

Determination of Rare- Earth Elements in White Marbles by Inductively Coupled Plasma Source Mass Spectrometry

Nurhayat Özdemir¹ & Şeref Güçer²

Abstract

Marmara (23), Afyon (31), Uşak (17) and Paros(9) white marble samples were analyzed by ICP-MS for the quantitative determination of rare earth element (REE) concentration. The levels of the isotopes of rare earth elements ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁷Er, ¹⁶⁹Tm, ¹⁷³Yb and ¹⁷⁵Lu

Keywords: white marble, rare earth elements, ICP-MS, NAA

Introduction

Characterization of white marbles from different sources is of outstanding importance in archaeology and history of art. Attempts to identify specific physical and chemical properties of marbles from different Mediterranean sources started in the late nineteenth century and still continue today. Whole-rock chemistry is one of the important parameters for characterization purposes.

¹ İnönü University Faculty of Arts and Science, Chemistry Dep. Malatya, Turkey. e-mail: nozdemir@inonu.edu.tr

² Department of Chemistry, Faculty of Arts and Science, University of Uludağ TR-16059 Bursa, Turkey. butal@tubitak.gov.tr

For this reason major and minor elements of marbles were analyzed by various techniques: such as complex metric titration (Ca), colorimetric (Si) conventional (Mg,Sr) or flameless (Al,V) atomic absorption spectrometry and instrumental neutron activation analysis (Na, K, Sc, Cr, Mn, Co, Fe, Zn, Sr, La, Ce, Sm, Eu, Tb, Yb, Hf, Th and U) (Moens et al, 1986).

It is shown that the levels of K, Mn and Hf would determinative parameters for different sources (Moens et al, 1988). In our present work, inductively coupled mass spectrometry (ICP-MS) was used for the determination of rare earth elements from lanthanum to Lutetium in white marbles.

Levels of isotopes ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{173}Yb and ^{175}Lu were analyzed by ICP-MS in marbles obtained from Marmara, Afyon and Uşak (Turkey) and Paros (Greece). Since the direct analysis was not possible due to the presence of high Ca level as matrix that caused column blockage and peak overlapping. Therefore, methods were sought to separate rare earth elements from Ca and it was seen that rare earth elements were effectively co precipitated with yttrium in basic medium after the dissolution of the sample. The efficiency of the analytical scheme followed was tested against neutron activation analysis (Carma et al. 1988).

Plasma Quad Operating Condition		Vacuum	
plasma		expansion stage	2.3 mbar
rf power	forward, 1.35 kW reflected, <10 W	intermediate	1.0×10^{-4} mbar
gas flows	plazma, 13.5L / min auxiliary, 1L / min nebulizer, 0.72 L / min	analyzer	2.0×10^{-6} mbar
peristaltic pump	Minipuls 2-Gilson pumped at 0.9 mL /	Data acquisition	
min		Quantitative scanning	
nebulizer	Meinhard concentric	sweeps	120
glass	nebulizer (type: Tr-30-	dwelt time	250s
A3)		channels	4096
spray chamber	double pass Scott type, water cooled (10 oC)	mass region	50-140 u
ion sampling		acquisition time	123 s
sampling cone	nickel, 1.0 mm orifice		
skimmer cone	nickel, 0.75 mm orifice		
sampling depth	10 mm (from load coil)		

The accuracy of the method was tested using MCG standard marble (British Museum).

Table 1: ICP-MS operating conditions

Before the analysis of marbles the recovery percentages of rare earth elements in CaCO₃ matrix were calculated. Results were multiplied by a correction factor. 178Hf was used as an internal standard to balance any changes in the analysis signal and to increase precision of measurement by correcting various sources of noise.

Experimental:

A commercially available ICP-MS instrument, The VG Plasma Quad (VG Elemental, Wins ford, U.K.), was used in its standard configuration with a Mein hard nebulizer and a spray chamber made of borosilicate glass. Details of the operating conditions are given in Table I.

Results and Discussion

Due to the overlapping of analyze peaks and blockage of columns by calcium in marble matrix, direct analysis by ICP-MS was not possible. A method of separating calcium from the rare earth matrix was applied. After a dissolution step, it was shown that rare earth metals could be precipitated with yttrium in basic environment. Thus, rare earth metals were separated and concentrated. The test for the efficiency of this method was compared, using the some analytical diagram, with neutron activation analysis. To balance any alteration in the analysis signal and the correction of different plasma sources together with the improvement of the measuring sensitivity, Hf was used as internal standard. In order to eliminate the interferences from CaO matrix is plasma the proposed analytical scheme is used which is shown in Figure 1.

Sample Preparation

(1.5-3 g marble is treated with 2N HNO₃. After washing and drying at 110°C nearly 2 g sample is taken

Dissolution

6N 10 mL HCl : Si is separated by filtration

Co precipitation

NH₄OH (aq) is added (pH>9). Then REE precipitated with 1mL 1000 mg/L Y⁺³ solutions.

Separation and Dissolution

Mixing, centrifugation and precipitate containing La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu in 2M HNO₃. Hf is added as internal standard

Detection

ICP-MS

Figure 1: Analytical Scheme

Analysis is carried out using only a two-point calibration, with one reference standard solution containing each REE at 10 ng mL⁻¹ and one reagent blank, and taking only the most abundant isobaric overlap-free isotope in each instance. Figure 2 shows the graph of the ratio of the levels REE to that of chondrite etc. mass number may be accepted as a parameter for characterization.

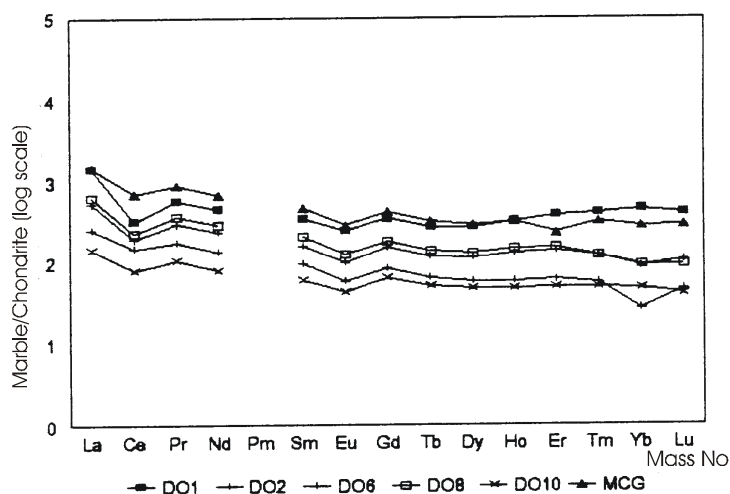


Figure 2: Logarithmic ratio of rare earth elements (REE) abundance marble/chondrite versus in increasing mass number DO1 (Afyon1), DO2 (Afyon2), DO6 (Afyon6), DO8 (Afyon8), DO10 (Afyon10).

Finally, the REE content of marbles is compared in Table 3 from different origins and in as a percentage figures illustrated. In Table 4 shown the cooperation of the analytical results for reference marble (MCG).

Conclusion

A novel methodology was applied for the determination of the rare elements in white marbles.

La : Lanthanum AA standard solution contains 1000 ppm Lanthanum in 5 % Nitric acid Janson Matthey Materials technology England
 Ce : Cerium AAS standard solution 1000 μ g Ce/mL 20 oC (NH₄)₃Ce(NO₃)₆ solvent deionized H₂O Ventron.
 Pr : Praseodymium /mL = 1 mg Pr (3+/4+) Art No: 9340 1.21 g Pr₆O₁₁ /lt 2 % HNO₃ Lot No:A0234
 Nd : Neodymium AAS standard solution 1000 μ g/ml solute: NdCl₃ solvent: deionized H₂O containing 4 % (v/v)HCl . Ventron
 Sm : Samarium 88D92 AAS Standard solution 1000 μ g Sm/ml @ 20oC solute: SmCl₃ solvent : deionized H₂O containing 5,4% (v/v) HCl
 Eu : Europium AA standard solution 1000 μ g Eu/ml @ 20oC solute: EuCl₃ solvent: deionized H₂O containing 2 % (v/v)HCl
 Alfa Products Thiokol / Ventron Division, Catalog no 88064
 Gd : Gadolinium AAS standard solution 1000 μ g Gd Table 2 ICP-MS operating conditions
 /ml solute: GdCl₃ solvent: deionized H₂O containing 1,3 % (v/v)HCl %1.3 (v/v) HCl Ventron
 Tb : Terbium / 1 ml = 1 mg Tb (3+ / 4+) Art no:938 1.18 g Tb₄O₇ /lt 2% HCl lot no:AO236 Servi Lab.
 Dy : Dysprosium AA standard solution contains 1015 μ g/ml Dy in 1 wt %HNO₃ d= 1.005 Aldrich Chemical Company, Inc USA.
 Ho: Holmium 1.15 g Ho₂O₃ /lt 2% HNO₃ Art no : 9410 Holmium / 1ml = 1 mg Ho (3+) lot no: S1141Servi Lab.
 Er : Erbium 1.15 g Er₂O₃ /lt 2 % HNO₃ Art no : 9420 Erbium / 1 ml = 1 mg Er (3+) lot no : AO237 Servi Lab.
 Tm : Thulium 1.15 g Tm₂O₃ /lt 2 % HNO₃ Art no : 9400 Thulium / 1ml = 1 mg Tm (3+) lot no : AU239 Servi Lab.
 Yb : Ytterbium AA standard solution contains 1015 μ g/ml of Yb in 1 wt % HNO₃ d = 1.005 Catalog no : 20.764 - 0

Aldrich Chemical Company, Inc, USA
Lu : Lutetium AAS standard solution 1000 ppm μ g Lu / ml solute: Lu ₂ O ₃ solvent : Deionized H ₂ O Ventron D 7500 Karlsruhe 1 gmbh postfach 6540
Hf : Hafnium AA standard solution 1 mg/ml Hf in 5% HF Nitrogen flushed Janssen Chimica B - 2440 Belgium
Y : Yttrium AA standard solution 1006 μ g Y /ml 2% HNO ₃ Aldrich Chemical Company Inc. USA (corrosive)
Eu : Eu ₂ O ₃ %99.999 TRONA American Potash & Chemical Corporation Rare Earth Division, West Chicago
La : La ₂ O ₃ %99.999 TRONA American Potash & Chemical Corporations Rare Earth Division, West Chicago
Solid lanthanum oxide was past trended at 900oC in an oven for an hour and kept in desiccators.
Yb : Yb ₂ O ₃ SPECPURE Spectrographically Standardized JMC Johnson Matthey Chemicals Limited Orchard Road Royston, Herts, SC8 5HE, England Catalog No. 1 MC 319
Ca : Ca ₂ CO ₃ Pro Analysis Precipitated, GR Merck 2066.02250 150 A 558666 [250 g net]
Y : Y ₂ O ₃ Pur zuiverpure 9288 RPL Grauwmeer B-3030 Leuven H.R Leuven 6172 Belgium

Table 3: Reagents used for ICP-MS Analyzes

Though the level of the elements follows a parallel trend in all samples, but the quantity of them differs. As a result, it is possible to classify white marbles according to the rare element contents.

Element	UŞAK(UŞ) ng.g-1		MARMARA (PR) ng.g-1		PAROS (PA) ng.g-1		AFYON (DO) ng.g-1 ng/g	
	Range	Median	Range	Median	Range	Median	Range	Median
139La	1836-27.3	410	893-0	173	585-69.7	166	1511-28.4	279
140Ce	458-13.7	116	636-6.66	125	774-35.9	154	1933-45.6	314
141Pr	213-3.86	58.2	137-1.23	27.9	108-6.5	24.4	281-8.9	54.4
146Nd	953-16.0	251	598-5.66	121	431-28.5	101	1081-34.3	223
147Sm	171-2.50	47.6	129-0	26.3	82.1-5.7	19.3	220-9.5	50.1
153Eu	44.5-0.46	12.1	34.2-0.08	6.85	18.2-1.34	4.54	54.2-2.4	12.2
157Gd	322-3.56	70.2	194-0.27	38.5	96.4-8.14	25.4	274-13.4	62.9
159Tb	44.4-0.35	10.3	30.3-0.35	5.9	12.9-1.15	3.45	42.3-2.4	9.3
163Dy	309-2.54	67.0	200-0	38.8	77.8-8	21.6	278-15.1	58.9
165Ho	83.0-0.78	17.0	48-0.52	9.8	17.9-2.14	5.26	66.2-3.4	14.0
166Er	257-2.41	53.1	136-0.99	29.4	53.3-6.55	15.5	215-9.9	42.8
169Tm	34.6-0.22	7.28	16.8-0.39	4.02	7.2-0.81	2.11	31.3-1.5	6.3
172Yb	563-0	87.8	9011-0	420	39.2-0	8.69	428-4.97	51.3
175Lu	36.1-0.28	7.6	12.7-0.46	3.65	6.97-0.76	1.98	30.4-1.4	5.96

Table 4: Comparison of rare earth elements content of marbles from Uşak (17 samples), Marmara (23 samples), Paros (9 samples) and Afyon(31 samples)

Element	NAA ng.g-1	ICP-MS ng.g-1
La	503 ± 20	494 ± 37
Ce	731 ± 24	627 ± 48
Pr	-	99 ± 7.5
Nd	334 ± 20	411 ± 24
Sm	87.1 ± 4.6	85 ± 5.3
Eu	23.02 ± 0.49	20 ± 1.16
Gd	-	105.3 ± 5.8
Tb	14.86 ± 0.43	15.27 ± 0.74
Dy	-	93.4 ± 4.0
Ho	-	22.84 ± 0.97
Er	-	47.36 ± 2.1
Tm	-	9.82 ± 0.10
Yb	67.0 ± 17.0	57.1 ± 0.6
Lu	-	9.91 ± 0.09

Table 5: Rare earth elements content of standard reference sample (MCG) is analyzed by ICP-MS and compared with NAA. Each result is quoted as the mean ± standard deviation

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