

Reduced partition function ratios of iron and oxygen in goethite

Marc Blanchard, N. Dauphas, M.Y. Hu, M. Roskosz, E.E. Alp, D.C. Golden,

C.K. Sio, F.L.H. Tissot, J. Zhao, L. Gao, et al.

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| 5 | M. Blanck | hard ^{a,} *, N. D | auphas ^b , M.Y. Hu ^c , M. Rosko | osz ^d , E.E. Alp ^c , D.C. |
| 6 | Golden ^e , | C.K. Sio ^b , F | F.L.H. Tissot ^b , J. Zhao ^c , L. Ga | ao ^c , R.V. Morris ^f , M. |
| 7 | | Fornace | ^b , A. Floris ^g , M. Lazzeri ^a , E. | Balan ^a |
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| 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 | ^a Institut de Sorbonne U d'Histoire I ^b Origins I Institute, T USA ^c Advanced Argonne, II ^d Unité Ma Villeneuve ^e Engineeri Houston, T ^f NASA Joh ^g Departme Kingdom | e Minéralogie, Jniversités - U Naturelle, IRD Laboratory, De he University l Photon Source L 60439, USA tériaux et Tran d'Ascq, France ng and Scienc X 77058, USA inson Space Ce nt of Physics, H | de Physique des Matériaux, et de PMC Univ Paris 06, UMR CNRS UMR 206, 4 Place Jussieu, F-7500 epartment of the Geophysical Sci- of Chicago, 5734 South Ellis Ave e, Argonne National Laboratory, 9 asformations, Université Lille 1, C e Contract Group-Hamilton Sunds enter, Houston, TX, USA King's College London, London, St | Cosmochimie (IMPMC), 7590, Muséum National 5 Paris, France. ences and Enrico Fermi enue, Chicago, IL 60637, 700 South Cass Avenue, 700 So |
| 26 | Correspond | ing Author: M | arc Blanchard (marc.blanchard@ir | npmc.upmc.tr) |
| 27 | 101. +33 1 | 44 27 98 22 | гах. +33 1 44 27 37 83 | |

Abstract

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30 First-principles calculations based on the density functional theory (DFT) with or without the addition of a Hubbard U correction, are performed on goethite in order 31 32 to determine the iron and oxygen reduced partition function ratios (β -factors). The 33 calculated iron phonon density of states (pDOS), force constant and β -factor are 34 compared with reevaluated experimental β -factors obtained from Nuclear Resonant 35 Inelastic X-ray Scattering (NRIXS) measurements. The reappraisal of old experimental data is motivated by the erroneous previous interpretation of the low-36 37 and high-energy ends of the NRIXS spectrum of goethite and jarosite samples 38 (Dauphas et al. 2012). Here the NRIXS data are analyzed using the SciPhon software 39 that corrects for non-constant baseline. New NRIXS measurements also demonstrate 40 the reproducibility of the results. Unlike for hematite and pyrite, a significant 41 discrepancy remains between DFT, NRIXS and the existing Mössbauer-derived data. 42 Calculations suggest a slight overestimation of the NRIXS signal possibly related to 43 the baseline definition. The intrinsic features of the samples studied by NRIXS and 44 Mössbauer spectroscopy may also contribute to the discrepancy (e.g. internal 45 structural and/or chemical defects, microstructure, surface contribution). As for 46 oxygen, DFT results indicate that goethite and hematite have similar β -factors, which 47 suggests almost no fractionation between the two minerals at equilibrium.

48

1. INTRODUCTION

50 For decades now, the isotopic compositions of natural samples have been 51 measured and found countless applications in all branches of geosciences (see for 52 reviews, Valley and Cole, 2001; Johnson et al. 2004; Eiler et al. 2014). In the meantime, isotope exchange experiments were performed to improve our 53 54 understanding of the processes responsible for stable isotope fractionation. More 55 recently, new approaches have emerged and are contributing to this field of research. 56 First-principles calculations give reduced partition function ratios (also called β -57 factors) that can be combined for two phases in order to obtain the equilibrium isotope 58 fractionation factor (α -factor), which is the quantity usually measured. These 59 theoretical methods are also of great interest for investigating the mechanisms 60 controlling the isotope fractionation at the molecular scale. For Mössbauer active 61 elements (like iron), β -factors can also be obtained using Mössbauer spectroscopy through the measurement of the temperature dependence of the isomer shift 62 63 (Polyakov and Mineev, 2000) or using Nuclear Resonant Inelastic X-ray Scattering (NRIXS, Polyakov et al., 2005, 2007; Dauphas et al., 2012, 2014). 64

Dauphas et al. (2012) and Hu et al. (2013) reported NRIXS data for ⁵⁷Fe-rich 65 66 goethite FeO(OH), hydronium-jarosite (H₃O)Fe₃(SO₄)₂(OH)₆ and potassium jarosite 67 KFe₃(SO₄)₂(OH)₆. From such measurements, one can deduce iron β -factors as a 68 function of temperature. Polyakov et al. (2007) had used projected partial phonon 69 density of states (pDOS) obtained using this technique to calculate β -factors for 70 various phases. Dauphas et al. (2012) and Hu et al. (2013) used a different approach 71 based on moment estimates of NRIXS scattering spectrum S(E), which simplifies 72 evaluation of measurement uncertainties and potential systematic errors. The study of 73 Dauphas et al. (2012) was the first of its kind in measuring NRIXS spectra

74 specifically for applications to isotope geochemistry. In doing so, they encountered a 75 difficulty that had been unappreciated before concerning the baseline at low and high 76 energies. Most previous studies in geosciences had focused on estimating the Debye 77 sound velocity (Hu et al. 2003; Sturhahn and Jackson, 2007), from which 78 compressional and shear wave velocities can be deduced if the bulk modulus and 79 density of the phase are known. These estimates are derived from parts of the spectra that are close to the elastic peak for the nuclear transition of ⁵⁷Fe at 14.4125 keV. On 80 81 the other hand, the force constant, which controls β -factors, is heavily influenced by 82 details of the spectrum at the low- and high-energy ends of the spectrum. As a result, 83 little attention had been paid to the accuracy of force constant measurements by 84 NRIXS. Dauphas et al. (2012) found that in some cases, significant counts were 85 present even at high energies. The projected partial phonon density of states, g(E), and 86 the scattering spectrum, S(E), never reached zero and as a result, the integrals that 87 gave the force constants did not plateau for goethite and H-jarosite. These were 88 interpreted to reflect the presence of multiple phonons at high energies. However, we 89 were unable to replicate the measurements during another session of NRIXS 90 measurements at the Advanced Photon Source synchrotron. This and other tests 91 performed on other phases convinced us that the high counts in the tails are not from 92 multiple phonons but rather reflect the presence of a non-constant baseline. To 93 address this issue, Dauphas and collaborators have developed a software (SciPhon) 94 that reliably corrects for non-constant baseline (Dauphas et al, 2014).

In the present study, the pDOS as well as the iron and oxygen β -factors of goethite are computed using first-principles calculations and compared to available experimental isotopic data. In parallel, the data published in Dauphas et al. (2012) have been re-evaluated using SciPhon and we present revised estimates for the force 99 constants of goethite and jarosite. To validate the approach and evaluate the long-term 100 reproducibility of force constant measurements by NRIXS, we have analyzed the 101 goethite sample two more times and the jarosite samples one more time. Those new 102 results, together with a re-evaluation of previous data, are reported here.

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2. MATERIALS AND METHODS

105 **2.1. NRIXS spectroscopy**

Nuclear resonant inelastic X-ray scattering is a nuclear spectroscopic 106 technique that uses the nuclear transition of ⁵⁷Fe at 14.4125 keV to probe the vibration 107 108 properties of iron (Seto et al. 1995; Sturhahn et al. 1995). The method as implemented 109 at sector 3-ID-B of the Advanced Photon Source at Argonne National Laboratory is 110 briefly described hereafter. The incident beam is a pulsed X-ray beam of 70 ps 111 duration and 153 ns interpulse duration. A monochromator restricts the energy spread 112 of the incident beam to 1 meV. When the pulse hits the sample, X-rays are scattered by electrons and this electronic contribution is almost instantaneous. On the other 113 hand, the excited ⁵⁷Fe nuclei have a finite lifetime of 141 ns and the electronic 114 contribution can be eliminated from the signal by applying some time discrimination. 115 116 The signal from NRIXS is measured using Avalanche Photodiodes (APD). The 117 energy is scanned around the nominal resonant energy over a typical interval of -150 118 to +150 meV. When the photon energy is higher than the resonance energy, the 119 excess energy can be lost to excitation of phonon modes in the lattice and the nuclear 120 excitation can still occur (phonon creation). When the energy is lower than the nominal resonance energy, the energy deficit can be provided by lattice vibrations and 121 122 the nuclear excitation can still occur (phonon annihilation).

From NRIXS spectra one can calculate β-factors by taking the moments of the scattering spectrum S(E) (Dauphas et al. 2012; Hu et al. 2013) or the projected partial phonon density of states g(E) (Polyakov et al. 2005, Dauphas et al. 2012). In the present study, all samples were fine powders (isotropic) and the calculated pDOS represents an average from contributions of all crystallographic orientations. The pDOS is partial in the sense that NRIXS is only sensitive to ⁵⁷Fe. Using S(E), the formula that gives β-factors is (Dauphas et al. 2012),

130
$$1000 \ln \beta \approx 1000 \left(\frac{M}{M^*} - 1\right) \frac{1}{E_R} \left[\frac{R_3^S}{8k^2T^2} - \frac{R_5^S - 10R_2^S R_3^S}{480k^4T^4} + \frac{R_7^S + 210(R_2^S)^2 R_3^S - 35R_3^S R_4^S - 21R_2^S R_5^S}{20160k^6T^6}\right]$$

131 , (Eq. 1)

where *M* and *M** are the masses of the two isotopes considered (*e.g.*, 56 and 54), *E_R* is the free recoil energy (1.956 meV for ⁵⁷Fe), *k* is Boltzmann's constant, *T* is the temperature, and R_i^S is the *i*th centered moment of S given by $R_i^S = \int_{-\infty}^{+\infty} S(E)(E - E_R)^i dE$. Equation (1) was derived by Dauphas et al. (2012) and Hu et al. (2013) using two different mathematical approaches (expansions in powers of temperature *vs*. thermalized moments).

138 The β -factors can also be calculated from g(E) using the formula that is valid for E/kT

139 < 2π (Polyakov et al. 2005, Dauphas et al. 2012),

140
$$1000 \ln \beta \approx 1000 \left(\frac{M}{M^*} - 1\right) \left[\frac{m_2^g}{8k^2T^2} - \frac{m_4^g}{480k^4T^4} + \frac{m_6^g}{20160k^6T^6}\right], \quad (Eq. 2)$$

141 where m_i^g is the *i*th moment of *g* given by $m_i^g = \int_0^{+\infty} g(E)E^i dE$. Polyakov et al. (2005) 142 obtained this formula using perturbation theory and an expression of the kinetic 143 energy while Dauphas et al. (2012) obtained this formula using a Bernoulli expansion 144 of the reduced partition function ratio. In general, β -factors can be expressed as,

145
$$1000 \ln \beta = \frac{A_1}{T^2} + \frac{A_2}{T^4} + \frac{A_3}{T^6}, \qquad (Eq. 3)$$

146 where the coefficients A_1 , A_2 , and A_3 can be calculated from either Eq. 1 (S) or Eq. 2 (g). The pDOS g is calculated from S using a Fourier-Log decomposition (Johnson 147 148 and Spence, 1974; Sturhahn et al. 1995; Sturhahn 2000; Kohn and Chumakov 2000) 149 and Eqs. 1 and 2 are mathematically equivalent. In practice, Eq. 1 is easier to use as 150 errors are not correlated between different energy channels and it is more 151 straightforward to assess the effects of the data reduction procedure (e.g., truncation 152 in energy, baseline subtraction) on the estimates of the β -factor coefficients. The 153 above-mentioned equations can also be written as (Dauphas et al. 2012),

154
$$1000 \ln \beta = \frac{B_1 \langle F \rangle}{T^2} - \frac{B_2 \langle F \rangle^2}{T^4}, \qquad (Eq. 4)$$

155 where $B_1 = 2853$, B_2 is a constant that depends on the shape of the pDOS and $\langle F \rangle$ is 156 the mean force constant (in N/m) of the bonds holding iron in position,

157
$$\langle F \rangle = \frac{M}{E_R \hbar^2} R_3^s = \frac{M}{\hbar^2} m_2^g.$$
 (Eq. 5)

158 The same samples as those initially measured by Dauphas et al. (2012) were used in 159 this study and details on the synthesis method can be found in Golden et al. (2008). All samples were made starting with ⁵⁷Fe-rich metal (95 % vs 2.1 % natural 160 161 abundance) as NRIXS is only sensitive to this Mössbauer isotope. The nature of the 162 minerals analyzed was checked by X-ray powder diffraction (XRD). The Rietveld 163 refinement (JADE software package, Materials Data Inc.) provided the following unit-cell parameters for the goethite sample: a = 4.58 Å, b = 9.94 Å, c = 3.02 Å 164 165 (Pbnm space group). The particle sizes (equivalent sphere diameters of coherent 166 domain sizes) were determined using the peak broadening of Rietveld-refined XRD, 167 yielding 19.8 nm for goethite and 223.0 nm for K-Jarosite. Goethite particles are

168 usually acicular. In Dauphas et al 2012, the powdered samples were mounted in 169 compressed pellets, which could impart preferential orientation of the samples, as 170 rightly noticed by Frierdich et al. (2014). However, the latter measurements were 171 done on the powdered samples mounted in vacuum grease at the tip of a kapton 172 capillary, which should keep a random orientation of the particles. One or two APDs 173 were mounted on the sides of the sample perpendicular to the incident beam, so as to 174 capture the maximum solid angle of scattered X-rays. The forward signal was 175 measured at the same time, providing an accurate estimate of the resolution function.

176 The data reduction was entirely done using a new software called SciPhon that 177 is introduced briefly in Dauphas et al. (2014) and will be the scope of a forthcoming 178 publication. The main difference with the data reduction protocol used by Dauphas et 179 al. (2012) is the recognition that signal is present at the low and high energy ends of 180 the spectrum at a level that is too high to be explained by the presence of multiple 181 phonons. The approach used in SciPhon is to remove a linear baseline that is 182 calculated by interpolating the data between the low and high-energy ends of the 183 spectrum and truncating the data when the signal reaches a constant value. This is an 184 effective method when a broad enough energy scan is acquired and one can clearly 185 make the cut between what is signal and what is baseline. After truncation and 186 baseline subtraction, the missing signal is reconstructed by calculating the 187 contribution from the missing multiple phonons using a first estimate of g obtained 188 from truncated S. When the baseline at the high-energy end is higher than at the low-189 energy end (most common situation), the correction for non-constant baseline brings 190 the force constant down. Conversely, when the baseline at the high-energy end is 191 lower than at the high-energy end, the correction brings the force constant up. The 192 other features of SciPhon are deconvolution of the resolution function using a steepest descent algorithm, removal of the elastic peak using a refined interpolation method, calculation of all parameters needed for application of NRIXS data to isotope geochemistry (Eqs. 1 and 2), and propagation of all uncertainties (not only counting statistics but also errors on baseline subtraction and energy scaling) on parameters derived from S. We applied the same algorithm to the new data reported here and to the raw data reported in Dauphas et al. (2012).

199

200 **2.2. Computational methods**

Goethite (α -FeOOH) has an orthorhombic unit cell (a = 4.598 Å, b = 9.951 Å, c 201 = 3.018 Å, *Pbnm* space group, Yang et al. 2006), containing four formula units. 202 203 Calculations are done with the PWscf code (Giannozzi et al., 2009; 204 http://www.quantum-espresso.org) using the density functional theory (DFT) and the generalized gradient approximation (GGA) to the exchange-correlation functional 205 206 with the PBE parameterization (Perdew et al. 1996). The ionic cores are described by 207 the ultrasoft pseudopotentials Fe.pbe-nd-rrkjus.UPF, O.pbe-rrkjus.UPF, H.pbe-208 rrkjus.UPF, as in Blanchard et al. (2009, 2010, 2014). The wave-functions and the 209 charge density are expanded in plane-waves with 40 and 480 Ry cutoffs, respectively. 210 Increasing these energy cutoffs to 60 and 720 Ry does not modify significantly the 211 vibrational frequencies (< 1%). For the electronic integration, the Brillouin zone is 212 sampled according to the Monkhorst-Pack scheme (Monkhorst and Pack 1976), using shifted $4 \times 2 \times 6$ k-point grids. Increasing the number of k-points does not modify the 213 214 structural and vibrational properties. Calculations are spin-polarized and set up to the 215 antiferromagnetic structure. The spins are oriented along the *c*-axis of goethite with 216 up and down spins in alternate chains of octahedra (Cornell and Schwertmann, 2003). 217 Magnetic moments are free to relax. Atomic positions are relaxed until the residual

218 forces on atoms are less than 10^{-4} Ry/a.u..

219 Additional calculations were performed using the GGA+U method since it is 220 known that the addition of a Hubbard U correction on the Fe atom improves the 221 description of the electronic and elastic properties of goethite by taking into account 222 the strong on-site Coulomb repulsion of Fe 3d electrons (e.g. Otte et al. 2009). The 223 value of the Hubbard U is determined using a linear response approach in an 224 internally consistent way following the procedure proposed by Cococcioni and de 225 Gironcoli (2005) and Kulik et al. (2006). Details about the practical procedure can be 226 found in Blanchard et al. (2008). The value of the Hubbard U is found equal to 3.34 227 eV, a value similar to the 3.30 eV found for hematite (Blanchard et al. 2008).

228 Following the method described in Blanchard et al. (2009), the β-factors were 229 calculated from the harmonic vibrational frequencies using

230
$$\beta(a,Y) = \left[\prod_{i=1}^{3N_{at}} \prod_{\{q\}} \frac{\boldsymbol{v}_{q,i}^*}{\boldsymbol{v}_{q,i}} \frac{e^{-h\boldsymbol{v}_{q,i}^*/(2kT)}}{1 - e^{-h\boldsymbol{v}_{q,i}^*/(kT)}} \frac{1 - e^{-h\boldsymbol{v}_{q,i}/(kT)}}{e^{-h\boldsymbol{v}_{q,i}/(2kT)}}\right]^{1/(N_qN)} \text{(Eq. 6)}$$

where v_{ai} are the frequencies of the phonon with wavevector q and branch index i = 231 1,3 N_{at} . N_{at} is the number of atoms in the unit cell, while $v_{q,i}$ and $v_{q,i}^*$ are the vibrational 232 233 frequencies in two isotopologues. N is the number of sites for the Y atom in the unit 234 cell, T is the temperature, h is the Planck constant and k is the Boltzmann constant. 235 Phonon frequencies were calculated within the harmonic approximation using the 236 linear response theory (Baroni et al. 2001, Floris et al. 2011) as implemented in the 237 PHonon code (Giannozzi et al., 2009; http://www.quantum-espresso.org). Phonon frequencies were computed on shifted $2 \times 2 \times 2$ *q*-point grids, for which the 238 convergence of the β -factors is achieved. 239

240 The β -factors calculated from the pDOS (Eq. 2) are identical to the β -factors 241 calculated directly from the harmonic vibrational frequencies (Eq. 6) providing that the highest energy of the pDOS is smaller than $2\pi kT$. When it is not the case (*i.e.* when OH stretching modes are considered in the pDOS) the formula derived from perturbation theory (Eq. 1-4 in Polyakov et al. 2005) must be used instead.

245

246

3. RESULTS

247 **3.1. Reappraisal of NRIXS data**

248 The two motivations for implementing a non-constant baseline subtraction 249 procedure were that (1) replicate measurements of a given phase over several years 250 yielded force constant values that were not reproducible and (2) the signal at the low 251 and high energy ends of the spectrum often did not reach zero, so that the force 252 constant integral did not converge. In Fig. 1, we show force constant determinations 253 with or without baseline subtraction for goethite and jarosite. The values without 254 baseline subtraction were processed in the same manner as in Dauphas et al. (2012), 255 meaning that a constant background was subtracted, which is given by the average 256 counts measured in a 10 meV window at the low-energy end of the spectrum (e.g., 257 from -130 to -120 meV). The values without baseline subtraction differ slightly from 258 those reported by Dauphas et al. (2012) and Hu et al. (2013) because we now only use 259 the phonon-creation side to calculate the force constant (the phonon-annihilation side 260 is calculated from the detailed balance and the temperature). The phonon annihilation 261 side is still measured to define the low-energy end of the baseline but this side of the 262 spectrum often suffers from low counting statistics, which is the reason why it is not 263 used to calculate the mean force constant. When no baseline is subtracted, the force 264 constant values show variations from one sample to another that far exceed individual error bars (reduced $\chi^2 = 13.2$). When the data are corrected for the presence of a non-265 constant baseline, the average force constant does not change but the sample-to-266

sample scatter is very much reduced (reduced $\chi^2 = 3.1$). The improvement in reproducibility (Fig. 1) and better consistency with force constant estimates from theory (see Sect. 3.2.1) justify our preference of the non-constant baseline data reduction algorithm (Dauphas et al., 2014). Below, we discuss the results for each phase individually.

272

273 *3.1.1. Goethite*

274 Including the measurements published by Dauphas et al. (2012), goethite was analyzed by NRIXS three times. As explained in Dauphas et al. (2014) and the 275 276 method section, the main difference in the data reduction approach used here versus 277 that used by Dauphas et al. (2012) is the recognition that the non-zero signals at the 278 low- and high-energy ends of the spectrum are not from multiple phonons but rather 279 some non-constant baseline. Dauphas et al. (2012) used the counts at the low energy 280 end as baseline and interpreted the non-zero counts at the high-energy end to reflect 281 the presence of multiple phonons. Because the signal never reached zero for goethite, 282 a correction for missing multiple phonons was even applied, which exacerbated the 283 problem. The new approach removes a linear baseline interpolated between the low-284 and high-energy ends of the spectrum using the SciPhon software (Dauphas et al. 285 2014). Various quantities calculated from S(E) and g(E) are compiled in Table 1. The 286 pDOS calculated for the three goethite samples are very reproducible and the average 287 pDOS is plotted in Fig. 2.

As shown in Table 1 and later in Table 5 for jarosite samples, B_2 (Eq. 4) is almost the same for the phases investigated (~59,000), so the force constant is the main controlling factor in iron isotopic fractionation even at low temperature and we will focus on the values of the force constants in comparing the results obtained by Dauphas et al. (2012) and Hu et al. (2013) with those presented here. The force constant values obtained from g are identical to those obtained from S, so we will only discuss the values obtained from S in the following.

295 For goethite, Dauphas et al. (2012) reported force constants of 307±9 N/m from S and 314±10 N/m from S after refinement. Hu et al. (2013) obtained similar 296 297 values using the same data reduction approach. Significant signal remained at the 298 high-energy end and as a result the force constant integral did not plateau (Fig. 6 of 299 Dauphas et al., 2012), the new truncation-linear baseline subtraction protocol applied 300 to the same data (using SciPhon) leads to a significant reduction of the force constant, 301 *i.e.* 277±15 N/m. The larger error bar reflects the fact that additional sources of 302 uncertainties associated with baseline subtraction and energy scaling are propagated 303 in the calculation of the force constant (Hu et al. 2013, Dauphas et al. 2014). The two 304 new goethite measurements yield force constants of 264±13 N/m and 267±13 N/m, 305 averaging to 268±8 N/m for the three goethite measurements.

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307 *3.1.2. Jarosite*

Including the measurements published by Dauphas et al (2012), hydronium (H-) jarosite and potassium (K-) jarosite were analyzed twice each. Like for goethite, various quantities calculated from S(E) and g(E), using the new data reduction algorithm, are compiled in Table 2. The pDOS calculated for the two H-jarosite, and two K-jarosite samples are very reproducible and the average pDOS are plotted in Fig. 3.

The force constant for H-jarosite reported by Dauphas et al. (2012) was 302±9 N/m from *S* and 310±9 from *S* after refinement. Data reduction using SciPhon yields a force constant for this sample of 273±15 N/m. A second measurement of this sample during a different session gives 289±17 N/m. The average force constant for the two
H-jarosite measurements is 280±11 N/m.

The force constant of K-jarosite reported by Dauphas et al. (2012) was 262 ± 6 N/m from *S* and 264 ± 6 from *S* after refinement. The revised estimate using SciPhon gives a force constant of 279 ± 16 N/m. A second force constant measurement of this sample during another session gives a force constant of 305 ± 18 N/m. The average of these two values is 290 ± 12 N/m.

324 In the case of H-jarosite, for which significant signal remained at the high-325 energy end and as a result the force constant integral did not converge (Fig. 6 of 326 Dauphas et al., 2012), the new data-reduction leads to a significant reduction of the 327 force constant. In the case of K-jarosite, the force constant integral plateaued and the 328 estimated force constant does not change significantly with the new data reduction 329 scheme used in SciPhon. Note that Dauphas et al. (2012) had no satisfactory 330 explanation as to why the force constant of H-jarosite was significantly higher than K-331 jarosite, other than invoking the presence of high-energy modes arising from 332 hydrogen vibrations. The results presented here show that the force constants of H-333 jarosite and K-jarosite are indistinguishable (280±11 N/m vs. 290±12 N/m).

334

335 3.2. First-principles determination of isotopic fractionation properties

336 3.2.1. Iron β -factor of goethite

In first-principles calculations, the goethite cell parameters were fixed to their experimental values (Yang et al., 2006) and atomic positions were relaxed using either GGA or GGA+U methods. GGA atomic positions are in excellent agreement with the experimental values (Table 3). Only the x atomic coordinate of H atoms shows a significant discrepancy revealing the difficulty of DFT to treat hydrogen 342 bonds as well as the difficulty to determine experimentally the H positions. The 343 GGA+U performs similarly as GGA for the description of interatomic distances 344 (Table 4). This is also true for the vibrational properties. We observe a good 345 correlation between experimental and theoretical frequencies for both GGA and GGA+U methods (Fig. 4). As already highlighted in Blanchard et al. (2014), the 346 347 effect of the Hubbard U correction is mostly visible on the OH bending and stretching 348 modes. The OH bending frequencies increase while the OH stretching frequencies 349 decrease, consistently with lengthening of the O-H bond. The pDOS and in particular 350 the iron contribution is calculated using a $8 \times 4 \times 12$ *q*-points grid obtained through a 351 Fourier (trigonometric) interpolation of the force constants (see Méheut et al., 2007, 352 for details). We observe a general good agreement between the calculated and 353 measured iron pDOS (Fig. 2a). In detail, small differences can be noted between the 354 average measured pDOS and the calculated ones. These differences are of the same 355 order of magnitude as the differences between the pDOS computed with GGA and 356 GGA+U, and are distributed all along the energy range, which suggests that they are 357 not related to any specific vibrational modes. However, these small divergences lead 358 to a significant difference in the calculated iron force constants that are equal to 233 359 N/m and 247 N/m using GGA and GGA+U, respectively. The force constant is 360 calculated from the pDOS g by using equation (5). The integral in the second moment 361 of g explains why the OH vibration modes with their high energies contribute a little 362 to the iron force constant while the corresponding pDOS signal is almost negligible 363 (Fig. 2). The difference between the DFT (233 N/m for GGA, 247 N/m for GGA+U) 364 and NRIXS (268±8 N/m) force constants is already present before the OH vibration 365 modes. Calculations show that the pDOS should be exactly zero over a certain energy 366 range between the lattice modes and the OH bending modes (Fig. 2b), which is not 367 the case for the NRIXS measurements and contributes to the overestimation of the 368 iron force constant. This is likely due to the position of the baseline that should be slightly higher. The variability of the calculated 57 Fe/ 54 Fe β -factor is shown in Fig. 5, 369 370 and the corresponding temperature dependences are reported in Tables 1 and 5. Its 371 variations follow variations in the iron force constant (Eq. 4). GGA and GGA+Uresults differ by ~ 8 % and it is not possible from the analysis of the vibrational 372 373 properties to identify which computational method gives the best description of 374 goethite. This difference should thus give an idea of the uncertainty intrinsic of DFT. 375 These theoretical values are lower than the NRIXS-derived β -factor but higher than 376 the β -factor determined by Polyakov and Mineev (2000) from the Mössbauer measurements done by de Grave and Vanderberghe (1986). Therefore with the new 377 378 NRIXS data reduction, the discrepancy between the various analytical approaches is 379 reduced but remains significant.

380 A general scaling factor reflecting the systematic underestimation of 381 vibrational frequencies by the GGA functional is sometimes applied (e.g. Schauble 382 2011) or a mineral-dependent scaling factor is taken, assuming an accurate preliminary assignment of the vibrational modes (e.g. Blanchard et al. 2009). Here the 383 384 theoretical β -factors were obtained by fixing the cell parameters to the experimental values and relaxing only the atomic positions. Following this procedure, we found 385 386 that the interatomic bond lengths and therefore the vibrational frequencies are 387 improved with respect to the fully optimized structure (i.e. relaxation of the cell parameters and atomic positions). No further frequency correction is needed. The iron 388 389 β -factors of goethite calculated here are equal to 10.2 ‰ or 11.0 ‰ at 22°C, using either GGA or GGA+U methods. These values compare well with 10.5 ‰, which is 390 391 the β -factor obtained from the fully relaxed structure and a frequency scale factor of 392 1.04 (quantified by taking the best linear-fit of the theoretical versus experimental 393 frequencies). The same approach was applied to hematite, by keeping fixed the cell 394 parameters of the rhombohedral primitive cell to the experimental values (a = 5.427Å, $\alpha = 55.28^{\circ}$, $R\overline{3}c$ space group, Finger and Hazen, 1980). Unlike goethite, the 395 396 addition of the Hubbard U clearly improves the atomic positions, interatomic 397 distances and vibrational frequencies of hematite. Therefore, only GGA+U results are 398 retained and it is found that the new GGA+U iron β -factor is undistinguishable from 399 the β -factor previously published in Blanchard et al. (2009) where a frequency scale 400 factor of 1.083 was used. In a similar way, we checked for pyrite that the iron β -factor 401 obtained with the experimental cell parameters (Brostigen and Kjekshus, 1969), i.e. 13.1 ‰ at 22°C, is close, within the expected uncertainty, to the value calculated in 402 403 Blanchard et al. (2009), *i.e.* 13.6 ‰. However we would like to emphasize that fixing 404 the cell parameters to the experimental values do not dispense with checking that the 405 calculated frequencies are in good agreement with the measured values.

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407 3.2.2. Oxygen β -factor of goethite and hematite

Beside iron β -factors, first-principles calculations provide the ¹⁸O/¹⁶O β -factor 408 409 of goethite as a function of temperature (Fig. 6 and Table 6). For goethite, GGA and 410 GGA+U results differ by ~4%. In the ideal goethite structure, half of the oxygen 411 atoms are hydroxylated and the others are not. Calculations show that these two 412 oxygen populations can be distinguished isotopically. At thermodynamic equilibrium, 413 heavier isotopes will concentrate preferentially in hydroxylated sites. The oxygen 414 isotope fractionation of goethite corresponds then to the average of all oxygen atoms of the system. Similar calculations were also performed on hematite, using the same 415 416 model as that previously used by Blanchard et al. (2009). As explained in section

417 3.2.1, only GGA+*U* results are considered. With ~62 ‰ at 25 °C, the oxygen β -factor 418 of hematite is found to be very close to the one of goethite, but with a slightly more 419 linear temperature dependence (Fig. 6).

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4. DISCUSSION

422 4.1. Iron β -factor of goethite: intercomparison of the different methods

In principle, DFT, NRIXS and Mössbauer spectroscopy should lead to 423 424 statistically undistinguishable iron β -factors. In the case of hematite, an excellent agreement is found between DFT-derived ${}^{57}\text{Fe}/{}^{54}\text{Fe}$ β -factor (*i.e.* 10.9 ‰ at 22 °C, 425 Blanchard et al. 2009) and NRIXS-derived 57 Fe/ 54 Fe β -factor (*i.e.* 11.3 ± 0.4 ‰ at 22 426 °C, Dauphas et al. 2012). In the case of pyrite, the apparent discrepancy between DFT 427 428 and Mössbauer results that was reported in Blanchard et al. (2009) and in Polyakov 429 and Soultanov (2011), could be resolved by using a better constrained temperature 430 dependence of the Mössbauer spectra (Blanchard et al. 2012). The first NRIXS-based 431 estimation has recently confirmed our pyrite iron β -factor (Polyakov et al. 2013). In light of these previous studies, it is essential to investigate the origin of the scattering 432 433 of the goethite iron β -factors obtained from the three analytical techniques.

434 The first obvious difference between goethite and hematite is the presence of 435 hydrogen atoms, and it is well known that the accurate description of hydrogen 436 bonding using DFT remains a concern. However, it is important to note that the 437 lengths of the Fe-O and Fe-OH bonds are well described (Table 4) and that all vibrational frequencies below 700 cm⁻¹ (*i.e.* excluding OH bending and stretching 438 439 modes) compare well with the experimental values (Fig. 4). These vibrational modes 440 are the main ones that contribute to the iron β -factor (Fig. 2c). The main difference 441 between GGA, GGA+U and NRIXS comes from the high-energy end of the lattice 442 modes (65 - 90 meV or 525 - 725 cm⁻¹) and the fact that the NRIXS pDOS does not
443 go down to zero between the lattice modes and OH bending modes (Fig. 2).

444 The nature and quality of the samples may also have an impact on iron isotope composition. On one hand, a 57 Fe-rich sample with particle sizes of ~ 20 nm was 445 446 synthesized for the NRIXS measurements, and on the other hand, Mössbauer 447 spectroscopy was done on natural sample from the Harz mountains, well-crystallized with particle size of ~1 µm (de Grave and Vandenberghe, 1986). Some kind of 448 449 internal disorder is however commonly observed in goethite, using e.g. differential 450 thermal analysis, infrared or magnetic measurements (Cornell and Schwertmann, 451 2003). This internal disorder may correspond to crystal defects and/or iron vacant 452 sites that are compensated for by extra, non-stoichiometric protons. All this amounts 453 to introducing distortions with respect to the ideal crystal structure. In "real" goethite 454 crystals, there will be a larger variation in the length of Fe-O bonds, which will lead to 455 a larger variation of the local iron β -factors (*i.e.* β -factors associated with each iron 456 atom). In a similar but simpler way, the ideal goethite structure displays already two 457 oxygen populations with specific isotopic signatures and the bulk oxygen β -factor 458 corresponds to the average of these two local β -factors (Fig. 6). The prediction of the 459 iron β -factor of a goethite crystal containing a certain amount of defects would require the accurate characterization of the sample at the molecular scale, which is 460 461 beyond the scope of the present paper. It is noteworthy that the presence of defective 462 sites is not necessarily expressed in the overall isotopic composition because 463 compensation of local β -factors may occur. For instance, Blanchard et al. (2010) 464 investigated the isotopic properties of hematite with iron vacant sites compensated by 465 protons. The local iron β -factors display variations over a significant range (1.1 % at 0 °C), but extreme values compensate each other, resulting for the model investigated, 466

in a negligible effect of these cationic vacancies on the iron isotope composition of hematite. Similarly, we built a 2 × 1 × 2 supercell of goethite containing one iron vacancy compensated by three protons. The overall 57 Fe/ 54 Fe β -factor is almost unchanged (11.99 ‰ instead of 11.94 ‰ at 0 °C using GGA), even if the local β factors display values ranging from 11.22 ‰ to 13.61 ‰ at 0 °C (the highest value, *i.e.* 13.61 ‰, corresponds to an iron atom surrounded by two vacancies because of the periodic repetition of the simulation cell).

474 Iron force constant and β -factor can also be affected by surface sites, the contribution of which should depend on the size of the crystals. Unlike for defects in 475 476 bulk, the molecular relaxation in vicinity of the surfaces will more likely give rise to a specific isotopic signature that will affect the overall isotopic composition. Beard et 477 478 al. (2010) and Frierdich et al. (2014) investigated the isotopic exchange between 479 aqueous Fe(II) and goethite, using two sizes of goethite. Their results demonstrate that 480 the equilibrium isotopic properties of nano-scale minerals may be distinct from 481 micron-scale or larger minerals. They found that iron surface sites are enriched in 482 heavy isotopes compared to bulk goethite. This fractionation is consistent with the 483 fact that the NRIXS-derived β -factor (for a nano-scale sample) is higher than the Mössbauer-derived β -factor (for a micron-scale sample). However the difference 484 485 observed in β -factors (Fig. 5) is large compared to the difference in equilibrium 486 fractionation measured by Frierdich et al. (2014) for various particle sizes. Rustad and 487 Dixon (2009) examined iron isotope fractionation between hematite and aqueous iron, 488 and found almost no difference between bulk and surface β -factors. This conclusion 489 applies to the (012) hematite surface with molecularly and dissociatively adsorbed 490 water, using DFT calculations and the embedded cluster approach. Only few

491 experimental and theoretical data exist on the topic. More studies are needed with492 other mineral surfaces and more structurally-complex surfaces.

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494 **4.2.** Isotopic fractionations between minerals (α -factors)

495 The experimental iron isotope fractionation factors between goethite, hematite 496 and pyrite in condition of thermodynamic equilibrium can be determined by 497 combining the measurements from Skulan et al. (2002), Welch et al. (2003), Syverson 498 et al. (2013) and Frierdich et al. (2014) (Table 7). Keeping in mind that these mineral-499 mineral isotopic fractionations do not represent direct measurements and involve 500 approximations like temperature extrapolations, we can compare them with the 501 equilibrium fractionation factors estimated from NRIXS, Mössbauer or DFT (Fig. 7). 502 The range of iron β -factors obtained for goethite (Fig. 5) leads to a significant spread 503 of iron α -factors for pyrite-goethite and hematite-goethite (Fig. 7). DFT α -factor is in 504 good agreement with the experimental pyrite-hematite value (0.62 ‰ compared to Δ^{57} Fe = 0.44 ± 1.0 ‰ at 350 °C). For pyrite-goethite, DFT α -factors (GGA and 505 GGA+U) are within the error bar of the experimental data. For hematite-goethite, 506 507 DFT curves are 1-2 ‰ lower than the experimental points at 98 °C. The Mössbauer-508 derived β -factor of goethite (Polyakov and Mineev 2000) seems to be in better 509 agreement with experimental points, while NRIXS data fall in the lowest part of the 510 range (*i.e.*, little iron isotopic fractionation between goethite and hematite). The same 511 conclusions could also be reached looking at the isotopic fractionation between 512 aqueous Fe(II) and goethite (Frierdich et al. 2014). However this would require to 513 combine the present mineral β -factors with a Fe(II)_{aq} β -factor obtained from a 514 different technique (for instance, the DFT values from Rustad et al., 2010, currently 515 considered as the most reliable, and based on an aperiodic model, B3LYP exchange516 correlation functional and localized basis sets). This practice should be considered 517 with caution and the combination of β -factors determined by a single methodology is 518 always preferable.

519 It often happens that the iron β -factors derived from Mössbauer are slightly different 520 and lower than the ones derived from NRIXS, but usually when the α -factors are 521 determined the agreement between these two methods and with the experimental data 522 is satisfactory. This is shown, for instance, for the isotopic fractionation between 523 molten silicate, FeS and metal (Dauphas et al., 2014).

For the oxygen isotopes, DFT results (GGA and GGA+U) indicate a small 524 525 equilibrium fractionation between hematite and goethite (between -3.1 and +0.8 % 526 over the whole temperature range, Fig. 8). These theoretical estimations are consistent 527 with the study of Yapp (1990), which suggests, from synthesis experiments conducted 528 in the temperature range 25-120 °C, that goethite and hematite are isotopically 529 indistinguishable at equilibrium. Several experimental studies also investigated 530 oxygen isotope fractionation in hematite-water and goethite-water systems (e.g. Bao 531 and Koch, 1999; Yapp, 2007). The hematite-goethite fractionation curve that can be 532 derived from Bao and Koch (1999) shows a similar temperature-dependence as our 533 GGA results but is slightly more positive (Fig. 8). In this study, experiments of 534 goethite synthesis were performed at a pH higher than 14. However Yapp's results 535 (2007) suggest that, in addition to temperature, pH can affect the measured oxygen 536 isotope fractionation between goethite and water. He found for goethite synthesized at 537 low pH (~1 to 2) a curve that differs significantly from the ones obtained at high pH 538 (>14). Using this low-pH curve for goethite-water from Yapp (2007) and the 539 hematite-water oxygen fractionation from Bao and Koch (1999), the hematite-goethite 540 fractionation curve falls in the range predicted by DFT methods but with an stronger

temperature-dependence (Fig. 8). According to Yapp (2007), data measured for goethite crystallized at low pH may approach isotopic equilibrium values. These data are therefore the ones that must be compared preferentially with the DFT results. In conclusion, theoretical estimations for oxygen isotopes are consistent with experimental measurements, even if the exact temperature-dependence remains uncertain.

547 Our data display a significant discrepancy with the results of the semi-empirical 548 approach of Zheng (1991, 1998), i.e. the modified increment method where the 549 equilibrium oxygen isotope fractionation factors of oxides are assessed with respect to 550 a reference mineral (quartz) by considering the bond-type in the crystal structure (e.g., 551 bond strength, effect of mass on isotopic substitution). Blanchard et al. (2010) already 552 reported a discrepancy for the oxygen isotope fractionation between hematite and corundum, suggesting that the modified increment method cannot be used to reliably 553 554 predict isotopic fractionation factors.

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725 TABLES

726 **Table 1**. Goethite properties derived from NRIXS, based on the scattering spectrum, *S*(E), or the projected partial phonon density of states, *g*(E).

| | Goe | ethit | e 1 | Goe | ethit | e 2 | Goe | ethit | e 3 | Mean for Goethite | | |
|---|------------|-------|-----------|------------|-------|-----------|------------|-------|-----------|-------------------|---|-----------|
| Parameters from S | | | | | | | | | | | | |
| Temperature from detailed balance (K) | 287 | | | 302 | | | 296 | | | 295 | | |
| Lamb-Mössbauer factor from S | 0.7741 | ± | 0.0026 | 0.7548 | \pm | 0.0020 | 0.7604 | \pm | 0.0020 | 0.7614 | ± | 0.0012 |
| Mean square displacement $\langle z^2 \rangle$ from S (Å ²) | 0.00481 | ± | 0.00006 | 0.00528 | ± | 0.00005 | 0.00514 | ± | 0.00004 | 0.00511 | ± | 0.00003 |
| Internal energy/atom from S (meV) | 29.00 | ± | 0.73 | 29.17 | ± | 0.67 | 28.95 | ± | 0.67 | 29.04 | ± | 0.40 |
| Kinetic energy/atom from S (meV) | 14.50 | ± | 0.37 | 14.58 | ± | 0.34 | 14.48 | ± | 0.34 | 14.52 | ± | 0.20 |
| Force constant from S (N/m) | 277 | ± | 15 | 264 | ± | 13 | 267 | ± | 13 | 268 | ± | 8 |
| (without truncation/baseline subtraction) | (319 | ± | 17) | (250 | ± | 16) | (260 | ± | 14) | | | |
| ⁵⁶ Fe/ ⁵⁴ Fe β coefficients from S | | | | | | | | | | | | |
| $1000 \ln \beta = A_1/T^2 + A_2/T^4 + A_3/T^6$ (T in K) | | | | | | | | | | | | |
| A_1 | 7.898E+05 | ± | 4.384E+04 | 7.537E+05 | ± | 3.755E+04 | 7.605E+05 | ± | 3.724E+04 | 7.659E+05 | ± | 2.264E+04 |
| A_2 | -5.074E+09 | ± | 6.634E+08 | -5.382E+09 | ± | 7.678E+08 | -5.474E+09 | ± | 6.729E+08 | -5.301E+09 | ± | 4.024E+08 |
| A_3 | 7.516E+13 | ± | 1.866E+13 | 1.154E+14 | ± | 3.225E+13 | 1.111E+14 | ± | 2.430E+13 | 9.318E+13 | ± | 1.345E+13 |
| 1000 ln $\beta = B_1 < F > /T^2 - B_2 < F > ^2 /T^4$ (T in K) | | | | | | | | | | | | |
| B_1 | 2853 | | | 2853 | | | 2853 | | | 2853 | | |
| B_2 | 55630 | | | 59269 | | | 60154 | | | 58351 | | |
| Parameters from g | | | | | | | | | | | | |
| Lamb-Mössbauer factor from g | 0.7740 | | | 0.7546 | | | 0.7602 | | | 0.7629 | | |
| Mean square displacement $\langle z^2 \rangle$ from g (Å ²) | 0.00481 | | | 0.00528 | | | 0.00515 | | | 0.00508 | | |
| $d < z^2 > /dT (Å^2/K)$ | 1.45E-05 | | | 1.60E-05 | | | 1.56E-05 | | | 1.54E-05 | | |
| Critical temperature (K) | 1295 | | | 1170 | | | 1203 | | | 1222 | | |
| Resilience (N/m) | 95 | | | 86 | | | 88 | | | 90 | | |
| Internal energy/atom from g (meV) | 29.76 | | | 29.92 | | | 29.70 | | | 29.80 | | |
| Kinetic energy/atom from g (meV) | 14.88 | | | 14.96 | | | 14.85 | | | 14.90 | | |
| Vibrational entropy (kb/atom) | 1.00 | | | 1.05 | | | 1.03 | | | 1.03 | | |
| Helmholtz free energy (meV) | 3.89 | | | 2.60 | | | 2.86 | | | 3.12 | | |
| Vibrational specific heat (kb/atom) | 0.87 | | | 0.89 | | | 0.88 | | | 0.88 | | |
| Lamb-Mössbauer factor at T=0 | 0.92 | | | 0.92 | | | 0.92 | | | 0.92 | | |
| Kinetic energy/atom at T=0 (meV) | 7.91 | | | 7.68 | | | 7.69 | | | 7.76 | | |
| Force constant from g (N/m) | 276 | | | 262 | | | 266 | | | 268 | | |

| ⁵⁶ Fe/ ⁵⁴ Fe β coefficients from g 1000 ln $\beta = A_1/T^2 + A_2/T^4 + A_3/T^6$ (T in K) | | | | |
|--|---------------|---------------|---------------|---------------|
| A_1 | 7.884E+05 | 7.490E+05 | 7.580E+05 | 7.652E+05 |
| A_2 | -5.060E+09 | -5.333E+09 | -5.442E+09 | -5.278E+09 |
| A ₃ | 7.814E+13 | 1.158E+14 | 1.128E+14 | 1.023E+14 |
| Velocities from g | | | | |
| Input density (g/cc) | 4.27 | 4.27 | 4.27 | 4.27 |
| Input bulk modulus (GPa) | 108.5 | 108.5 | 108.5 | 108.5 |
| Debye velocity (m/s) | 3934 ± 43 | 3808 ± 39 | 3899 ± 46 | 3874 ± 25 |
| p-wave velocity (m/s) | 6480 ± 29 | 6395 ± 26 | 6456 ± 31 | 6439 ± 17 |
| s-wave velocity (m/s) | 3526 ± 41 | 3409 ± 37 | 3493 ± 44 | 3470 ± 23 |
| Poisson ratio | 0.290 | 0.302 | 0.293 | 0.295 |

Table 2. Hydronium-jarosite and potassium-jarosite properties derived from NRIXS, based on the scattering spectrum, S(E), or the projected

| 738 | partial | phonon | density | of states, | g (E). |
|-----|---------|--------|---------|------------|---------------|
| | | | | | |

| | H-J | aros | ite 1 | H-J | aros | ite 2 | Mean fo | or H | -Jarosite | K-J | aros | ite 1 | K-J | aros | ite 2 | Mean fo | or K | -Jarosite |
|--|---------|------|---------|---------|------|---------|---------|------|-----------|---------|-------|---------|---------|-------|------------|---------|------|-----------|
| Parameters from S | | | | | | | | | | | | | | | | | | |
| Temperature from | | | | | | | | | | | | | | | | | | |
| detailed balance | | | | | | | | | | | | | | | | | | |
| (K) | 300 | | | 297 | | | 298 | | | 302 | | | 304 | | | 303 | | |
| Lamb-Mössbauer | | | | | | | | | | | | | | | | | | |
| factor from S | 0.6576 | ± | 0.0023 | 0.6415 | ± | 0.0022 | 0.6492 | ± | 0.0016 | 0.6920 | ± | 0.0016 | 0.6724 | ± | 0.0018 | 0.6832 | ± | 0.0012 |
| Mean square | | | | | | | | | | | | | | | | | | |
| displacement | 0.00505 | | 0.0000 | 0.00022 | | 0.0000 | 0.00010 | | 0.00004 | 0.00/01 | | 0.00004 | 0.00745 | | 0.00005 | | | 0.0000 |
| $\langle z^2 \rangle$ from S (A ²) | 0.00/8/ | ± | 0.00006 | 0.00833 | ± | 0.00006 | 0.00810 | ± | 0.00004 | 0.00691 | ± | 0.00004 | 0.00/45 | ± | 0.00005 | 0.00715 | ± | 0.00003 |
| internal | | | | | | | | | | | | | | | | | | |
| S (meV) | 20.58 | + | 0.74 | 29 59 | + | 0.74 | 29 59 | + | 0.52 | 29.70 | + | 0.73 | 20.02 | + | 0.73 | 20.81 | + | 0.52 |
| Kinetic | 27.50 | - | 0.74 | 27.57 | - | 0.74 | 27.37 | - | 0.32 | 29.70 | - | 0.75 | 2).)2 | - | 0.75 | 27.01 | - | 0.32 |
| energy/atom from | | | | | | | | | | | | | | | | | | |
| S (meV) | 14.79 | ± | 0.37 | 14.80 | ± | 0.37 | 14.79 | ± | 0.26 | 14.85 | ± | 0.37 | 14.96 | ± | 0.37 | 14.90 | ± | 0.26 |
| Force constant | | | | | | | | | | | | | | | | | | |
| from S (N/m) | 273 | ± | 15 | 289 | ± | 17 | 280 | ± | 11 | 279 | ± | 16 | 305 | ± | 18 | 290 | ± | 12 |
| (without | | | | | | | | | | | | | | | | | | |
| truncation/baselin | | | | | | | | | | | | | | | | | | |
| e subtraction) | (316 | ± | 17) | (241 | ± | 20) | | | | (281 | ± | 13) | (294 | ± | 17) | | | |
| 50 Fe/ 54 Fe β | | | | | | | | | | | | | | | | | | |
| coefficients from | | | | | | | | | | | | | | | | | | |
| S | | | | | | | | | | | | | | | | | | |
| $1000 \ln p$ | | | | | | | | | | | | | | | | | | |
| $=A_1/1 + A_2/1 + A_3$ $/T^6 (T in K)$ | | | | | | | | | | | | | | | | | | |
| /1 (1 m K) | 7 778F+ | | 4 156E+ | 8 254E+ | | 4 881E+ | 7 979F+ | | 3 164F+ | 7 951E+ | | 4 551E+ | 8 705E+ | | 5.071E+ | 8 287F+ | | 3 387F+ |
| A ₁ | 05 | ± | 04 | 0.2041 | ± | 04 | 05 | ± | 04 | 05 | ± | 04 | 0.7051 | ± | 04 | 0.20711 | ± | 04 |
| 1 | - | | ~ · | - | | ~ • | - | _ | ~ • | - | | - · | - | | ~ · | - | _ | ~ • |
| | 4.864E+ | | 5.725E+ | 7.939E+ | | 1.150E+ | 5.475E+ | | 5.126E+ | 5.208E+ | | 9.136E+ | 8.989E+ | | 1.444E+ | 6.289E+ | | 7.720E+ |
| A_2 | 09 | ± | 08 | 09 | ± | 09 | 09 | ± | 08 | 09 | ± | 08 | 09 | ± | 09 | 09 | ± | 08 |
| A_3 | 6.032E+ | ± | 1.438E+ | 2.269E+ | ± | 5.105E+ | 7.257E+ | ± | 1.384E+ | 8.178E+ | \pm | 3.445E+ | 2.941E+ | \pm | 7.686E+ | 1.173E+ | ± | 3.143E+ |

| | 13 | 13 | 14 | 13 | 13 | 13 | 13 | 13 | 14 | 13 | 14 | 13 |
|--|----------|----|----------|----|----------|----|----------|----|----------|----|----------|----|
| 1000 ln β | | | | | | | | | | | | |
| $=B_1 < F > /T^2$ - | | | | | | | | | | | | |
| $B_2 < F >^2 / T^4$ (T in | | | | | | | | | | | | |
| K) | | | | | | | | | | | | |
| B ₁ | 2853 | | 2853 | | 2853 | | 2853 | | 2853 | | 2853 | |
| B_2 | 56692 | | 65584 | | 61138 | | 55698 | | 62457 | | 59078 | |
| Parameters from | | | | | | | | | | | | |
| g | | | | | | | | | | | | |
| Lamb-Mössbauer | | | | | | | | | | | | |
| factor from g | 0.6569 | | 0.6404 | | 0.6487 | | 0.6914 | | 0.6716 | | 0.6815 | |
| Mean square | | | | | | | | | | | | |
| displacement | | | | | | | | | | | | |
| $\langle z^2 \rangle$ from g (Å ²) | 0.00789 | | 0.00836 | | 0.00812 | | 0.00692 | | 0.00747 | | 0.00720 | |
| $d < z^2 > / dT (Å^2 / K)$ | 2.47E-05 | | 2.63E-05 | | 2.55E-05 | | 2.15E-05 | | 2.33E-05 | | 2.24E-05 | |
| Critical | | | | | | | | | | | | |
| temperature (K) | 760 | | 714 | | 737 | | 873 | | 805 | | 839 | |
| Resilience (N/m) | 56 | | 53 | | 54 | | 64 | | 59 | | 62 | |
| Internal | | | | | | | | | | | | |
| energy/atom from | | | | | | | | | | | | |
| g (meV) | 30.24 | | 30.25 | | 30.24 | | 30.39 | | 30.61 | | 30.50 | |
| Kinetic | | | | | | | | | | | | |
| energy/atom from | | | | | | | | | | | | |
| g (meV) | 15.12 | | 15.12 | | 15.12 | | 15.20 | | 15.30 | | 15.25 | |
| Vibrational | | | | | | | | | | | | |
| entropy (kb/atom) | 1.12 | | 1.13 | | 1.13 | | 1.09 | | 1.10 | | 1.10 | |
| Helmholtz free | | | | | | | | | | | | |
| energy (meV) | 1.17 | | 0.90 | | 1.03 | | 2.08 | | 2.05 | | 2.06 | |
| Vibrational | | | | | | | | | | | | |
| specific heat | | | | | | | | | | | | |
| (kb/atom) | 0.89 | | 0.89 | | 0.89 | | 0.89 | | 0.89 | | 0.89 | |
| Lamb-Mössbauer | | | | | | | | | | | | |
| factor at T=0 | 0.91 | | 0.90 | | 0.91 | | 0.91 | | 0.91 | | 0.91 | |
| Kinetic | | | | | | | | | | | | |
| energy/atom at | | | | | | | | | | | | |
| T=0 (meV) | 7.69 | | 7.67 | | 7.68 | | 7.84 | | 7.93 | | 7.88 | |
| Force constant | | | | | | | | | | | | |
| from g (N/m) | 271 | | 288 | | 279 | | 276 | | 303 | | 290 | |
| 56 Fe/ 54 Fe β | | | | | | | | | | | | |

| coefficients from g 1000 ln β =A ₁ /T ² +A ₂ /T ⁴ +A ₃ /T ⁶ (T in K) | | | | | | | | | | | | | | | | | | |
|--|--------------|---|-----|--------------|---|----|--------------|---|----|--------------|---|-----|--------------|---|----|--------------|---|----|
| (1 | 7.721E+ | | | 8.208E+ | | | 7.964E+ | | | 7.882E+ | | | 8.642E+ | | | 8.262E+ | | |
| A_1 | 05 | | | 05 | | | 05 | | | 05 | | | 05 | | | 05 | | |
| | - 4.840E+ | | | - 7.911E+ | | | - 6.375E+ | | | - 5.151E+ | | | - 8.936E+ | | | - 7.043E+ | | |
| A_2 | 09 | | | 09 | | | 09 | | | 09 | | | 09 | | | 09 | | |
| | 6.296E+ | | | 2.306E+ | | | 1.468E+ | | | 8.212E+ | | | 2.962E+ | | | 1.891E+ | | |
| A ₃ | 13 | | | 14 | | | 14 | | | 13 | | | 14 | | | 14 | | |
| Velocities from g | | | | | | | | | | | | | | | | | | |
| Input density | 2 | | | 2 | | | | | | 2.25 | | | 2.25 | | | | | |
| (g/cc) | 3 | | | 3 | | | 3 | | | 3.25 | | | 3.25 | | | 3.25 | | |
| Input bulk | - / | | | - / | | | | | | - / | | | - (| | | - | | |
| modulus (GPa) | 56 | | | 56 | | | 56 | | | 56 | | | 56 | | | 56 | | |
| Debye velocity | 22(4 | | 124 | 2172 | | 40 | 2100 | | 20 | 25// | | 104 | 2075 | | 50 | 2220 | | 47 |
| (m/s) | 3364 | ± | 134 | 31/3 | ± | 40 | 3189 | ± | 39 | 3566 | ± | 104 | 32/5 | ± | 50 | 3330 | ± | 45 |
| p-wave velocity | 5540 | | 01 | 5400 | | 26 | 5422 | | 25 | 55(7 | | 74 | 52(0 | | 24 | 5207 | | 21 |
| (m/s) | 5549 | ± | 91 | 5422 | ± | 26 | 5432 | ± | 25 | 5567 | ± | /4 | 5360 | ± | 34 | 5397 | ± | 31 |
| s-wave velocity | 2015 | | 120 | 2027 | | 20 | 2952 | | 27 | 2010 | | 00 | 2027 | | 10 | 2000 | | 42 |
| (m/s) | 3015 | ± | 128 | 2837 | ± | 38 | 2852 | ± | 31 | 3212 | ± | 99 | 2937 | ± | 48 | 2989 | ± | 43 |
| Poisson ratio | 0.291 | | | 0.312 | | | 0.301 | | | 0.250 | | | 0.285 | | | 0.268 | | |

739 and experimental atomic Table 3. Theoretical coordinates $[\pm(x,y,3/4),$

 $\pm(1/2+x,1/2+y,1/4)$] of goethite. Values in brackets give the differences with respect 740

| | xFe | yFe | хH | yН | xO | yО | xOh | yOh |
|-------|---------|----------|---------|---------|----------|----------|----------|---------|
| GGA | 0.0503 | 0.8523 | 0.4041 | 0.0855 | 0.6978 | 0.2001 | 0.1989 | 0.0528 |
| | (0.001) | (-0.001) | (0.026) | (0.004) | (-0.008) | (0.001) | (0.000) | (0.000) |
| GGA+U | 0.0603 | 0.8559 | 0.4011 | 0.0940 | 0.6798 | 0.1946 | 0.1959 | 0.0570 |
| | (0.011) | (0.002) | (0.023) | (0.012) | (-0.026) | (-0.005) | (-0.003) | (0.004) |
| Exp.* | 0.0489 | 0.8537 | 0.3781 | 0.0817 | 0.7057 | 0.1991 | 0.1987 | 0.0530 |
| | | | | | | | | |

to the experimental values. 741

742 *Yang et al. (2006)

- 743
- 744
- 745

Table 4. Theoretical and experimental interatomic distances (Å). Values in brackets 746

| | | Fe-O | Fe-Oh | O-H |
|-----|--------------|-----------------|-----------------|----------------|
| | GGA | 1.8963 (-0.037) | 2.1091 (0.010) | 0.9975 (0.125) |
| | | 1.9725 (0.017) | 2.1167 (0.011) | |
| | GGA+U | 1.9484 (0.015) | 2.0958 (-0.004) | 1.0130 (0.140) |
| | | 1.9889 (0.033) | 2.1018 (-0.004) | |
| | Exp.* | 1.9332 | 2.0994 | 0.8729 |
| | | 1.9560 | 2.1059 | |
| 748 | *Yang et al. | (2006) | | |
| | | | | |
| 749 | | | | |
| | | | | |

give the differences with respect to the experimental values. 747

- 749
- 750
- 751
- **Table 5**. Fits of the calculated $10^3 \ln \beta$ based on the function $ax + bx^2 + cx^3$, with x =752
- $10^{6}/T^{2}$ (T on K) for ⁵⁷Fe/⁵⁴Fe isotope fractionation in goethite. 753

| | a | b | с |
|-------|-------------------------|--------------------------|-------------------------|
| GGA | 9.384×10^{-1} | -4.7789×10^{-3} | 4.9888×10^{-5} |
| GGA+U | 10.248×10^{-1} | -5.8539×10^{-3} | 6.8122×10^{-5} |

754

756 **Table 6**. Fits of the calculated $10^3 \ln \beta$ based on the function $ax + bx^2 + cx^3$, with x =

| | | а | b | С |
|------------------|-------|--------|--------------------------|-------------------------|
| Goethite O total | GGA | 6.9558 | -1.9730×10^{-1} | 5.7833×10^{-3} |
| Goethite O total | GGA+U | 7.1664 | -1.8753×10^{-1} | 5.2786×10^{-3} |
| Goethite O | GGA | 5.2325 | -4.2571×10^{-2} | 4.3992×10^{-4} |
| Goethite O | GGA+U | 5.5402 | -4.9704×10^{-2} | 5.8375×10^{-4} |
| Goethite Oh | GGA | 8.6748 | -3.5227×10^{-1} | 1.1134×10^{-2} |
| Goethite Oh | GGA+U | 8.7932 | -3.2570×10^{-1} | 9.9755×10^{-3} |
| Hematite O | GGA+U | 6.0030 | -5.1020×10^{-2} | 5.1786×10^{-4} |

757 $10^6/T^2$ (T on K) for ¹⁸O/¹⁶O isotope fractionation in goethite and hematite.

759

Table 7. Mineral-mineral iron isotope fractionations determined from experimental measurements. The extrapolation to higher temperature is made assuming a linear dependence as a function of $10^6/T^2$ and a fractionation equal to zero at infinite temperature. Δ^{56} Fe shown here are subsequently converted in Δ^{57} Fe for comparison in Fig. 6.

| | Pyrite-Fe(II) _{aq} | Fe(II) _{aq} -Goethite | | Pyrite-Goethite |
|---|--------------------------------|---|---------------------------------|------------------------|
| | Syverson et al. (2013) | Frierdich et al. (2014) | | |
| | 0.99 ± 0.3 ‰ | -0.23 ± 0.1 ‰ | | 0.76 ± 0.3 ‰ |
| | at 350 °C | -0.27 ± 0.1 ‰* | | $0.72 \pm 0.3 \ $ % |
| | | extrapol. to 350 °C | | at 350 °C |
| | Hematite-Fe(III) _{aq} | Fe(III) _{aq} -Fe(II) _{aq} | Fe(II) _{aq} -Goethite | Hematite-Goethite |
| | Skulan et al. (2002) | Welch et al. (2003) | Frierdich et al. (2014) | |
| | 0.1 ± 0.2 ‰ | 1.87 ± 0.2 ‰ | -0.66 ± 0.1 ‰ | $1.31 \pm 0.3 \%$ |
| | at 98 °C | extrapol. to 98 °C | $-0.77 \pm 0.1 \%$ * | $1.2 \pm 0.3 \%$ |
| | | | extrapol. to 98 °C | at 98 °C |
| | Pyrite-Fe(II) _{aq} | Fe(II) _{aq} -Fe(III) _{aq} | Fe(III) _{aq} -Hematite | Pyrite-Hematite |
| | Syverson et al. (2013) | Welch et al. (2003) | Skulan et al. (2002) | |
| | 0.99 ± 0.3 ‰ | -0.66 ± 0.2 ‰ | -0.04 ± 0.2 ‰ | $0.29\pm0.4~\%$ |
| | at 350 °C | extrapol. to 350 °C | extrapol. to 350 °C | at 350 °C |
| 5 | * smaller particles | | | |

Figure Captions

767

Figure 1. Comparison between iron mean force constant determinations by NRIXS with or without baseline subtraction. The baseline is a linear interpolation between signal measured at the low- and high-energy ends of the NRIXS spectrum, where no phonon contributions are expected. Baseline subtraction yields force constant values that display better long-term reproducibility compared to no baseline subtraction (the different replicates were measured at during several beamline sessions spanning three years).

775

776 Figure 2. (a) Average measured (NRIXS) and calculated (GGA, GGA+U) phonon 777 density of states (pDOS) of iron atoms in goethite. (b) The iron pDOS and total pDOS 778 calculated with GGA are plotted along with the calculated (circles) and experimental 779 (triangles) infrared and Raman frequencies (Cambier, 1986; de Faria and Lopes, 780 2007). This highlights the energy gap existing between lattice modes and OH bending 781 modes. (c, d) The force constant is calculated from the pDOS by using the formula $\langle F \rangle = \frac{M}{\hbar^2} \int_0^{\lambda} g(E) E^2 dE$, with the upper limit $\lambda = \infty$ (Eq. 5). The term $g(E) E^2$ is 782 783 plotted in (c), while the force constant integral for different values of the integration 784 upper-limit is plotted in (d).

785

Figure 3. Average phonon density of states of iron atoms in hydronium-jarosite and
potassium-jarosite measured using NRIXS.

788

Figure 4. Calculated (GGA and GGA+U) versus experimental infrared and Raman
frequencies of goethite (Cambier, 1986; de Faria and Lopes, 2007).

Figure 5. Temperature dependence of the iron β -factor of goethite.

793

Figure 6. Temperature dependence of the oxygen β -factor of goethite and hematite.

795

796 **Figure 7.** Temperature dependence of the iron α -factor between pyrite and goethite, 797 and between hematite and goethite. The experimental points have not been measured 798 directly and are estimated instead from several experiments, which are compiled in 799 Table 7 (Skulan et al., 2002; Welch et al., 2003; Syverson et al., 2013; Frierdich et al., 800 2014). For Mössbauer, pyrite, hematite and goethite data are taken from Blanchard et 801 al. (2012), Polyakov et al. (2007) and Polyakov and Mineev (2000), respectively. For 802 GGA and GGA+U, pyrite and hematite data are from Blanchard et al. (2009) while 803 goethite data correspond to this study. For NRIXS, hematite data are from Dauphas et 804 al. (2012) and goethite data are from this study. No NRIXS iron β -factor is published 805 yet for pyrite.

806

807 **Figure 8.** Temperature dependence of the oxygen α -factor between hematite and 808 goethite. For GGA and GGA+U, hematite data are from Blanchard et al. (2009) while 809 goethite data are from this study. Results of the semi-empirical approach of Zheng 810 (1991, 1998) are shown for comparison, as well as the following experimental data: 811 Exp. 1 corresponds to data from Bao and Koch (1999) where goethite was synthesized 812 at high pH (>14), and Exp. 2 combines the hematite-water isotopic fractionation 813 factors from Bao and Koch (1999) with goethite-water data at low pH (~1 to 2) from 814 Yapp (2007).





Figure 1.



Figure 3.





Figure 4.





Figure 5.













Figure 8.