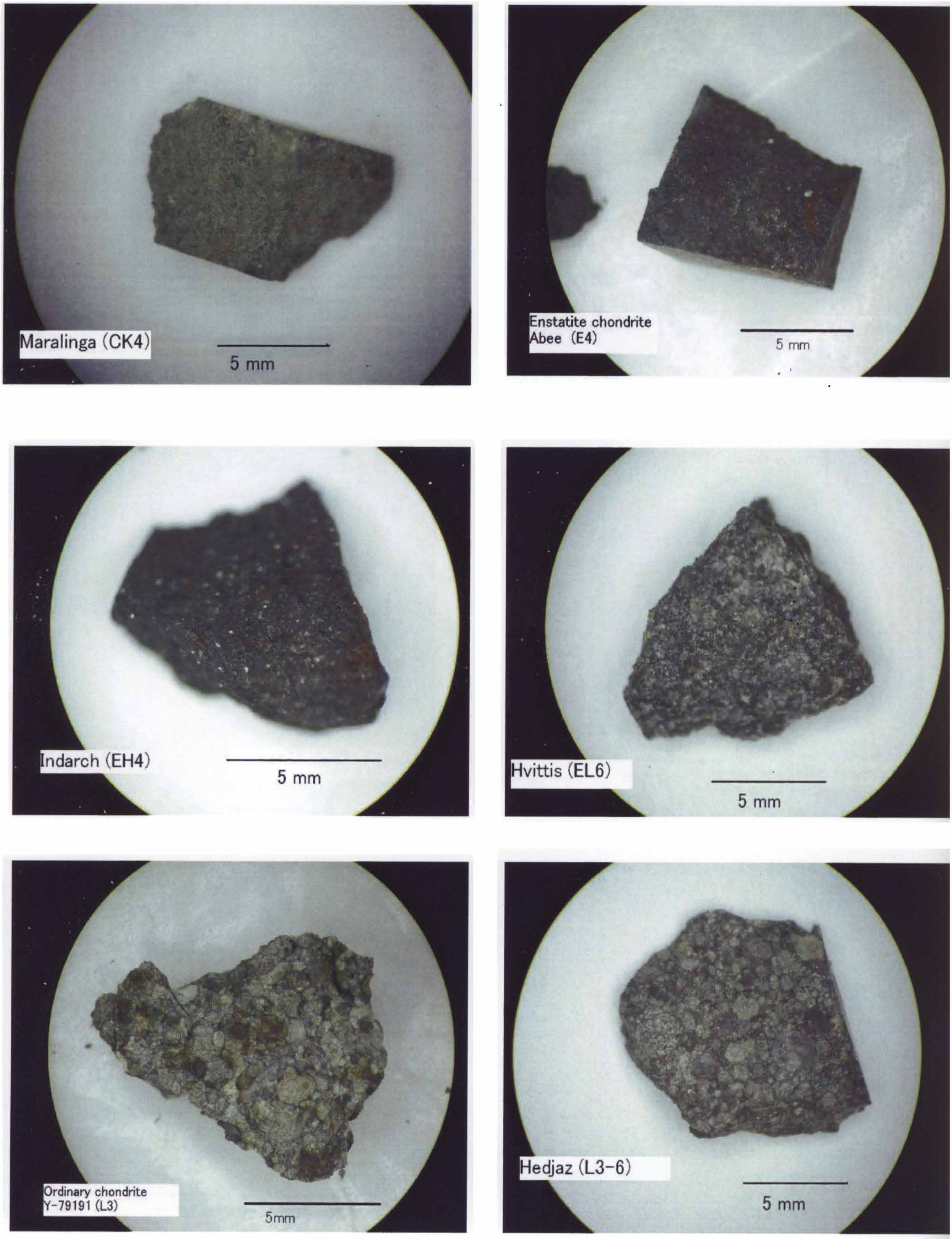


Figure A-2. Photograph of Maralinga, Abee, Indarch, Hvittis, Y-74191 and Hedjaz chondrites.

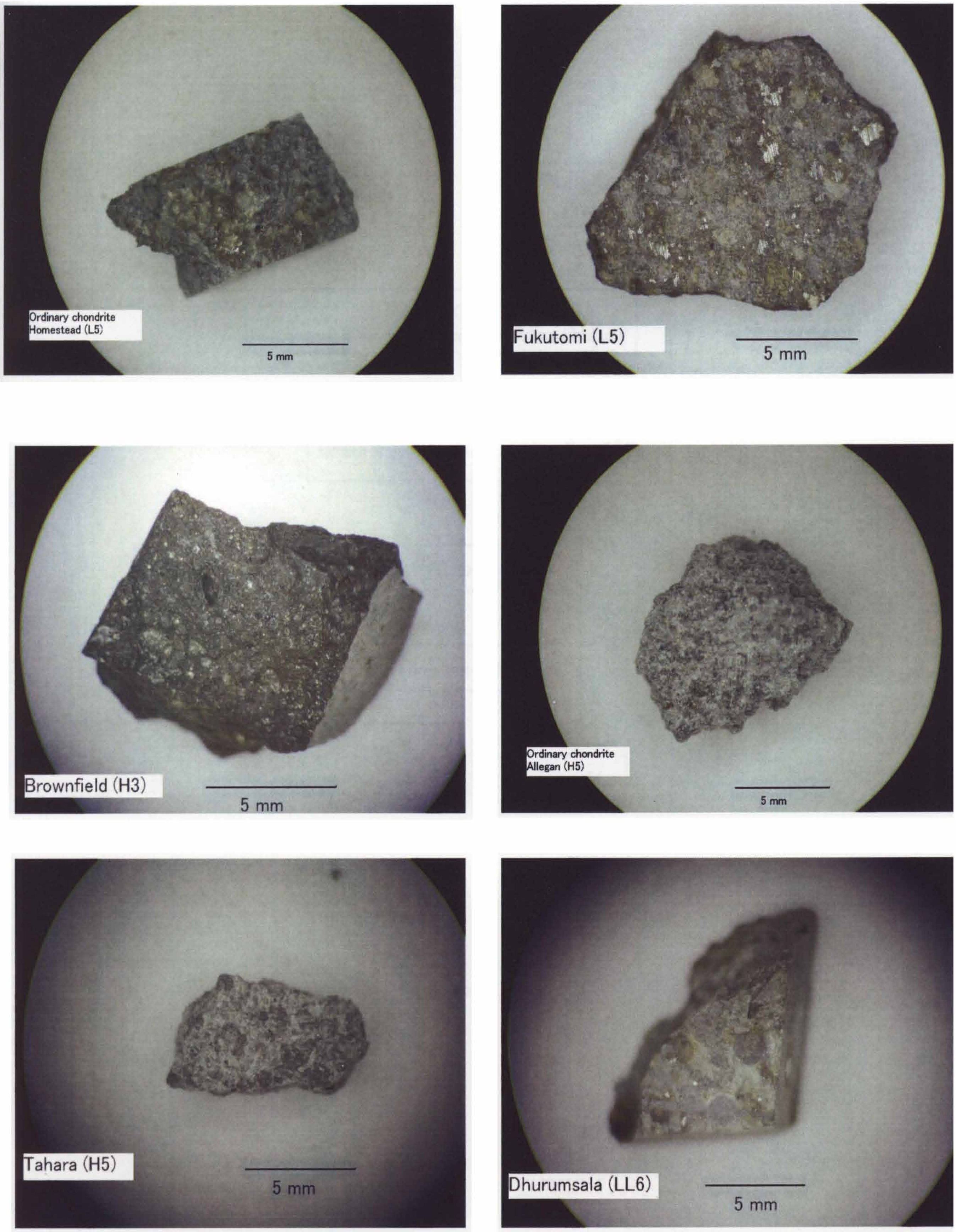


Figure A-3. Photograph of Homestead, Fukutomi, Brownfield, Allegan, Tahara and Dhurumsala meteorites.

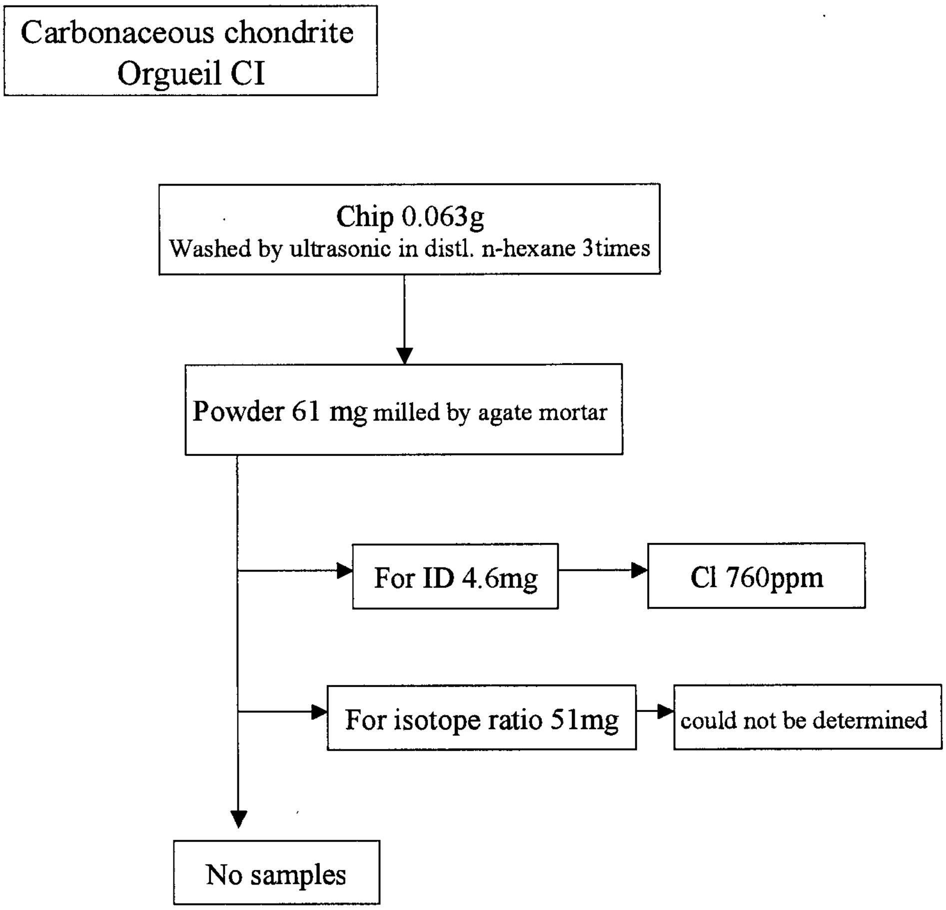


Figure A-4. A record of sample preparation for Orgueil.

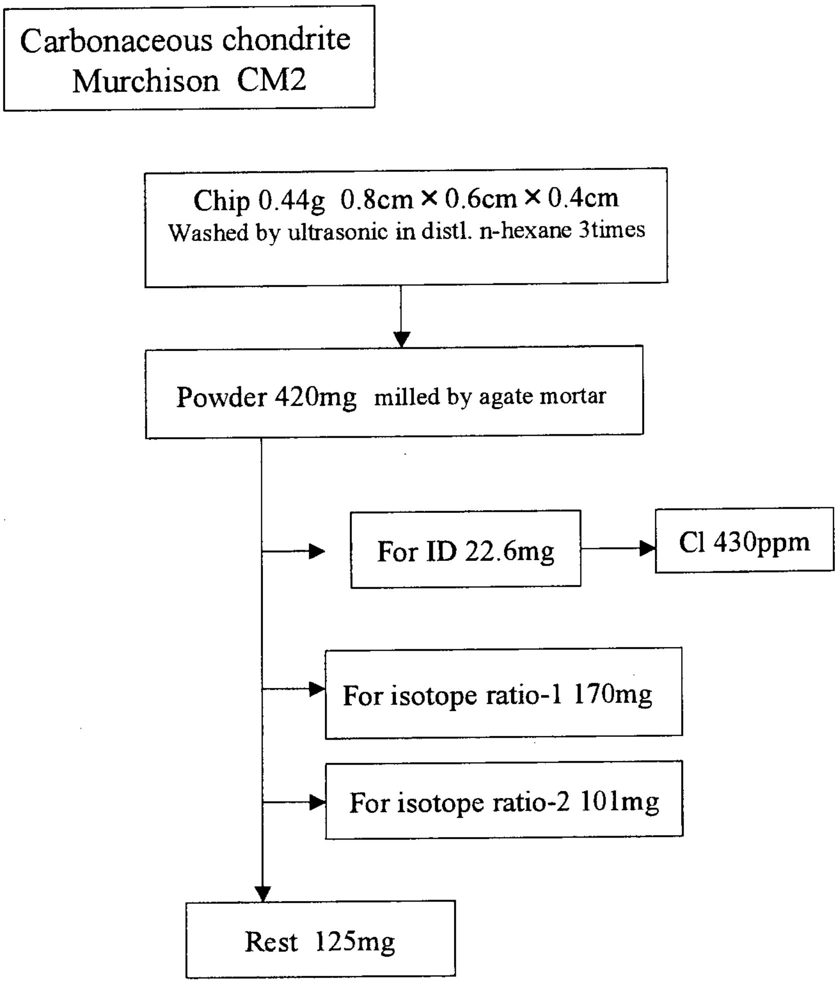
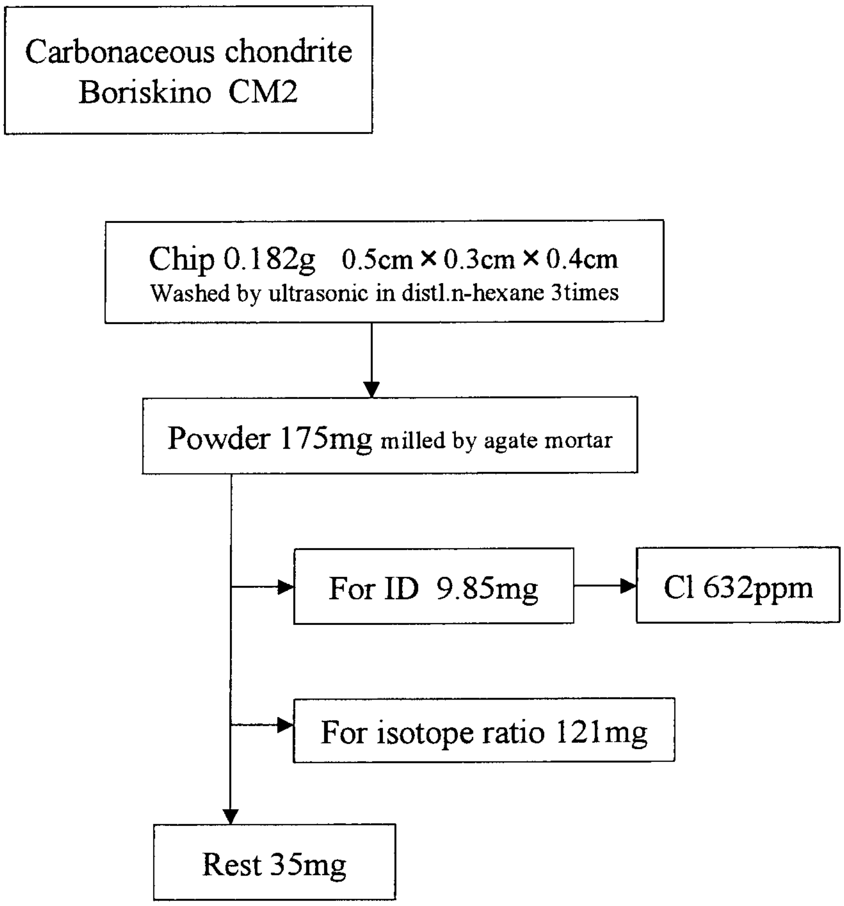


Figure A-5. A record of sample preparation for Murchison.



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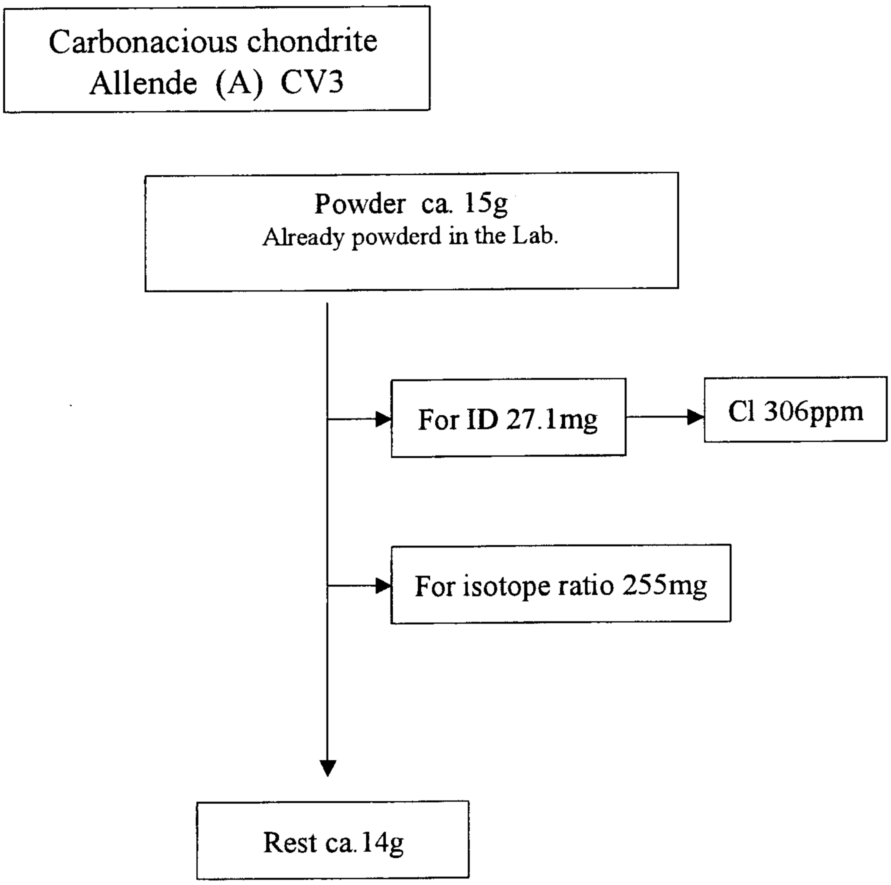


Figure A-7. A record of sample preparation for Allende (A).

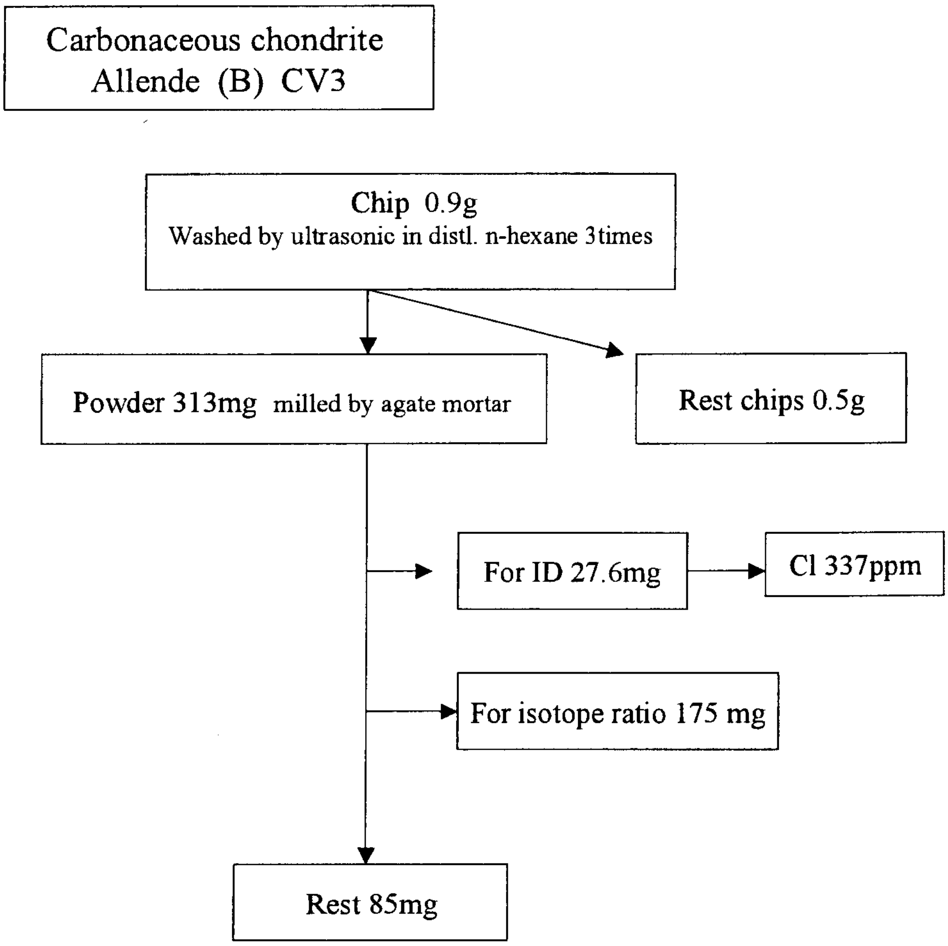


Figure A-8. A record of sample preparation for Allende (B).

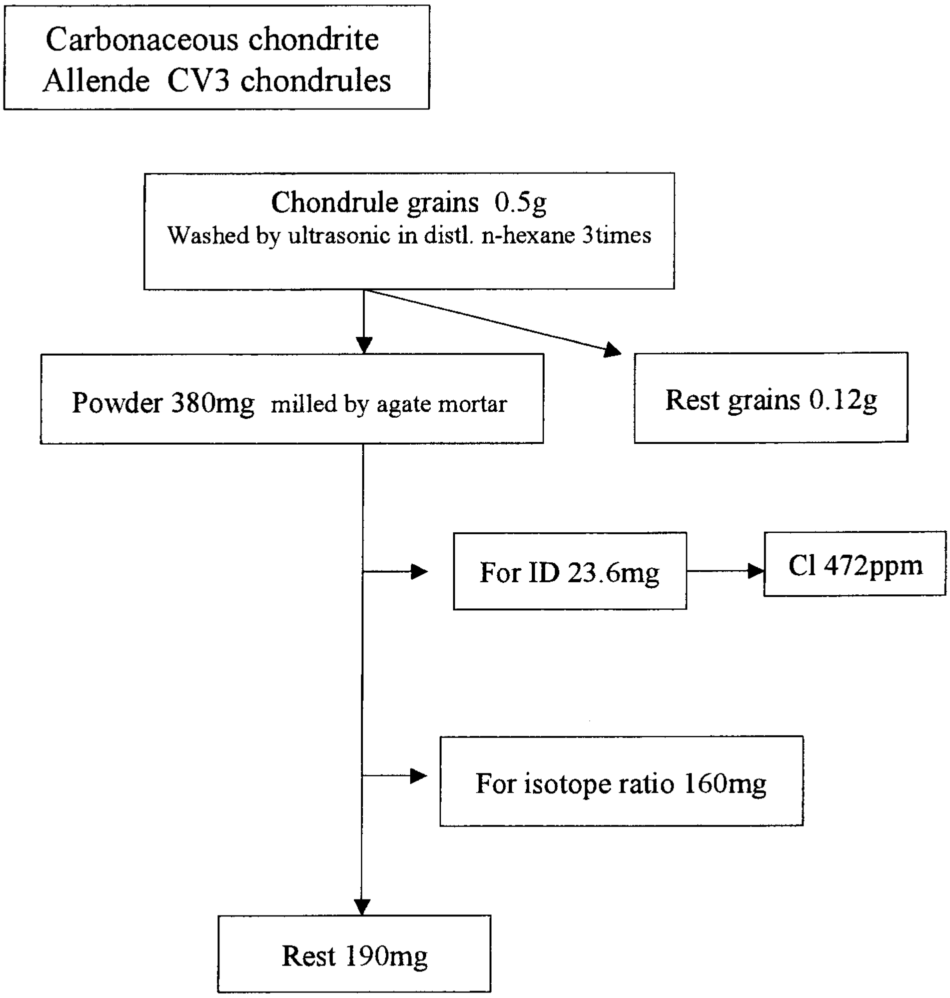


Figure A-9. A record of sample preparation for Allende chondrules.

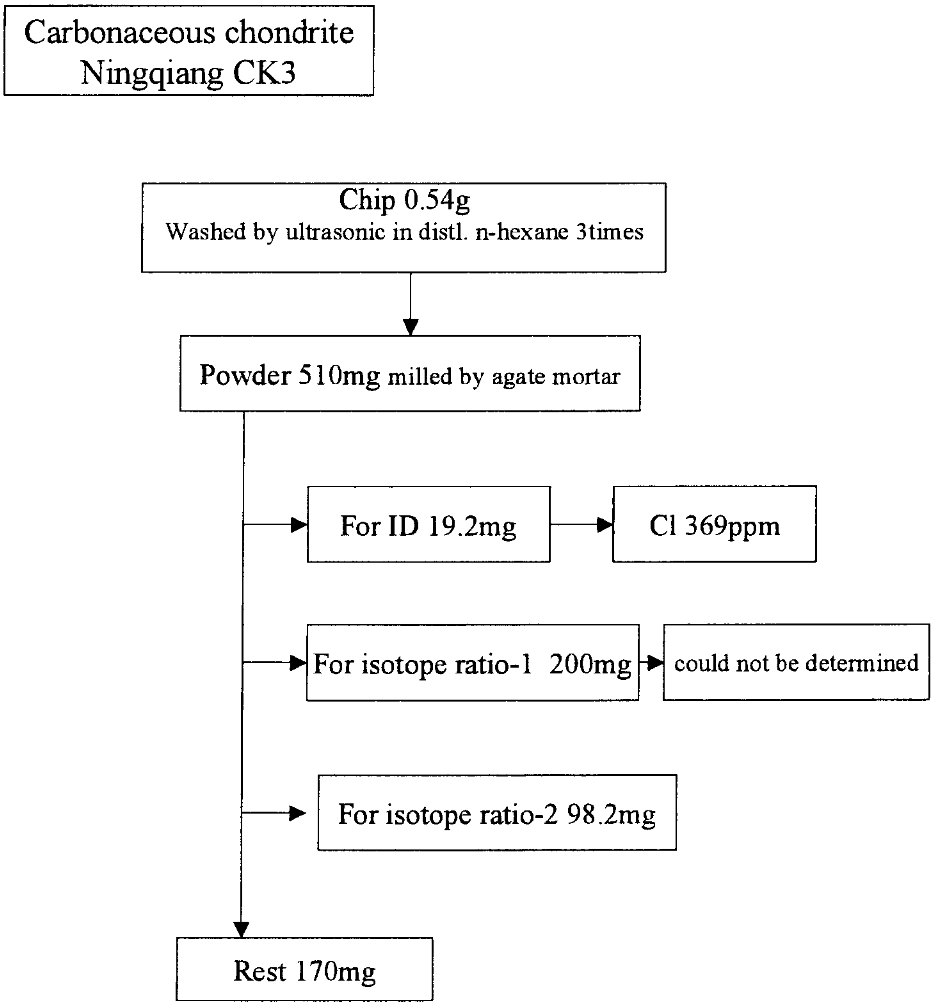
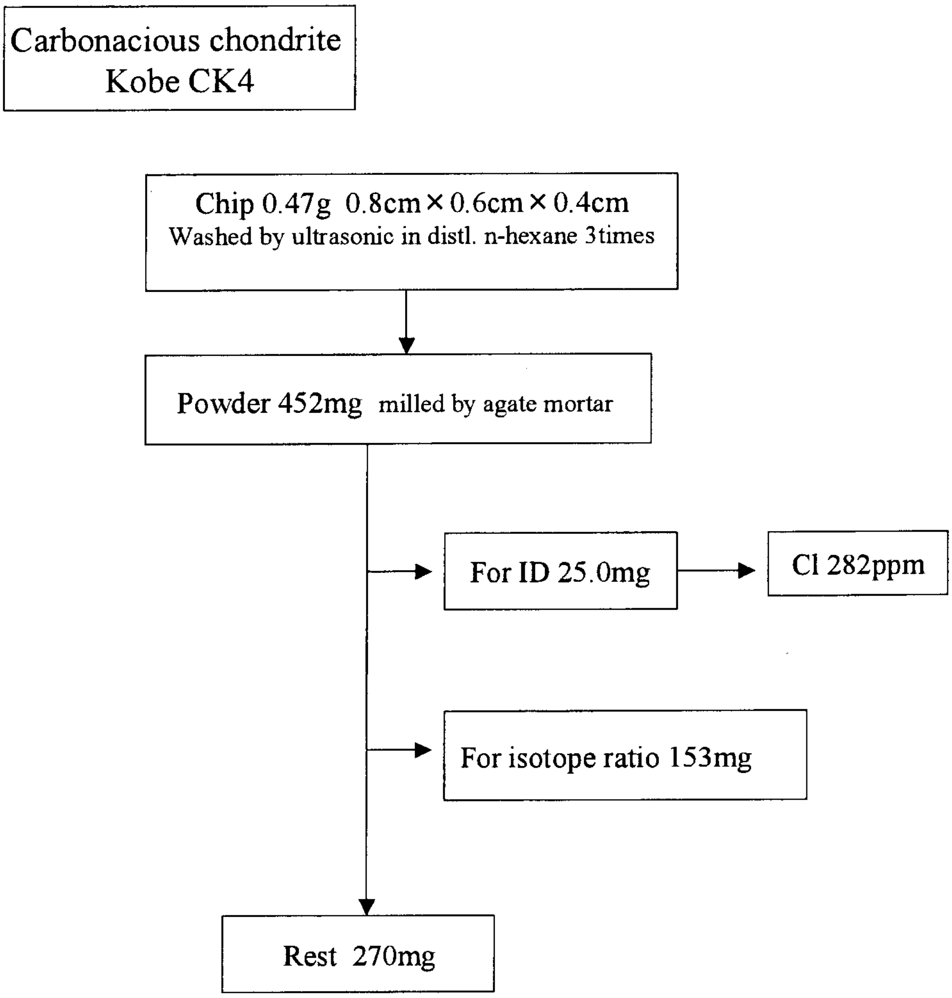


Figure A-10. A record of sample preparation for Ningqiang.



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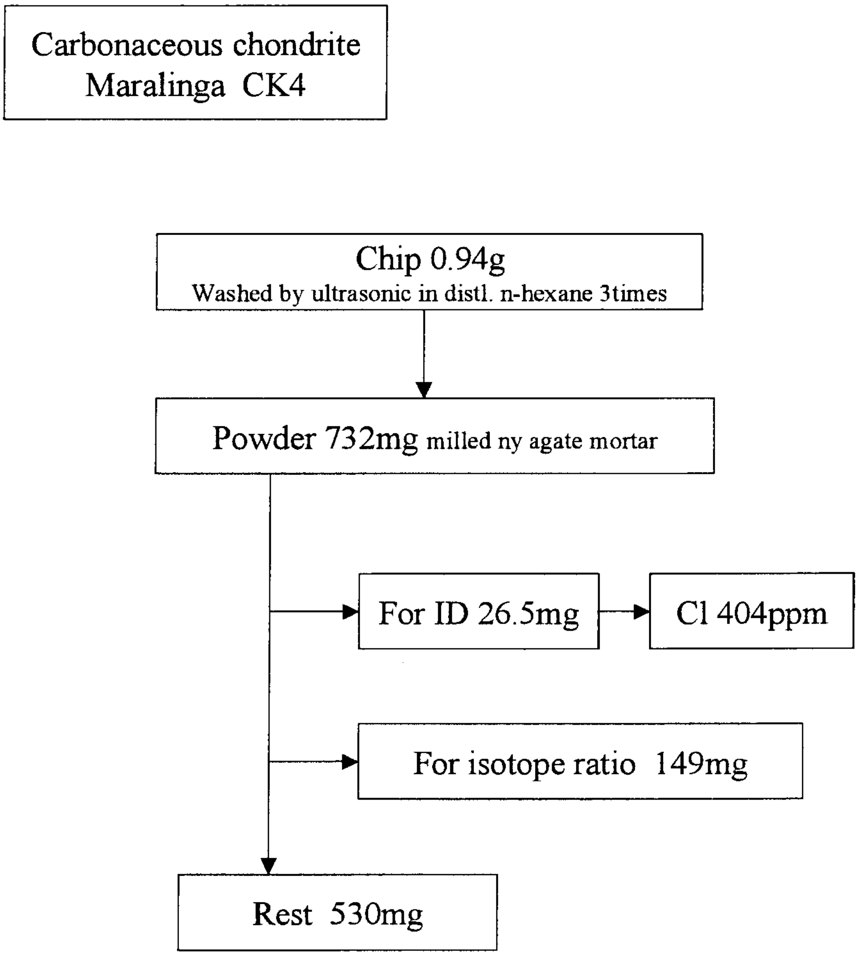

Figure A-12. A record of sample preparation for Maralinga.

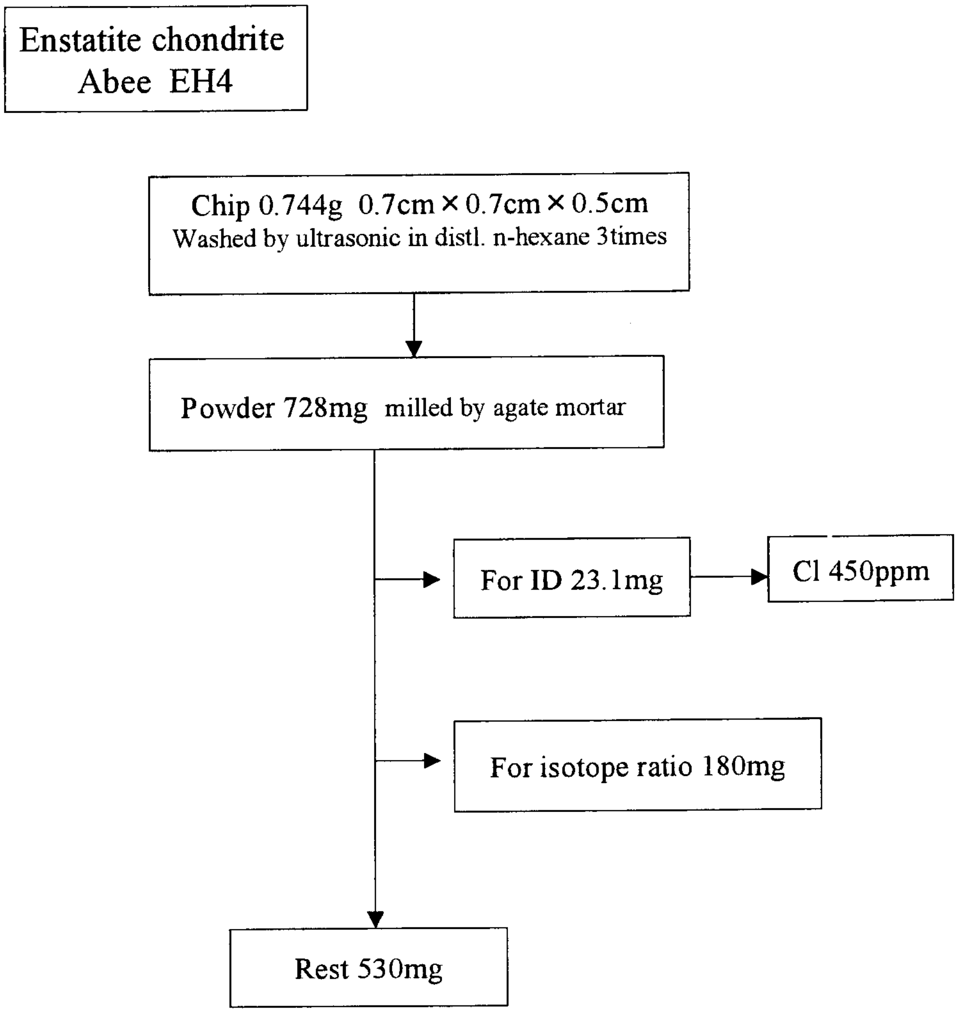

Figure. A-13. A record of sample preparation for Abee.

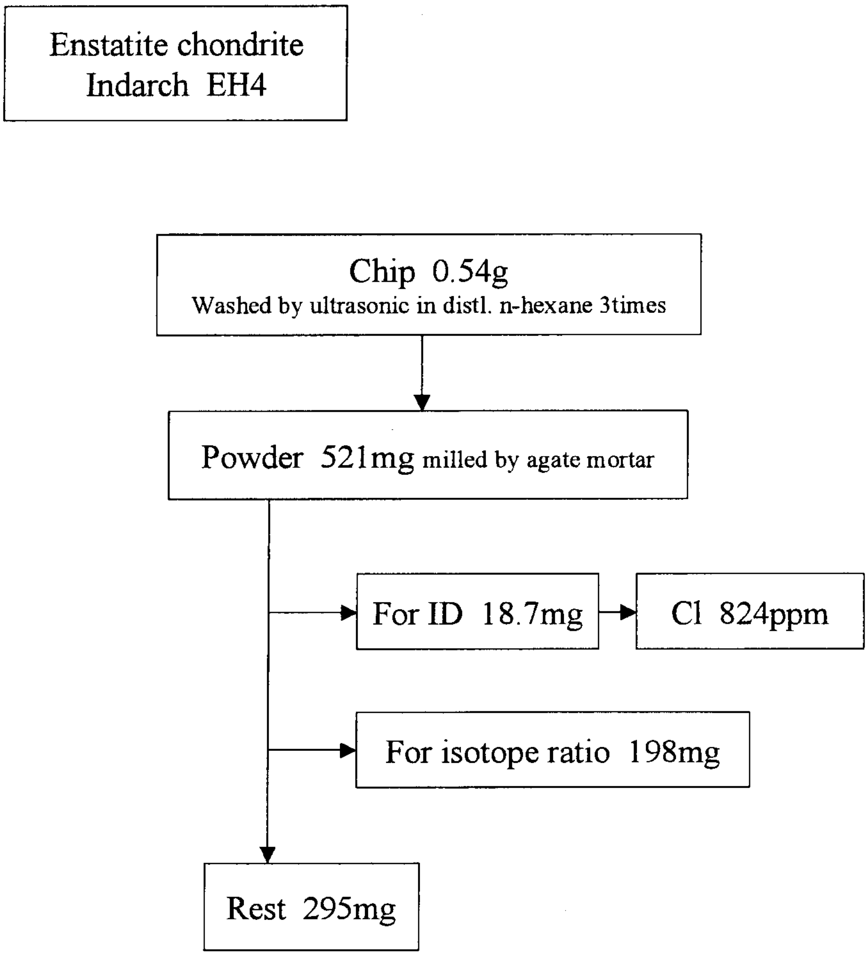

Figure A-14. A record of sample preparation for Indarch.

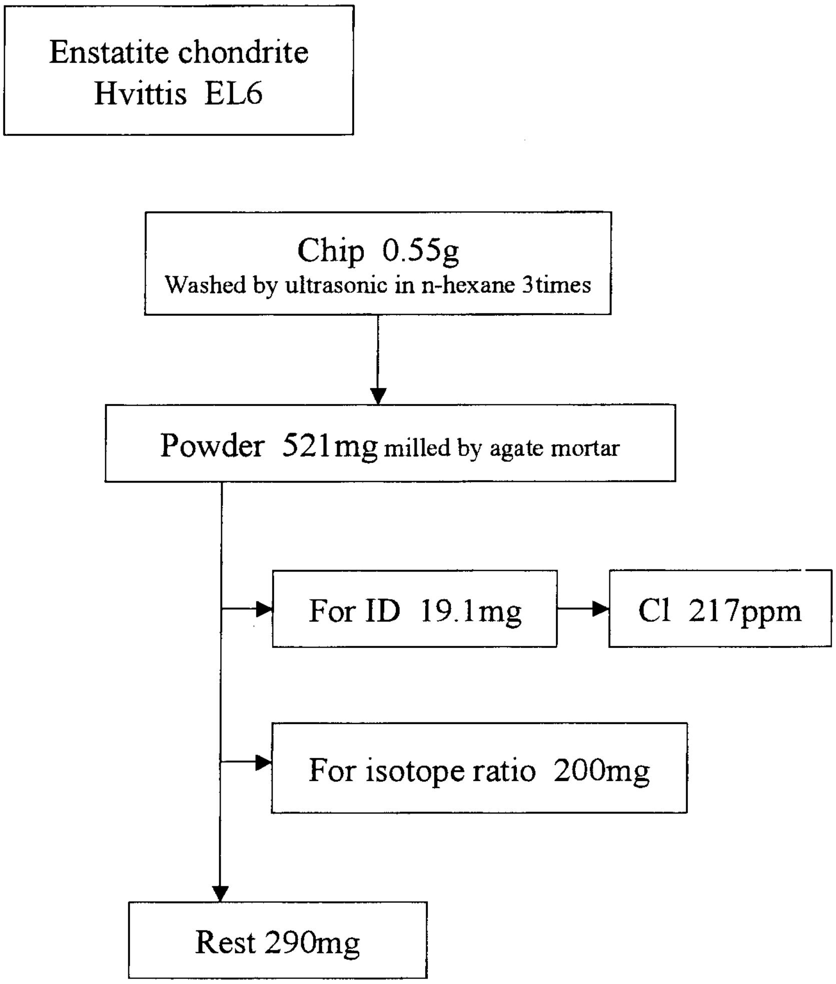

Figure A-15. A record of sample preparation for Hvittis.

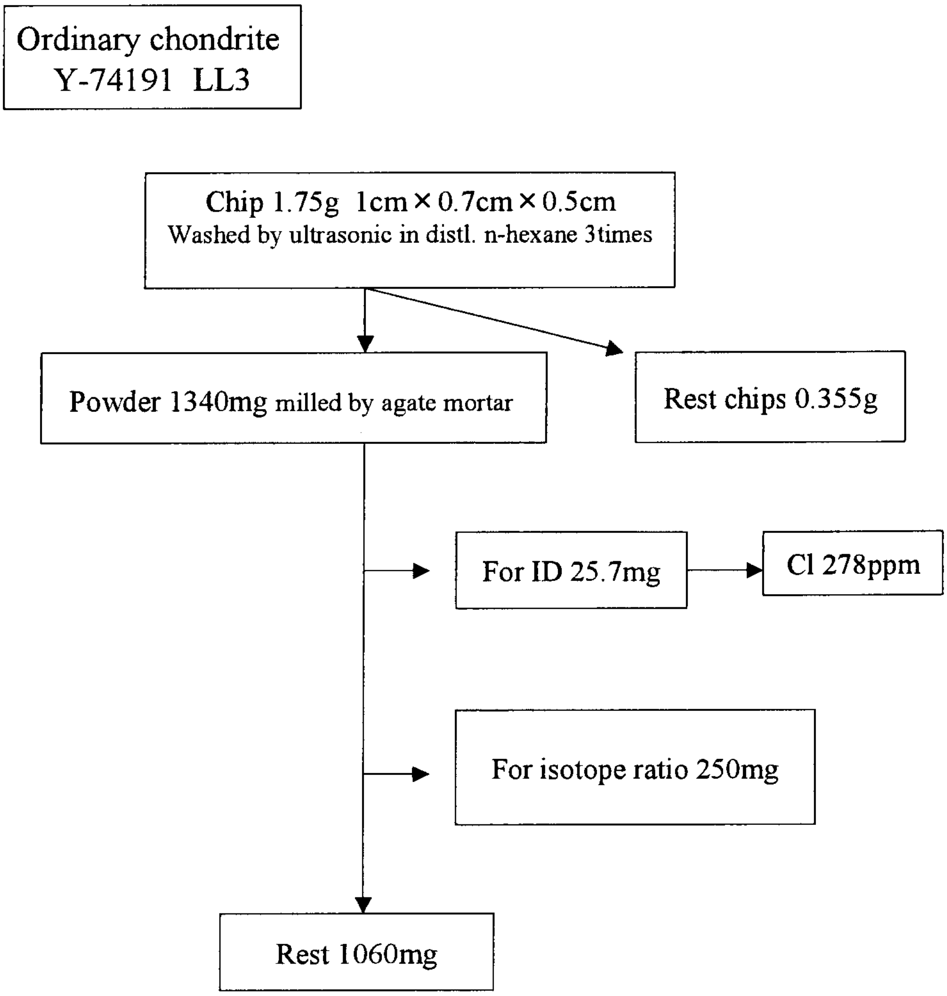

Figure A-16. A record of sample preparation for Y-74191.

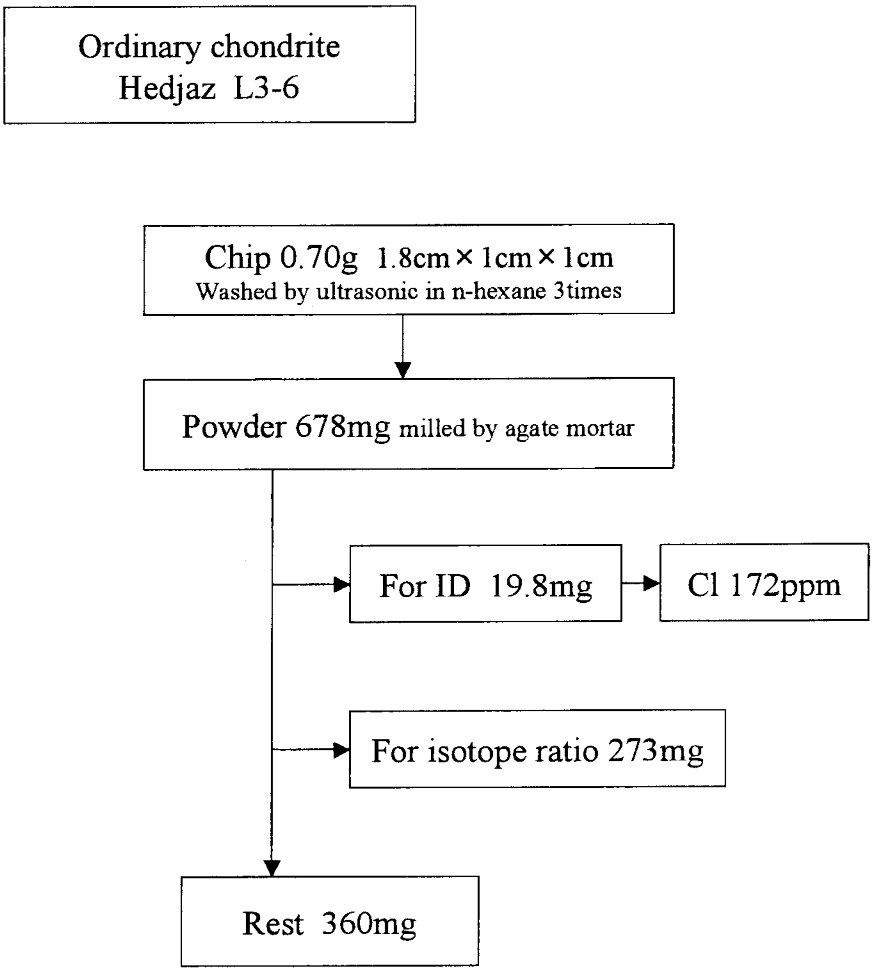

Figure A-17. A record of sample preparation for Hedjaz.

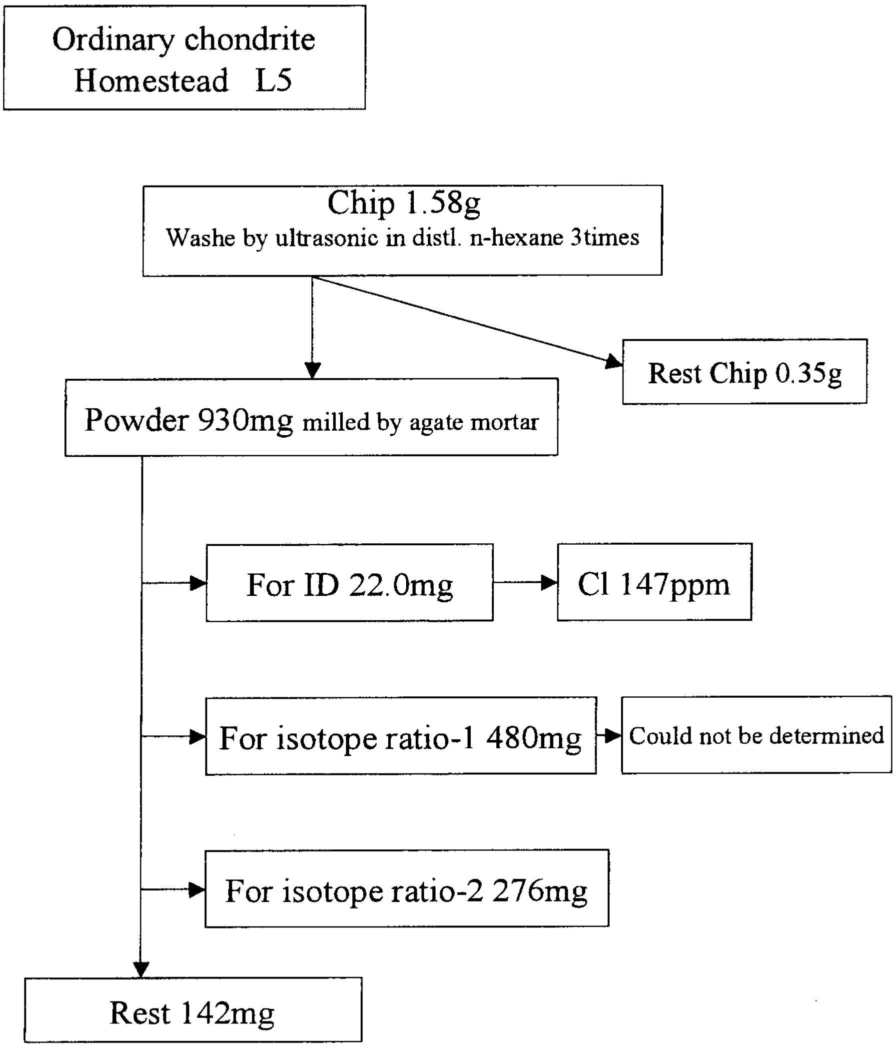

Figure A-18. A record of sample preparation for Homestead.

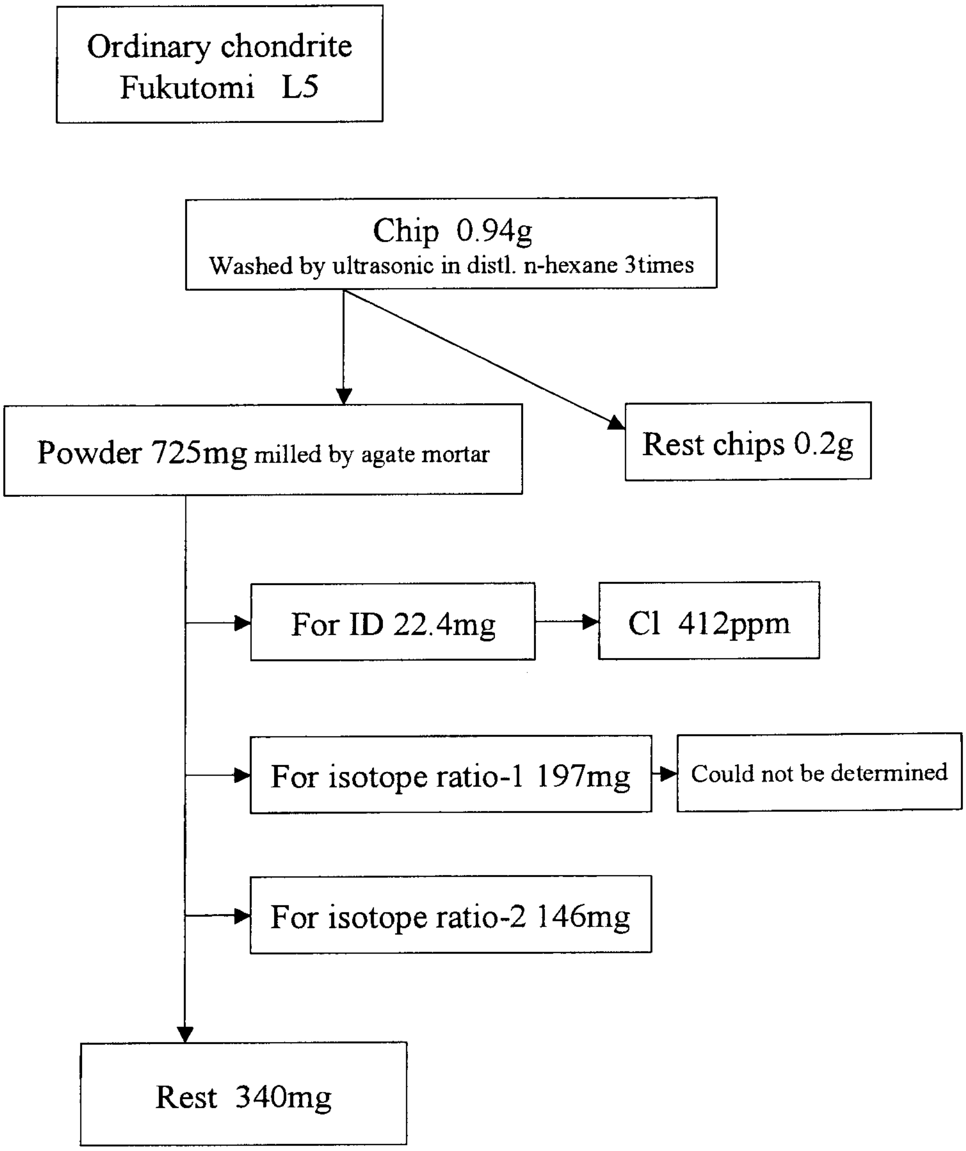

Figure A-19. A record of sample preparation for Fukutomi.

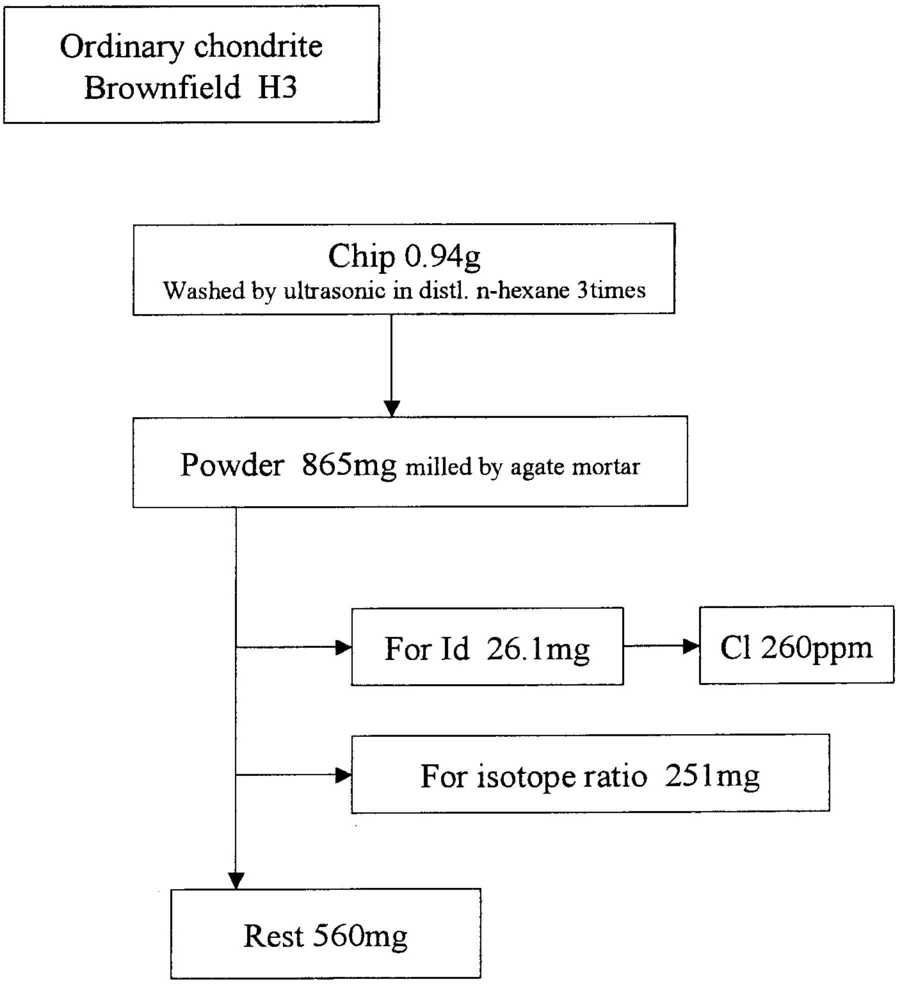

Figure A-20. A record of sample preparation for Brownfield.

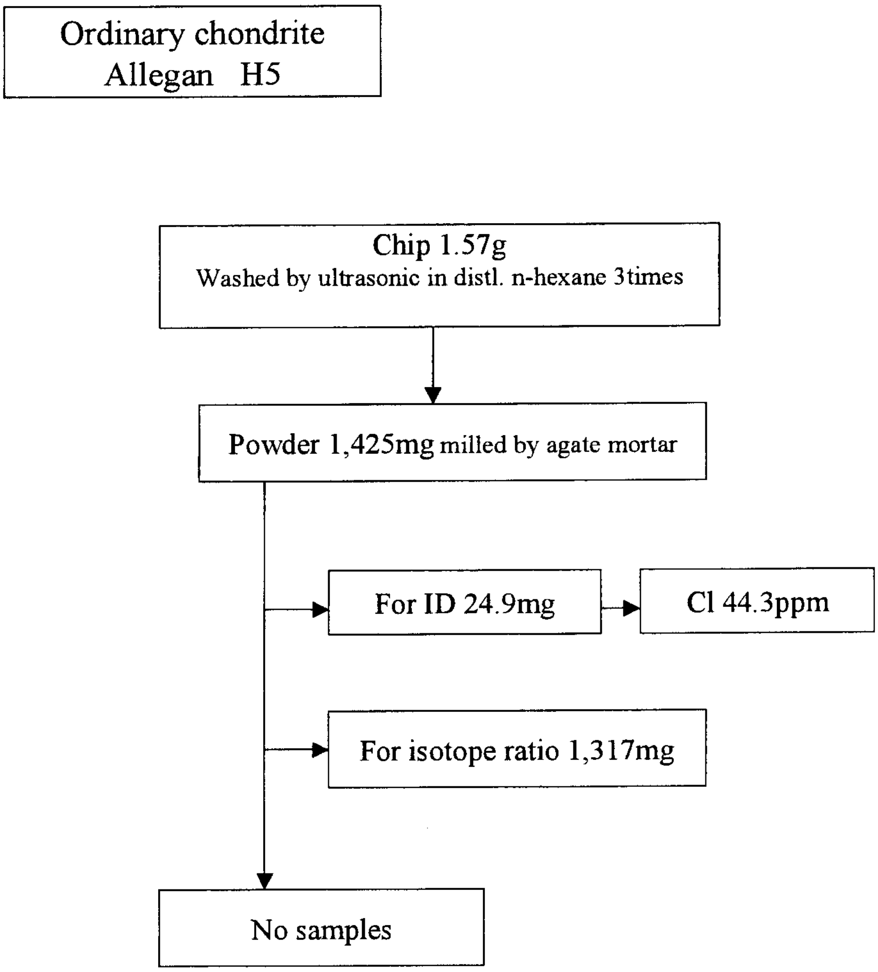

Figure A-21. A record of sample preparation for Allegan.

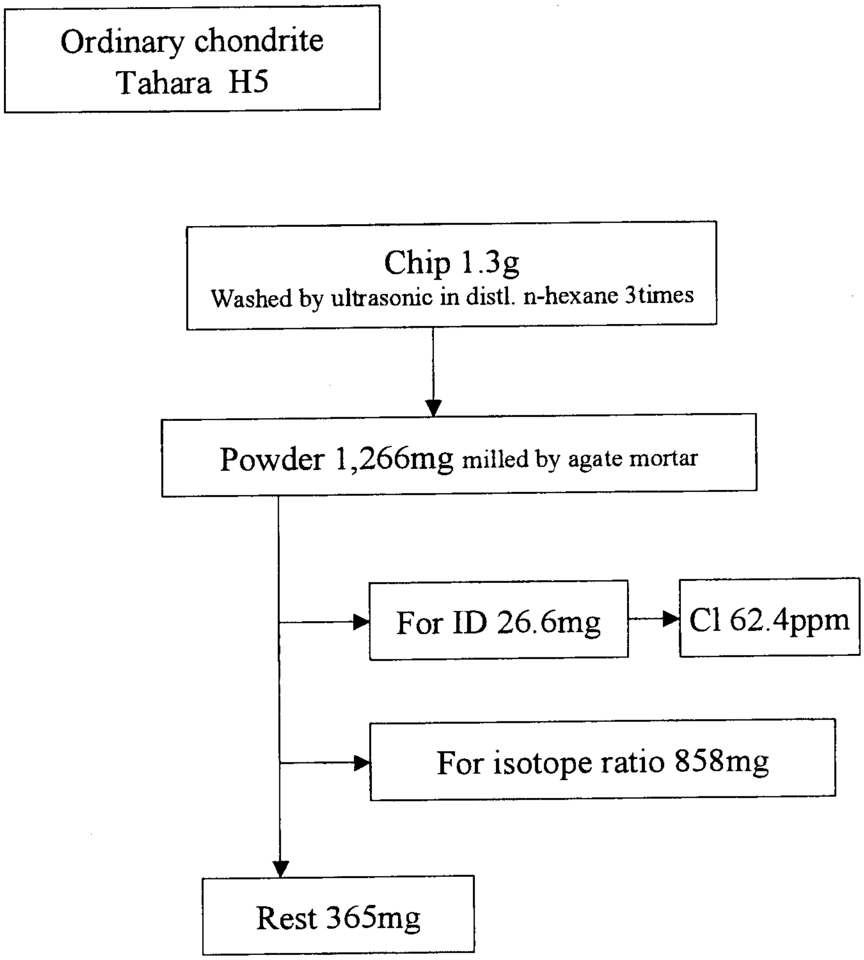

Figure A-22. A record of sample preparation for Tahara.

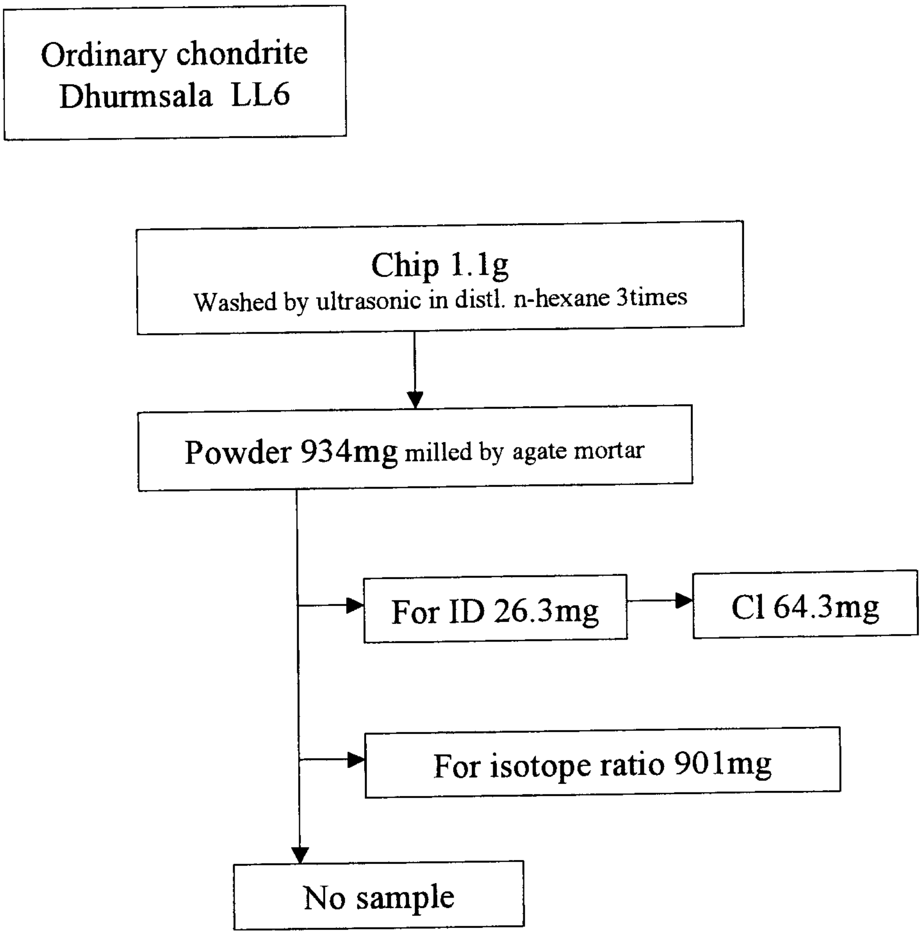

Fig. A-23. A record of sample preparation for Dhurmsala.