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AN ASSESSMENT OF RARE EARTH ELEMENTS COMPOSITION OF ROMANIAN METEORITIC MATERIAL USING AN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY METHOD

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ABSTRACT. Inductively coupled plasma mass spectrometry method was used for assessing rare earth elements (REE) concentrations in two Romanian ordinary chondritic meteorites, Mocs (L5-6) and Pleşcoi (L5-6). The obtained results show that the two rare earth elements compositions are, as expected, similar. The lowest concentration was obtained for Tm in both meteorites: 0.032 ± 0.003 mg/kg for Mocs and 0.034 ± 0.003 mg/kg for Pleșcoi, while the highest values are shared between Ce in the case of Mocs (0.606 ± 0.048), and Nd in the case of Pleşcoi (0.512 ± 0.041). Our results were compared with mean carbonaceous chondrite values found in literature; a scaling factor of 1.7 ± 0.2 was found for our ordinary chondrites.

Keywords: *inductively coupled plasma mass spectrometry, meteorite, rare earth elements, ultrasonic nebulization*

INTRODUCTION

Eight meteorite falls were officially recorded within Romania's borders, the most recent one being Pleşcoi, on June 12, 2008. However, the best know and studied Romanian meteorite is also the one with the largest recovered mass (around 300 kg). Its fall in the area of Mocs village (current locality name: Mociu, Cluj County), on February 3, 1882, was witnessed all around Transylvania and partly in the neighbouring regions. Both meteorites are classified as L5-6 type chondrites [1], [2]. Meteorites are rare natural materials, of high scientific and cultural value. Thus, in general, only small samples can be used for investigations using destructive methods, such as inductively coupled plasma spectrometry. In such cases, one has to find methods to optimise the data acquisition efficiency.

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An ultrasonic nebulizer was used in order to achieve higher sensitivity for rare earth elements (REE) determination in the studied meteorites. Information on rare earth elements concentration in chondrites allows performing further geochemical studies involving solar system dynamics [3],[4]. It was investigated if there is any direct relationship between the REE composition of the two ordinary chondrites and carbonaceous chondrites. Carbonaceous chondrites (classified into CI, CM, CV, CO, CK, CR, CH, CB, and C ungrouped) are considered to represent the most primitive and unaltered meteorites. Accordingly, they are compositionally closest to the nebula from which the Solar System formed [6]. This is particularly true for the CI group ("I" originates from the type meteorite in this group, *i.e.*, Ivuna). CI meteorites are thus used as a standard for evaluating the degree of chemical fractionation of materials formed throughout the solar system, including ordinary chondritic meteorites. Rare earth elements concentration was measured in this study and compared with literature values for the same meteorite class, confirming the chondritic nature of both Mocs from Pleşcoi from REE composition point of view and providing new data for the both meteorites.

RESULTS AND DISCUSSION

Rare earth elements compositions of Mocs and Pleşcoi meteorites are listed in Table 1. The graphical relationship between the two samples is displayed in Figure 1 where 14 points are displayed. The slope for the linear regression is 0.983 ± 0.159 (95% confidence interval) and the interception

Table 1. Rare earth elements concentrations measured in Mocs and Pleșcoi meteorites (± one standard deviation), five measurements were performed for each sample. Obtained values are compared with CI carbonaceous chondrites mean concentration (literature data [6]).

Element	Concentration (mg/kg)		
	Mocs	Pleșcoi	CI mean
La	0.470 ± 0.038	0.470 ± 0.038	0.237
Ce	0.606 ± 0.048	0.512 ± 0.041	0.613
Pr	0.086 ± 0.007	0.085 ± 0.007	0.093
Nd	0.532 ± 0.043	0.567 ± 0.045	0.457
Sm	0.256 ± 0.020	0.216 ± 0.017	0.148
Eu	0.118 ± 0.009	0.061 ± 0.005	0.056
Gd	0.367 ± 0.029	0.375 ± 0.030	0.199
Tb	0.054 ± 0.004	0.055 ± 0.004	0.036
Dy	0.429 ± 0.034	0.460 ± 0.037	0.246
Ho	0.090 ± 0.007	0.097 ± 0.008	0.055
Er	0.283 ± 0.023	0.308 ± 0.025	0.160
Tm	0.032 ± 0.003	0.034 ± 0.003	0.025
Yb	0.283 ± 0.023	0.308 ± 0.025	0.161
Lu	0.044 ± 0.004	0.040 ± 0.003	0.025

plots at 0.0001 ± 0.01707 thus, the data for the two samples show a strong positive correlation. The REE mean values for CI carbonaceous chondrites, as indicated in the literature [6], were considered for comparison. A scaling factor was computed for the Romanian ordinary chondrites for Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Other elements (La, Ce, Pr, Nd, Eu) were excluded given their higher concentration or factor variation. The scaling factor was calculated as the corresponding value for the studied ordinary chondrites divided by the CI mean value for each considered element. The obtained value is 1.7 ± 0.2, which is consistent with other studies [7], [8]. The difference in the mean REE concentration of CI and the two ordinary chondrites is caused by the different cosmic history experienced by the two categories of meteorites.

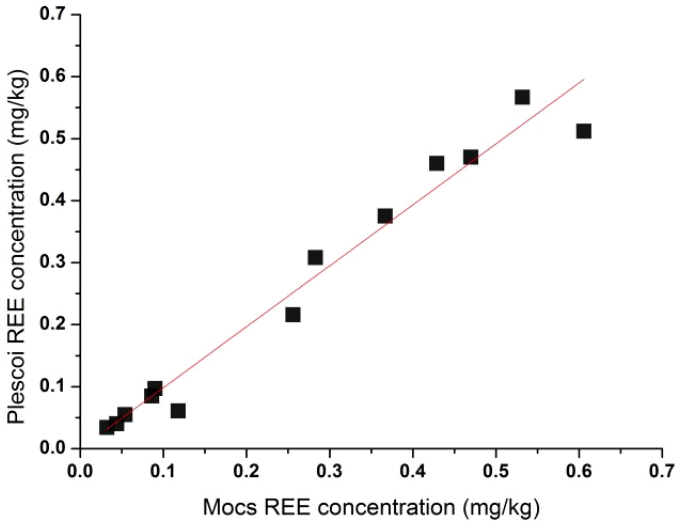

Figure 1. Rare earth elements correlation between Mocs and Pleșcoi meteorites.

CONCLUSIONS

Using a simple, four step method, an ICP-MS protocol for determining rare earth concentration in highly valuable samples was developed. In particular, this approach was used for the investigation of two Romanian chondrites, Mocs and Pleșcoi - the latest one being a relatively recent fall. For achieving a better sensitivity an ultrasonic nebulizer was used that successfully increased the ion signal up to 20 times, allowing a much better detector response. Rare earth elements concentrations are reported for both meteorites and compared with literature values for CI carbonaceous chondrites.

Our results represent the first REE data for the two meteorites. The consistency of our data suggests that the experimental set up we propose yields reliable results concerning the rare earth elements contents in meteorites, and in similar materials. Also, based on linear regression interpretation of the REE results, both meteorites share the same chondritic class.

EXPERIMENTAL

A SCIEX Perkin-Elmer DRC II (Ontario, Canada) inductively coupled plasma mass quadrupole spectrometer paired with CETAC UA6000AT ultrasonic nebulizer (Omaha, USA) was used for the measurements. Parameters of the instrument are expressed in Table 2. Ultrapure DI water (18 MΩ cm^{-1}) for sample preparation was produced by a Millipore Milli-Q Integral Water Purification System. Solution Standard II containing 16 rare earth elements, also purchased from Perkin Elmer, was used for calibration during the analysis. All other reagents used for sample treatment were purchased from Merck (Darmstadt, Germany).

Calibration was performed by diluting Multi-element Calibration Standard 2 solution (purchased from Perkin Elmer, containing a concentration of 10 mg/L from each of the following elements: Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Th, Tm, Y, Yb). The calibration ranged between 1.10^{-4} mg/L and 1.10^{-2} mg/L. The ICP-MS detector was set in pulse mode since ion counts were less than 10^6 per second (the highest cps count was obtained for 0.010 mg/L Tm, *i.e.*, $8.2\cdot10^5$, while the lowest cps count for 1.10^{-4} mg/L Gd, *i.e.*, $1.7\cdot10^4$).

Table 2. ICP-MS general experimental parameters

Plasma power	1100 W
Plasma gas flow	12 L/min
Auxiliary gas Flow	1.2 L/min
Nebuliser gas flow	0.91 L/min
Sample/Skimmer cone	Platinum
Quadrupole rod offset	0 V
Cell rod offset	-8 V
Cell path Voltage	-16 V
Dwell time	200 V
RPq	0.25
Rpa	0
Replicates	5
Lens voltage	7.1 V

Before measuring every sample batch, the instrument was optimized for best signal/noise ratio, using a standard set-up solution purchased from Perkin Elmer containing 0.001 mg/L In. This element is used for verifying instrument stability and general performance. Also, Ce and Ba included in the same solution offered a good view on oxides (CeO) and double ionized species (Ba^{++}) produced in the plasma region. We acted to keep those levels below 3 % threshold, in order to avoid any significant interference.

Samples were washed with ultrapure water and then processed into a fine powder; 0.2 grams of each were used for measurements [9]. Nitric acid was added in the first step, followed by hydrofluoric and perchloric acid. The mix was heated to 100 °C for a few hours then the temperature was increased to allow the perchloric acid to evaporate. After the sample dried and cooled down, a mixture of nitric acid and deionized water was added to make a total volume of 10 ml. This represented the final solution that was further analysed directly by ICP-MS.

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