Determination of ultra-trace rare earth elements in iron minerals using HR-ICP-MS after chemical purification by polyurethane foam

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Formula S1 is used to calculate the absorption capacity of PUF in Fig 2 and 3:

The amount of iron absorbed by PUF was measured indirectly by comparing the iron concentration in equal aliquots of a solution before and after absorption. As the PUF weight was known, the absorption capacity of PUF (mg g^{-1}) could be calculated as follows:

$$Q = \frac{(C_0 - C_1) \times V_0}{1000 \times m} \quad (1)$$

Where **Q** is the capacity of PUF (mg g^{-1}); $\mathbf{C_0}$ is the iron concentration before absorption (μg mL^{-1}); $\mathbf{C_1}$ is the iron concentration after absorption (μg mL^{-1}); $\mathbf{V_0}$ is the solution volume (mL); and **m** is the weight of PUF (g).

Table S1 REE (μg g^{-1}) results from this study and references of FER-1

Element	Published values [a]				This study
	[1]	[2] Mean ± 1S (n=4)	[3A] Mean ± 1S (n=7)	[3B] Mean ± 1S (n=4)	Mean ± 1S (n=5)
Y	18	18.3 ± 0.2	17.3 ± 0.2	18.6 ± 0.1	17.3 ± 0.1
La	9.8	9.2 ± 0.5	9.2 ± 0.2	9.4 ± 0.4	9.33 ± 0.32
Ce	7.5	8.3 ± 0.3	8.2 ± 0.1	8.7 ± 0.1	8.12 ± 0.33
Pr	- [b]	1.64 ± 0.04	1.55 ± 0.02	1.65 ± 0.4	1.56 ± 0.04
Nd	7	7.0 ± 0.2	7.2 ± 0.1	7.60 ± 0.04	7.30 ± 0.14
Sm	1.7	1.66 ± 0.08	1.7 ± 0.1	1.84 ± 0.04	1.70 ± 0.06
Eu	3.1	3.33 ± 0.05	3.29 ± 0.05	3.51 ± 0.02	3.21 ± 0.06
Gd	1.5	1.81 ± 0.02	1.76 ± 0.05	1.89 ± 0.01	1.71 ± 0.03
Tb	0.2	0.267 ± 0.004	0.271 ± 0.006	0.286 ± 0.003	0.268 ± 0.003
Dy	1.8	1.77 ± 0.03	1.78 ± 0.03	1.90 ± 0.01	1.75 ± 0.04
Ho	0.4	0.401 ± 0.004	0.412 ± 0.006	0.43 ± 0.01	0.387 ± 0.011
Er	1	1.18 ± 0.02	1.19 ± 0.03	1.25 ± 0.01	1.13 ± 0.03
Tm	0.2	0.157 ± 0.006	0.153 ± 0.003	0.165 ± 0.001	0.150 ± 0.002
Yb	0.98	0.96 ± 0.04	0.93 ± 0.02	0.98 ± 0.01	0.911 ± 0.011
Lu	0.15	0.132 ± 0.002	0.129 ± 0.004	0.134 ± 0.004	0.130 ± 0.002

[a] Published values : [1] from Govindaraju (1994),[41] [2] from Dulski (2001),[42] [3A] and [3B] from Sampaio et al. (2015).[43] n, number of digestions.

[b] Not reported (no value exist in the reference).

Table S2 REE (μg g^{-1}) results from this study and references of FER-2

Element	Published values [a]							This study
	[1]	[2] Mean ± 1S (n=3)	[3]	[4A] Mean ± 1S (n=7)	[4B] Mean ± 1S (n=4)	[5] (n=3)	[6] (n=3)	Mean ± 1S (n=3)
Y	16	13.3 ± 0.2	12.4	12.3 ± 0.3	14.2 ± 0.5	13.2 ± 0.6	12.6 ± 0.2	12.3 ± 0.1
La	12	12.8 ± 0.5	11.8	12.2 ± 0.5	12.3 ± 0.7	13.4 ± 0.2	12.4 ± 0.16	12.2 ± 0.4
Ce	25	26 ± 1	24.1	24.8 ± 0.9	26 ± 2	25.8 ± 0.2	25.5 ± 0.5	25.2 ± 0.5
Pr	3	3.2 ± 0.1	2.83	3.0 ± 0.1	3.1 ± 0.2	3.31 ± 0.05	3.14 ± 0.04	3.08 ± 0.09
Nd	12	12.0 ± 0.6	11.5	12.3 ± 0.5	12.7 ± 0.6	13.2 ± 0.2	11.7 ± 0.1	11.7 ± 0.3
Sm	2.5	2.6 ± 0.1	2.44	2.6 ± 0.1	2.7 ± 0.1	2.65 ± 0.06	2.56 ± 0.03	2.55 ± 0.02
Eu	1.25	1.28 ± 0.02	1.2	1.29 ± 0.05	1.32 ± 0.06	1.30 ± 0.20	1.32 ± 0.02	1.32 ± 0.02
Gd	2	2.33 ± 0.07	2.25	2.3 ± 0.1	2.39 ± 0.06	2.32 ± 0.14	2.32 ± 0.01	2.36 ± 0.04
Tb	0.32	0.354 ± 0.005	0.332	0.36 ± 0.01	0.37 ± 0.01	0.36 ± 0.01	0.382 ± 0.003	0.386 ± 0.004
Dy	2	2.21 ± 0.03	2.1	2.3 ± 0.1	2.36 ± 0.04	2.17 ± 0.18	2.23 ± 0.06	2.24 ± 0.02
Ho	0.6	0.463 ± 0.004	0.436	0.49 ± 0.02	0.50 ± 0.01	0.47 ± 0.03	0.493 ± 0.005	0.491 ± 0.016
Er	1.5	1.38 ± 0.02	1.31	1.45 ± 0.06	1.48 ± 0.03	1.38 ± 0.12	1.42 ± 0.01	1.44 ± 0.01
Tm	0.2	0.207 ± 0.008	0.187	0.21 ± 0.02	0.217 ± 0.003	0.19 ± 0.01	0.218 ± 0.002	0.221 ± 0.005
Yb	1.25	1.35 ± 0.03	1.23	1.39 ± 0.08	1.44 ± 0.02	1.41 ± 0.04	1.343 ± 0.003	1.41 ± 0.01
Lu	0.2	0.203 ± 0.006	0.191	0.21 ± 0.01	0.213 ± 0.005	0.22 ± 0.02	0.216 ± 0.003	0.217 ± 0.007

[a] Published values: [1] from Govindaraju (1994),[41] [2] from Dulski (2001),[42] [3] from Alexander et al. (2009),[44] [4A] and [4B] from Sampaio et al. (2015),[43] [5] from Li et al. (2014),[19] [6] from Li et al. (2016).[21] n, number of digestions.

“The variability of iron minerals”

With regard to the variability of iron minerals, the possible effects on the sample digestion and PUF separation steps are discussed.

Sample digestion:

Compared to magnetite, pyrite is more difficult to dissolve. However, with our acid digestion method, both minerals are dissolved thoroughly without any precipitation. The following picture shows the digested solution of GBW07267 (pyrite).

PUF separation:

Based on the results of Drtil et al.,[32] only Fe^{3+} can be extracted by PUF in HCl media. Therefore, as long as the iron in the minerals is present in the acid-digested solution in the form of Fe^{3+}, PUF can quantitatively separate the iron matrix. This suggestion can be verified by the high iron recovery rate of PUF measured for the three RMs. For the recoveries of REE, the spiked recovery experiments of GBW07267 (pyrite) and FER-1 (rich in magnetite) demonstrated that there is no influence.

Based on the above points, we think that the variability of iron minerals has no impact on the results obtained in our current work.