

## **DETERMINATION OF THE RARE EARTH ELEMENTS OF ROCK SAMPLES BY ICP-MS USING DIFFERENT SAMPLE DECOMPOSITION METHODS**

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### **ABSTRACT**

Rare earth elements were determined in 12 international standard reference rock samples using inductively coupled plasma mass spectrometry technique. Aim of this work was to find a relatively simple but reliable decomposition method for the purposes of REE determination. Sample solutions were produced by different sample decomposition methods: 1. closed vessel decomposition in a microwave digestion oven by different acid mixtures; 2. decomposition by LiBO<sub>2</sub> fusion in platinum crucibles. Effect of dilution was investigated. Final sample concentration of 0.2 gL<sup>-1</sup> was found to be optimal. Indium was used as internal standard.

HCl-HNO<sub>3</sub>-H<sub>2</sub>F<sub>2</sub> digestion followed by an evaporation step was not efficient enough to obtain a total recovery. In the case of digestion with acid mixtures there could occur some recovery problems for the heavy REEs, mainly with the mixture of HCl-HNO<sub>3</sub>-H<sub>2</sub>F<sub>2</sub> which is less aggressive than the H<sub>3</sub>PO<sub>4</sub>-HNO<sub>3</sub>-H<sub>2</sub>F<sub>2</sub> mixture, used alternatively. Fusion with LiBO<sub>2</sub> is a very simple process used extensively in our laboratory and gave good recovery data.

### **INTRODUCTION**

Determination of rare earth element (REE) concentrations and plotting of the REE patterns are very useful tools at understanding geochemical and petrogenetic processes. REE contents of the rocks deliver important information about the geological environment of the earth when they were formed.

There are several instrumental techniques suitable for REE determination like neutron activation analysis (NAA), X-ray fluorescent spectrometry (XRF), inductively coupled plasma atomic emission spectrometry (ICP-AES) and, more recently, inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS has very advantageous detection limits for the REEs which are considerably better than the other methods mentioned above.

Decomposition of the rock samples is a key question in the ICP-MS technique when the sample introduction happens by conventional solution nebulisation. Samples can contain acid-resistant mineral phases which can remain as an insoluble residue even after a strong mixed-acid attack. Decomposition by fusion is mostly successful but this method will significantly increase the total dissolved solids (TDS) content of the solution. ICP-MS technique can generally tolerate a TDS content of about 1 gL<sup>-1</sup>. So, the increased TDS level should be taken into consideration (i.e. samples must be diluted).

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In an early paper, DATE and HUTCHISON (1987) dissolved the samples by a mixture of  $\text{HNO}_3$ ,  $\text{HClO}_4$  and  $\text{HF}$  in open PTFE vessels. Insoluble residue was filtered, silica was removed by expelling as  $\text{SiF}_4$ , residue was dissolved and solutions were combined.

HIRATA et al. (1988) used a rather simple mixed acid decomposition procedure in PTFE beakers. For the purposes of comparison, they treated further an aliquot of the sample by removing of major elements on a cation-exchange resin column. Results were compared with thermal ionisation mass spectrometry isotope dilution (TIMS-ID) analysis results. They found that separation of REEs from matrix elements is essential to accurate determination. Their results obtained from the original solution (without separation of matrix), however, showed a reasonable agreement between the ICP-MS and TIMS-ID results, too. (Deviation was less than 10 %.) Regarding this fact, separation step may be omitted in some cases.

JENNER et al. (1990) describe a very simple  $\text{HF}$ - $\text{HNO}_3$  dissolution in screw-top PTFE bombs for sample preparation. Matrix correction was made by use of standard addition. They reported good or excellent accuracy and precision for most of the elements studied.

JARVIS (1990) evaluated two sample preparation techniques for determination of some geologically incompatible elements including REEs. She found good agreement between acid digestion and fusion results in a range of silicate and carbonate matrices. In some cases she obtained inaccurate data for some elements, probably due to dissolution problems with resistant mineral phases.

Similarly, SHOLKOVITZ (1990) made a comparison of sediment dissolution methods by  $\text{HF}$ -containing acid mixture and lithium metaborate fusion. His study showed that using  $\text{HF}$  dissolution some insoluble residues can remain which can host heavy REEs. Main component of these residues is the heavy mineral zircon. Fusion data yielded real total REE concentrations.

RIVOLDINI and FADDA (1994) used potassium-based fluxes ( $\text{K}_2\text{CO}_3$  and  $\text{K}_2\text{B}_4\text{O}_7$ ) for dissolution of the samples. Potassium and boron were removed from the solution, to keep the level of total dissolved solids content sufficiently low. This procedure was carried out by precipitation of K as  $\text{KClO}_4$  and by expelling of B as  $\text{BF}_3$ .

UCHINO et al. (1995) dissolved the rock samples by mineral acids in 5 subsequent steps. They carried out open vessel digestion using  $\text{HNO}_3$ ,  $\text{HClO}_4$  and finally  $\text{HF}$ . Final solution was made up by  $\text{HNO}_3$ . Samples studied in this paper were rather special because of their extremely high iron contents.

In a recent work, PERKINS and PEARCE (1996) report some aspects of the determination of REEs by laser ablation ICP-MS in fused glass samples. Finally they returned to the sample introduction by solution nebulisation to overcome the problems of sample inhomogeneity and standardisation. They used lithium borate flux (commonly used for XRF analysis) and dissolved the fused glasses. They are satisfied with the results obtained.

Summarizing all these experiences, it seemed to be worth to perform a systematic comparison of different decomposition methods.

## EXPERIMENTAL

### Instrumentation

Microwave assisted decompositions were carried out by a microwave digestion system made by MILESTONE, type: MEGA MLS 1200 with an MDR-100/6/100/110 rotor (high

pressure system, allowing maximum 110 bar internal pressure). Samples were transferred into TFM digestion vessels provided with a protection shield made of HTC. Acids were added, bombs were closed and placed into the rotor body. FAM-40 Acid Scrubber module was used for evaporation of samples if applied. Details of decomposition programs are listed in Table 1.

The ICP-MS instrument used was a VG PlasmaQuad II STE (FISONS Instruments). Instrumental operating conditions are listed in Table 2. Samples were introduced using a V-groove type nebulizer. Instrument was optimised for the  $^{115}\text{In}$  signal. No any mathematical correction was used to eliminate isobaric spectral interferences (interference by  $\text{BaO}^+$  on Eu and LREE oxides on HREEs). The ions chosen for the determinations are listed in Table 3.

### **Samples**

Two sets of international standard reference materials were used. One of them was a set of Chinese made rock samples. These samples were attested for more than 60 elements including REEs, of course. Others were selected standard reference rock samples made for the former COMECON, in the former GDR (German Democratic Republic). These samples were attested very well for the main components but for some trace elements only. Attestation for REEs was carried out mainly on the basis of NAA analyses. SRMs used are listed in Table 4.

### **Chemicals and Reagents**

High purity distilled, deionised water was used throughout the work (Purite HP Still Plus reverse osmosis system). Acids used for decomposition were at least analytical-reagent grade products. Hydrochloric acid 36% and nitric acid 70% were BDH products, 'SpectrosoL' quality. Hydrofluoric acid 40% was from BDH, 'Aristar' grade (analytical-reagent grade by Carlo Erba was not pure enough). Ortho-phosphoric acid 85% was from MERCK, 'Suprapur' grade. Boric acid was analytical-reagent grade and used in saturated solution.

Lithium metaborate fluxing agent was from BDH, 'SpectrosoL' grade.

Stock solution for calibration standards was a mixed solution containing La, each REE plus Y and Th ( $10\text{ mgL}^{-1}$  each) and was from SPEX Industries (SPEX-1 ICP-MS Calibration Standard solution). Analytical standard solutions were made up by dilution of this stock solution. Final acid concentration was 1% of nitric acid.

Stock solution for indium internal standard was a monoelement solution ( $1\text{ gL}^{-1}$ ) and was from BDH, 'SpectrosoL' grade. This solution was diluted to give a concentration of  $1\text{ mgL}^{-1}$ . The latter solution was added to the sample solutions to give a final concentration of  $10\text{ }\mu\text{gL}^{-1}$ .

### **Sample Preparation Procedures**

Samples were finely powdered and homogenised in ball mills (average grain size was below  $60\text{ }\mu\text{m}$ ).

Amongst the aims of this work was to find a decomposition procedure which is suitable for determination of REEs but simple and rapid for routine work. For this reason we tried out several procedures including dissolution procedures with different acid mixtures and a fusion. Decomposition procedures with acid mixtures were carried out in microwave decomposition unit.

Decomposition with acid mixtures is generally preferred for the purposes of ICP-MS analysis in order to keep the total dissolved solid level sufficiently low. (TDS should remain below  $1 \text{ gL}^{-1}$ .) Decomposition procedures in this study were aimed to obtain total dissolution of samples. For this reason, use of hydrofluoric acid was unavoidable to destroy silica lattice structure. To bind the excess amount of fluoride we generally add boric acid to the solution. TDS level, however, will increase because of this fact. In order to keep TDS level low, we made a trial to remove the excess fluoride by evaporation (Method 1.1., see below). We tried out decompositions with mixed acids and addition of boric acid, too. This procedure was carried out in two steps: acidic decomposition first, boric acid addition afterwards. Because of this fact, procedure is rather time-consuming (Method 1.2., see below). For that reason we tried to apply a decomposition procedure in one step only. In this method boric acid was added already into the acid mixture. In this case phosphoric acid as a more effective agent was used instead of hydrochloric acid (Method 1.3., see below).

### 1. Microwave assisted decomposition procedures using different acid mixtures

#### 1.1. Decomposition in two steps including an evaporation step

0.2 g of samples were weighed into TFM digestion vessels. Samples were digested by a mixture of concentrated HCl, HNO<sub>3</sub> and H<sub>2</sub>F<sub>2</sub> (1 mL of each acid was used). Vessels were closed and digestion program (program 1.1., see Table ) was started. After finishing program, vessels were cooled down, opened and placed into the evaporation tray. (Lids were handled carefully, rinsing solution droplets into the vessel body to avoid any loss.) Evaporation stage was started. After finishing, evaporation residues were dissolved in 5 mL of 2N nitric acid and made up to 50 mL with deionised water. Before analysis these solutions were diluted by a factor of 20, so the final sample concentration was  $0.2 \text{ gL}^{-1}$ . Final solutions contained  $10 \text{ }\mu\text{gL}^{-1}$  In as internal standard.

#### 1.2. Decomposition in two steps including a step with addition of boric acid

0.25 g of samples were weighed into TFM digestion vessels. Samples were digested by a mixture of concentrated HCl, HNO<sub>3</sub> and H<sub>2</sub>F<sub>2</sub> (1 mL of each acid was used). Vessels were closed and digestion program (program 1.2., see Table ) was started. After finishing program, vessels were cooled down, opened and 10 mL of saturated boric acid solution was added. Vessels were closed again and second stage of temperature program was started. After finishing, vessels were cooled down and opened. Solutions were transferred into volumetric flasks containing 5 mL of 2N nitric acid and made up to 50 mL with deionised water. These solutions were diluted 25-fold before analysis, so the final sample concentration was  $0.2 \text{ gL}^{-1}$ . Final solutions contained  $10 \text{ }\mu\text{gL}^{-1}$  In as internal standard.

#### 1.3. Decomposition in one step

0.25 g of samples were weighed into TFM digestion vessels. Samples were digested by a mixture of 1 mL of cc. H<sub>3</sub>PO<sub>4</sub>, 1 mL of cc. HNO<sub>3</sub> and 1.5 mL of cc. H<sub>2</sub>F<sub>2</sub>. Also 0.4 g of crystalline boric acid was added in this step. Vessels were closed and digestion program was run (program 1.3., see Table ). After finishing digestion, vessels were cooled down and opened. Solutions were transferred into volumetric flasks containing 5 mL of 2N nitric acid and made up to 50 mL with deionised water. These solutions were diluted 25-fold before analysis, so the final sample concentration was  $0.2 \text{ gL}^{-1}$ . Final solutions contained  $10 \text{ }\mu\text{gL}^{-1}$  In as internal standard.

## 2. Fusion with LiBO<sub>2</sub>

0.5 g of samples were weighed into platinum crucibles. 1.16 g of lithium metaborate was added and mixed thoroughly. Crucibles were covered with platinum lids and were placed into electric furnace. Temperature was gradually increased up to 1060 °C. Reaching final temperature, samples were fused for 30 minutes. Crucibles were allowed to cool and then transferred into 100 mL glass beakers, covered with sufficient amount (about 50 mL) of deionised water and 10 mL of 1:1 HCl. Fusion melt was dissolved on a magnetic stirrer plate. After complete dissolution solution was transferred into volumetric flask and made up to 250 mL. Before analysis, this solution was diluted tenfold, so the final sample concentration was 0.2 gL<sup>-1</sup>. (Total dissolved solid content remained below 1gL<sup>-1</sup>.) Final solution contained 10 µgL<sup>-1</sup> In as internal standard.

## RESULTS

Method 1.1. (decomposition in two steps including an evaporation step) seems to have the advantages as follows: keeps the total dissolved solids level sufficiently low and this is a method which does not introduce boron (neither as boric acid nor as lithium metaborate) into the analysis system. This fact is very important in the practice because boron has got a strong memory effect in the ICP-MS technique. Washing-out from the system takes extremely long, even some days. Unfortunately, this method did not prove suitable for our purposes. Evaporation step could not be controlled, the efficiency is different from sample to sample. Recovery was found very poor, less than 1% for analyte elements because of the low solubility of the REE fluorides.

Use of reagents containing boron was unavoidable, consequently. We tried out three decomposition methods using boron-containing reagents. Decomposition methods by acid mixtures were carried out in microwave oven. The differences between the two methods are as follows: Method 1.2. is carried out in two steps (addition of boric acid takes place in a second step). Method 1.3. consists of one step only, so the capacity of the method is twice better. Moreover, this method applies phosphoric acid which allows to use higher decomposition temperature because of the higher boiling point of the phosphoric acid. So, in some cases this method can be considered as more effective one.

For most samples these methods gave similar recoveries, close to 100 %. In the case of the SRM Clay shale TB-2, Method 1.2. (decomposition with HCl-HNO<sub>3</sub>-H<sub>2</sub>F<sub>2</sub> mixture) gave poorer recoveries for the heavy REEs while recoveries for the light REEs were reasonably good. This fact can be clearly explained by the presence of small amount of refractory mineral phases. The HREEs are enriched in these phases. Method 1.2. is not effective enough to destroy these refractory minerals.

Method 2. (fusion with LiBO<sub>2</sub>) gave good recoveries, too. This method is rapid, simple and very well-known for our laboratory staff because we use that regularly for determination of main components of rock samples. The only disadvantage is the relatively high blank value of the fusion agent for La and Ce. The blank level is some ppm calculated for the original solid sample. Despite of this drawback, in the future we will apply mostly this fusion procedure for REE determination.

Detection limits (10σ values) listed in Table are obtained with the LiBO<sub>2</sub> fusion method, calculated for the solid sample. The ICP-MS instrument is sensitive enough to determine isotopes even with an isotope abundance of about 10 % only (Nd, Sm, Yb).

Sample concentration was generally 2-5 gL<sup>-1</sup> using decomposition methods listed above. This concentration is necessary for the determination of a number of trace elements by ICP-AES technique. For the ICP-MS measurements, however, a significant dilution is necessary. Using V-groove nebuliser, a dilution factor of 10 was found to be optimal for the LiBO<sub>2</sub> fusion, while for the closed vessel decompositions with acid mixtures a dilution factor of 25 was found to be suitable. This generally means a final sample concentration of 0.2 gL<sup>-1</sup> and a further amount of 0.5 gL<sup>-1</sup> of the decomposition reagents. The total dissolved solids (TDS) content is about 0.7 gL<sup>-1</sup>, consequently. Using a Meinhardt nebuliser, especially on a long workday, it is practical to decrease the sample concentration by a further factor of 2. So, the total dissolved solids contents will decrease below 0.4 gL<sup>-1</sup>.

One of the main problems is the choice of isotopes used for determinations. In the case of monoisotopic elements there is no possibility of choice. In the case of elements having several isotopes it is important to be careful to use an isotope without isobaric overlap. For example, Nd is determined on the isotope 143 because isotopes 142 and 144 are interfered by the <sup>142</sup>Ce and <sup>144</sup>Sm isotopes. Measurement on an isotope with an isotope abundance of about 10 % means that the analytical sensitivity of the element in question will be only the 10 % of the sensitivity of a monoisotopic element.

Interference of the BaO on the isotopes of Eu is an existing problem. This interference is not significant but in the case of higher Ba concentrations (over some thousands ppm Ba) must be corrected for.

Interferences by the light REE oxides on the heavy REEs must be corrected for only in the case of extremely high HREE concentrations. Regarding the data obtained by HIRATA et al. or RIVOLDINI and FADDA, percentages of metal oxide to parent ion are generally below 1%, so correction for isobaric interference from oxide ions may be omitted. Unnecessary application of correction can increase the level of uncertainties.

For the calibration diluted, aqueous calibration solutions were used. 10 µgL<sup>-1</sup> In was used as internal standard. Use of internal standard is necessary because the occurrence significant instrumental drift is very well-known in the ICP-MS technique. Indium is very suitable internal standard in the mass range of 139-175 amu. Serious drift problems usually occur at the low (below 70 amu) and the high (above 200 amu) mass numbers.

Our experiences from element to element were as follows.

Lanthanum:

There is no any serious problem except for the high blank value using decomposition by fusion with LiBO<sub>2</sub>.

Cerium:

The situation is very similar to the lanthanum..

Praseodymium:

Chinese SRMs are very reliable for all certified elements while the former COMECON SRMs are not accurate enough. This is the case for the SRM Clay shale TB-2. Certified concentration value is not correct.

Neodymium:

Isotope 143 was used. There is no problem with the sensitivity although the isotope abundance of this isotope is 12.2% only.

Samarium:

No problem.

#### Gadolinium:

There are several problems. In the case of SRMs Granite GM, Basalt BM and Clay shale TB-2 certified concentration values seem to be incorrect. Interference by praseodymium does not seem to be significant.

#### Europium:

Measured concentration values are in pretty good agreement with the certified values. Well-known interference by the  $\text{BaO}^+$  polyatomic ion was not significant. (Maximum barium concentration in the samples remained below 2000 ppm.)

#### Terbium:

Problems with the certified concentration value in the SRM Clay shale TB-2 can be seen again. Interference by neodymium is negligible. Going in the direction of the heavier REEs, beginning from the terbium, in the SRM Clay shale TB-2 the measured concentration values in the solutions decomposed by acid mixtures (Method 1.2. and 1.3.) and  $\text{LiBO}_2$  fusion are different for the heavy REEs. This phenomenon will be discussed further on.

#### Dysprosium:

Certified concentration values in the SRMs Clay shale TB-2 and Granite GM seem to be incorrect. In the Clay shale TB-2 measured concentrations are different in the case of acidic and fusion decomposition.

#### Holmium:

Certified concentration values in the SRMs Clay shale TB-2 and Granite GM seem to be incorrect. Deviation of the measured concentration values is higher (absolute concentration values are rather low). In the SRM Clay shale TB-2 the measured concentrations are different in the case of acidic and fusion decomposition.

#### Erbium:

In the SRM Clay shale TB-2 the measured concentrations are different in the case of acidic and fusion decomposition.

#### Thulium:

In the SRM Clay shale TB-2 the measured concentrations are different in the case of acidic and fusion decomposition. Problems with the certified concentration values.

#### Ytterbium and lutetium:

In the SRM Clay shale TB-2 the measured concentrations are different in the case of acidic and fusion decomposition.

So, a difference could be seen very well from the analytical results of the SRM Clay shale TB-2 between the two kinds of closed vessel acidic decompositions. Decomposition by  $\text{HCl-HNO}_3\text{-H}_2\text{F}_2$  mixture was proven significantly less efficient than the decomposition with  $\text{H}_3\text{PO}_4\text{-HNO}_3\text{-H}_2\text{F}_2$  mixture. The latter one can provide higher decomposition temperature. So, its efficiency is comparable with the fusion method. This fact might be explained by the presence of refractory mineral phases in the Clay shale. Heavy REEs are probably enriched in these phases. Decomposition method should be efficient enough to destroy these phases, too.

## CONCLUSIONS

Although the decomposition techniques were not specially developed for ICP-MS analysis (they are commonly used in the laboratory for the determination of major and trace elements of rocks), most of them produced acceptable results for the rare earth elements comparing with the certified values of SRMs. Method 1.1 (decomposition in two

steps including an evaporation step) was the only method producing unacceptable results. 0.2 gL<sup>-1</sup> sample concentration proved to be optimal for the analysis.

Chinese standard reference rock samples are very reliable for the REE concentration values but some of the former COMECON standards are not. For example at the clay shale TB-2 the praseodymium, gadolinium, terbium, holmium and thulium or at the basalt BM and granite GM standards the gadolinium, dysprosium and holmium contents do not show good agreement with the reference values. In some cases perhaps the number of analyses (done for the purposes of certification) was not sufficient to provide proper precision.

No mathematical correction was used to eliminate the BaO polyatomic ion interference or the light REE oxides polyatomic ion interference on the heavy REEs. In the case of extreme high barium or light REE concentrations the correction is necessary.

There is a huge difference between the recovery values of the light and heavy REEs in clay shale TB-2 comparing the last three decomposition methods (methods 1.2., 1.3. and 2.). The LREEs gave the same results in the case of all the three decompositions, the HREEs showed much less decomposition efficiency by the HCl-HNO<sub>3</sub>-H<sub>2</sub>F<sub>2</sub> method (method 1.2.) than the more aggressive H<sub>3</sub>PO<sub>4</sub>-HNO<sub>3</sub>-H<sub>2</sub>F<sub>2</sub> method (method 1.3.) or the alkaline fusion (method 2.). The reason of this difference is, the HREEs accumulate in the refractory minerals of the clay shale TB-2.

In the case of the refractory minerals forming elements the microwave decompositions are not efficient enough, for total decomposition of those elements the alkaline fusion is necessary.

## REFERENCES

- DATE, A. R. and HUTCHISON, D. (1987): Determination of Rare Earth Elements in Geological Samples by Inductively Coupled Plasma Source Mass Spectrometry *J. Anal. At. Spectrom.*, **2**, 269-276
- HIRATA, T., SHIMIZU, H., AKAGI, T., SAWATARI, H. and MASUDA, A. (1988): Precise Determination of Rare Earth Elements in Geological Standard Rocks by Inductively Coupled Plasma Source Mass Spectrometry *Anal. Sci.*, **4**, 637-643
- JARVIS, K. E. (1990): A critical evaluation of two sample preparation techniques for low-level determination of some geologically incompatible elements by inductively coupled plasma-mass spectrometry *Chem. Geol.*, **83**, 89-103
- JENNER, G. A., LONGERICH, H. P., JACKSON, S. E. and FRYER, B. J. (1990): ICP-MS – A powerful tool for high-precision trace-element analysis in Earth sciences: Evidence from analysis of selected U.S.G.S. reference samples *Chem. Geol.*, **83**, 133-148
- PERKINS, W. T. and PEARCE, N. J. G. (1996): Problems and Progress in the Determination of Trace and Ultra Trace Elements by ICP-MS and the Application to Petrogenetic Studies of Igneous Rocks V. M. Goldschmidt Conference, Heidelberg, 1996 *J. of Conf. Abstr.*, **1**, 459
- RIVOLDINI, A. and FADDA, S. (1994): Inductively Coupled Plasma Mass Spectrometric Determination of Low-level Rare Earth Elements in Rocks Using Potassium-based Fluxes for Sample Decomposition *J. Anal. At. Spectrom.*, **9**, 519-524
- SHOLKOVITZ, E. R. (1990): Rare-earth elements in marine sediments and geochemical standards *Chem. Geol.*, **88**, 333-347
- UCHINO, T., EBIHARA, M. and FURUTA, N. (1995): Determination of Rare Earth Elements in Precambrian Sediments at Isua by Inductively Coupled Plasma Mass Spectrometry *J. Anal. At. Spectrom.*, **10**, 25-30

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*Sample preparation details*

## Microwave decompositions - MILESTONE MEGA MLS 1200

## Program 1.1.

| Time(min) | Power (W)    |
|-----------|--------------|
| 5         | 250          |
| 5         | 400          |
| 10        | 500          |
| 5         | 250          |
| 2         | ventillation |

cool down and put into evaporation module

|    |              |
|----|--------------|
| 10 | 700          |
| 3  | ventillation |

## Program 1.2.

| Time (min) | Power (W)    |
|------------|--------------|
| 8          | 250          |
| 6          | 400          |
| 6          | 500          |
| 5          | 250          |
| 2          | ventillation |

cool down and add 10 ml saturated boric acid

|   |              |
|---|--------------|
| 5 | 250          |
| 5 | 400          |
| 2 | ventillation |

## Program 1.3.

| Time (min) | Power (W)    |
|------------|--------------|
| 8          | 250          |
| 5          | 400          |
| 15         | 600          |
| 2          | ventillation |

TABLE 2.

*ICP-MS operating parameters:*

|                    |                                     |
|--------------------|-------------------------------------|
| Instrument         | : VG Elemental PlasmaQuad II STE    |
| Plasma             | : all argon                         |
| Forward power      | : 1350 W                            |
| Reflected power    | : <5 W                              |
| Coolant gas flow   | : 14.0 l/min                        |
| Auxiliary gas flow | : 1.4 l/min                         |
| Nebuliser gas flow | : 0.956 l/min                       |
| Peristaltic pump   | : Gilson Minipuls 3                 |
| Uptake rate        | : about 0.9 ml/min                  |
| Nebuliser          | : V-groove                          |
| Spray chamber      | : double-pass, water-cooled (10 °C) |
| Sampling cone type | : Ni, 1 mm orifice                  |
| Skimmer            | : Ni, VG design                     |
| Acquisition mode   | : scan                              |
| Detector mode      | : dual                              |
| Channels/amu       | : 20                                |
| Dwell time         | : 320 µs/channel                    |
| Acquisition time   | : 60 s                              |
| Scanned region     | : 111.6-180.4 amu                   |
| Skipped region     | : 117.4-133.6 amu                   |
| Internal standard  | : <sup>115</sup> In (10 µg/l)       |

TABLE 3.

*Isotopes chosen for analysis*

| Element | Isotope | Isotope abundance<br>% | Crustal abundance<br>ppm | Detection limit-10s<br>ppm |
|---------|---------|------------------------|--------------------------|----------------------------|
| La      | 139     | 99.9                   | 18                       | 0.5                        |
| Ce      | 140     | 88.5                   | 46                       | 0.5                        |
| Pr      | 141     | 100                    | 6                        | 0.1                        |
| Nd      | 143     | 12.2                   | 24                       | 0.1                        |
| Sm      | 147     | 15                     | 7                        | 0.1                        |
| Eu      | 151     | 47.8                   | 1                        | 0.1                        |
| Gd      | 157     | 15.7                   | 6                        | 0.1                        |
| Tb      | 159     | 100                    | 0.9                      | 0.1                        |
| Dy      | 163     | 24.9                   | 5                        | 0.1                        |
| Ho      | 165     | 100                    | 1                        | 0.1                        |
| Er      | 166     | 33.6                   | 3                        | 0.1                        |
| Tm      | 169     | 100                    | 0.2                      | 0.1                        |
| Yb      | 171     | 14.3                   | 0.8                      | 0.1                        |
| Lu      | 175     | 97.5                   | 0.8                      | 0.1                        |

*International Standard Reference Rock Samples used in this study*

## Chinese Rock Standards\*:

GBW 7109 Ijolite-Syenite  
GBW 7110 Trachite Andesite  
GBW 7111 Granodiorite  
GBW 7112 Gabbro  
GBW 7113 Rhyolite  
GBW 7114 Dolomite

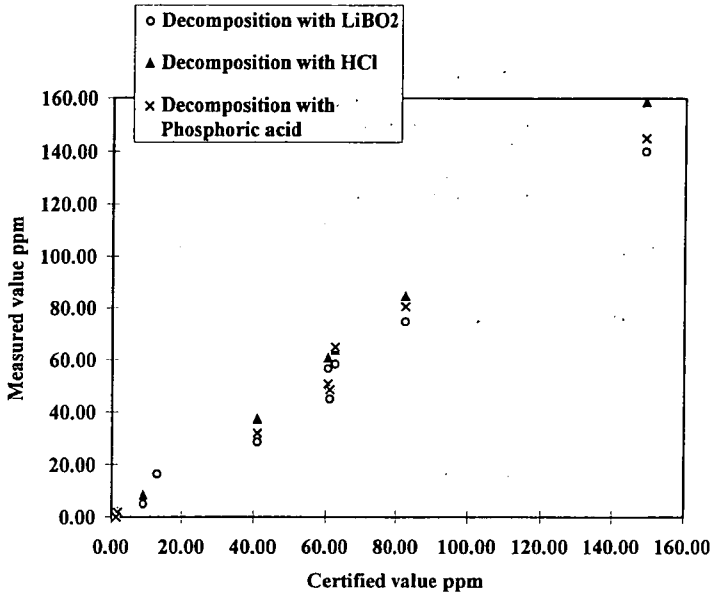
\*Source: Institute of Geophysical and Geochemical Exploration, Langfang, P. R. of China

## Former COMECON Rock Standards\*:

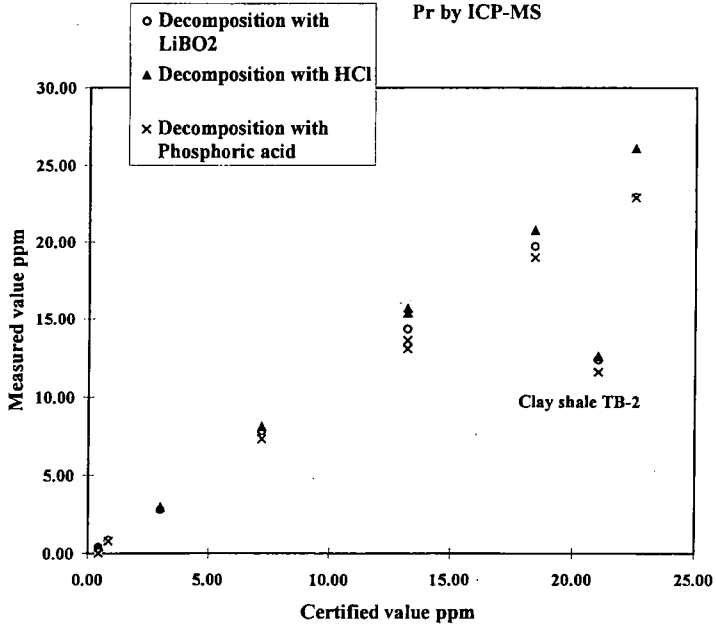
Basalt BM  
Granite GM  
Clay shale TB-2  
Greisen GnA  
Limestone KH  
Serpentinite SW

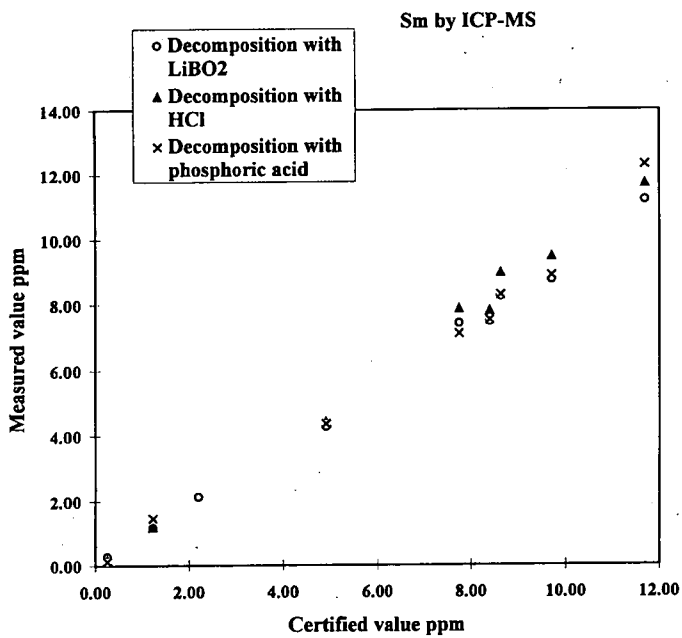
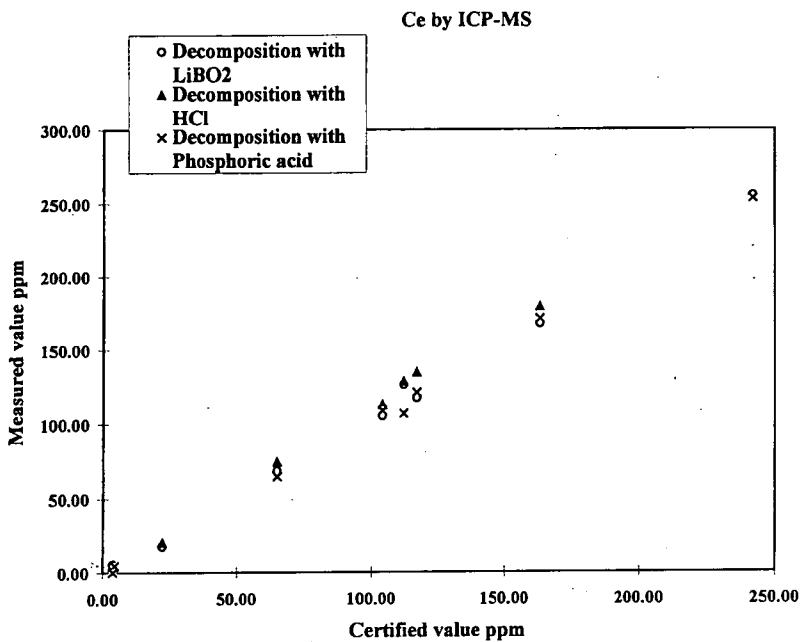
\*Source: (former) Zentrales Geologisches Institut, Berlin, (former) GDR

La by ICP-MS

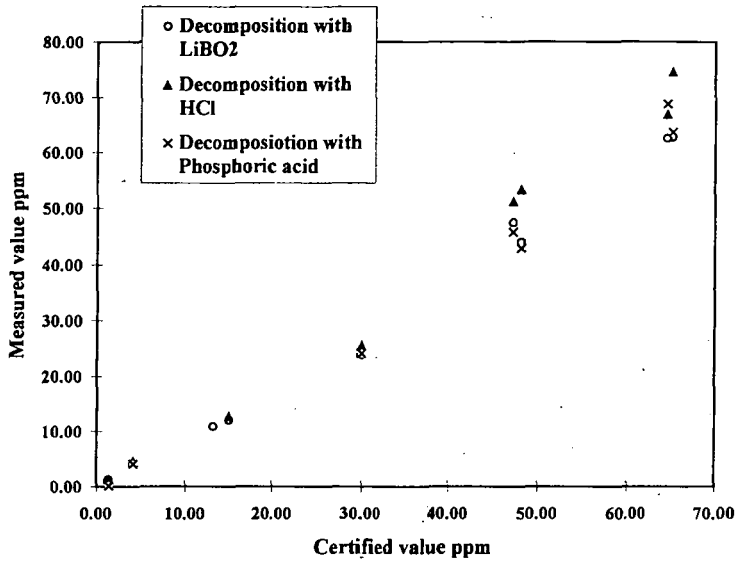


Pr by ICP-MS

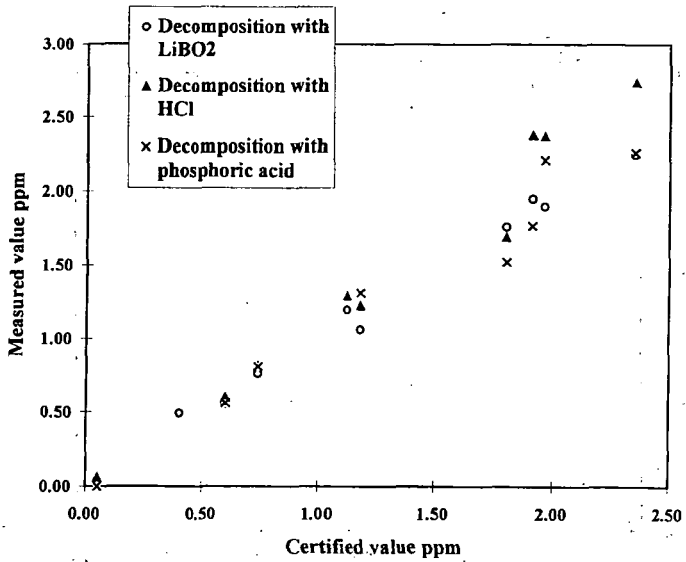




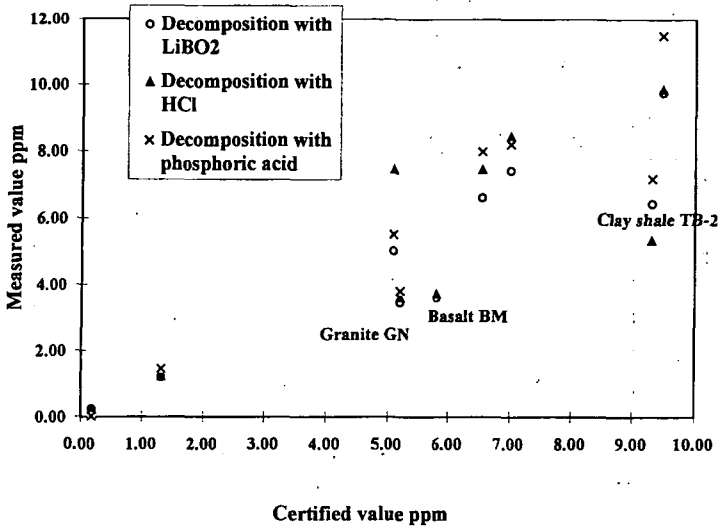
Nd by ICP-MS



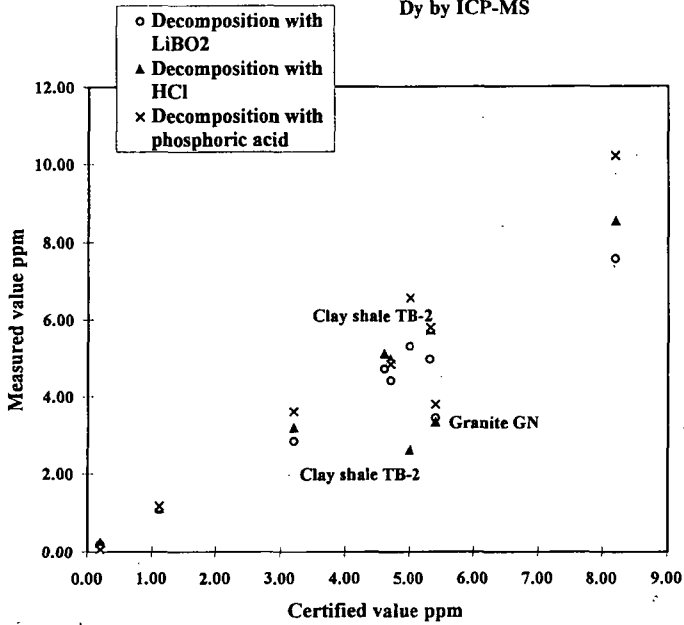
Eu by ICP-MS



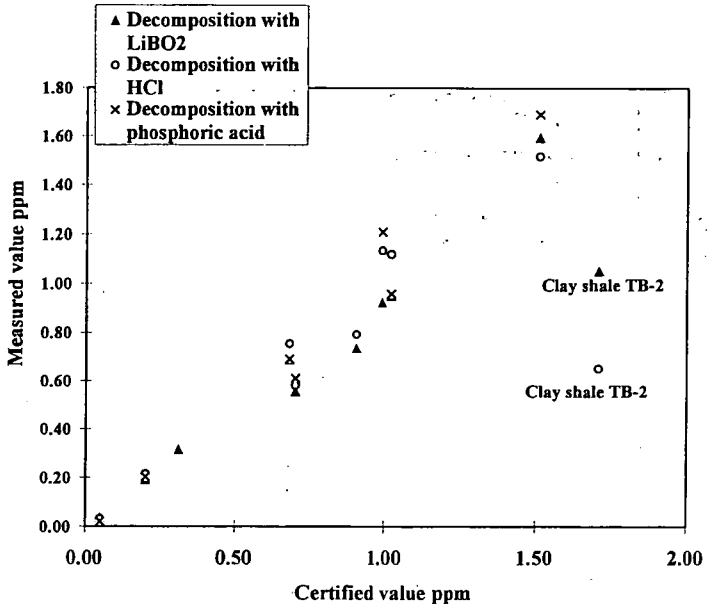
Gd by ICP-MS



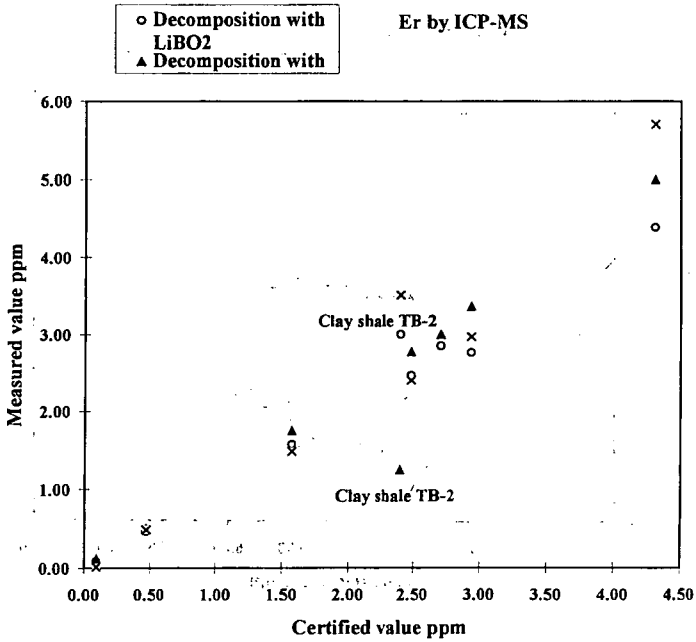
Dy by ICP-MS



Tb by ICP-MS

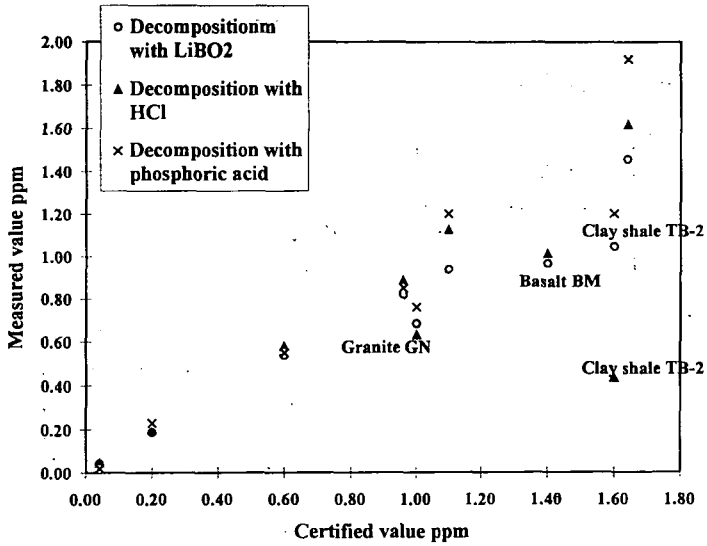


Er by ICP-MS

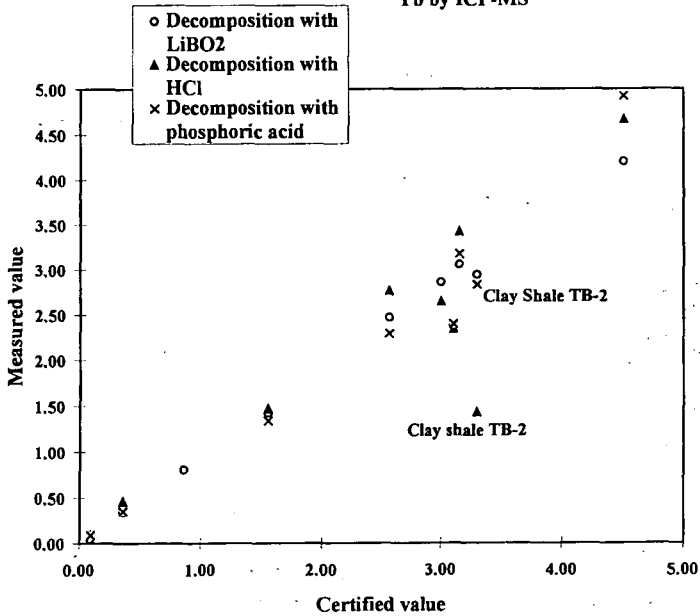




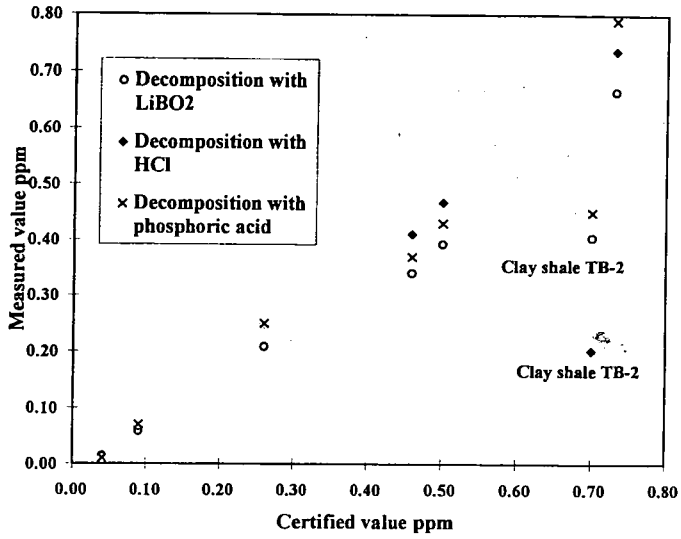
Ho by ICP-MS



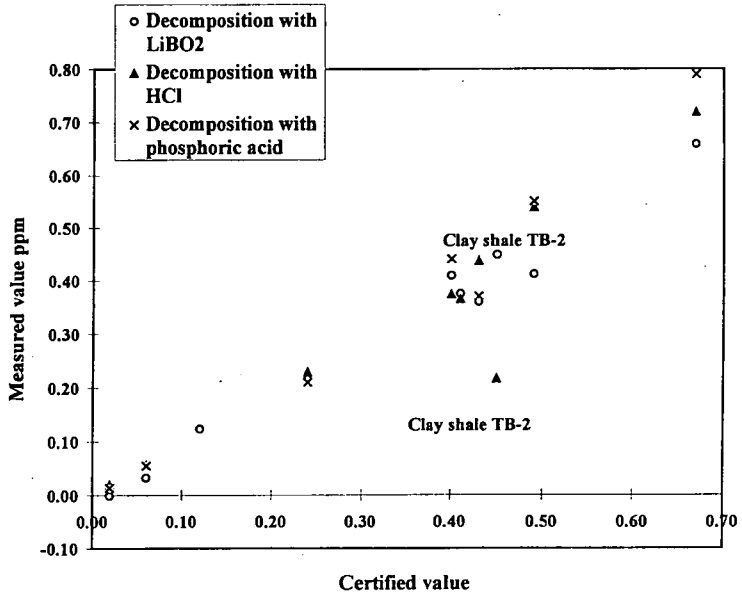
Yb by ICP-MS



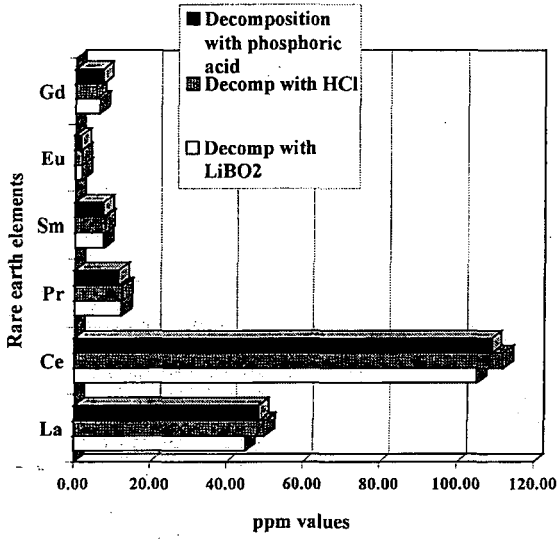
Tm by ICP-MS



Lu by ICP-MS



Recoveries of light rare earth elements of clay shale TB-2



Recoveries of heavy rare earth elements of clay shale TB-2

