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PRELIMINARY INVESTIGATION OF MOCS METEORITE BY LEAD ISOTOPIC RATIO USING QUADRUPOLE INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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ABSTRACT. Lead isotopic ratios ($^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$) were measured on a sample of Mocs L5-6 chondritic meteorite (from the collection of meteorites of the Museum of Mineralogy of the Babeş-Bolyai University, Cluj-Napoca, Romania), using a inductively coupled plasma quadrupole mass spectrometry method. A NIST 981 standard reference material was used for calibration and control. The obtained data for the standard reference material were within the certified range; the isotopic ratio values measured for Mocs meteorite were 0.8656 ± 0.0084 for $^{207}\text{Pb}/^{206}\text{Pb}$ and 2.1011 ± 0.0036 for $^{208}\text{Pb}/^{206}\text{Pb}$ and they were compared with other chondritic meteorites. The measured total Pb content was 0.888 ± 0.005 mg/kg. Due to isobaric interferences with ^{204}Hg , ^{204}Pb was excluded, but further method improvement is planned to include all lead stable isotopes due to their importance to geochronology dating.

Keywords: Pb isotopes, ICP-MS, Mocs meteorite, L5-6 chondrite

INTRODUCTION

Mocs meteorite, classified as L5-6 chondrite [1] fell as a shower of stones on 3rd February 1882, in Transylvania region over an area of several dozen squared kilometers near Mocs village (now Mociu, Cluj County, Romania, coordinates 46°48' N, 24°2' E). The number of recovered fragments was estimated at 3000, with a total weight of about 300 kg [2]. According to the Meteoritical Bulletin Database, Mocs is one of the 31 approved meteorites classified as L5-6. The exact fall location of the investigated Mocs meteorite sample (inv. no. I.34B) is Chesău village (Keszú, in the official catalogues of meteorites, e.g. [2]), Mociu Commune, Cluj County). Due to the large amount

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of material present in more than 30 museums worldwide [2], Mocs meteorite has been intensely studied before; however, no lead isotopes measurements have been done so far. Our experiments concerned whole rock fragments.

With a wide spreading among analytical laboratories, ICP-MS technique has become an important tool for trace elements determination; the same technique allows isotopic ratio measurements, since the core of the instrument is represented by a quadrupole that can differentiate between different isotopes.

SAMPLE PREPARATION

A meteorite sample was provided for this study by Museum of Mineralogy, Babeş-Bolyai University, Cluj-Napoca, Romania. Prior to the measurements, the samples were well wash using ultrapure water and were carefully manipulated afterwards, avoiding any lead contamination. The samples had the fusion crust removed and then the fragment was precisely weighted and divided into three sub-samples with various mass. The sample was not fragmented by using a saw, in order to avoid contamination during processing into fine powder. The powder mass was weighted (0.2 grams each) and compared with the original mass of the bulk sample. Every sub-samples was digested separately and the dissociation was performed in a Teflon beaker on a sand box. The Teflon device was cleaned with *aqua regia* before measurements. Temperature of the sand box was kept constant ($T = 90^{\circ}\text{C}$). Every step uses a combination of strong acids as each step destroyed a part of the complex compound matrix. Following the dissociation, the solution was filtered into a 25 ml flask. The purpose of the procedure was to obtain enough concentrated solution that could be precisely measured with the ICP-MS. The steps are listed in Table 1.

Table 1. Four-step mineralization method for Mocs meteorite

| Step 1 | Step 2 | Step 3 | Step 4 |
|--|--|--|--|
| 2x5 ml HNO ₃ heat until 2ml left | 5 ml HF 1.5 ml HClO ₄ heat until 2ml left | No heating 1 ml HCl 5 ml HNO ₃ ultrapure water | 5 ml HNO ₃ 6.5 ml HF 5 ml HCl 1 ml H ₂ SO ₄ heat until 2ml left |

For calibration and mass bias correction, a solution of NIST 981 standard reference material (natural lead standard, $^{204}\text{Pb}/^{206}\text{Pb} = 0.059042 \pm 0.000037$, $^{207}\text{Pb}/^{206}\text{Pb} = 0.91464 \pm 0.00033$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.1681 \pm 0.0008$) was used. From the initial solid, wire-shaped material, a 20 ppb solution was prepared for daily use, by dissolving a weighted fragment of the reference material in nitric acid. The NIST 981 SRM sample was purchased directly from the National

Institute for Standards and Technology, NIST (USA). All other reagents were supplied by Merck. 18 M Ω cm⁻¹ DI water was prepared in the laboratory, using a Millipore- Milli-Q® ultrapure water purification system.

INSTRUMENTATION

SCIEX Perkin Elmer Elan DRC II (Canada) inductively coupled plasma mass spectrometer (with quadrupole and single detector setup) was used for this study. The operating parameters are listed in Table 2. The instrument's running parameters were checked and adjusted each analysis day, using a solution with 1 ppb In, 1 ppb Ce, 10 ppb Ba and 1 ppb Th and Mg. Oxides levels and double ionized levels were kept under 3%, backgrounds for both low and high mass were below 1 cps and all the other parameters were chosen considering the best signal/noise ratio. The detector was used in pulse mode, for better sensitivity. The dynamic reaction chamber (DRC) was used in rf-only mode (no gas); its parameters optimization procedure has been described elsewhere [3].

Table 2. Elan DRC II running parameters.

| Parameter | Value |
|---------------------------------------|---|
| Plasma | |
| Power / W | 1350 |
| Plasma gas flow /min ⁻¹ | 12.00 |
| Auxiliary gas flow /min ⁻¹ | 1.20 |
| Nebuliser gas flow /min ⁻¹ | 1.05 |
| Sample/Skimmer cone | Platinum |
| Quadrupole | |
| Quadruple rod offset (QRO) / V | 0.00 |
| Cell rod offset (CRO) / V | - 8.00 |
| Cell path voltage (CPV) / V | - 20.00 |
| Measurement mode | Peak hopping |
| Dwell time / ms | 100 (²⁰⁶ Pb, ²⁰⁷ Pb), 70 (²⁰⁸ Pb) |
| Integration time / ms | 5000 (²⁰⁶ Pb, ²⁰⁷ Pb), 3500 (²⁰⁸ Pb) |
| Reading per point | 300 |
| Reading per replicate | 1 |
| Replicate measurements | 4 |
| DRC | |
| Reaction Gas | None |
| Lens voltage / V | 11.00 |

RESULTS AND DISCUSSION

For this study, ^{206}Pb , ^{207}Pb and ^{208}Pb were selected for measurement. Due to isobaric interferences, the quadrupole cannot differentiate between ^{204}Pb and ^{204}Hg isotopes and mercury was found at a level of 1.047 mg/kg (other studies [4] found 1.120 mg/kg), which is impossible to ignore in our lead measurements. For terrestrial samples with known Hg isotopic ratio, mathematical correction can be performed for subtracting ^{204}Hg counts from the total counts at mass 204. Since no data about Hg isotopic ratio in Mocs meteorite are yet provided, no such mathematical correction could be applied; interferences from Hg would have caused a false signal on mass 204 that would have rendered correct ^{204}Pb determination to be impossible with current method. Isotopic ratio determination for Hg by hydride generation would be able to improve ^{204}Pb measurements.

No internal standard was used during the measurements, but after every two sample, the NIST 981 SRM calibration solution was read, to correct for any mass bias effect. Correction factor was automatically calculated by the instrument's software.

The obtained solutions for Mocs sample and NIST 981 SRM were measured in three consecutive days. Settings for dwell time distribution were chosen according to previous studies [5] thus tuned for maximizing the sensibility - in this case, without using ^{204}Pb isotope but keeping the same ratio, meaning: 37% ^{206}Pb , 37% ^{207}Pb and 26% ^{208}Pb .

Table 3. Measured averages (\pm Standard Deviation)

| | | $^{207}\text{Pb}/^{206}\text{Pb}$ | $^{208}\text{Pb}/^{206}\text{Pb}$ |
|-----------------------------|------------------|-----------------------------------|-----------------------------------|
| NIST 981 | <i>Measured</i> | 0.9142 ± 0.0005 | 2.1683 ± 0.0015 |
| | <i>Certified</i> | 0.9146 ± 0.0003 | 2.1681 ± 0.0008 |
| Mocs (L5-6) | | 0.8656 ± 0.0084 | 2.1011 ± 0.0036 |
| Sharps (H3.7)* | | 1.0918 ± 0.0021 | 3.1029 ± 0.0005 |
| Mező-Madaras (L3.7)* | | 1.0985 ± 0.0014 | 3.1317 ± 0.0003 |

* average corrected ratios, according to [9].

Quantitative analysis revealed 0.888 ± 0.005 mg/kg concentration of Pb in Mocs sample (which is in good agreement with the results from literature [4]). The average values for the measured Pb isotopic ratios in NIST SRM and Mocs meteorite are reported in Table 3, together with comparative data on two other chondrites from references [9]. Other works on lead isotopic ratio on soils revealed $^{207}\text{Pb}/^{206}\text{Pb}$ ratio between 1.187 – 1.199 and $^{206}\text{Pb}/^{206}\text{Pb}$ ratio between 2.476 – 2.530 [14].

Lead isotopes in meteoritic materials are used for studying and dating early events in the solar system. "Initial" Pb isotope ratios obtained on troilite (FeS) in the least-radiogenic Canyon Diablo iron meteorite were used either as complementary reference for terrestrial ore Pb values, or as the assumed initial composition of Earth Pb ("primordial lead") that further evolved into all the other Pb-containing terrestrial phases [7]. There are no significant differences between the initial Pb ratios in Canyon Diablo troilite as compared to some chondritic meteorites selected for their low degree of early planetary metamorphism [9].

The oldest recorded Pb-Pb meteoritic age, obtained on Ca-Al-rich inclusions in Allende (CV3) carbonaceous chondritic meteorite [6] and the Angra dos Reis achondrite (angrite) [12], is of about 4.56 Ga (1 Ga = 10^9 years) [9]. When calculating internal $^{207}\text{Pb}/^{206}\text{Pb}$ ages for chondrites, caution should be taken in order to exclude pre-analysis contamination with terrestrial lead. This can be done by comparing isotope correlations between the acid-washes of analyzed samples, which basically would contain all the contamination lead induced by some type of fluid transport, and the residual washed samples [9].

Mocs is an ordinary chondrite with a relatively high degree of thermal metamorphism (petrologic type L5-6) and heterogeneous degrees of shock metamorphism, from S3 to S5 [1]. Extreme crushing and distortion of all mineral components was found on Mocs meteorite [11]. By taking these into consideration, as expected, the average lead concentration in Mocs sample (0.888 ± 0.005 mg/kg) is much lower than that in less metamorphosed whole rock chondrites, e.g. 5.44 mg/kg in Mezö-Madaras (L3.7) or 1.93 mg/kg in Sharps (H3.7) [9] due to the greater amounts of volatile elements in type 3 chondrites [13]. The same is true for the values of the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (Table 3).

CONCLUSIONS

An inductively plasma mass spectrometer with single detector and a quadrupole for mass discrimination was used for lead isotopic ratio measurements on Mocs meteoritic sample. The proposed method was tested using a NIST 981 standard reference material and it offered good results for lead determination. Even if the calculation of radiometric ages is not possible by using the current results, they may provide some comparative grounds for Pb isotope compositions on other chondritic meteorites. Further method improvements for including determination of ^{204}Pb isotope is currently underway.

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