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Dedicated to Professor Emil Cordoș on the occasion of his 80th anniversary

REVISED RARE EARTH ELEMENTS COMPOSITION OF MOCS METEORITE USING HR-ICP-MS AND ICP-QMS ANALYSIS

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ABSTRACT. Rare earth elements composition of Mocs meteorite was analyzed using two inductively coupled plasma mass spectrometry methods: a quadrupole and a single-detector sector-field high-resolution instrument. The obtained results are in good agreement with previous studies found in literature for both Mocs and chondritic materials analysis regarding REE composition. Allende meteorite reference material was used for calibration. Sample preparation for ICP-MS analysis was carried out following a custom protocol derived from the literature: the samples were finely ground, then treated in a multi-step procedure [1]. A mix of hydrofluoric acid, nitric acid and perchloric acid was used to digest the sample, which was finally dissolved in nitric acid and diluted accordingly, before being measured directly by ICP-MS instruments. Mocs samples were made available from Museum of Mineralogy, Babeș-Bolyai University Cluj-Napoca and Allende meteorite reference sample was provided by Smithsonian Institution (split 7, position 17) [2].

Keywords: *HR-ICP-MS, ICP-QMS, meteorite, chondrite, Mocs, REE*

INTRODUCTION

Mocs meteorite, classified as L5-6 chondrite [3], fell as a shower of stones on 03 February 1882, over an area of several dozen squared kilometers, near Mocs village (now called Mociu, Cluj County, Romania, coordinates 46°48'N, 24°2'E; meteorites are usually named after the settlement closest to their recovery area and their name [4] doesn't change afterwards to reflect any future

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change of settlement's name). The number of recovered fragments was estimated at 3000, with a total weight of about 300 kg [5]. According to the Meteoritical Bulletin Database, Mocs is one of the 48 approved meteorites classified as L5-6 and one of the 9 approved meteorite recovered from current Romania territory [6]. About 86% of the total number of meteorites falling on Earth are ordinary chondrites, divided into the H, L and LL groups, based on iron, nickel and other metals content [7]. From a total number of over 53000 recorded meteorites, over 46000 are classified as ordinary chondrites [8]. Our experiments concerned whole rock fragments (no crust), from the collection of the Museum of Mineralogy, Babeș-Bolyai University, Cluj-Napoca. Rare earth elements composition offers clues for a variety of geochemical and cosmochemical processes and meteorites display variations in REE concentration and abundances patterns that offers clues about their origin and past history [9].

RESULTS AND DISCUSSION

Due to sample matrix difference between samples and standard, a multiple point calibration curve was found unsuitable for these analyses. Thus, a bracketing calibration, involving a sample from Allende reference material was used. A standard sample was always run before and after each Mocs sample and sample concentration was calculated from standard know concentration and signal counts. In this way, the matrix for the samples and the standards matched, and issues like signal drifting and recovery were avoided.

Table 1. Rare earth elements composition of Mocs meteorite, using data from both high-resolution (HR-ICP-MS) and quadrupole (ICP-QMS) and methods inductively coupled plasma mass spectrometry methods

mg/kg	HR-ICP-MS	*3σ*	ICP-QMS	*3σ*
La	0.41	*0.05*	0.47	*0.05*
Ce	1.31	*0.17*	1.52	*0.17*
Pr	0.17	*0.01*	0.20	*0.02*
Nd	0.86	*0.08*	0.97	*0.11*
Sm	0.27	*0.01*	0.28	*0.03*
Eu	0.04	*0.01*	0.03	*0.01*
Gd	0.34	*0.01*	0.38	*0.04*
Tb	0.07	*0.01*	0.07	*0.01*
Dy	0.36	*0.03*	0.37	*0.03*
Ho	0.09	*0.01*	0.10	*0.01*
Er	0.26	*0.01*	0.27	*0.03*
Tm	0.04	*0.01*	0.04	*0.01*
Yb	0.26	*0.01*	0.26	*0.03*
Lu	0.04	*0.01*	0.05	*0.01*

Previous studies for rare earth content of Mocs [10] used the same meteorite as source of sample material, but different sample preparation method was used. Current method implies two spectrometric methods and a different calibration method, using bracketing and a suitable reference standard material. Data are listed in Table 1 and patterns for rare earth elements composition from Figure 1 are normalized to Solar System abundances [11]. Mocs samples appear slightly enriched than the other CI chondrites (a group of carbonaceous chondrites) reported and respectively than the reported mean for L chondrites [6]. The pattern is similar with Aumiers and Milena L-type chondrites [13], being slight enrichment in low mass rare earth elements in respect to high mass rare earth elements and negative Europium anomaly. However, the Europium anomaly of Mocs samples is more pronounced showing a strong depletion in Europium relative to the CI line, while the Dysprosium slight depletion is similar with other chondrites.

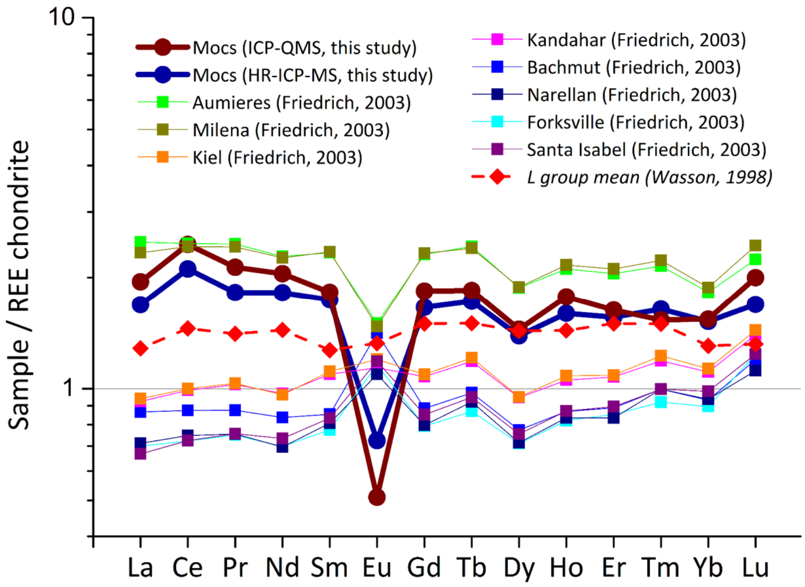

Figure 1. Rare earth elements patterns for Mocs chondrite and other chondrites [6,7], normalized to Solar System abundances

CONCLUSIONS

Despite having significant lower sensitivy than HR-ICP-MS, quadrupole ICP-MS can successfully be used for direct rare earth elements determination (microwave acid digestion of samples, without intermediary pre-concentration steps), if a suited certified reference material is provided for calibration. Rare earth elements patterns for Mocs meteorite, normalized to solar system abundances, show a general enrichment for almost all the rare elements concentration, with the exception of Europium. Data for both HR-ICP-MS and ICP-QMS are in good agreement for all the measured elements, even if HR-ICP-MS provided up to two orders of magnitude higher sensitivity.

EXPERIMENTAL SECTION

Nu Instruments AttoM high-resolution ICP-MS (HR-ICP-MS) from Department of Geology, Faculty of Biology and Geology, Babeș-Bolyai University, Cluj-Napoca, and Perkin-Elmer Elan DRC II quadrupole inductive coupled mass spectrometer (ICP-QMS) from INCDO-INOE 2000 Research Institute for Analytical Instrumentation Cluj-Napoca were used. Both instruments were carefully optimized before each sample batch, using routine procedures, providing best signal/noise ratio during analysis, thus ensuring best sensitivy. Elan DRC II was used in DRC *rf-only* mode (no gas) and pulse detector mode, providing maximum sensitivity; for reading, peak-hoping mode was selected. AttoM instrument was used on low-resolution mode and for the detector no attenuation was necessary, since the concentration were low enough not to generate high counts and trigger mode change; deflector jump mode was used for data acquisition.

Mocs samples were ground to very fine powder and 100 mg for Mocs and Allende meteorites were used for analysis. Two digested methods were performed, both involving microwaves. In the first stage, 3 mL HNO_3, 3 ml HF and 2 mL H_2O were added to the sample and then placed in the microwave oven for 30 minutes (up to 22°C in the first 10 minutes, no change for another 10 minutes, then up to 240°C for the remaining time). After cooling, the digested solutions were evaporated and dried down on a hot plate. The second stage of acid treatment consisted on 1 mL HNO_3, 2 mL HCL and 5 mL H_2O and placed again in the microwave oven for 35 minutes (up to 200°C in the first 15 minutes, then the temperature was kept constant). After cooling, the final solution was brought to a total volume of 50 mL with deionized water in a volumetric flask, ready for direct ICP-MS analysis. A blank solution was prepared and its contribution was extracted from samples detector counts (cps level). No intermediary pre-concentration steps were involved, both instruments used being able to directly measure the samples.

While for HR-ICP-MS instrument the sensitivy varied from 4079 cps/ppb for Dysprosium to 289955 cps/ppb for Lanthanum, for the quadrupole system it varied less, with only one order of magnitude, from 559 cps/ppb for

Neodymium to 3354 cps/ppb for Lutetium, but we still had measurable signal for all the elements considered for this study. Allende meteorite sample was used as a calibration standard and its counts per second values for every element was used to quantify the Mocs samples, after applying a mass correction coefficient, due to different weighted masses considered.

Results of rare earth elements analysis with both HR-ICP-MS and ICP-QMS are listed in Table 1. Results are expressed in ppm (mg/kg), with 3σ level standard deviation. In both cases, Allende certified reference material was used for calibration, using the bracketing technique, since it was the best reference material found that matched the matrix of chondritic samples. Figure 1 shows the values normalized to solar system abundances [5], together with other chondrites from L5-6 group [6] and also an average [7] for group L chondrites.

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