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Abstract

The oxidation state of iron in mantle-derived melts is commonly used to determine the oxygen fugacity (fO_2) of magmas and their related sources. The accurate and precise determination of the iron oxidation state ratio of Mid-Oceanic Ridge Basalt (MORB) glasses has been a matter of controversy for the last three decades. None of the wet chemical methods used in the literature to measure this ratio converge toward a consensus value. The same difficulties have been observed for the most recent data obtained by XANES spectroscopy, which allows the measurement of the iron oxidation state ratio at high spatial resolution. This study unravels the origin of the analytical biases observed between the colorimetric and direct titration wet chemistries used in the studies of Christie et al. (1986) and Bézos and Humler (2005), respectively. We demonstrate that colorimetric measurements overestimate the ferrous iron contents of sulfide-bearing samples whereas the direct titration method does not suffer from such sulfide interference. Because MORB glasses contain significant amount of sulfur in the +2 valence state, we re-assessed the average MORB FeO/FeO_{total} ratio by using the bulk FeO_{total} and FeO data from this study and from Bézos and Humler (2005),

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respectively. We calculated for 49 MORB glasses an average FeO/FeO_{total} of 0.90±0.02. This result agrees with colorimetric measurements corrected for sulfide interference and with the results of Bézos and Humler (2005), if corrected for the presence of plagioclase in the sample powders. The average MORB FeO/FeO_{total} that we determined in this study agrees also within uncertainty with the most recent XANES spectroscopic data of Berry et al. (2018) (0.90±0.02).

Keywords: MORB, iron, oxidation sate, wet chemistry, XANES spectroscopy

1. Introduction

The oxygen fugacity (fO_2) is a fundamental parameter that plays a role in producing the calc-alkaline and tholeiitic differentiation trends (Gill, 1981; Grocke et al., 2016; Chin et al., 2018), in determining the speciation of the magmatic gases released into the atmosphere (Holland, 2002; Brounce et al., 2017), and in influencing the valence state and partitioning behaviors of redox sensitive elements in magmas. Iron is the only major element for which two valence states co-exist in terrestrial mafic magmas. Therefore, special attention has been paid to develop precise and accurate analytical methods to measure the $Fe^{3+}/\Sigma Fe$ ratio (Mysen et al., 1985; Fialin et al., 2004; Bézos and Humler, 2005; Cottrell and Kelley, 2011; Shorttle et al., 2015; Zhang et al., 2018; Berry et al., 2018; Le Losq et al., 2019; Gaborieau et al., 2020) and to relate this ratio to fO_2 (Kress and Carmichael, 1991; O'Neill et al., 2018). The $Fe^{3+}/\Sigma Fe$ ratio of MORB magmas has been regularly debated in the literature during the last three decades (Carmichael and Ghiorso, 1986;

Christie et al., 1986; Bézos and Humler, 2005; Cottrell and Kelley, 2011; Zhang et al., 2018; Berry et al., 2018). There is yet no real consensus on the absolute value of this ratio. This is mainly due to the analytical difficulties encountered to measure the $Fe^{3+}/\Sigma Fe$ ratio using either the Mössbauer spectroscopy method (Mysen et al., 1985; Rossano et al., 1999; Cottrell and Kelley, 2011; Zhang et al., 2018; Berry et al., 2018), which is used to calibrate the results of XANES spectroscopy, or wet chemical methods (Christie et al., 1986; Bézos and Humler, 2005). Important variations are observed in the iron redox state ratio of basic magmas from different tectonic settings (Kelley and Cottrell, 2012; Brounce et al., 2015; Gaborieau et al., 2020), and even within a given setting (Sinton, 2003; Brounce et al., 2017; Hartley et al., 2017; Novella et al., 2020). The lack of analytical consistency in the $Fe^{3+}/\Sigma Fe$ ratio measurements severely obscures our global view and understanding of present and past earth magma's fO_2.

The main analytical challenge of wet chemistries relies on the preservation of the iron redox state during sample digestion (Yokoyama and Nakamura, 2002). On this point, the studies of Christie et al. (1986) and Bézos and Humler (2005) have followed different strategies using the colorimetric and direct titration methods, respectively. In the former method, the sample is dissolved at room temperature for several days, in the presence of a strong oxidising agent: the pentavalent vanadium. The ferrous iron released from the sample matrix is thus immediately oxidized in ferric iron by V^{5+} (eq. 1), which preserves the sample from uncontrolled oxidation by air (Wilson,

1960).

$$V^{5+} + Fe^{2+} \rightleftharpoons V^{4+} + Fe^{3+} \quad (1)$$

This problem of Fe^{3+} oxidation by atmospheric O_2 has been investigated by Bézos and Humler (2005) in the context of a quite different sample dissolution protocol, which involved hot boiling acids for three minutes. The authors compare FeO measurements of vanadium-free dissolutions performed under inert (Ar) and ambiant atmospheres. The results of these experiments show no evidence of accidental Fe^{2+} oxidation by air.

On the other hand, the issue of the reduction of ferric to ferrous iron by sample sulfides during sample digestion has often been invoked (Wilson, 1960; Saikkonen and Rautiainen, 1993; Sossi and O'Neill, 2011; Berry et al., 2018), but never demonstrated for the case of oceanic basaltic glasses analyses. Nonetheless, the accurate measuring of the iron redox state ratio in MORB glasses requires a thoughtful evaluation of the potential interference of sulfides during sample dissolution. For this purpose, we used the colorimetric method — optimised to measure both FeO and FeO_{total} in the same aliquot of solution — and determined the FeO/FeO_{total} ratios of 6 reference materials and 49 MORB glassy samples. We quantified the interference of S^{2-} on the colorimetric and direct titration methods and proposed a re-evaluation of the average FeO/FeO_{total} of MORB glasses (0.90±0.02). We compared this results to the most recent XANES spectroscopic data calibrated by Mössbauer spectroscopy (Cottrell and Kelley, 2011; Zhang et al., 2018; Berry et al., 2018).

2. Reference materials and MORB samples

We analysed 6 natural reference powders of mafic rocks, BE-N, BR, BHVO-1, BCR-1, W-2 and JB-2 (see Table A1 and A2 in appendix A). They display recommended total iron contents, FeO/FeO_{total} ratios, and sulfur contents ranging from 9.5 to 13 wt. %, 0.56 to 0.87, and 20 to 400 μ g/g, respectively (Govindaraju, 1994; Jochum et al., 2016).

From the 49 Mid-Oceanic Ridge Basaltic (MORB) glassy samples selected from global sources, forty-six correspond to the same sample powders analysed by Bézos and Humler (2005) and/or Christie et al. (1986). Three new MORB glasses are specific to our study. They come from the South West Indian (ED-DR1-1-1), South East Indian (MD57-D2-3) and the Mid-Atlantic (MAPCO CH98-DR07) ridges (Bézos, 2003). All powders correspond to chips of glass that have been carefully hand-picked under a binocular microscope to discard all visible signs of alteration or micro-phenocrysts and were gently hand-ground in agate mortar (Christie et al., 1986; Bézos and Humler, 2005).

3. Colorimetric FeO/FeO_{total} analyses

The colorimetric method derives from the experimental protocols developed by Wilson (1960) and Schuessler et al. (2008). When used conjointly, these two protocols allow the determination of the FeO/FeO_{total} ratio in the same sample aliquot. The basic principle of FeO colorimetric measurements relies on the introduction of an oxidising agent (V^{5+}) before sample digestion to prevent undesired and accidental oxidation of Fe^{2+} (Wilson, 1960). As the digestion proceeds and breaks down the silicate network, the ferrous iron re-

leased into the low pH acid solution is immediately oxidised into ferric iron by pentavalent vanadium (eq. 1). The excess of V^{5+} during sample digestion ensures the quantitative oxidation of all Fe^{2+} into Fe^{3+}. Once the digestion is completed, the addition of an acetate buffer increases the pH of the solution up to 5. The reaction 1 is therefore reversed and proceeds now from right to left. The initial ferrous iron thereby regenerated can be analyzed by colorimetry (Wilson, 1960). The total iron content is then measured in its ferrous form by adding a strong reducing agent to convert all the remaining Fe^{3+} into Fe^{2+} (Schuessler et al., 2008).

3.1. FeO/FeO$_{total}$ analytical protocol

About 3-7 mg of sample powders were weighed with a precision of 10^{-3} mg in 7 mL crystal polypropylene beakers and digested for three days at room temperature in a mixture of 1 mL HF (40%) and 1mL of 1.41×10^{-2} mol.L^{-1} ammonium vanadate solution to guarantee V^{5+} excess. After complete digestion, 5 mL of beryllium sulfate solution (2.82 mol.L^{-1}) were added to the beakers to neutralise the excess of HF and to break down all insoluble fluorides. The prepared solutions were then transferred into 100 mL borosilicate glass volumetric flasks containing 10 mL ammonium acetate buffer solution (6.48 mol.L^{-1}) and 5 mL of a 2:2'-dipyridyl colorimetric reagent solution (6.9×10^{-3} mol.L^{-1}). All the flasks were then filled up to 100 mL with ultra-pure water. All samples and procedural blanks were stirred for 20 minutes before analysis to ensure full homogeneity of the solutions. The FeO$_{\mathrm{total}}$ analytical solutions were prepared by adding 100 mg of the strong reducing agent hydroxylamine hydrochloride to 15 mL of the FeO solutions. We prepared ferrous stock solution at 3.7×10^{-2} mol.L^{-1} by dissolving 14.5 g of ammonium

ferrous sulfate hexahydrate in 1L 2.9 % (m/m) H_2SO_4. This stock solution was then diluted to 0.0014 mol.L^{-1} and used to prepare the FeO and FeO_{total} external standard calibration solution at 2, 4, 6, 8, and 9.5 mg.L^{-1} Fe^{2+}.

3.2. Spectroscopic measurements

All colorimetric measurements reported in this study were acquired with the UV/VIS spectrophotometer CARY UV 500 (Varian) of the Laboratoire de Planétologie et Géodynamique (LPG, Université de Nantes, France). The optical density measurements were done at 525 nm where the ferrous- 2:2-dipyridil complex absorption is maximum (Wilson, 1960). All peak heights were determined relative to the baseline measured at 700 nm. The FeO/FeO_{total} ratios were determined by dividing the absorbance signals corrected for the baseline measured at 700 nm and for the procedural blanks. The typical regression parameters obtained for our external FeO and FeO_{total} standard calibrations display r^2= 0.9999 and intercepts that range between -0.01 $\pm$ 0.02 (1σ).

4. Analytical experiments in presence of sulfide

The presence of reduced species such as sulfide (S^{2-}) in natural samples has often been invoked as a potential source of interferences during FeO wet chemistries (Saikkonen and Rautiainen, 1993; Cottrell and Kelley, 2011; Sossi and O'Neill, 2011; Berry et al., 2018). Below, we present the experimental protocols that we have designed to characterise and quantify the potential sulfide interference on colorimetric and direct titration FeO measurements.

4.1. Cold sample digestion in presence of vanadium (colorimetric method)

We used simple S^{2-}, Fe^{3+} and V^{5+} reagent solutions to quantify the redox reactions that occur between these species during the three-day low temperature sample digestion.

In a first experiment, a synthetic solution of S^{2-} at 4.16×10^{-2} mol.L^{-1} was prepared by dissolving sodium sulfide hydrated salts ($Na_2S \cdot 9H_2O$) in pure H_2O. We then poured 0.1 g of $NH_4 \cdot VO_3$ salt (V^{5+}) into 5 mL of the S^{2-} solution and let the mixture rest at room temperature for between one hour and 72 hours. The titration of the V^{5+} left after the redox reaction with S^{2-} was done using a solution of Fe^{2+} (3.69×10^{-2} mol.L^{-1}) with 10 mL of pure H_2O and 10 mL of the coloured indicator barium diphenylamine sulfonate prepared following Crabtree and Lange (2012). The same protocol was then duplicated but without the addition of S^{2-}. The difference between the two titrations quantifies the number of S^{2-} moles that has reacted with V^{5+}.

In a second experiment, we tested the potential reaction between the S^{2-} and Fe^{3+} species. We poured 5 mL of the S^{2-} solution (4.16×10^{-2} mol.L^{-1}) into 20 mL of Fe^{3+} solution at $4 \times 10^{2-}$ mol L^{-1} and let it rest between 1 and 72 hours at room temperature. The titration of the Fe^{2+} was done using a solution of Cr^{6+} solution at 6.2×10^{-3} mol.L^{-1}, 5 mL of barium diphenylamine sulfonate as a coloured indicator and a few drops of concentrated HCl to lower the pH of the solution for titration.

Finally, the third experiment follows the conceptual approach of the standard addition method. We selected two MORB glassy samples that display natural sulfur contents of 1400 μg/g for the JDF-D2 and 1128 μg/g for GN02-02 (Bézos, 2003). We dissolved 3 aliquots of each sample in the exact same

conditions as those described in section 3.1 and added for two of them varying amounts of S^{2-} solution — one aliquot remained therefore free of S^{2-} addition. The FeO/FeO_{total} ratio, FeO and FeO_{total} contents were then measured by colorimetry.

4.2. Hot sample digestion in absence of vanadium (direct titration method)

Following the analytical protocol of Bézos and Humler (2005), we proceed to several dissolutions of the BR basaltic reference material with, and without the addition of a S^{2-} prior to sample digestion. The sample powder batches ($\approx$ 0.5 g) were then dissolved during three minutes in a mixture of boiling sulfuric and hydrofluoric acids. The released ferrous iron was immediately titrated against a potassium dichromate solution in a mixture of H_2SO_4 and H_3PO_4, using barium diphenylamine sulphonate as the redox indicator (for more details see Bézos and Humler, 2005).

5. Results

Historically, we have become used to report the iron redox state in the form of the $Fe^{3+}/\Sigma Fe$ ratio, which corresponds to the ratio of the quantity of Fe_2O_3 normalized to the total iron expressed as ferric iron. Because only few wet chemical methods are available to determine the ferric iron in geological samples (Roex and Watkins, 1995; Tarafder and Thakur, 2013), this latter oxide is usually recalculated by difference between FeO_{total} — the total iron expressed as ferrous iron — and FeO measurements. However, for the sake of analytical consistency and coherent error propagation calculations, we consider that it is more relevant to present our results in the form of the

FeO/FeO_{total} ratio. Both ratios are related by the relationship $Fe^{3+}/\Sigma Fe$ = 1- FeO/FeO_{total}.

5.1. Colorimetric measurements on geological reference materials

Comparisons of our FeO_{total}, FeO, and FeO/FeO_{total} measurements with recommended (Govindaraju, 1994; Jochum et al., 2016) or previously published (Bézos and Humler, 2005) values are presented in Fig.1 (see also Table A.1 in supplementary materials). Although, the FeO_{total} data are offset on average by 0.20% FeO_{total} above the 1:1 line in Fig. 1-A, our results agree within 2 sigma error with the recommended values of Jochum et al. (2016), except for BHVO-1. Our FeO and FeO/FeO_{total} results match all reference values, except for the FeO/FeO_{total} ratio of BHVO-1 (Fig. 1-B and -C). The reproducibility of our measurements varied between 0.6 and 2.2% (1σ relative) for FeO, 0.5 and 1.8% (1σ relative) for FeO_{total}, and from 0.5 to 1.2% for the FeO/FeO_{total} ratio (Table A.1).

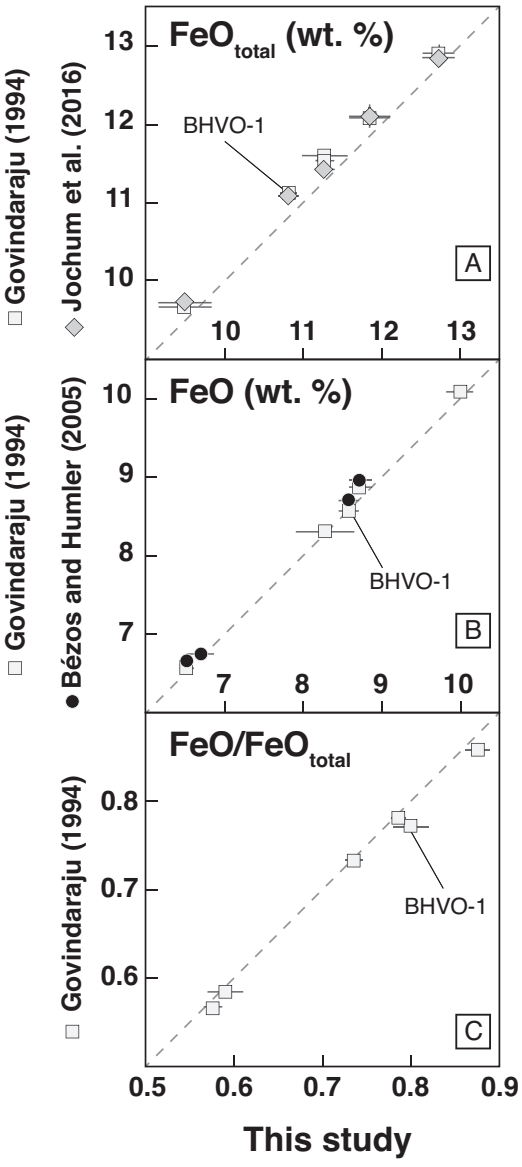
FeO$_{total}$ (wt. %)
BHVO-1
A
Govindaraju (1994)
Jochum et al. (2016)
FeO (wt. %)
BHVO-1
B
Govindaraju (1994)
Bézos and Humler (2005)
FeO/FeO$_{total}$
BHVO-1
C
Govindaraju (1994)
This study

Figure 1: Comparison of FeO_{total} (A), FeO (B), and FeO/FeO_{total} (C) results from this study with recommended values from Govindaraju (1994) (white squares), preferred values from Jochum et al. (2016) (grey diamonds), and with Bézos and Humler (2005) (black dots) for 6 reference materials of mafic compositions. Dashed line: 1:1 line, error bars are 2 σ errors.

5.2. Colorimetric measurements on MORB glassy samples

To begin with, it is important to remind briefly the discrepancies of the analytical protocols used by Bézos and Humler (2005), Christie et al. (1986) and this study. The present study and that of Christie et al. (1986) display the closest match in their analytical methodologies. Indeed, both studies determined the bulk FeO and FeO_{total} contents for the same powder aliquots and both studies used the same vanadium-based FeO colorimetric method, which involves the cold dissolution of less than 10 mg of sample during three days (Wilson, 1960). The only notable difference would be that Christie et al. (1986) analyzed the bulk FeO_{total} contents using a Direct Current Plasma (DCP) spectrometer instrument whereas we used the colorimetric method adapted from Schuessler et al. (2008). The differences between Bézos and Humler (2005) and this study are, however, more fundamental. Bézos and Humler (2005) analyzed the FeO contents by direct titration using a Cr^{6+} solution (Grillot et al., 1964), which does not require pentavalent vanadium. Moreover, the sample digestion in Bézos and Humler (2005) which involved 500 mg of material, was performed during 3 minutes above the boiling point of an acid mixture composed of 7 mL of H_2SO_4 (9 $mol.L^{-1}$) and 3 mL HF (22

mol.L^{-1}). Finally, Bézos and Humler (2005) analyzed the FeO_{total} contents using the in-situ electron microprobe technique. Some discrepancies between the bulk colorimetric or DCP methods (Christie et al., 1986, and this study) and the in-situ FeO_{total} electron microprobe data (Bézos and Humler, 2005) may occur. Indeed, we cannot guarantee that the sample powders were totally devoid of micro-crystals of plagioclase or olivine. The presence of the former mineral has the effect to lower the measured iron content whereas the latter increases it.

The 13 replicate analyses of the GN02-02 MORB powder over a period of 3 years yielded a reproducibility (relative 1σ error) of 0.74% for FeO, 1.12% for FeO_{total}, and 1.17% for the FeO/FeO_{total} ratio (Table A.2 in supplementary materials). All other MORB results are reported in Table A.3 and presented in Fig. 2. In Fig.2-A our FeO_{total} colorimetric results on MORB glasses display systematically lower values ($\approx$ -0.28 wt.% on average) when compared to microprobe data (Bézos and Humler, 2005, black dots). Although this offset is comparable to that observed in Fig. 1-A, the good match between our FeO_{total} results and that of bulk DCP analysis from Christie et al. (1986) (white dots) strongly support that this offset is more likely related to the use of bulk and in-situ analytical methods. As proposed by Bézos and Humler (2005) the presence of $\approx$ 1.5% plagioclase micro-crystals — an iron-free phase — in sample powders may account for the offset observed in Fig. 1-A. In Fig. 2-B, our FeO data display on average higher contents (+0.21 wt.% on average) when compared to the direct titration data of Bézos and Humler (2005). Because both data sets were produced from the exact same batches of powders with bulk analytical methods, such difference cannot be explained

by the presence of plagioclase micro-crystals in the powders. The FeO colorimetric data from our study match with that of Christie et al. (1986). Finally, we report an average FeO/FeO_{total} ratio of 0.92±0.01 for our MORB sample set, which is in good agreement with the study of Christie et al. (1986).

The MORB data presented in Fig. 2 thus reveal a methodological bias between bulk and in-situ FeO_{total} analyses and an analytical bias between vanadium-based (Christie et al., 1986, this study) and direct titration FeO data (Bézos and Humler, 2005).

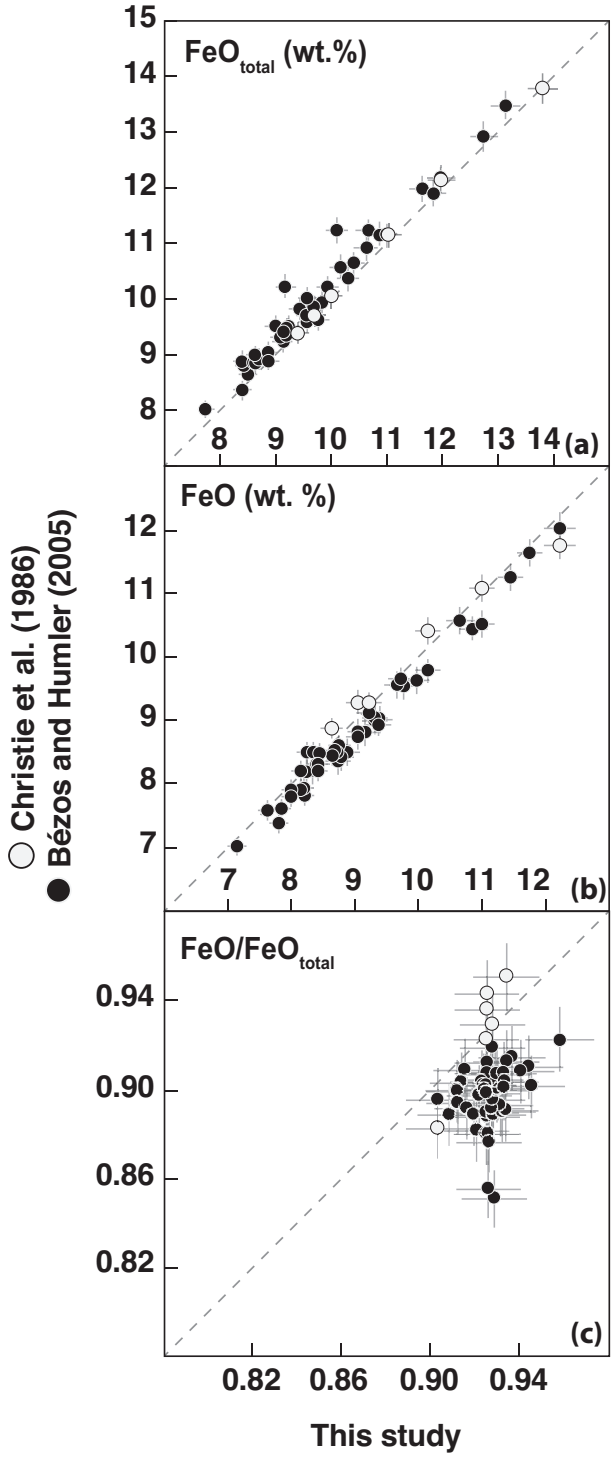
FeO$_{total}$ (wt.%)
(a)
FeO (wt. %)
(b)
FeO/FeO$_{total}$
(c)
○ Christie et al. (1986)
● Bézos and Humler (2005)
This study

Figure 2: Comparison of FeO_{total} (A), FeO (B) and FeO/FeO_{total} (C) measurements from this study with results from Christie et al. (1986) (white dots) and Bézos and Humler (2005) (black dots). The analyses were made on the same batches of powders. Error bars corresponds to a 95% confidence level. Dashed line: 1:1 line.

5.3. Sulfide interferences on FeO measurements

5.3.1. Colorimetric method

In a first experiment, we investigated the redox reaction that might occur between pentavalent vanadium and sulfide during sample digestion. We prepared a solution with known amounts of S^{2-} and V^{5+} that we set aside at room temperature for one to 72 hours. We then titrated the amount of V^{5+} left in the final solution with a Fe^{2+} solution (all the results are in Table B.1 in supplementary materials). From this data, we calculated the amount of V^{4+} formed during the redox reaction with S^{2-} and determined a $n_{V^{4+}}/n_{S^{2-}}$ molar ratio of 1.9 ± 0.1 for this reaction. In the context of ferrous colorimetric measurements, the presence of V^{4+} implies that when eq. 1 is reversed, the number of mole of V^{4+} is not equal to $n_{Fe^{2+}}$ but to $n_{Fe^{2+}} + 1.9 \pm 0.1 \times n_{S^{2-}}$.

In a second experiment, we tested more specifically the potential interference of S^{2-} on Fe^{3+} during sample digestion. We prepared 25 mL of a solution with known quantities of sulfide and ferric iron and left the solution at room temperature for one to 72 hours. During this experiment, we noticed the formation of black solid particles. After one night, the black solid turned into white solid. Raman spectroscopy of these particles revealed that

the black solids corresponds to FeS mackinawite and white solids to sulfur α-S_8 (Bourdoiseau et al., 2008). Because of the presence of particles, the solution was centrifuged and the Fe^{2+} formed was determined in a 20 mL aliquot using a direct Cr^{6+} titration. The final $n_{Fe^{2+}}$ was recalculated by normalising it to the initial volume of the solution (25 mL). We measured significant amount of Fe^{2+} and determined a molar ratio $n_{Fe^{2+}}/n_{S^{2-}}$ of 1.7 (see Table B.2 in supplementary materials).

These two experiments clearly demonstrate that sample digestion in presence of S^{2-} reduces V^{5+} into V^{4+} and Fe^{3+} into Fe^{2+}. These two redox reactions artificially increase the FeO content, and therefore FeO/FeO_{total} ratio, measured by colorimetry.

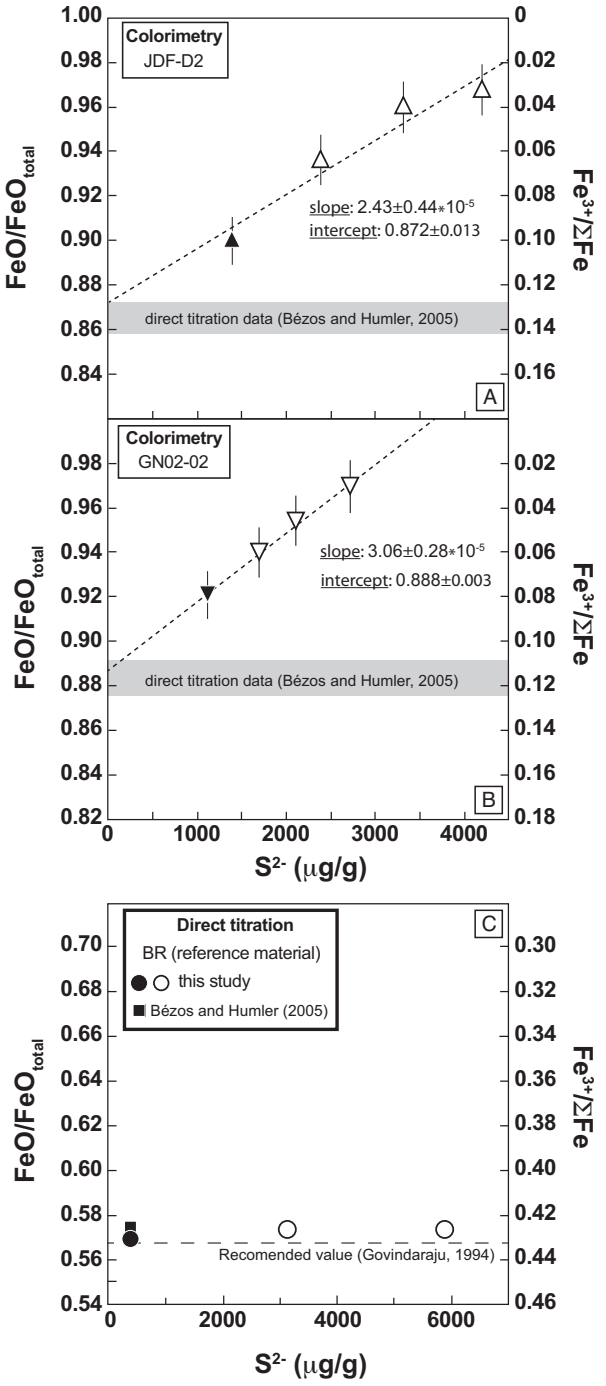
Colorimetry
JDF-D2
slope: 2.43±0.44*10-5
intercept: 0.872±0.013
direct titration data (Bézos and Humler, 2005)
A
Colorimetry
GN02-02
slope: 3.06±0.28*10-5
intercept: 0.888±0.003
direct titration data (Bézos and Humler, 2005)
B
FeO/FeOtotal
Fe3+/ΣFe
S2- (μg/g)
Direct titration
BR (reference material)
this study
Bézos and Humler (2005)
C
Recomended value (Govindaraju, 1994)

Figure 3: Quantification of sulfide (S^{2-}) interference on the FeO/FeO_{total} measurements for the vanadium-based colorimetric method (panels A and B) and for the direct titration method (panel C). A & B: experiments on the two natural MORB glassy matrices JDF-D2 and GN02-02, respectively. C: experiments on the BR basaltic rock reference material. Open symbols: samples spiked with varying amounts of a S^{2-} solution; solid symbols: un-spiked samples; Gray area: direct titration data from Bézos and Humler (2005).

Our third experiment was designed to quantify the interference of S^{2-} on the measured FeO/FeO_{total} ratio in the presence of the sample matrix and under standard analytical conditions (section 3.1). Prior to sample dissolution, we added various amounts of S^{2-} to the natural glassy samples JDF-D2 and GN02-02. These two samples have natural sulfur contents of 1400 and 1128 μ g/g respectively (Bézos, 2003), mostly in the form of S^{2-}. In Fig. 3, the solid symbols correspond to the results for un-spiked samples and open symbols to the S^{2-}-spiked samples. The higher the sulfide content is during sample digestion, the higher the measured FeO/FeO_{total} ratio. Because the slopes in Fig. 3 depend upon the $n_{Fe^{2+}}/n_{S^{2-}}$ mole ratio of the redox reaction and the total iron content, they cannot be compared directly. Therefore, we calculated from these data that for each mole of S^{2-} added to the JDF-D2 and GN-02-02 samples, 1.32±0.24 and 1.29±0.12 moles of Fe^{2+} were produced respectively. Although this mole ratio is slightly lower than those calculated from our two first experiments (i.e. 1.9-1.7), this result confirms that S^{2-} interferes under the standard analytical conditions of the colorimetric method. We also note that both mole ratios are close enough to suggest the same sulfide effect for both matrices.

5.3.2. Direct titration method

We first proceed to three dissolutions of the BR reference material — a continental basalt, see Table A1 and A2 in appendix A — with no addition of S^{2-} solution prior to sample digestion. The average ferrous iron content recovered from these analyses is 6.59 ± 0.04% m/m (Table B.3), which is in very good agreement with the recommended value of Govindaraju (1994) and with the measurements from Bézos and Humler (2005) (6.57% and 6.65%, respectively). Two dissolutions were then carried out in presence of varying amount of a S^{2-} solution prepared from sodium sulfide hydrated salts (Na_2S). The BR reference material contains naturally 390 μg/g of sulfur. Assuming that this sulfur is in the -2 valence state, the sulfide concentrations of the spiked experiments would thus be 3129 and 5870 μg/g (Fig. 3 and Table B.3). The measured ferrous iron contents of these two spiked-dissolutions yielded 6.63% for both experiments, which is indistinguishable from the sulfide-free experiments (6.59 ± 0.04% m/m) and from the recommended value (6.57 %, Govindaraju, 1994). These experiments suggest the absence of sulfide interference in the case of the direct titration method.

6. Discussion

Three important analytical results arise from our study. Firstly, our vanadium-based colorimetric results for reference materials are in close agreement with both the recommended values (Govindaraju, 1994; Jochum et al., 2016) and the direct titration results from Bézos and Humler (2005). Secondly, the FeO and FeO/FeO_{total} MORB data of Christie et al. (1986) can be reproduced using the same sample powders and vanadium-based colorimet-

ric method (Fig. 2). Finally, our S^{2-} experiments demonstrate that reduced sulfur clearly interferes with ferrous iron measurements in the case of the vanadium-based wet chemistry whereas it has no effect during direct titration experiments. In the following discussion, we first review the nature of the redox reactions triggered by the presence of S^{2-} during sample digestion. We then discuss the implications of these results for the determination of the iron redox state in MORB samples by wet chemistries. Finally, we compare wet chemical results free of sulfide interaction to the most recent MORB data obtained by XANES spectroscopy.

6.1. Identifying the redox reactions with sulfide during the vanadium-based wet chemistry

The sulfide experiments designed in this study demonstrate that V^{5+} is reduced to V^{4+} by the oxidation of S^{2-}. Sulfur exhibits mostly oxidation state of -2, 0, +2, +4, and +6. According to the standard electrode potentials of the vanadium, sulfur and iron redox couples of interest (see appendix C, Fig. C.1), the spontaneous reaction that should occur involves the oxidant having the strongest standard electrode potential and the reducing agent of the couple having the lowest potential. Therefore, the predicted redox reaction that prevails in our experiment is:

$$2\,V^{5+} + S^{2-} \longrightarrow 2\,V^{4+} + S^{0}\downarrow \tag{2}$$

The reaction 2 will eventually stop when all the V^{5+} is reduced. However, if the quantity of sulfides is large enough to ensure $n_{S^{2-}} > 0.5 \times n_{V^{4+}}$, then

the following redox reaction will take over:

$$2\,Fe^{3+} + S^{2-} \longrightarrow 2\,Fe^{2+} + S^{0}\downarrow \tag{3}$$

Because pentavalent vanadium is added in large excess in the colorimetric method, there is little chance that reaction 3 occurs during sample digestion. Would this happen, the same effect would be expected on ferrous iron measurements, as both equations have the same stoichiometric ratios of two. The $n_{V^{4+}}$ or $n_{Fe^{2+}}$ to $n_{S^{2-}}$ mole ratios determined in our experiments, with, and without sample matrix, are ≈1.8 and 1.3, respectively. Although these results do not conform to the stoichiometric coefficients of reactions 2 and 3, the identification of S^0 in our experiments — as black solid particles of mackinawite — indicates that the oxidation of sulfide may not proceed beyond the formation of elemental sulfur. The low experimental mole ratios that we determined from our experiments could result from several origins. First, V^{5+} could react with other reduced vanadium species or with other reduced polyvalent elements such as chromium. In terrestrial magmas, chromium have a valence of +3 and vanadium, which partitions between the valences of +3, +4 and +5, is largely dominated by the +4 valence (Sutton et al., 2005; Papike, 2005). Once again, according to the standard redox potentials of the half redox reactions reported in appendix C, none of these species is expected to react spontaneously with V^{5+}. Such low mole ratios could also be achieved if S^{2-} were to be lost during sample digestion in presence of concentrated sulphuric acid — for example via the formation and partial degassing of volatile compounds such as H_2S or SO_2. We believe that the lack of sulfide interference in the direct titration method could be explained

by such process which would be enhanced in boiling sulphuric acid (Zhang et al., 2000). It may also be possible that the kinetic of eq. 3 is too slow compared to the duration of the sample digestion (i.e. three minutes). Further experimental work is clearly needed to understand how S^{2-} might escape or be neutralized to different extent in both wet chemistries .

6.2. Settling analytical discord between wet chemistries

The study of Bézos and Humler (2005) was the first to suspect the presence of an analytical bias on the measurements of the iron redox state in oceanic ridge basaltic glasses. The comparison of the vanadium-based colorimetric data (Christie et al., 1986) with the direct (vanadium-free) titration data (Bézos and Humler, 2005) revealed more reduced FeO/FeO_{total} ratios when using the former analytical method. However, the lack of data on common reference materials between both studies hampered the clarification of this analytical issue. Our study provides the keys to solve this analytical discord.

First, we show that both wet chemistries agree for the reference materials FeO and FeO/FeO_{total} measurements (Fig. 1), but on the other hand disagree when MORB samples are concerned (Fig. 2). There are important differences between these two kinds of materials. The MORB samples display glassy textures with high sulfur content (S$\approx$1000 μg/g Jenner and O'Neill, 2012), whereas the reference materials display fine-grained volcanic (BE-N, BR, BHVO-1, BCR-1, JB-2) to coarse-grained plutonic (W-2) textures with low sulfur contents (S<410 μ g/g, Table A.1). Second, our sulfide spiked experiments clearly demonstrate that reduced sulfur interferes with ferrous iron measurements in the case of the vanadium-based wet chemistry whereas

it does not for the direct titration method (section 6.1). Several studies have analyzed the JDF-D2 sample — a MORB glass from the East Pacific Rise from the study of Christie et al. (1986) — using either the vanadium-based or the direct titration wet chemistries (Carmichael and Ghiorso, 1986; Christie et al., 1986; Lange and Carmichael, 1989; Wallace and Carmichael, 1992; Nilsson and Peach, 1993; Bézos and Humler, 2005). All data derived from vanadium-based methods, whether they involved back-titration or colorimetric measurements (Carmichael and Ghiorso, 1986; Christie et al., 1986; Lange and Carmichael, 1989; Wallace and Carmichael, 1992; Nilsson and Peach, 1993, this study), present homogeneous but higher FeO/FeO_{total} ratios (>0.910) compared to the direct titration data (0.864±0.007, Bézos and Humler, 2005). This confirms that the S^{2-} derived from the sample matrix contributes, just as the S^{2-} added to the experiments, to increase the FeO/FeO_{total} ratio during sample digestion. A classical counter-argument would be to explain such difference by the undesired oxidation of Fe^{2+} to Fe^{3+} by atmospheric O_2 in the case of the direct titration method. It is for this specific reason that Wilson (1960) developed the vanadium-based method. However, this issue has been examined in details by Bézos and Humler (2005) as notified in the introduction (see section 1).

On the basis on the sulfide-bearing experiments carried out on the JDF-D2 and GN02-02 MORB glassy samples, we propose to define a colorimetric sulfide-free FeO/FeO_{total} ratio which might be retrieved from the intercept values of the linear regressions in Fig. 3. The resulting sulfide-free ratios agree within error with the direct titration data of Bézos and Humler (2005) (Table 1 and Fig. 3). This approach demonstrates that ferrous iron deter-

mination by different wet chemistries on MORB samples can be reconciled if vanadium-based data are corrected for sulfide interference.

	FeO		FeO_{total}		FeO/FeO_{total}
	Method	Wt.%	Method	Wt.%	
JDF-D2					
Carmichael and Ghiorso (1986)	Colorimetry [1]	11.11		12.14[3]	0.915
Christie et al.(1986)	Colorimetry [1]	11.08			
	Back-titration[1]	11.11			
Nilsson and Peach (1993)	Colorimetry [1]	11.07	EMPA	12.17	0.910
Lange and Carmichael(1989)	Colorimetry [1]	10.93			
	Back-titration[1]	11.12			
Wallace and Carmichael (1992)	Colorimetry [1]	11.08	EMPA	12.09	0.916
Bézos and Humler (2005)	Direct titration	10.52 ± 0.05	EMPA	12.17 ± 0.08	0.864 ± 0.007
This study	Colorimetry [1]	10.99 ± 0.05	Colorimetry	11.99 ± 0.09	0.917 ± 0.011
	Sulfide-free ratio[2]				0.872 ± 0.013
Cottrell and kelley (2010)	XANES spectroscopy				0.833 ± 0.004
Zhang et al. (2018)	XANES spectroscopy				0.849 ± 0.010
Berry et al. (2018)	XANES spectroscopy				0.876 ± 0.010
GN02-02					
Bézos and Humler (2005)	Direct titration	8.50 ± 0.04	EMPA	9.61 ± 0.07	0.884 ± 0.008
This study	Colorimetry [1]	8.72 ± 0.06	Colorimetry	9.49 ± 0.11	0.918 ± 0.011
	Sulfide-free ratio[2]				0.888 ± 0.003

Table 1: Compilation of JDF-D2 and GN02-02 measurements by wet chemistries and XANES spectroscopic methods. [1]: Vanadium-based wet chemical methods; [2] ratio corrected for sulfide interference; [3] LDEO (Lamont -Doherty Earth Laboratory) reference value (Christie et al., 1986); EMPA: Electron Micro-Probe Analyzer.

6.3. The FeO/FeO_{total} ratio of MORB glasses

The average FeO/FeO_{total} ratio of the 49 MORB glasses analyzed in this study by the colorimetric method is 0.92±0.01 (Fig. 4a). This result agrees with the average ratio of 0.93±0.02 from Christie et al. (1986) (Fig. 4b). Christie et al. (1986) data can therefore be reproduced not only for the JDF D2 sample but also for a sample set representative of the global MORB database of Bézos and Humler (2005). As we have demonstrated

that vanadium-based wet chemistries overestimate the FeO/FeO_{total} ratio, the average MORB ratio that we report in this study should be corrected for sulfide interference. This could be done for example by using the sulfur content of each sample — assuming 100% S^{2-}(Mathez, 1976; Métrich et al., 2009) — and by applying the $n_{Fe^{2+}}/n_{S^{2-}}$ reaction ratio of ≈ 1.30 (see section 5.3) to calculate the sulfide-free ratios. When using the sulfur data determined by Bézos (2003) and Bézos et al. (2005) on the MORB analyzed in this study, such first order correction gives a FeO/FeO_{total} ratio of 0.89 $\pm$0.02 (Fig. 4a). However, in the absence of more comprehensive data exploring the behaviour of the $n_{Fe^{2+}}/n_{S^{2-}}$ ratio during analysis of MORB matrices, we do not recommend to use the vanadium-based wet chemistry to analyze the ferrous iron content of S^{2-}-bearing samples.

Although we have demonstrated that ferrous iron data from Bézos and Humler (2005) are not affected by the presence of sulfide, we must put a caveat with respect to their calculated FeO/FeO_{total} ratio that is not strictly speaking self-consistant (Cottrell and Kelley, 2011; Berry et al., 2018). Indeed, this latter study measured the FeO_{total} in MORB glasses using an Electron Micro-Probe Analyzer (EMPA) whereas the ferrous iron were determined on sample powders by direct titration. Bulk analyses were thus normalised to in-situ data. Even if both analytical methods are highly reliable, they do not refer to the exact same material. Indeed, as mentioned in section 5.2, the glass powders prepared for ferrous iron analysis may contain variable amount of plagioclase micro-crystals from sample to sample. As a consequence, in Fig. 2 the bulk colorimetric FeO_{total} data display systematically lower contents compared to the in-situ EMPA data gather by Bézos and

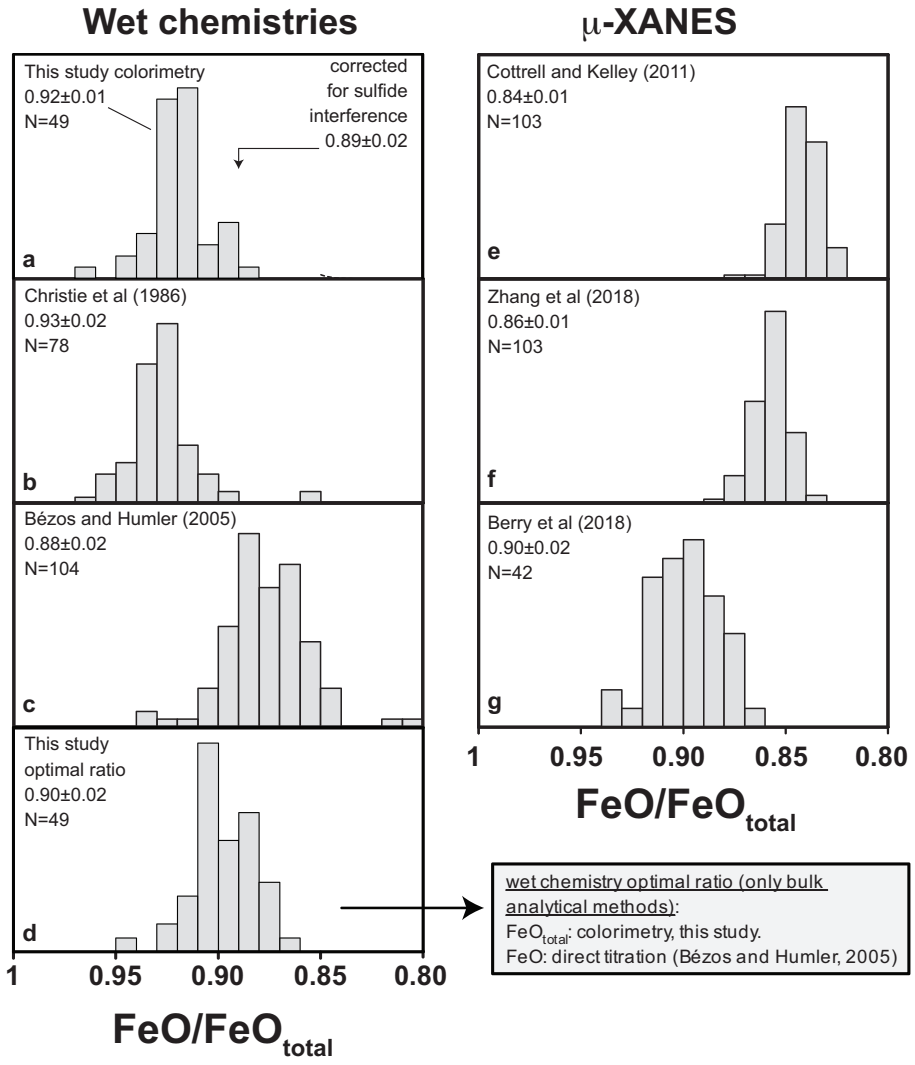

Figure 4: Comparison of the FeO/FeO_{total} histograms (bin size 0.01, origin 1) of MORB glasses determined by wet chemistry: (a) colorimetry, this study; (b) colorimetry, Christie et al. (1986); (c) direct titration, Bézos and Humler (2005); (d) optimal wet chemistry ratio (FeO (Bézos and Humler (2005))/FeO^{total} (this study) and by m-XANES: (e) Cottrell and Kelley (2011); (f) Zhang et al. (2018); (g) Berry et al. (2018). N: number of sample analyzed. The standard deviation of the average ratio is reported in each panel. Arrow in panel (a): average ratio of colorimetric data corrected for sulfide interference (see section 6.3).

Humler (2005) on the corresponding chips of glass. Such difference could be accounted for by the presence of $\approx$ 1.5 weight % plagioclase micro-crystals in MORB glassy rims (Bézos and Humler, 2005). As mentioned by Bézos and Humler (2005), if their ferrous iron analysis were to be corrected for the presence of such micro-crystals in sample powders, the ratio would increased from 0.88$\pm$0.02 to 0.89$\pm$0.02. However, such first order correction should not be applied to single analyses. Some samples might have negligible amounts of micro-crystals as it is, for example, the case for the JDF-D2 and GN02-02 samples that display both similar bulk and in-situ FeO_{total} contents (Table 1).

On the other hand, the presence of olivine micro-crystals (FeO>15 %m/m) in the sample powders would inevitably distort wet chemical results (Cottrell and Kelley, 2011). However, given the plagioclase-to-olivine abundance ratio of $\sim$ 70:30 — expected from the cotectic crystallisations of MORB (Grove et al., 1992), and the relatively low plagioclase contents in our sample powders ($<$ 1.5% on average), the presence of such small amounts of olivine in our sample powders would have no noticeable effect on the measured FeO/FeO_{total} ratio, as long as FeO_{total} is measured on the same sample powders as FeO.

We calculated a self consistent FeO/FeO_{total} ratio — that we named the optimal ratio — of 0.90$\pm$0.02 (Fig. 4d) using the bulk FeO and FeO_{total} data from Bézos and Humler (2005) and this study, respectively. This result agrees within uncertainty with the plagioclase corrected ratio (0.89$\pm$0.02) of Bézos and Humler (2005) and with the colorimetric sulfide-free ratio from this study (0.89 $\pm$0.02, Fig. 4a).

6.4. Comparison of wet chemical and XANES spectroscopic data

The iron redox state of the JDF-D2 sample has not only been determined many times by wet chemistry (section 6.2), but also by XANES spectroscopy (see Table 1: Cottrell and Kelley, 2011; Zhang et al., 2018; Berry et al., 2018). One critical aspect of this spectroscopic method resides in the calibration of XANES spectra using an independent technique. To date, the Mössbauer spectroscopy has been the most widely used method to determine the FeO/FeO_{total} ratio of calibration materials (Cottrell et al., 2009; Zhang et al., 2018; Berry et al., 2018; Farges et al., 2004). However, the acquisition and interpretation of Mössbauer analyses is a matter of active debate in the literature (Cottrell et al., 2009; Zhang et al., 2018; Berry et al., 2018). The detailed discussion on the difference of Mössbauer data used to calibrate XANES data is beyond the scope of this paper, but it involves, among other things, varying temperature of data acquisition and the interpretation of the most reduced spectra (Cottrell et al., 2009; Zhang et al., 2018; Berry et al., 2018). As an illustration of this analytical difficulty, the XANES FeO/FeO_{total} ratios measured on the JDF-D2 sample vary from 0.833 up to 0.876 (Table 1). Even when considering the improved Mössbauer calibration of Zhang et al. (2018), the XANES JDF-D2 data appeared to be more varied than wet chemical data free of sulfide interference (Bézos and Humler (2005) and sulfide-free ratio from this study, see Table 4). Notably, these latter chemical data agree within errors with the XANES JDF-D2 data from Berry et al. (2018) (Table 1).

The comparison of the global MORB data base reveals the same differences as those observed on the JDF-D2 (Fig. 4). The study of Cottrell et al.

(2009) reports the lowest average FeO/FeO_{total} ratio of 0.84±0.01 (Fig.4e), the study of Zhang et al. (2018) re-evaluates this ratio to be 0.86±0.01 (Fig.4f), and finally, the study of Berry et al. (2018) reports the most reduced XANES data with an average value of 0.90±0.02 (Fig. 4g). In line with the JDF-D2 results, the XANES results of Berry et al. (2018) agree within uncertainty with sulfide-free, plagioclase-corrected or optimal ratios determined in this study (Table 1 and Fig. 4).

7. Conclusions

New colorimetric measurements of the iron redox state ratio for the selected reference materials and MORB glasses from the study of Bézos and Humler (2005) and Christie et al. (1986) revealed the presence of an analytical bias between the colorimetric and the direct titration methods. Both wet chemistries agree on reference materials but not on MORB samples. The colorimetric measurements display on MORB samples systematically more reduced FeO/FeO_{total} ratios (0.93-0.92: Christie et al., 1986, this study) compared to direct titration data (Bézos and Humler, 2005, 0.88:).

We have established that the presence of reduced sulfur in MORB samples interferes with ferrous iron measurements in the case of the colorimetric method whereas it has no effect on direct titration measurements. This difference of behaviour is certainly related to the difference of sample digestion procedures between both methods. We demonstrated on two MORB samples that, when corrected for the interference of S^{2-}, colorimetric data agree within uncertainty with direct titration data.

The average FeO/FeO_{total} ratio of 49 MORB glasses calculated from the

bulk FeO and FeO_{total} data from Bézos and Humler (2005) and this study, respectively, is 0.90±0.02. Acknowledging that MORB colorimetric data need to be corrected for the interference of sulfide and that the FeO/FeO_{total} ratio of Bézos and Humler (2005) needs to be corrected for the presence of plagioclase micro-crystals in the sample powders, all the wet chemical methods agree within errors. This result is also consistent with the XANES data from Berry et al. (2018).

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