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3 **Reduced partition function ratios of iron and oxygen in goethite**

4

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28

28

Abstract

29

30 First-principles calculations based on the density functional theory (DFT) with
31 or without the addition of a Hubbard U correction, are performed on goethite in order
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
36 experimental data is motivated by the erroneous previous interpretation of the low-
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

49

49

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
53 meantime, isotope exchange experiments were performed to improve our
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
62 through the measurement of the temperature dependence of the isomer shift
63 (Polyakov and Mineev, 2000) or using Nuclear Resonant Inelastic X-ray Scattering
64 (NRIXS, Polyakov et al., 2005, 2007; Dauphas et al., 2012, 2014).

65 Dauphas et al. (2012) and Hu et al. (2013) reported NRIXS data for ^{57}Fe -rich
66 goethite $\text{FeO}(\text{OH})$, hydronium-jarosite $(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ and potassium jarosite
67 $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$. 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
80 that are close to the elastic peak for the nuclear transition of ^{57}Fe at 14.4125 keV. On
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).

95 In the present study, the pDOS as well as the iron and oxygen β -factors of
96 goethite are computed using first-principles calculations and compared to available
97 experimental isotopic data. In parallel, the data published in Dauphas et al. (2012)
98 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.

103

104

2. MATERIALS AND METHODS

2.1. NRIXS spectroscopy

106 Nuclear resonant inelastic X-ray scattering is a nuclear spectroscopic
107 technique that uses the nuclear transition of ^{57}Fe at 14.4125 keV to probe the vibration
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
113 by electrons and this electronic contribution is almost instantaneous. On the other
114 hand, the excited ^{57}Fe nuclei have a finite lifetime of 141 ns and the electronic
115 contribution can be eliminated from the signal by applying some time discrimination.
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
121 nominal resonance energy, the energy deficit can be provided by lattice vibrations and
122 the nuclear excitation can still occur (phonon annihilation).

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

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

130
 131 , (Eq. 1)

132 where M and M^* are the masses of the two isotopes considered (*e.g.*, 56 and 54), E_R is
 133 the free recoil energy (1.956 meV for ^{57}Fe), k is Boltzmann's constant, T is the
 134 temperature, and R_i^S is the i^{th} centered moment of S given by
 135 $R_i^S = \int_{-\infty}^{+\infty} S(E)(E - E_R)^i dE$. Equation (1) was derived by Dauphas et al. (2012) and
 136 Hu et al. (2013) using two different mathematical approaches (expansions in powers
 137 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 $< 2\pi$ (Polyakov et al. 2005, Dauphas et al. 2012),

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

140

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

146 where the coefficients A_1 , A_2 , and A_3 can be calculated from either Eq. 1 (S) or Eq. 2
 147 (g). The pDOS g is calculated from S using a Fourier-Log decomposition (Johnson
 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
$$1000 \ln \beta = \frac{B_1 \langle F \rangle}{T^2} - \frac{B_2 \langle F \rangle^2}{T^4}, \quad (\text{Eq. 4})$$

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

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).
 160 All samples were made starting with ^{57}Fe -rich metal (95 % vs 2.1 % natural
 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
 164 unit-cell parameters for the goethite sample: $a = 4.58 \text{ \AA}$, $b = 9.94 \text{ \AA}$, $c = 3.02 \text{ \AA}$
 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

193 descent algorithm, removal of the elastic peak using a refined interpolation method,
194 calculation of all parameters needed for application of NRIXS data to isotope
195 geochemistry (Eqs. 1 and 2), and propagation of all uncertainties (not only counting
196 statistics but also errors on baseline subtraction and energy scaling) on parameters
197 derived from S. We applied the same algorithm to the new data reported here and to
198 the raw data reported in Dauphas et al. (2012).

199

200 **2.2. Computational methods**

201 Goethite (α -FeOOH) has an orthorhombic unit cell ($a = 4.598 \text{ \AA}$, $b = 9.951 \text{ \AA}$, c
202 $= 3.018 \text{ \AA}$, $Pbnm$ space group, Yang et al. 2006), containing four formula units.
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
205 generalized gradient approximation (GGA) to the exchange-correlation functional
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
213 shifted $4 \times 2 \times 6$ k -point grids. Increasing the number of k -points does not modify the
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

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

231 where $\nu_{q,i}$ are the frequencies of the phonon with wavevector q and branch index $i =$
232 $1, 3N_{at}$. N_{at} is the number of atoms in the unit cell, while $\nu_{q,i}$ and $\nu_{q,i}^*$ are the vibrational
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
238 frequencies were computed on shifted $2 \times 2 \times 2$ q -point grids, for which the
239 convergence of the β -factors is achieved.

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

242 the highest energy of the pDOS is smaller than $2\pi kT$. When it is not the case (*i.e.*
243 when OH stretching modes are considered in the pDOS) the formula derived from
244 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
265 error bars (reduced $\chi^2 = 13.2$). When the data are corrected for the presence of a non-
266 constant baseline, the average force constant does not change but the sample-to-

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

272

273 3.1.1. Goethite

274 Including the measurements published by Dauphas et al. (2012), goethite was
275 analyzed by NRIXS three times. As explained in Dauphas et al. (2014) and the
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.

288 As shown in Table 1 and later in Table 5 for jarosite samples, B_2 (Eq. 4) is
289 almost the same for the phases investigated ($\sim 59,000$), so the force constant is the
290 main controlling factor in iron isotopic fractionation even at low temperature and we
291 will focus on the values of the force constants in comparing the results obtained by

292 Dauphas et al. (2012) and Hu et al. (2013) with those presented here. The force
293 constant values obtained from g are identical to those obtained from S , so we will only
294 discuss the values obtained from S in the following.

295 For goethite, Dauphas et al. (2012) reported force constants of 307 ± 9 N/m
296 from S and 314 ± 10 N/m from S after refinement. Hu et al. (2013) obtained similar
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.

306

307 3.1.2. Jarosite

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

314 The force constant for H-jarosite reported by Dauphas et al. (2012) was 302 ± 9
315 N/m from S and 310 ± 9 from S after refinement. Data reduction using SciPhon yields a
316 force constant for this sample of 273 ± 15 N/m. A second measurement of this sample

317 during a different session gives 289 ± 17 N/m. The average force constant for the two
318 H-jarosite measurements is 280 ± 11 N/m.

319 The force constant of K-jarosite reported by Dauphas et al. (2012) was 262 ± 6
320 N/m from S and 264 ± 6 from S' after refinement. The revised estimate using SciPhon
321 gives a force constant of 279 ± 16 N/m. A second force constant measurement of this
322 sample during another session gives a force constant of 305 ± 18 N/m. The average of
323 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*

337 In first-principles calculations, the goethite cell parameters were fixed to their
338 experimental values (Yang et al., 2006) and atomic positions were relaxed using
339 either GGA or GGA+ U methods. GGA atomic positions are in excellent agreement
340 with the experimental values (Table 3). Only the x atomic coordinate of H atoms
341 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
346 GGA+ U methods (Fig. 4). As already highlighted in Blanchard et al. (2014), the
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
369 slightly higher. The variability of the calculated $^{57}\text{Fe}/^{54}\text{Fe}$ β -factor is shown in Fig. 5,
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+ U
372 results differ by $\sim 8\%$ and it is not possible from the analysis of the vibrational
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
377 measurements done by de Grave and Vanderberghe (1986). Therefore with the new
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
383 preliminary assignment of the vibrational modes (*e.g.* Blanchard et al. 2009). Here the
384 theoretical β -factors were obtained by fixing the cell parameters to the experimental
385 values and relaxing only the atomic positions. Following this procedure, we found
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
388 parameters and atomic positions). No further frequency correction is needed. The iron
389 β -factors of goethite calculated here are equal to 10.2 ‰ or 11.0 ‰ at 22°C, using
390 either GGA or GGA+ U methods. These values compare well with 10.5 ‰, which is
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 ($a = 5.427$
395 \AA , $\alpha = 55.28^\circ$, $R\bar{3}c$ space group, Finger and Hazen, 1980). Unlike goethite, the
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.*
402 13.1 ‰ at 22°C, is close, within the expected uncertainty, to the value calculated in
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.

406

407 3.2.2. Oxygen β -factor of goethite and hematite

408 Beside iron β -factors, first-principles calculations provide the $^{18}\text{O}/^{16}\text{O}$ β -factor
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
415 of the system. Similar calculations were also performed on hematite, using the same
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).

420

421

4. DISCUSSION

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

423 In principle, DFT, NRIXS and Mössbauer spectroscopy should lead to
424 statistically undistinguishable iron β -factors. In the case of hematite, an excellent
425 agreement is found between DFT-derived $^{57}\text{Fe}/^{54}\text{Fe}$ β -factor (*i.e.* 10.9 % at 22 °C,
426 Blanchard et al. 2009) and NRIXS-derived $^{57}\text{Fe}/^{54}\text{Fe}$ β -factor (*i.e.* 11.3 ± 0.4 % at 22
427 °C, Dauphas et al. 2012). In the case of pyrite, the apparent discrepancy between DFT
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
432 light of these previous studies, it is essential to investigate the origin of the scattering
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
438 vibrational frequencies below 700 cm^{-1} (*i.e.* excluding OH bending and stretching
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
445 composition. On one hand, a ^{57}Fe -rich sample with particle sizes of ~ 20 nm was
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
448 with particle size of ~ 1 μm (de Grave and Vandenberghe, 1986). Some kind of
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
460 require the accurate characterization of the sample at the molecular scale, which is
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
466 0 °C), but extreme values compensate each other, resulting for the model investigated,

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

474 Iron force constant and β -factor can also be affected by surface sites, the
475 contribution of which should depend on the size of the crystals. Unlike for defects in
476 bulk, the molecular relaxation in vicinity of the surfaces will more likely give rise to a
477 specific isotopic signature that will affect the overall isotopic composition. Beard et
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
484 Mössbauer-derived β -factor (for a micron-scale sample). However the difference
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 with
492 other mineral surfaces and more structurally-complex surfaces.

493

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
505 $\Delta^{57}\text{Fe} = 0.44 \pm 1.0$ ‰ at 350 °C). For pyrite-goethite, DFT α -factors (GGA and
506 GGA+ U) are within the error bar of the experimental data. For hematite-goethite,
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 exchange-

516 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).

524 For the oxygen isotopes, DFT results (GGA and GGA+*U*) indicate a small
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

541 temperature-dependence (Fig. 8). According to Yapp (2007), data measured for
542 goethite crystallized at low pH may approach isotopic equilibrium values. These data
543 are therefore the ones that must be compared preferentially with the DFT results. In
544 conclusion, theoretical estimations for oxygen isotopes are consistent with
545 experimental measurements, even if the exact temperature-dependence remains
546 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
553 corundum, suggesting that the modified increment method cannot be used to reliably
554 predict isotopic fractionation factors.

555

556

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- 724

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

	Goethite 1	Goethite 2	Goethite 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 ± 0.0020	0.7604 ± 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 $\beta = B_1 \langle F \rangle / T^2 - B_2 \langle F \rangle^2 / T^4$ (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 $\langle z^2 \rangle$ /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

⁵⁶Fe/⁵⁴Fe 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

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737 **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-Jarosite 1		H-Jarosite 2		Mean for H-Jarosite		K-Jarosite 1		K-Jarosite 2		Mean for 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 $\langle z^2 \rangle$ from S (Å ²)	0.00787	± 0.00006	0.00833	± 0.00006	0.00810	± 0.00004	0.00691	± 0.00004	0.00745	± 0.00005	0.00715	± 0.00003
Internal energy/atom from S (meV)	29.58	± 0.74	29.59	± 0.74	29.59	± 0.52	29.70	± 0.73	29.92	± 0.73	29.81	± 0.52
Kinetic 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) (without truncation/baseline subtraction)	273	± 15	289	± 17	280	± 11	279	± 16	305	± 18	290	± 12
⁵⁶ Fe/ ⁵⁴ Fe β coefficients from S	(316 ± 17)		(241 ± 20)				(281 ± 13)		(294 ± 17)			
1000 ln β = A ₁ /T ² +A ₂ /T ⁴ +A ₃ /T ⁶ (T in K)												
A ₁	7.778E+05	± 4.156E+04	8.254E+05	± 4.881E+04	7.979E+05	± 3.164E+04	7.951E+05	± 4.551E+04	8.705E+05	± 5.071E+04	8.287E+05	± 3.387E+04
A ₂	4.864E+09	± 5.725E+08	7.939E+09	± 1.150E+09	5.475E+09	± 5.126E+08	5.208E+09	± 9.136E+08	8.989E+09	± 1.444E+09	6.289E+09	± 7.720E+08
A ₃	6.032E+	± 1.438E+	2.269E+	± 5.105E+	7.257E+	± 1.384E+	8.178E+	± 3.445E+	2.941E+	± 7.686E+	1.173E+	± 3.143E+

coefficients from
 g
 $1000 \ln \beta$
 $= A_1/T^2 + A_2/T^4 + A_3$
 $/T^6$ (T in K)

A ₁	7.721E+05	8.208E+05	7.964E+05	7.882E+05	8.642E+05	8.262E+05
A ₂	4.840E+09	7.911E+09	6.375E+09	5.151E+09	8.936E+09	7.043E+09
A ₃	6.296E+13	2.306E+14	1.468E+14	8.212E+13	2.962E+14	1.891E+14
Velocities from g						
Input density (g/cc)	3	3	3	3.25	3.25	3.25
Input bulk modulus (GPa)	56	56	56	56	56	56
Debye velocity (m/s)	3364 ± 134	3173 ± 40	3189 ± 39	3566 ± 104	3275 ± 50	3330 ± 45
p-wave velocity (m/s)	5549 ± 91	5422 ± 26	5432 ± 25	5567 ± 74	5360 ± 34	5397 ± 31
s-wave velocity (m/s)	3015 ± 128	2837 ± 38	2852 ± 37	3212 ± 99	2937 ± 48	2989 ± 43
Poisson ratio	0.291	0.312	0.301	0.250	0.285	0.268

739 **Table 3.** Theoretical and experimental atomic coordinates [$\pm(x,y,3/4)$,
740 $\pm(1/2+x,1/2+y,1/4)$] of goethite. Values in brackets give the differences with respect
741 to the experimental values.

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

742 *Yang et al. (2006)

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746 **Table 4.** Theoretical and experimental interatomic distances (Å). Values in brackets
747 give the differences with respect to the experimental values.

	Fe-O	Fe-Oh	O-H
GGA	1.8963 (-0.037) 1.9725 (0.017)	2.1091 (0.010) 2.1167 (0.011)	0.9975 (0.125)
GGA+ <i>U</i>	1.9484 (0.015) 1.9889 (0.033)	2.0958 (-0.004) 2.1018 (-0.004)	1.0130 (0.140)
Exp.*	1.9332 1.9560	2.0994 2.1059	0.8729

748 *Yang et al. (2006)

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

	a	b	c
GGA	9.384×10^{-1}	-4.7789×10^{-3}	4.9888×10^{-5}
GGA+ <i>U</i>	10.248×10^{-1}	-5.8539×10^{-3}	6.8122×10^{-5}

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755

756 **Table 6.** Fits of the calculated $10^3 \ln \beta$ based on the function $ax + bx^2 + cx^3$, with $x =$
 757 $10^6/T^2$ (T on K) for $^{18}\text{O}/^{16}\text{O}$ isotope fractionation in goethite and hematite.

		a	b	c
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}

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

Pyrite-Fe(II)_{aq} Syverson et al. (2013)	Fe(II)_{aq}-Goethite Friedrich et al. (2014)	Pyrite-Goethite	
$0.99 \pm 0.3 \text{ ‰}$ at 350 °C	$-0.23 \pm 0.1 \text{ ‰}$ $-0.27 \pm 0.1 \text{ ‰}^*$ extrapol. to 350 °C	$0.76 \pm 0.3 \text{ ‰}$	$0.72 \pm 0.3 \text{ ‰}$ at 350 °C
Hematite-Fe(III)_{aq} Skulan et al. (2002)	Fe(III)_{aq}-Fe(II)_{aq} Welch et al. (2003)	Fe(II)_{aq}-Goethite Friedrich et al. (2014)	Hematite-Goethite
$0.1 \pm 0.2 \text{ ‰}$ at 98 °C	$1.87 \pm 0.2 \text{ ‰}$ extrapol. to 98 °C	$-0.66 \pm 0.1 \text{ ‰}$ $-0.77 \pm 0.1 \text{ ‰}^*$ extrapol. to 98 °C	$1.31 \pm 0.3 \text{ ‰}$ $1.2 \pm 0.3 \text{ ‰}$ at 98 °C
Pyrite-Fe(II)_{aq} Syverson et al. (2013)	Fe(II)_{aq}-Fe(III)_{aq} Welch et al. (2003)	Fe(III)_{aq}-Hematite Skulan et al. (2002)	Pyrite-Hematite
$0.99 \pm 0.3 \text{ ‰}$ at 350 °C	$-0.66 \pm 0.2 \text{ ‰}$ extrapol. to 350 °C	$-0.04 \pm 0.2 \text{ ‰}$ extrapol. to 350 °C	$0.29 \pm 0.4 \text{ ‰}$ at 350 °C

765 * smaller particles

766

Figure Captions

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768 **Figure 1.** Comparison between iron mean force constant determinations by NRIXS
769 with or without baseline subtraction. The baseline is a linear interpolation between
770 signal measured at the low- and high-energy ends of the NRIXS spectrum, where no
771 phonon contributions are expected. Baseline subtraction yields force constant values
772 that display better long-term reproducibility compared to no baseline subtraction (the
773 different replicates were measured at during several beamline sessions spanning three
774 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
782 $\langle F \rangle = \frac{M}{\hbar^2} \int_0^\lambda g(E) E^2 dE$, with the upper limit $\lambda = \infty$ (Eq. 5). The term $g(E)E^2$ is
783 plotted in (c), while the force constant integral for different values of the integration
784 upper-limit is plotted in (d).

785

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

788

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

791

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

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

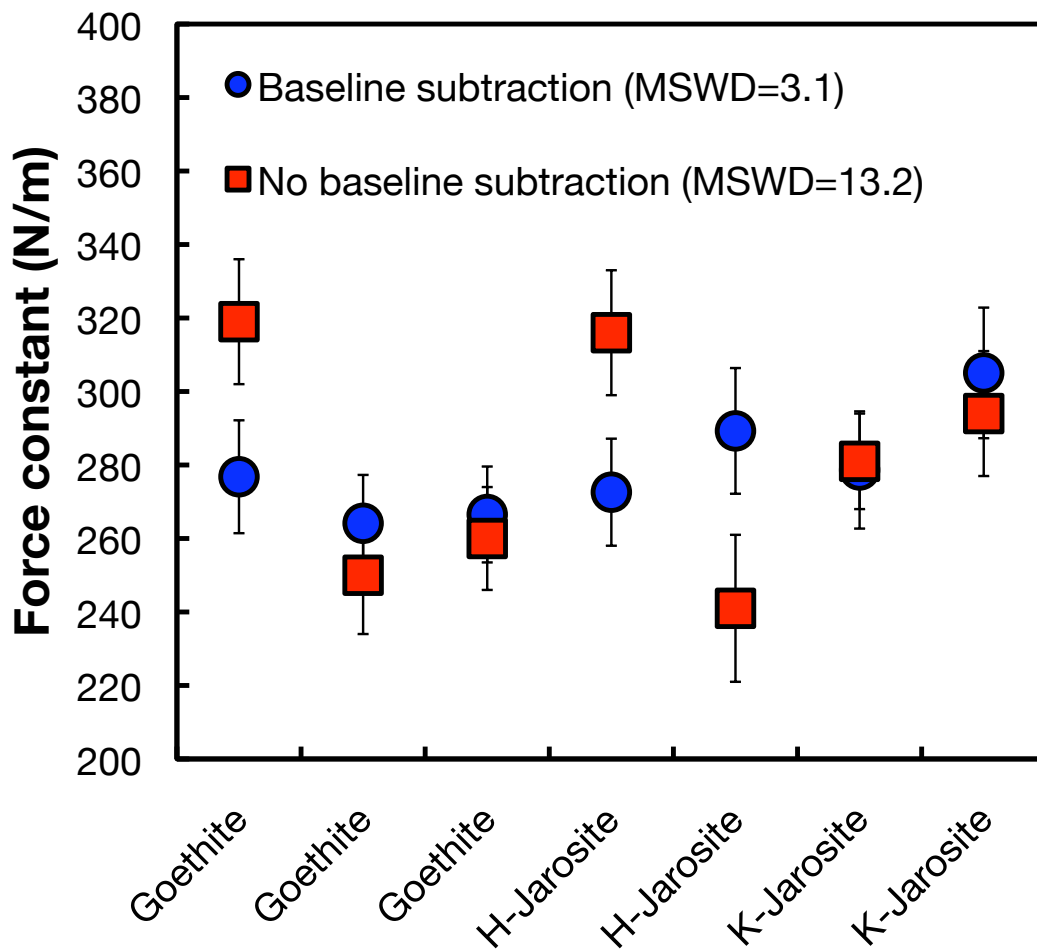
795

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).

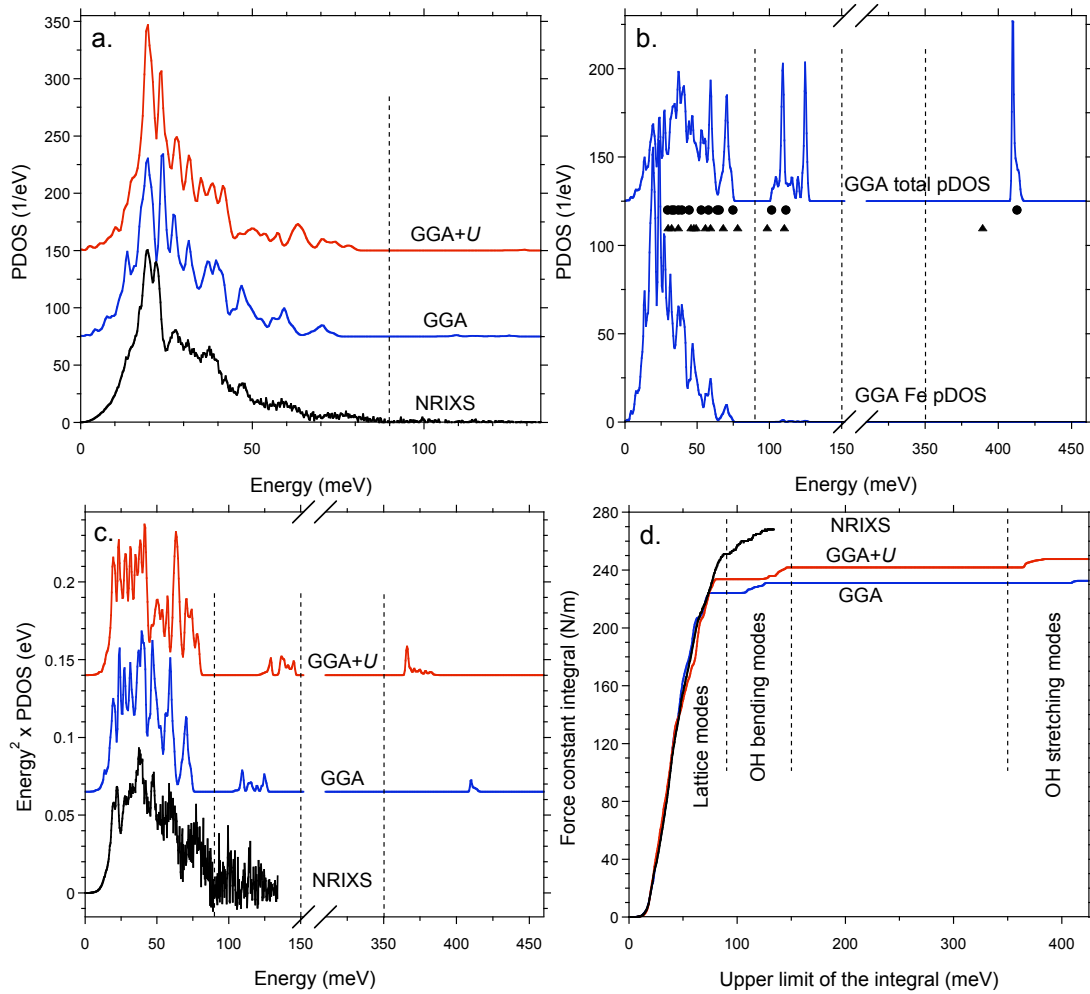
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816 **Figure 1.**

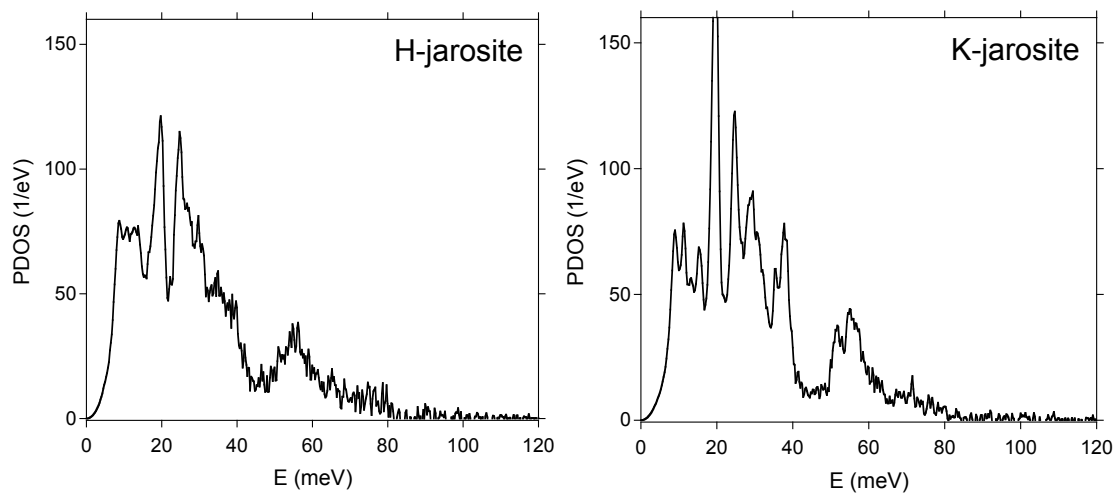
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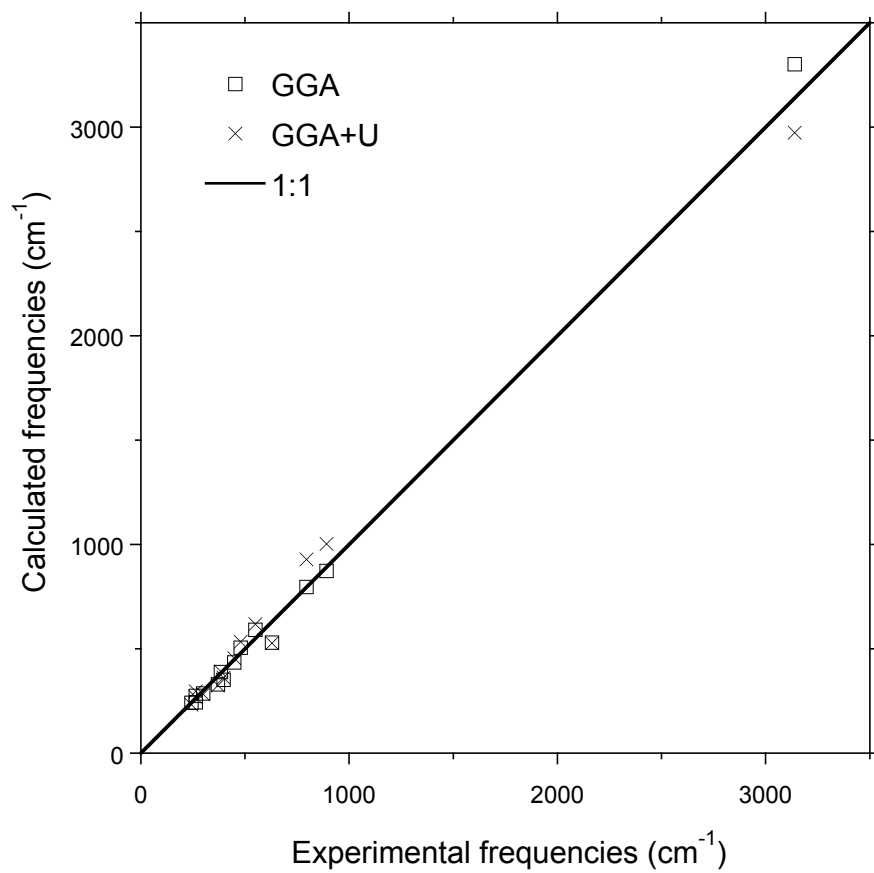
820 **Figure 2.**

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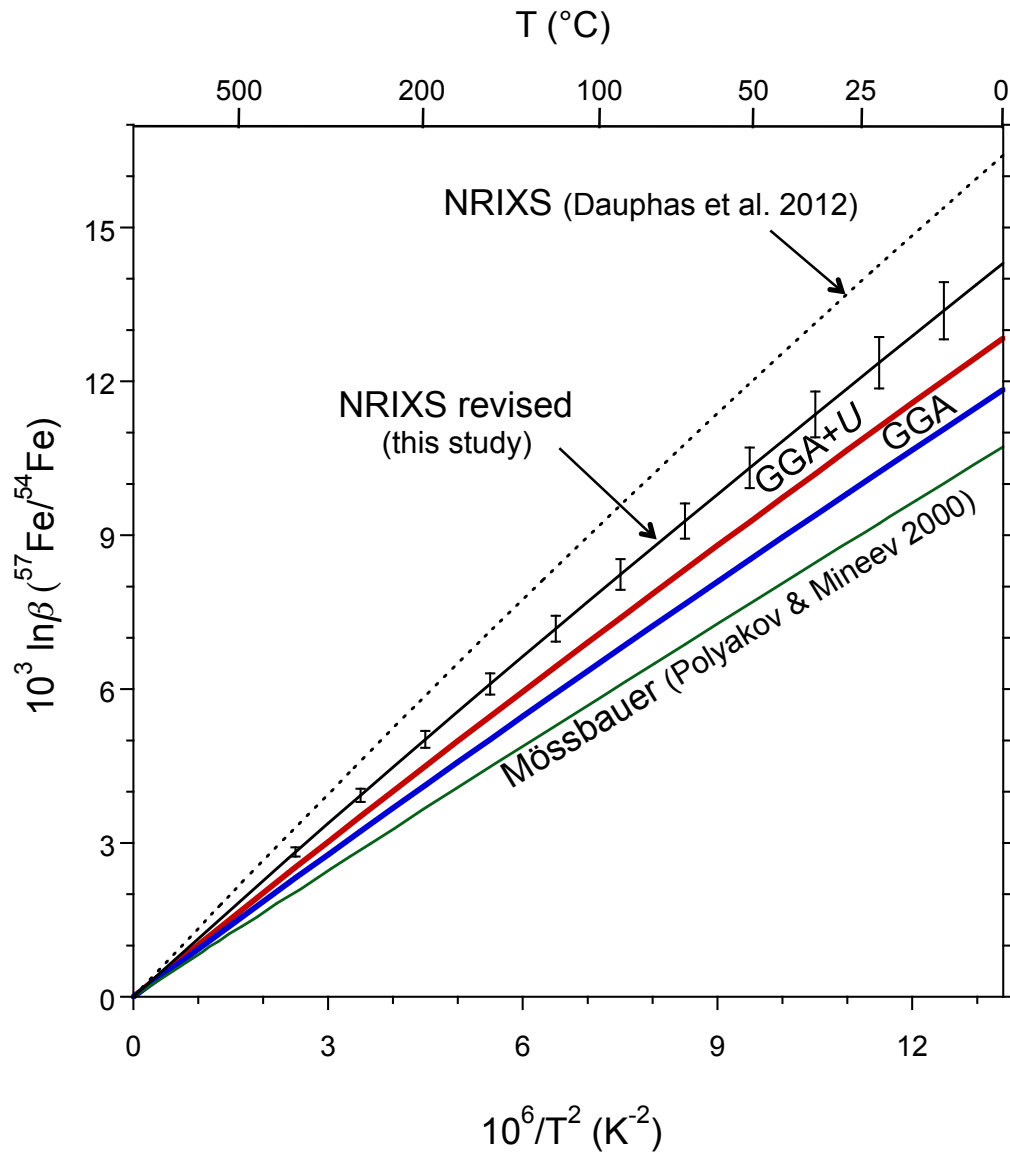
824 **Figure 3.**



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826 **Figure 4.**

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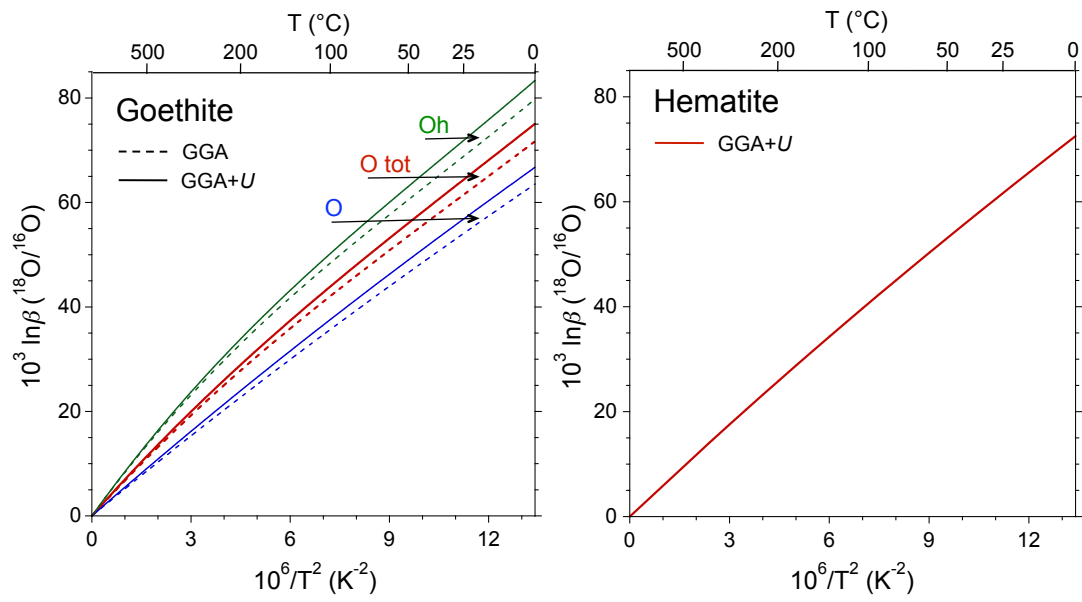
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829 **Figure 5.**

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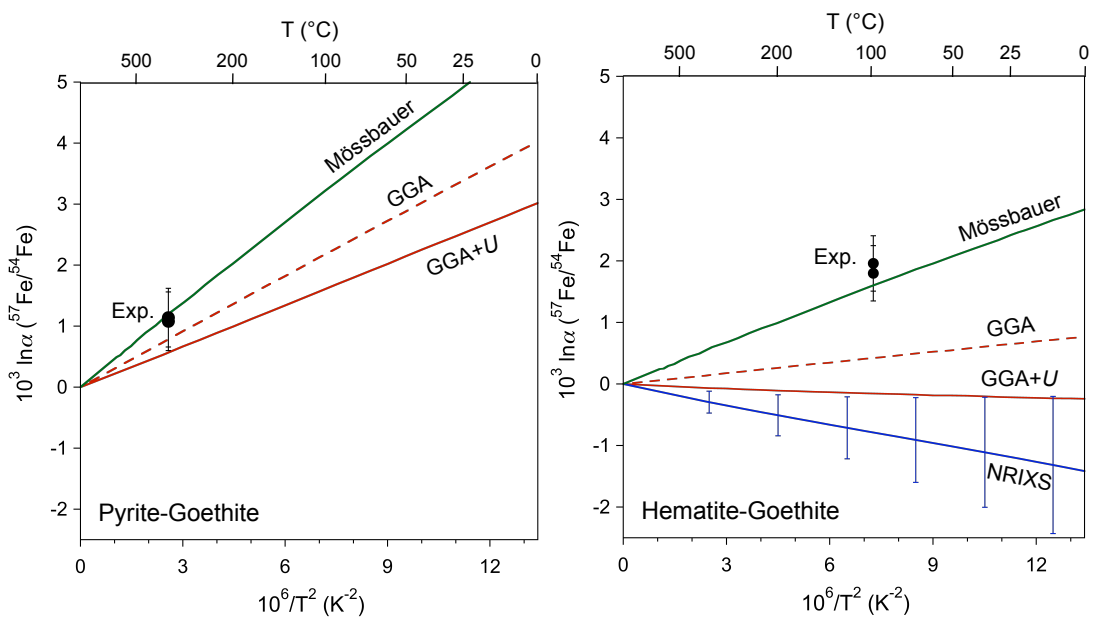
834 **Figure 6.**

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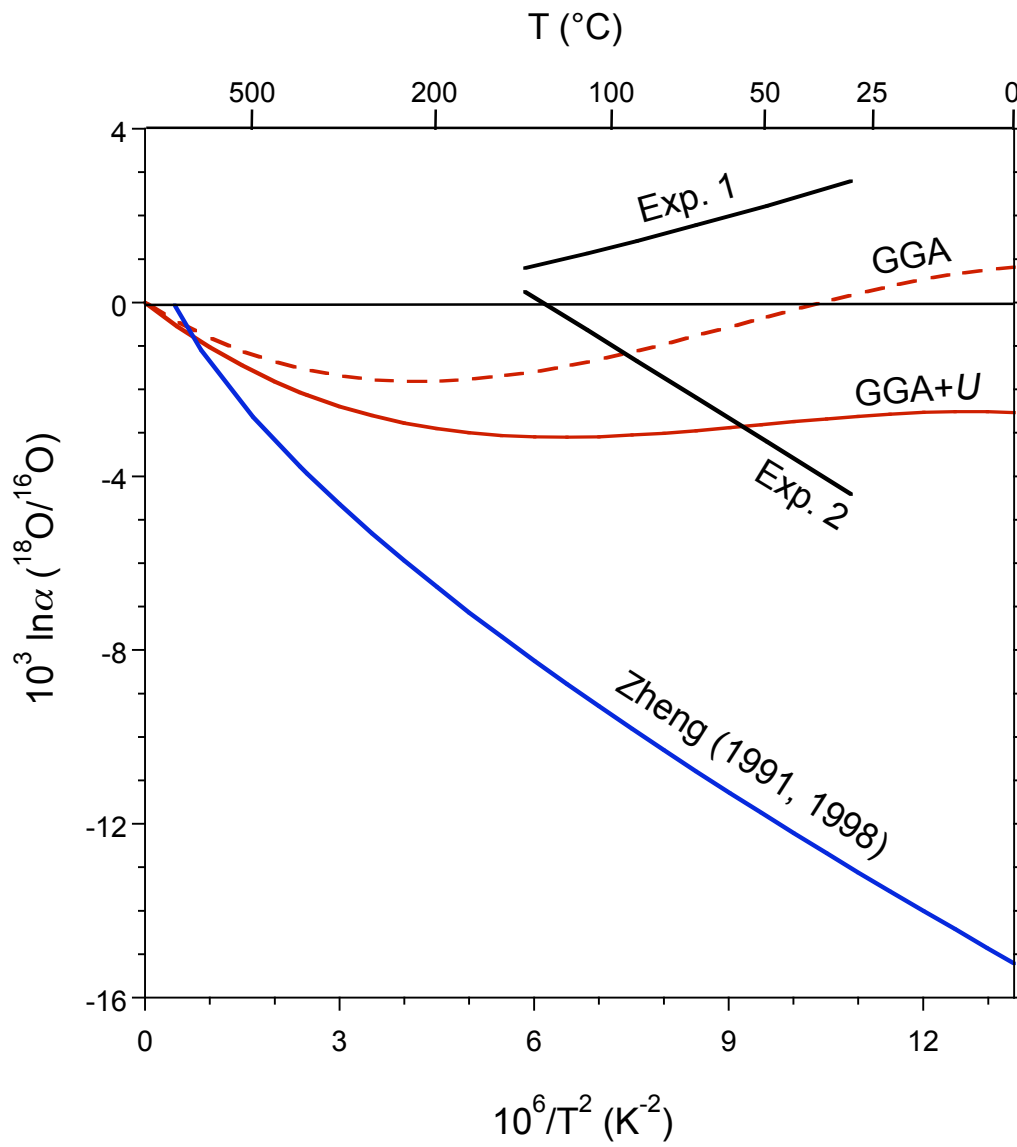
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840 **Figure 7.**

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843 **Figure 8.**