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Review

Trace element determinations in Fe–Mn oxides by high resolution ICP-MS after Tm addition

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ABSTRACT

In order to propose an optimal analytical procedure specific to ferromanganese (Fe–Mn) oxides, we investigated different modes of data acquisition using inductively coupled plasma mass spectrometry (ICP-MS). The results of trace element and Rare Earth Element (REE) determination in eight Fe–Mn nodules and crusts (FeMn-1, GSMC-1, GSMC-2, GSMC-3, GSPN-2, GSPN-3, NOD-A-1 and NOD-P-1) are presented here. The analytical procedure involves chemical dissolution of the Fe–Mn oxides and addition of a thulium (Tm) spike. The correction of measured values from potential isobaric interferences was investigated using both corrections based on mono-elemental solutions, and data acquisition in the high-resolution mode. The obtained results show that the high-resolution acquisition mode is unnecessary to achieve high quality data for REE in Fe–Mn oxides. Using our revised method, we provide a consistent set of precise and accurate values for eight widely used but poorly characterized certified reference materials.

1. Introduction

Fe–Mn oxides are ubiquitous in the ocean and are produced by three main processes or combination of these [1–3]: (1) precipitation of Fe–Mn oxyhydroxide colloids from cold ambient seawater, (2) precipitation from pore water and (3) precipitation from hydrothermal fluids. Whereas Fe–Mn mineralizations that precipitate from the third process are mainly composed of Fe or Mn and Si, polymetallic nodules and Fe–Mn crusts that form from the two other mechanisms can be enriched in base metals (e.g., Cu, Ni) and critical metals (e.g., Co, REE, Zr, Nb, Y, Te and Pt) [4–6]. Consequently, Fe–Mn crusts and polymetallic nodules are now seen as a potential mineral resource and recent studies highlight the growing interest for REE and Y (REY) [e.g., [7]].

Besides their economic potential, REY can be used as geochemical proxies for deciphering between the different types of Fe–Mn oxides, and REY are now widely used in recently published discrimination diagrams [2,8]. Normalized REY patterns (e.g., Post-Archean Australian Shale; Mud of Queensland) [9,10] is an easy way to visualize anomalies for redox-sensitive elements (e.g., Ce ± Eu) as well as non-redox-sensitive elements (e.g., La, Gd, Y) which are linked to the behavior of REY during geochemical processes [2,11]. For example, as a redox-sensitive element and part of the REY suite [12,13], Ce (and its anomaly) can provide insights to identify the distinct water mass layers in the oceans [14–16]. Even though REE fractionation during surface-complexation on Mn and Fe oxides must be carefully assessed when studying Fe–Mn oxides [13], crucial information can be gleaned from comparative studies of REE and Y [12]. Apart from these anomalies (i.e., Ce, Eu, La, Gd, Y), normalized REY patterns are smooth functions of ionic radius and can be used to estimate the analytical quality of the data [2].

Therefore, it is of prime importance to establish a precise and time-effective method to quantify trace elements abundances, especially the REY, in Fe–Mn oxides. The most widely technique used for determining trace element concentrations is inductively coupled plasma mass spectrometry (ICP-MS). This technique offers several advantages such as very low limits of detection and high data accuracy. Moreover, ICP-MS is powerful in rapidly and simultaneously determining numerous trace elements. However, the presence of isobaric interferences, a common issue in mass spectrometry, can affect the results, as exemplified for REE [17–20]. Three alternatives exist to overcome isobaric interferences: (a) the purification of samples, (b) the correction of interferences using solutions of pure elements to estimate their contributions, and (c) data acquisition in high-resolution mode. The first is not suitable for our case:

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Table 1
ICP-MS operating conditions and measurement parameters.

RF power	1200 W
Sample uptake rate	100 μL/min
Coolant argon flow rates	16 L/min
Auxiliary argon flow rates	0.9 L/min
Nebuliser argon flow rates	1.031 L/min
Torch	Quartz
Nebuliser	PFA ST micro-flow
Spray chamber	Quartz cyclonic
Cones	Nickel
Low resolution mode (LRM)	^{9}Be, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{133}Cs, ^{135}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, $^{143,146}Nd$, $^{147,149}Sm$, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{174}Yb, ^{175}Lu, $^{177,178}Hf$, ^{181}Ta, ^{232}Th, ^{238}U
Medium resolution mode (MRM)	^{31}P, ^{45}Sc, ^{47}Ti, ^{51}V, ^{52}Cr, ^{66}Zn, ^{69}Ga, ^{85}Rb, ^{88}Sr, ^{90}Zr, ^{93}Nb, ^{111}Cd, ^{133}Cs, ^{181}Ta,
High resolution mode (HRM)	^{39}K, ^{43}Ca, ^{45}Sc, ^{52}Cr, ^{139}La, ^{140}Ce, ^{141}Pr, $^{143,146}Nd$, $^{147,149}Sm$, $^{151,153}Eu$, $^{155,157}Gd$, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{174}Yb, ^{175}Lu
Acquisition mode	Mass Accuracy
Number of scans	3*2
Ion lens settings	Acquisition to obtain maximum signal intensity
Wash time	100 s

purifying the sample would add extra workload with the separation of elements. Consequently, fewer elements per run would be acquired (e.g., Eu without Ba) for a higher degree of work.

The main goal of this study is to compare the two other possibilities to correct measured abundances from potential isobaric interferences: the use of mono-elemental solutions and data acquisition using the high-resolution mode. The use of this latter method appeared to be well suited considering the typically high trace element and REE content in Fe–Mn oxides. To process, we decide to follow a well-established analytical procedure for trace element determination by ICP-MS based on the addition of Tm spike [21–23]. The addition of Tm spike in the samples before ICP-MS measurements produces a positive Tm anomaly in the resulting REE patterns, which can be used to calculate trace element abundances in the sample solutions. This procedure was initially developed to allow the determination of REE abundances after separation and concentration and intensively described [21,24–26]. We subsequently systematized this technique for all our samples because it simplifies the preparation of solutions [e.g., [22, 27]], and largely reduces the errors associated with the correction of signal drift during analytical sessions.

The resulting data produced in both low and high-resolution modes will be compared and a new set of reference values for a suite of commonly-used certified reference materials will be proposed.

2. Standards and analytical method

Eight certified reference materials of Fe–Mn oxides were analyzed in this study. They correspond to some of the most widely used Fe–Mn standards by the scientific community for the characterization of major and trace elements (FeMn-1, GSMC-1, GSMC-2, GSMC-3, GSPN-2, GSPN-3, NOD-A-1, NOD-P-1). Additionally, two other certified reference materials were also used to validate our ICP-MS measurements (BE-N and BCR-2, two well-characterized basalts). Another certified reference material (basalt BHVO-2) was analyzed to correct measured values from instrumental drift and for calibration purposes.

All sample preparations were conducted in a Class 1000 (ISO 6) clean laboratory. Deionized water purified with a Milli-Q system (Millipore®) at 18.2 MΩ was used for material cleaning and preparation of acid solutions. The following reagents were used: nitric and hydrochloric acid solutions (commercial grade, Merck, Darmstadt, Germany), and ultra-pure hydrofluoric acid solution (HIPERPUR-PLUS®, Panreac, Barcelona, Spain), all of them were purified by sub-boiling. About 1 g of each Fe–Mn certified reference materials was dried in an oven at about 60 °C for a period of one day. One hundred mg of powder were dissolved in closed screw-top Teflon vessels (Savillex®) at about 120 °C for one day with 2 ml of 32 N HF and 2 ml of 14 N HNO_3. The vessels were then opened for evaporation at about 110 °C. After evaporation to dryness, 2 ml of 14 N HNO_3 was added. The vessels were capped and put back on the hotplate for 12 h at about 120 °C. The samples were dried a second time and taken up in about 20 ml of Quartex 6 M HCl to prepare the "mother solutions". No residual particles were observed in the mother solutions. The solutions were then transferred to acid cleaned polypropylene bottles. For analysis, aliquots of each mother solution were spiked with a Tm solution (30 ng of Tm per mg of sample) and then evaporated to dryness. Finally, a few hours before measurements, the residues were taken up in 0.4 N HNO_3 containing traces of HF (6 drops of 32 N HF/l). The total dilution factors are comprised between 0.05 and 0.06 mg of sample per g of solution.

Trace element abundances were determined with a high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) Thermo Electron Element XR (Thermo Scientific, Bremen, Germany) at the PSO ("Pôle Spectrométrie Océan") in Plouzané, France. This instrument can be operated in low (LRM, m/Δm approx. 300), medium (MRM, m/Δm = 4500) and high (HRM, m/Δm = 9200) resolution modes, depending on the required sensitivity and potential interferences for each element. Basic operating conditions and measuring parameters are summarized in Table 1. The REE were determined (a) in low-resolution mode to enhance sensitivity and were corrected for oxide and hydroxide interferences by analyzing solutions of ultra-pure water, Ba + Ce, Pr + Nd and Sm + Eu + Gd + Tb at the beginning of the measurement cycle, and (b) in high-resolution mode. A solution prepared with BHVO-2 was run after every three samples and used for both calibration and instrumental drift corrections following the procedure of Barrat et al. [21–24].

The raw data were first corrected for drift, procedural blank and interferences. Raw elemental concentrations were then calculated from corrected data, but these concentrations do not correspond to absolute abundances. At this stage, the Er and Yb measured concentrations were used to interpolate the content of Tm in the sample solutions. From these

Table 2
BHVO-2 working values used in this study, abundances (oxides in wt%, other elements in μg/g) and relative standard deviations (in italic) for the certified reference materials.

	Be	P_2O_5	K_2O	CaO	Sc	TiO_2	V	Cr	Zn	Ga	Rb	Sr	Y	Zr	Nb	Cs	Ba	Hf	Ta	Pb	Th	U
BHVO-2, working values																						
Barrat et al. (2012)	1.1	0.27	0.52	11.4	32.3	2.73	317	280	101	20.6	9.08	396	27.6	164.9	16.82	0.096	131	4.474	1.1	1.51	1.21	0.41
BE-N (n = 6)	**1.95**	**1.10**	**1.42**	**14.04**	**22.64**	**2.58**	**231**	**342**	**118**	**16.73**	**47.57**	**1409**	**30.90**	**260**	**103.0**	**0.75**	**1055**	**5.81**	**5.13**	**4.22**	**10.61**	**2.45**
RSD %	***2.12***	***2.02***	***2.77***	***1.57***	***1.32***	***3.04***	***1.60***	***1.37***	***1.87***	***1.78***	***3.58***	***1.80***	***0.83***	***1.79***	***1.72***	***3.47***	***1.52***	***1.90***	***6.57***	***3.82***	***1.59***	***1.16***
Jochum et al. (2016)	1.9	1.04	1.42	13.99	22.55	2.612	231.9	353.1	122.9	17.20	47.61	1392	29.44	272.9	113.2	0.73	1039	5.72	5.64	4.081	10.58	2.44
BCR-2 (n = 5)	**2.37**	**0.356**	**1.82**	**7.15**	**33.93**	**2.27**	**418**	**15.01**	**132**	**21.46**	**47.04**	**344**	**38.15**	**180**	**11.44**	**1.13**	**676**	**4.95**	**0.747**	**9.47**	**5.889**	**1.652**
RSD %	***3.48***	***1.44***	***0.98***	***2.18***	***1.34***	***1.18***	***0.93***	***1.85***	***2.87***	***1.10***	***0.63***	***1.00***	***0.76***	***0.75***	***0.83***	***1.08***	***0.48***	***0.80***	***0.95***	***3.98***	***0.65***	***0.44***
Jochum et al. (2016)	2.17	0.359	1.774	7.11	33.53	2.265	417.6	15.85	129.5	22.07	46.02	337.4	36.07	186.5	12.44	1.160	683.9	4.972	0.785	10.59	5.828	1.683
NOD-A-1 (n = 6)	**5.45**	**1.19**	**0.55**	**14.57**	**11.36**	**0.444**	**562**	**20.82**	**539**	**5.31**	**9.79**	**1472**	**128**	**289**	**42.61**	**0.58**	**1451**	**6.14**	**0.73**		**22.80**	**6.90**
RSD %	***2.44***	***1.77***	***1.04***	***1.93***	***1.53***	***1.35***	***1.44***	***5.66***	***1.32***	***2.17***	***1.32***	***1.90***	***1.82***	***1.22***	***1.07***	***2.23***	***1.48***	***1.74***	***1.09***		***1.70***	***1.80***
Flanagan and Gottfried (1980)		1.40	0.60	15.40		0.53	770		590			1750					1670					
Dulski (2001)											9.7	1467	116	233		0.56	1352	4			23.4	7
Axelsson et al. (2002)	5.60	1.36	0.60	16.06	12.4	0.51	660	20.9	800	6.30	10.6	1630	120	310	43.1	0.61	1530	5.80	0.76		25.1	7.00
Bau et al. (2014)													117									
Laurila et al. (2014)					12.1		614						122.6	321.5			1479	6.2			23.9	
NOD-P-1 (n = 6)	**2.21**	**0.44**	**1.15**	**2.86**	**9.67**	**0.429**	**446**	**14.21**	**1479**	**24.24**	**23.89**	**630**	**96.99**	**263**	**20.06**	**1.66**	**2537**	**4.13**	**0.35**		**15.63**	**4.03**
RSD %	***1.41***	***1.20***	***0.99***	***1.40***	***0.79***	***0.96***	***0.96***	***1.78***	***1.16***	***1.08***	***0.65***	***1.10***	***0.98***	***0.35***	***0.43***	***1.44***	***0.46***	***1.00***	***1.05***		***0.45***	***0.55***
Flanagan and Gottfried (1980)		0.46	1.20	3.10		0.50	570		1600			649					3350					
Dulski (2001)											24.5	680	91	298			2453				16.6	4.21
Axelsson et al. (2002)	2.30	0.47	1.20	3.15	9.70	0.45	510	13.3	2020	28.1	23.7	670	90.0	280	21.3	1.80	2690	4.20	0.33		16.7	4.00
Bau et al. (2014)													88.9									
Laurila et al. (2014)					10.25		492.5						93	287			2611	4			16.4	
FeMn-1 (n = 5)	**1.57**	**0.33**	**0.92**	**2.35**	**7.98**	**0.257**	**426**	**8.22**	**1742**	**23.16**	**12.01**	**682**	**73.76**	**298**	**12.34**	**0.78**	**3012**	**4.67**	**0.21**		**6.70**	**4.17**
RSD %	***2.72***	***2.90***	***5.69***	***4.64***	***2.86***	***3.46***	***2.15***	***8.47***	***1.57***	***1.63***	***2.99***	***2.80***	***1.93***	***1.50***	***2.23***	***3.65***	***1.85***	***1.63***	***3.33***		***1.80***	***1.46***
Webb et al. (2008)		0.352*		2.50	8.095*	0.29*	468.5*		1845		12.5*	683.3	69.11	325	13.4	0.85*	3158*	4.74	0.26*		6.87	4.39
Kriete (2011)	1.66	0.356	0.911	2.53	9.31	0.297	483		1821	31	12.9	683	69.1	326	13.8	0.822	3176	4.89	0.252		7.12	4.39
Bau et al. (2014)													66.7									
GSPN-2 (n = 5)	**3.53**	**0.49**	**0.994**	**2.44**	**14.08**	**1.19**	**423**	**13.53**	**809**	**20.42**	**15.24**	**835**	**149**	**558**	**45.65**	**0.83**	**1693**	**9.93**	**0.64**		**24.23**	**6.51**
RSD %	***0.44***	***1.22***	***0.91***	***1.10***	***0.91***	***1.29***	***0.81***	***4.66***	***2.43***	***1.34***	***1.18***	***0.90***	***0.80***	***0.68***	***0.88***	***0.85***	***0.69***	***0.74***	***0.92***		***0.77***	***0.98***
Wang et al. (1998)		0.58	1.08	2.67	13.7	1.37	425.9	17	918	27	16	869	133	618		0.84	1800	10			26	6.2
Dulski (2001)											16.2	875	144	614		0.89	1716	9.8			26.5	6.98
Laurila et al. (2014)					14.1		439.1						139.5	610			1729	9.55			25.1	
GSPN-3 (n = 5)	**1.75**	**0.32**	**1.094**	**2.09**	**10.03**	**0.47**	**403**	**11.03**	**1522**	**32.12**	**18.07**	**547**	**92.6**	**239**	**19.09**	**1.12**	**2370**	**3.90**	**0.31**		**15.34**	**3.77**
RSD %	***1.17***	***3.40***	***6.75***	***5.71***	***3.11***	***1.90***	***1.64***	***3.78***	***1.87***	***1.91***	***3.05***	***1.34***	***1.34***	***0.96***	***0.61***	***13.12***	***0.46***	***1.14***	***5.83***		***1.14***	***1.62***
Wang et al. (1998)		0.37	1.14	2.25	9.4	0.54	442	18	1600	38	17	561	84	256	21	1.2	2400	3.9	0.31		15	3.8
Dulski (2001)											18.8	565	87.4	274		1.26	2323	4.1			16.2	3.99
Bau et al. (2014)													83.3									
GSMC-1 (n = 5)	**5.35**	**1.45**	**0.70**	**4.34**	**11.56**	**1.93**	**574**	**14.11**	**618**	**2.93**	**9.72**	**1449**	**259**	**597**	**58.75**	**0.63**	**1745**	**10.27**	**1.17**		**20.12**	**12.07**
RSD %	***4.18***	***3.09***	***2.41***	***1.75***	***1.73***	***1.52***	***1.53***	***7.16***	***4.75***	***2.52***	***1.77***	***1.37***	***0.76***	***0.92***	***1.32***	***1.61***	***1.23***	***0.30***	***1.04***		***0.88***	***0.90***

(*continued on next page*)

Table 2 (*continued*)

	Be	P_2O_5	K_2O	CaO	Sc	TiO_2	V	Cr	Zn	Ga	Rb	Sr	Y	Zr	Nb	Cs	Ba	Hf	Ta	Pb	Th	U
Wang et al. (2003)		1.59	0.76	4.6		2.2	617		676		11	1481	239	656	58	0.6	1847	9.3	1.1		25	12
Bau et al. (2014)													244									
GSMC-2 (n = 5)	**5.27**	**3.08**	**0.67**	**7.09**	**10.60**	**1.68**	**586**	**12.58**	**547**	**3.03**	**9.01**	**1518**	**273**	**533**	**50.25**	**0.63**	**1852**	**8.78**	**0.97**		**15.16**	**11.60**
RSD %	***0.81***	***0.48***	***0.81***	***1.61***	***0.90***	***0.39***	***0.43***	***6.20***	***0.42***	***1.22***	***0.68***	***0.64***	***0.56***	***0.59***	***0.52***	***0.61***	***0.48***	***0.43***	***0.81***		***0.54***	***0.49***
Wang et al. (2003)		3.3	0.71	7.4	13	1.9	617		606		12	1551	251	602	53	0.9	1840	10.1			16.2	11
GSMC-3 (n = 5)	**4.86**	**3.48**	**0.79**	**7.55**	**10.70**	**1.72**	**524**	**12.48**	**538**	**4.05**	**10.59**	**1426**	**267**	**578**	**50.23**	**0.58**	**2029**	**9.62**	**1.12**		**14.19**	**11.25**
RSD %	***0.73***	***1.00***	***0.77***	***1.59***	***0.38***	***0.60***	***0.69***	***18.24***	***1.15***	***0.84***	***1.19***	***0.90***	***0.65***	***0.84***	***0.76***	***1.01***	***1.00***	***0.49***	***0.69***		***0.59***	***0.44***
Wang et al. (2003)		3.7	0.83	7.8	12.4	1.9	556		592		12	1466	247	642	53	0.5	2066	10			17	11

*Provisional.

abundances and the amount of Tm added during the chemical procedure, it was possible to calculate the element concentrations in the samples. The advantage of this calculations is that possible effects of the signal drift have no or negligible impact here [21,23]. Each solution was analyzed in triplicate and the results were averaged. The concentrations are provided in Tables 2 and 3, relative to our working values for the USGS basalt BHVO-2 [22]. In the event of future change to these BHVO-2 values, the data need only to be corrected by the ratio of the new and old values.

3. Results and discussion

The results and precision of the measurements as the relative standard deviation (RSD) are provided in Tables 2 and 3 For basalt standards BE-N and BCR-2, precisions are generally better than 4% for most elements and typically below 1.5% for the REE. Our data are in excellent agreement with the recommended values [28].

The eight Fe–Mn certified reference materials display high abundances of trace elements and REE. The results are also shown in Tables 2 and 3, while corresponding patterns are presented in Fig. 1. A Queensland alluvial sediment composite (MUQ) was used for normalization [9, 29] since it presents many well-characterized elements. Precision is mostly better than 4% for most elements and typically below 2.5% for the REE. Although the majority of our results are highly comparable to those obtained previously in the literature [2,30–37], important differences (>10%) exist between some of our data. For example, this is the cases for V (e.g., NOD-P-1 : 614 μg/g [37] vs. 562 μg/g in this study) and Zr (e.g., GSMC-2 : 602 μg/g [32] vs. 533 μg/g in this study). These variations are systematic for the eight Fe–Mn certified reference materials as illustrated in Fig. 2. Results from the other laboratories are higher than our data. Whereas the results obtained in this study for the basalt standards are in perfect agreement with the data published by Jochum et al. (2016) and used in the geochemical database GeoReM (Geological and Environmental Reference Materials). Our values are perfectly aligned on the x = y line (Fig. 2). These observations show the main differences between our data and those from previous studies come from a calibration bias and also confirm the high quality of our instrument calibration and the analytical procedure from homogeneous powder.

Comparisons between low-resolution and high-resolution REE results are provided in Table 4. The patterns and concentrations of REE are very similar whether in low or high-resolution modes. The Eu anomalies are calculated as the ratio of the normalized values of the element by the interpolation of the adjacent elements such as:

$$Eu \,/\, Eu^{*} = Eu_{MUQ} / (Sm_{MUQ} \times Gd_{MUQ})^{1/2} \quad (1)$$

and determined after data acquisition in low and high-resolution modes were also compared and appear to be very similar, within 3%, as well as in the basaltic certified references materials (Fig. 3). The isobaric interferences normally generated on Eu (BaO+, BaOH+) and on Gd (CeOH+, PrO+) are therefore well corrected in low-resolution mode. The RSD are generally less than 2% for the nodules and less than 1.5% for the crusts. The patterns are smooth (Fig. 1), which indicate excellent analytical quality [2]. The elementary ratios such as Zr/Hf [$(Zr/Hf)_{MUQ}$ = 1.25–1.71], La/Sm [$(La/Sm)_{MUQ}$ = 0.64–1.36] and Gd/Yb [$(Gd/Yb)_{MUQ}$ = 0.81–1.22] are characteristic of marine Fe–Mn oxides [2,8,38] and the well-known anomalies such as positive Ce anomalies (average Ce/Ce* = 1.73) and negative Y anomalies (average $(Y/Ho)_{MUQ}$ = 0.86) are clearly apparent [12,39–42]. The Ce anomaly is calculated using the same procedure as for the Eu anomaly calculation, such as:

$$Ce \,/\, Ce^{*} = Ce_{MUQ} / (La_{MUQ} \times Pr_{MUQ})^{1/2} \quad (2)$$

Although RSD from analyses obtained in high-resolution mode are generally better than 5%, they are nevertheless 1.5 to 14.5 times greater than those obtained in low-resolution mode. Results with RSD as low as

Table 3
BHVO-2 working values used in this study, REE abundances (μg/g) and relative standard deviations (in italic) for the certified reference materials.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu
BHVO-2, working values													
Barrat et al. (2012)	15.2	37.5	5.31	24.5	6.07	2.07	6.24	0.94	5.31	1.00	2.54	2.00	0.27
BE-N (n = 6)	**83.05**	**153.4**	**17.30**	**66.85**	**12.17**	**3.69**	**10.17**	**1.305**	**6.46**	**1.108**	**2.58**	**1.85**	**0.242**
RSD %	***0.88***	***0.79***	***1.12***	***0.90***	***1.02***	***1.04***	***2.07***	***1.28***	***0.77***	***0.44***	***0.76***	***0.88***	***0.35***
Jochum et al. (2016)	82.55	153.00	17.39	66.35	12.03	3.68	10.09	1.30	6.48	1.08	2.61	1.82	0.249
BCR-2 (n = 5)	**24.99**	**52.98**	**6.80**	**28.78**	**6.57**	**1.93**	**6.68**	**1.048**	**6.39**	**1.322**	**3.68**	**3.38**	**0.491**
RSD %	***0.72***	***0.79***	***0.67***	***0.71***	***0.54***	***0.82***	***0.67***	***0.44***	***0.75***	***0.73***	***0.76***	***0.49***	***0.95***
Jochum et al. (2016)	25.08	53.12	6.83	28.26	6.55	1.99	6.81	1.08	6.42	1.31	3.67	3.39	0.50
NOD-A-1 (n = 6)	**111.2**	**745**	**23.85**	**99.55**	**21.79**	**5.28**	**24.28**	**3.84**	**23.08**	**4.96**	**14.31**	**13.48**	**2.08**
RSD %	***1.68***	***1.75***	***1.74***	***1.70***	***1.81***	***2.29***	***2.08***	***1.63***	***1.68***	***1.73***	***1.93***	***1.69***	***1.79***
Flanagan and Gottfried (1980)	120	730		94	21	5	26		23		12	14	2.2
Dulski (2001)	112	743	24.3	93	19.8	5.4	24.9	3.9	23.5	4.9	14.6	13.7	2.2
Axelsson et al. (2002)	115	720	25.0	98.0	21.9	5.20	25.4	4.00	23.8	5.00	14.4	13.9	2.10
Bau et al. (2014)	115	792	24.8	103	22.3	5.51	26.1	3.98	24	5.06	15.1	14.1	2.27
Laurila et al. (2014)	115.4	750	25.1	104.3	22.8	5.5	25	4	24.1	5	14.2	14	2.2
NOD-P-1 (n = 6)	**106.4**	**319**	**31.40**	**132.2**	**31.87**	**7.68**	**30.28**	**4.71**	**26.29**	**5.00**	**13.42**	**12.70**	**1.82**
RSD %	***0.35***	***0.55***	***0.32***	***0.46***	***0.54***	***1.31***	***1.40***	***0.83***	***0.51***	***0.61***	***0.76***	***0.69***	***0.69***
Flanagan and Gottfried (1980)	104	290		120	30	7.5	28		27		12	13	1.8
Dulski (2001)	110	329	33	128	30	8	31.7	4.8	27.5	5.13	14.15	13.3	1.99
Axelsson et al. (2002)	105	305	31.0	130	31.0	7.60	30.4	4.90	27.1	5.00	13.6	12.9	1.80
Bau et al. (2014)	104	322	31.5	127	31.9	7.97	32.2	4.89	27.9	5.01	14	13.4	1.96
Laurila et al. (2014)	110.5	325	33	138	33.2	7.9	30.95	4.9	27.3	5.05	13.2	13.15	1.93
FeMn-1 (n = 6)	**66.69**	**107.8**	**14.22**	**62.62**	**13.65**	**3.53**	**15.68**	**2.48**	**15.81**	**3.37**	**9.77**	**9.90**	**1.49**
RSD %	***1.80***	***1.99***	***1.57***	***2.05***	***0.61***	***0.97***	***2.31***	***2.39***	***2.28***	***0.91***	***1.45***	***1.96***	***1.52***
Webb et al. (2008)	68.22	110	14.11*	62.95	14.03	3.8	15.63	2.52	15.8	3.42	9.80	10	1.59*
Kriete (2010)	68.2	109	14.3	63	14.1	3.75	15.6	2.53	15.8	3.44	9.81	9.88	1.57
Bau et al. (2014)	65	108	14.3	59.5	13.7	3.61	16.1	2.5	16.5	3.38	10.1	10.3	1.58
GSPN-2 (n = 5)	**175**	**617**	**49.19**	**201**	**47.07**	**11.60**	**47.33**	**7.42**	**41.81**	**8.00**	**21.47**	**20.22**	**2.97**
RSD %	***1.01***	***0.93***	***1.22***	***0.79***	***0.83***	***0.74***	***0.74***	***0.86***	***0.91***	***0.78***	***0.78***	***0.88***	***0.52***
Wang et al. (1998)	184	620	49	198	46	11	48	7.6	42	8.2	21	20	2.9
Dulski (2001)	191	657	53	201	46	12.5	50.6	7.82	44.7	8.4	23.2	21.7	3.3
Laurila et al. (2014)	180.1	607.05	49.5	204.3	47.6	11.6	46.55	7.45	42.15	7.85	20.65	20.35	3
GSPN-3 (n = 5)	**92.20**	**252**	**29.06**	**123**	**30.54**	**7.42**	**29.21**	**4.67**	**26.11**	**4.93**	**13.16**	**12.47**	**1.79**
RSD %	***0.36***	***0.75***	***0.44***	***1.03***	***1.08***	***1.01***	***1.59***	***1.17***	***1.74***	***1.71***	***1.91***	***0.76***	***0.95***
Wang et al. (1998)	96	249	29	121	31	7.6	28	4.6	27	5.1	13	12	1.8
Dulski (2001)	97	262	30.9	120	29	7.95	30.8	4.87	27.4	5	13.9	13.2	1.95
Bau et al. (2014)	95.9	267	29.1	124	31	7.46	29.6	4.68	26.8	4.92	13.8	12.9	1.9
GSMC-1 (n = 5)	**326**	**1246**	**68.74**	**283**	**58.40**	**14.36**	**61.68**	**9.53**	**56.48**	**11.58**	**31.93**	**29.20**	**4.26**
RSD %	***1.76***	***1.73***	***0.84***	***1.16***	***0.80***	***0.99***	***1.08***	***0.70***	***0.51***	***0.65***	***0.47***	***0.57***	***0.18***
Wang et al. (2003)	352	1315	72	293	61	15	65	9.5	58	11.3	32	31	4.5
Bau et al. (2014)	349	1370	71			15.2	68.4	10.3	60.1	12.1	34.1	30.9	4.68
GSMC-2 (n = 5)	**317**	**1134**	**60.52**	**249**	**49.31**	**12.12**	**54.34**	**8.28**	**49.98**	**10.55**	**29.70**	**27.28**	**4.10**
RSD %	***0.49***	***1.40***	***0.53***	***0.48***	***0.44***	***0.49***	***0.63***	***0.58***	***0.60***	***0.55***	***0.53***	***0.46***	***0.57***
Wang et al. (2003)	323	989	63	246	49	12	58	8.1	52	10.5	30	28	4.2
GSMC-3 (n = 5)	**289**	**1014**	**58.06**	**240**	**49.27**	**12.19**	**54.53**	**8.24**	**48.95**	**10.24**	**28.49**	**26.34**	**3.91**
RSD %	***0.78***	***1.01***	***0.91***	***0.84***	***0.69***	***0.64***	***1.34***	***0.56***	***0.74***	***0.56***	***0.86***	***0.72***	***0.47***
Wang et al. (2003)	306	1080	62	246	51	12	55	8	51	10.2	29	27.4	4.2

*Provisional.

those acquired in low-resolution are conceivable in high-resolution provided exclusive usage of more concentrated solutions to enhance the entering signal. However, such protocol would generate an important risk of saturation of the collector in low-resolution requiring a substantial increase of the rinse time and overall cleaning procedure between each analytical session. Therefore, the high-resolution acquisition seems not to be relevant for REE characterization in Fe–Mn oxides.

4. Conclusion

In this study, the determination by ICP-MS of REE and other trace element abundances in eight certified reference materials of Fe–Mn oxides (FeMn-1, GSMC-1, GSMC-2, GSMC-3, GSPN-2, GSPN-3, NOD-A-1 and NOD-P-1) was investigating, using a Tm addition analytical procedure. Two different approaches were investigated for the correction of

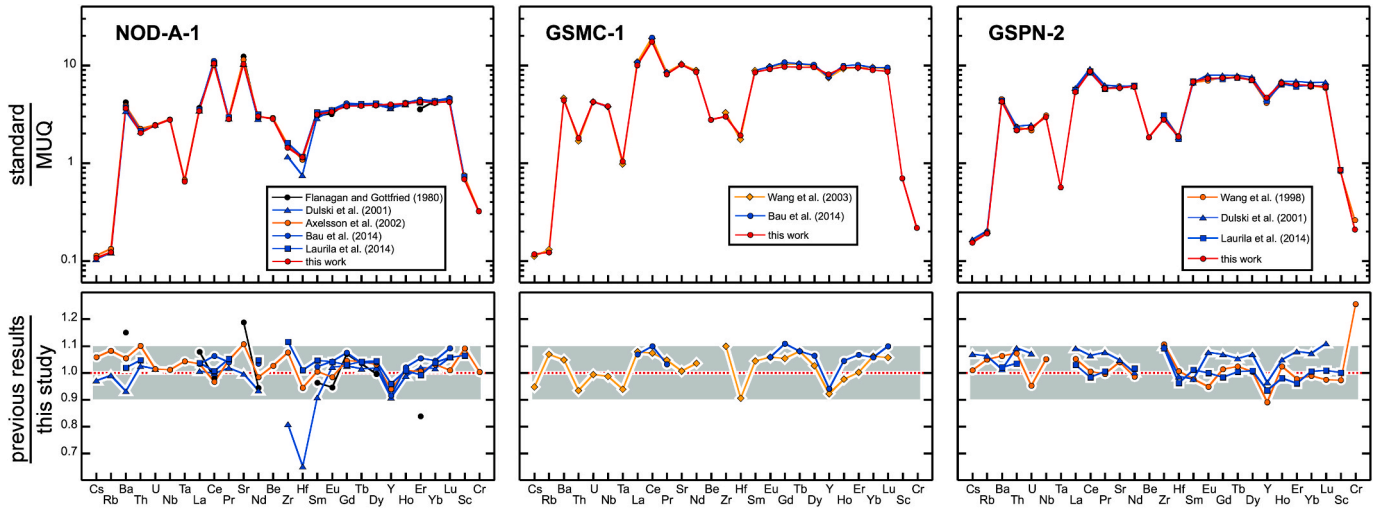

Fig. 1. MUQ normalized trace elements and REE patterns measured in LR mode from the certified reference materials NOD-A-1, GSMC-1 and GSPN-2.

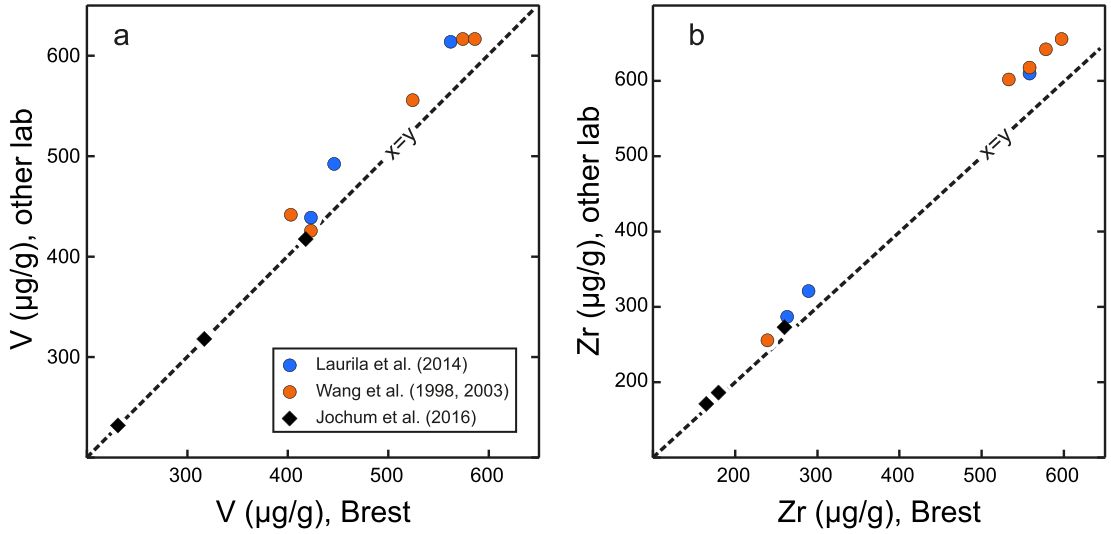

Fig. 2. A comparison of the V (µg/g) and the Zr (µg/g) values obtained in LR mode in this study and from literature studies showing a calibration bias. The black diamonds represent the basalt standards (including BHVO-2) and the points correspond to the Fe–Mn oxides.

isobaric interferences that can significantly affect measured concentrations during ICP-MS analyses: the use of mono-elemental solutions and the data acquisition in high-resolution mode. Our data demonstrate that the high-resolution acquisition mode is not the preferred choice for REE measurements in Fe–Mn oxides. Indeed, despite accurate data, the RSD are greater (<6.5%) than those obtained with the low resolution mode after correction of interferences using mono-elemental solutions (RSD < 2.5%).

The procedure was developed and validated using two silicate reference materials (BCR-2, BEN) providing precise and accurate data, before being applied to Fe–Mn oxides and calibrated with a silicate standard (BHVO-2). Although notable differences exist between our values and some data of the literature, the obtained results for two silicate certified reference materials (BCR-2 and BEN) are in excellent agreement with published reference values demonstrating the high-quality calibration of our analytical procedure. Using our revised protocol, we propose a new set of fair and accurate reference values for eight Fe–Mn certified reference materials that are widely used, but which were so far poorly characterized for trace elements.

As tracers of processes, sources and physicochemical parameters, REE and Y can provide crucial information concerning the mechanisms of formation of Fe–Mn oxides. REE and Y are also essential for deciphering between the different types of Fe–Mn oceanic deposits. Quantifying them precisely is a key step to discriminate mineral resources before targeting deposits and driving deep-sea exploration. Thus, this new set of data will serve as useful reference values for studies aiming at precisely quantifying REE (and other trace element) abundances in Fe–Mn oxides.

Declaration of competing interest

The authors declare that they have no known competing financial

Table 4
Comparisons between low and high-resolution REE values for the certified reference materials.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu
Basalts													
BE-N													
LR, n = 6 (*RSD%*)	83.1 (*0.88*)	153 (*0.79*)	17.30 (*1.12*)	66.85 (*0.90*)	12.17 (*1.02*)	3.69 (*1.04*)	10.17 (*2.07*)	1.305 (*1.28*)	6.46 (*0.77*)	1.108 (*0.44*)	2.58 (*0.76*)	1.85 (*0.88*)	0.242 (*0.35*)
HR, n = 6 (*RSD%*)	83.0 (*4.39*)	152 (*5.51*)	17.09 (*5.72*)	66.53 (*5.77*)	12.22 (*6.26*)	3.66 (*6.41*)	9.81 (*5.22*)	1.299 (*7.74*)	6.59 (*6.09*)	1.115 (*6.20*)	2.61 (*4.41*)	1.81 (*5.35*)	0.232 (*6.56*)
HR/LR	0.999	0.993	0.988	0.995	1.004	0.990	0.965	0.995	1.021	1.006	1.008	0.977	0.958
BCR-2													
LR, n = 5 (*RSD%*)	24.99 (*0.72*)	52.98 (*0.79*)	6.80 (*0.67*)	28.78 (*0.71*)	6.57 (*0.54*)	1.93 (*0.82*)	6.68 (*0.67*)	1.048 (*0.44*)	6.39 (*0.75*)	1.322 (*0.73*)	3.68 (*0.76*)	3.38 (*0.48*)	0.491 (*0.95*)
HR, n = 5 (*RSD%*)	24.50 (*1.33*)	52.83 (*3.04*)	6.77 (*3.60*)	28.61 (*2.99*)	6.45 (*3.35*)	1.97 (*1.51*)	6.70 (*2.38*)	1.036 (*5.95*)	6.31 (*2.22*)	1.304 (*2.24*)	3.67 (*3.83*)	3.35 (*5.97*)	0.480 (*4.20*)
HR/LR	0.980	0.997	0.996	0.994	0.980	1.021	1.003	0.989	0.987	0.987	0.998	0.991	0.977
Nodules													
NOD-A-1													
LR, n = 6 (*RSD%*)	111.2 (*1.68*)	745 (*1.74*)	23.85 (*1.74*)	99.55 (*1.70*)	21.79 (*1.81*)	5.28 (*2.29*)	24.28 (*2.08*)	3.84 (*1.63*)	23.08 (*1.68*)	4.96 (*1.73*)	14.31 (*1.93*)	13.48 (*1.69*)	2.08 (*1.79*)
HR, n = 6 (*RSD%*)	110.0 (*3.03*)	740 (*2.38*)	23.79 (*2.18*)	99.45 (*1.77*)	21.73 (*3.37*)	5.41 (*2.70*)	24.75 (*2.54*)	3.90 (*2.12*)	22.92 (*2.18*)	5.02 (*2.83*)	14.52 (*5.22*)	13.69 (*3.09*)	2.14 (*5.37*)
HR/LR	0.989	0.994	0.997	0.999	0.997	1.024	1.019	1.015	0.993	1.013	1.015	1.016	1.029
NOD-P-1													
LR, n = 6 (*RSD%*)	106.4 (*0.35*)	319 (*0.55*)	31.40 (*0.32*)	132.2 (*0.46*)	31.87 (*0.54*)	7.68 (*1.31*)	30.28 (*1.40*)	4.71 (*0.83*)	26.29 (*0.51*)	5.00 (*0.61*)	13.42 (*0.76*)	12.70 (*0.69*)	1.82 (*0.69*)
HR, n = 6 (*RSD%*)	107.1 (*3.02*)	321 (*2.20*)	31.84 (*2.38*)	134.5 (*2.14*)	32.41 (*2.63*)	7.97 (*3.30*)	30.85 (*2.35*)	4.74 (*3.75*)	27.03 (*4.00*)	5.16 (*3.14*)	13.58 (*4.33*)	13.08 (*4.61*)	1.93 (*5.73*)
HR/LR	1.006	1.005	1.014	1.018	1.017	1.037	1.019	1.007	1.028	1.031	1.012	1.030	1.058
FeMn-1													
LR, n = 6 (*RSD%*)	66.69 (*1.80*)	107.8 (*1.99*)	14.22 (*1.57*)	62.62 (*2.05*)	13.65 (*0.61*)	3.53 (*0.97*)	15.68 (*2.31*)	2.48 (*2.39*)	15.81 (*2.28*)	3.37 (*0.91*)	9.77 (*1.45*)	9.90 (*1.96*)	1.49 (*1.52*)
HR, n = 6 (*RSD%*)	65.43 (*6.05*)	106.0 (*4.78*)	14.20 (*4.02*)	62.63 (*3.20*)	13.75 (*4.85*)	3.64 (*3.75*)	15.44 (*2.85*)	2.48 (*4.72*)	15.74 (*5.68*)	3.36 (*4.57*)	9.89 (*5.42*)	10.07 (*2.03*)	1.51 (*3.98*)
HR/LR	0.981	0.983	0.999	1.000	1.008	1.029	0.985	0.999	0.995	0.996	1.012	1.017	1.014
GSPN-2													
LR, n = 5 (*RSD%*)	175 (*1.01*)	617 (*0.93*)	49.19 (*1.22*)	201 (*0.79*)	47.07 (*0.83*)	11.60 (*0.74*)	47.33 (*0.74*)	7.42 (*0.86*)	41.81 (*0.91*)	8.00 (*0.78*)	21.47 (*0.78*)	20.22 (*0.88*)	2.97 (*0.52*)
HR, n = 5 (*RSD%*)	174 (*2.44*)	609 (*2.86*)	47.81 (*2.47*)	199 (*1.87*)	46.31 (*2.37*)	11.62 (*2.51*)	46.82 (*1.62*)	7.27 (*2.45*)	41.61 (*2.68*)	7.85 (*2.52*)	21.85 (*2.38*)	19.74 (*1.85*)	2.87 (*4.45*)
HR/LR	0.997	0.986	0.972	0.990	0.984	1.002	0.989	0.980	0.995	0.981	1.018	0.976	0.964
GSPN-3													
LR, n = 5 (*RSD%*)	92.19 (*0.36*)	251 (*0.75*)	29.06 (*0.44*)	123 (*1.03*)	30.54 (*1.08*)	7.42 (*1.01*)	29.21 (*1.59*)	4.67 (*1.17*)	26.11 (*1.74*)	4.93 (*1.71*)	13.16 (*1.91*)	12.47 (*0.76*)	1.79 (*0.95*)
HR, n = 5 (*RSD%*)	90.19 (*5.24*)	245 (3.41)	28.51 (*3.93*)	122 (*3.28*)	30.32 (*3.59*)	7.37 (*2.78*)	28.60 (*2.50*)	4.63 (*3.05*)	25.57 (3.76)	4.81 (*4.76*)	13.47 (*4.47*)	12.40 (*4.43*)	1.81 (*6.17*)
HR/LR	0.978	0.974	0.981	0.995	0.993	0.993	0.979	0.991	0.979	0.977	1.024	0.994	1.016
Crusts													
GSMC-1													
LR, n = 5 (*RSD%*)	326 *(1.76)*	1245 *(1.73)*	68.74 *(0.84)*	283 *(1.16)*	58.40 *(0.80)*	14.36 *(0.99)*	61.68 *(1.08)*	9.53 *(0.70)*	56.48 *(0.51)*	11.58 *(0.65)*	31.93 *(0.47)*	29.20 *(0.57)*	4.26 *(0.18)*
HR, n = 5 (*RSD%*)	331 *(4.09)*	1237 *(3.19)*	67.41 *(3.80)*	283 *(3.14)*	58.54 *(3.69)*	14.45 *(3.03)*	63.71 *(3.91)*	9.32 *(3.45)*	56.53 *(2.89)*	11.60 *(3.60)*	32.32 *(3.54)*	29.16 *(4.07)*	4.21 *(3.65)*
HR/LR	1.015	0.994	0.981	1.000	1.002	1.006	1.033	0.978	1.001	1.002	1.012	0.999	0.988
GSMC-2													
LR, n = 5 (*RSD%*)	317 *(0.49)*	1134 *(1.40)*	60.52 *(0.53)*	249 *(0.48)*	49.31 *(0.44)*	12.12 *(0.49)*	54.34 (*0.63*)	8.28 (*0.58*)	49.98 (*0.60*)	10.55 (*0.55*)	29.70 (*0.53*)	27.28 (*0.46*)	4.10 (*0.57*)
HR, n = 5 (*RSD%*)	312 *(2.57)*	1117 *(1.97)*	59.64 *(2.78)*	246 *(2.56)*	49.54 *(1.11)*	12.25 *(2.70)*	54.64 (*3.18*)	8.16 (*2.58*)	49.78 (*1.71*)	10.55 (*2.85*)	29.75 (*2.37*)	27.32 (*3.18*)	4.11 (*3.98*)
HR/LR	0.986	0.986	0.986	0.988	1.005	1.011	1.006	0.986	0.996	0.999	1.002	1.002	1.004
GSMC-3													
LR, n = 5 (*RSD%*)	289 *(0.78)*	1014 *(1.01)*	58.06 *(0.91)*	240 *(0.84)*	49.27 *(0.69)*	12.19 *(0.64)*	54.53 (*1.34*)	8.24 (*0.56*)	48.95 (*0.74*)	10.24 (*0.56*)	28.49 (*0.86*)	26.34 (*0.72*)	3.91 (*0.47*)
HR, n = 5 (*RSD%*)	300 *(2.21)*	1042 *(1.19)*	59.98 *(1.46)*	249 *(1.56)*	51.09 *(1.01)*	12.62 *(2.21)*	56.64 (*2.50*)	8.58 (*0.76*)	50.24 (*1.71*)	10.53 (*0.76*)	29.24 (*2.08*)	27.33 (*1.88*)	4.04 (*2.71*)
HR/LR	1.039	1.028	1.033	1.038	1.037	1.035	1.039	1.042	1.026	1.028	1.027	1.038	1.032

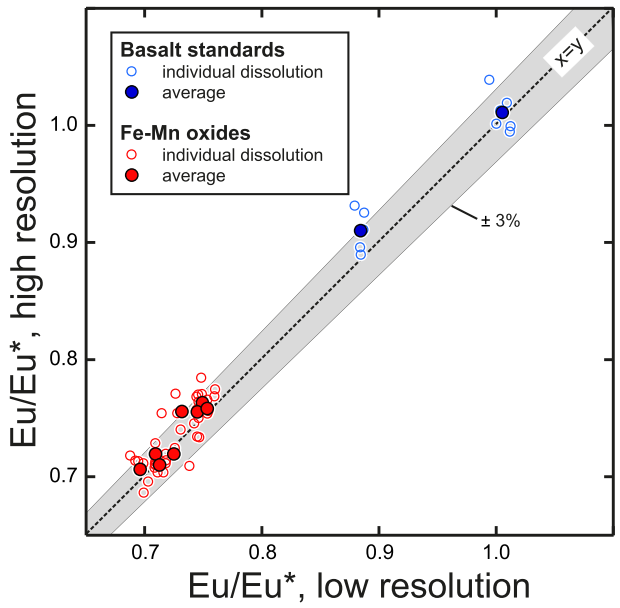

Fig. 3. A comparison of measured Eu/Eu* ratio in LR and HR modes for the basalt standards and the studied Fe–Mn oxides.

interests or personal relationships that could have appeared to influence the work reported in this paper.

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