



HAL
open science

Crystal–chemical and biological controls of elemental incorporation into magnetite nanocrystals

Matthieu Amor, J. Frederick W. Mosselmans, Ernesto Scoppola, Chenghao Li,
Damien Faivre, Daniel Chevrier

► **To cite this version:**

Matthieu Amor, J. Frederick W. Mosselmans, Ernesto Scoppola, Chenghao Li, Damien Faivre, et al.. Crystal–chemical and biological controls of elemental incorporation into magnetite nanocrystals. ACS Nano, 2023, 17 (2), pp.927-939. 10.1021/acsnano.2c05469 . cea-03993863

HAL Id: cea-03993863

<https://cea.hal.science/cea-03993863v1>

Submitted on 20 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

1
2
3
4 1 **Crystal-chemical and biological controls of trace and**
5
6
7 2 **minor element incorporation into magnetite nanocrystals**
8
9

10 3
11
12 4 *Matthieu Amor^a \perp *, J. Frederick W. Mosselmans^b, Ernesto Scoppola^c, Chenghao Li^c, Damien*
13
14
15 5 *Faivre^a, Daniel M. Chevrier^a **
16

17 6
18
19 7 *^a Aix-Marseille Université, CEA, CNRS, BIAM, 13108 Saint-Paul-lez-Durance, France*

20
21
22 8 *^b Diamond Light Source, Diamond House, Harwell Campus, Chilton, Didcot, OX11 0DE,*
23
24 9 *United Kingdom*

25
26 10 *^c Biomaterials, Hierarchical Structure of Biological and Bio-inspired Materials, Max Planck*
27
28 11 *Institute of Colloids and Interfaces, Potsdam 14476, Germany*

29
30
31 12
32
33 13
34
35 14 \perp Present address: Univ. Lyon, ENSL, UCBL, UJM, CNRS, LGL-TPE, F-69007 Lyon,
36 15 France

37 16
38 17 * To whom correspondence should be addressed:
39 18 matthieu.amor@ens-lyon.fr (MA); daniel.chevrier@cea.fr (DMC)

21 **Abstract**

22 Magnetite nanoparticles possess numerous fundamental, biomedical and industrial applications,
23 many of which depend on tuning the magnetic properties. This is often achieved by the
24 incorporation of trace and minor elements into the magnetite lattice. Such incorporation was
25 shown to depend strongly on the magnetite formation pathway (*i.e.*, abiotic *vs* biological), but
26 the mechanisms controlling element partitioning between magnetite and its surrounding
27 precipitation solution remain to be elucidated. Here, we used a combination of theoretical
28 modelling (lattice and crystal field theories) and experimental evidence (high-resolution
29 inductively coupled plasma mass spectrometry and X-ray absorption spectroscopy) to
30 demonstrate that element incorporation into abiotic magnetite nanoparticles is controlled
31 principally by cation size and valence. Elements from the first series of transition metals (Cr to
32 Zn) constituted exceptions to this finding as their incorporation appeared to be also controlled
33 by the energy levels of their unfilled 3d orbitals, in line with crystal field mechanisms. We
34 finally show that element incorporation into biological magnetite nanoparticles produced by
35 magnetotactic bacteria (MTB) cannot be explained by crystal-chemical parameters alone,
36 which points to the biological control exerted by the bacteria over the element transfer between
37 MTB growth medium and the intracellular environment. This screening effect generates
38 biological magnetite with a purer chemical composition than the abiotic materials formed in a
39 solution of similar composition. Our work establishes a theoretical framework for
40 understanding the crystal-chemical and biological controls of trace and minor cation
41 incorporation into magnetite, thereby providing predictive methods to tailor the composition of
42 magnetite nanoparticles for improved control over magnetic properties.

43
44 **Keywords:** Trace Element Partitioning, Magnetotactic Bacteria, Magnetite Nanoparticles,
45 Biomineralization, Lattice and Crystal Field Theories

Main Text

Magnetite [Fe(II)Fe(III) O] is a naturally-occurring ubiquitous Fe oxide that can be precipitated through abiotic chemical reactions.¹ Microorganisms can also promote magnetite formation. Among them, only magnetotactic bacteria (MTB) are known to synthesize nanoparticles of magnetite in a genetically controlled manner by incorporating Fe into organelles called magnetosomes for magnetite formation.² MTB are proposed to represent some of the most ancient microorganisms on Earth,³ and are markers of oxic/anoxic transitions in the environment.⁴ Nanoparticles of magnetite are of fundamental scientific interest in industrial and biomedical applications,^{5,6,7} with many of these interests relying on careful tuning and optimization of magnetic properties. A particular way of doing so directly relies on modifying the chemical composition of magnetite, into which cations can substitute for Fe, incorporating into the magnetite lattice structure and thereby modifying its magnetic properties such as coercivity, saturation magnetization or heat release capacity.^{8,9} Cation incorporation has been shown to depend strongly on the nature of the magnetite formation pathways (*i.e.*, abiotic or biologic),¹⁰ but the mechanisms controlling such incorporation remain unknown.

The content of trace and minor elements in magnetite is also of critical interest for the detection of extra-terrestrial and ancient terrestrial life⁴ as exemplified by the controversial origin of magnetite in the Martian meteorite ALH84001.¹¹ This meteorite contains nanocrystals of magnetite encapsulated in (Ca, Mg, Fe)-carbonates showing a pure chemical composition (*i.e.*, they contain no detectable dopant elements).¹² They were proposed to be produced from the thermal decomposition of the carbonate matrix,¹³ although laboratory experimentation showed that incorporation of Mg and Ca into the generated magnetite should occur during such processes.¹⁴ An alternative biological origin of this Martian magnetite was thus suggested, since only MTB were shown to generate magnetite with pure chemical composition.¹⁰ Such characteristic property of biological magnetite was proposed as a reliable tool for the identification of fossils of MTB in ancient terrestrial and extra-terrestrial environments.⁴ Therefore, understanding the mechanisms leading to trace and minor element incorporation into magnetite, as well as the capacity of MTB to screen for element incorporation, has important implications in exobiology and (paleo)environmental sciences.⁴

The goal of the present work is to establish the crystal-chemical parameters controlling the incorporation of trace and minor elements into magnetite nanocrystals. Scheme 1 illustrates the partitioning of tested elements into magnetite nanocrystals of synthetic and biological origin. Using the concentrations of chemical elements in magnetite and residual solution ($[X_{\text{magnetite}}]$ and $[X_{\text{solution}}]$, respectively) measured from high-resolution inductively coupled plasma mass

1
2
3
4 80 spectrometry (HR-ICP-MS)¹⁰ in abiotic magnetite, we show that the cation incorporation is
5 81 controlled by the ionic radius and the valence. Identifying this comprehensive framework of
6
7 82 the crystal-chemical processes controlling element incorporation into magnetite enables us to
8
9 83 investigate the biological control exerted by the magnetotactic strain *Magnetospirillum*
10 84 *magneticum* AMB-1 on element partitioning between magnetite and the external solution.¹⁰ We
11
12 85 find that the behavior of elements during biological formation of magnetite cannot be explained
13
14 86 by crystal-chemical parameters alone: their incorporation into MTB magnetite is more limited
15 87 than expected given their ionic radius and valence. These results point towards an active
16
17 88 screening of elements by the bacteria to limit the transfer of trace and minor elements from the
18
19 89 external solution to internally formed magnetite nanoparticles.

20 90 We report a few exceptions¹⁰ to this general picture: elements from the first series of transition
21
22 91 metals (Cr, Mn, Co, Ni, Cu, Zn) are more stabilized into the magnetite lattice during abiotic
23
24 92 precipitation than predicted from their size and valence, but they do not show any specific
25 93 behavior in AMB-1. To establish the consistency of these findings as well as their crystal-
26
27 94 chemical and biological relevance, we prepared a second round of abiotic and biological
28
29 95 magnetite samples produced in the presence of Co, Mn and Zn following distinct protocols.
30 96 Abiotic magnetite was synthesized at constant pH using a titration device. The incorporation
31
32 97 behavior of Co, Mn and Zn into MTB-produced magnetite was then confirmed by cultivating
33
34 98 a distinct magnetotactic strain (*Magnetospirillum gryphiswaldense* MSR-1) to test the potential
35 99 biological variability of iron-series metal incorporation in MTB induced by distinct bacterial
36
37 100 strains. The choice of MSR-1 was motivated by the extensive literature characterizing the
38
39 101 coordination of transition metals in MSR-1 magnetite using X-ray spectroscopy (XAS). HR-
40 102 ICP-MS analyses of abiotic magnetite produced in the titration device yielded results similar to
41
42 103 those produced in batch, validating the enhanced stabilization of 3d metals in magnetite. In
43
44 104 addition, Co, Mn and Zn incorporation into MSR-1 magnetite was also similar to what was
45 105 previously observed in AMB-1, demonstrating that these elements have no specific behavior
46
47 106 during magnetite precipitation in either strain of MTB. X-ray absorption spectroscopy (XAS)
48
49 107 analyses specifically on Co, Mn and Zn were performed to confirm the incorporation into the
50 108 magnetite nanocrystals and to identify the possible local structure of these metals, helping to
51
52 109 reveal the origin of their enhanced stabilization in abiotic magnetite. They demonstrate that the
53
54 110 preferential incorporation of first series transition metals can be explained by the energy levels
55 111 of unfilled 3d electron orbitals according to the crystal field theory, and further demonstrate the
56
57 112 active screening of trace elements induced by MTB.

58
59 113
60

114 **Results and Discussion**

115 **Chemical composition of abiotic and biological magnetite**

116 Magnetite possesses an inverse spinel structure, with trivalent cations [Fe(III)] contained in
117 both octahedral (6-coordination) and tetrahedral sites (4-coordination) while divalent cations
118 [Fe(II)] occupy octahedral sites only.¹ During abiotic or biological formation, distinct trace and
119 minor cations can substitute Fe(II) or Fe(III) by incorporating into the lattice structure. A
120 previous study quantified the trace element content of abiotic and biological (AMB-1 strain)
121 magnetite nanoparticles.¹⁰ Magnetite nanoparticles were thoroughly purified in order to
122 eliminate adsorbed elements (see ref.¹⁰ for high-resolution TEM). X-ray diffraction and high-
123 resolution electron microscopy analyses of the samples revealed pure magnetite crystals, with
124 no additional precipitated phases potentially induced by element doping.¹⁰ The concentrations
125 of trace and minor elements (X) in magnetite and in the residual solution after nanoparticle
126 formation were measured using HR-ICP-MS. For each element, a partition coefficient (D^X)
127 between magnetite and solution was calculated from the equation:
128

$$129 \quad D^X = \frac{[X_{magnetite}]}{[X_{solution}]} \quad (1)$$

130
131 where $[X_{magnetite}]$ and $[X_{solution}]$ are the massic concentrations of an element X in magnetite and
132 in the residual solution after precipitation, respectively, expressed in ppb. Thus, the partition
133 coefficient quantifies the capacity of an element to incorporate into magnetite and does not
134 depend on the initial concentration of trace elements in the precipitation solution, at least in
135 first approximation. We show below that element partitioning can be explained by crystal-
136 chemical parameters according to established models, demonstrating that the element
137 concentration used (100 ppb for each element) did not induce competition between elements
138 for incorporation into magnetite. The same set of partition coefficients was calculated in the
139 case of biological formation by AMB-1 with identical dopant concentrations in the initial
140 study.¹⁰ Elemental concentrations in the residual growth media as well as magnetite samples
141 thoroughly purified were quantified using HR-ICP-MS. Measured elemental concentrations
142 and partition coefficients are given in Tables S1 and S2.

143 144 **Lattice strain control of element incorporation into magnetite**

145 The partitioning of a trace element between a given lattice site (M) and melts under high
146 temperature and pressure conditions is controlled by the ion radius and valence.¹⁵ For a given
147 valence ($n+$, with $n = 1, 2, 3$ or 4), incorporation of a trace element is maximized when the ionic

1
2
3
4 148 radius (r^X) matches the size of the site M ($r_n^{0(M)}$). A shift from this ideal size generates an elastic
5 149 deformation that is accommodated by the neighboring crystal lattice, translating into a penalty
6
7 150 in energy for the ion incorporation and, consequently, into a decrease of D^X . A size shift of the
8
9 151 same magnitude but with opposite sign corresponds to the same energy penalty. The
10 152 distribution of D^X values for an isoivalent series of elements thus follows a parabolic trend with
11
12 153 a maximum value ($D_n^{0(M)}$) corresponding to a fictive element perfectly matching the size of the
13
14 154 lattice site (*i.e.*, strain-compensated D^X)¹⁵ (see Eqs. 2 and 3 in Materials and Methods).
15 155 Similarly, heterovalent cation substitution entails accommodation of excess electric charge by
16
17 156 the crystal lattice that will also translate into a penalty in energy for element incorporation.¹⁵
18 157 Thus, $D_n^{0(M)}$ corresponding to each valence also follow a parabolic trend with a maximum
19
20 158 coefficient $D^{00(M)}$ corresponding to an ion causing no electrostatic charging (*i.e.*, homovalent
21
22 159 substitution).
23

24 160 We tested such a model in the case of magnetite to determine the role of ion radius and
25 161 valence in the distribution of D^X but under different conditions at ambient temperature and
26
27 162 atmospheric pressure. For all valences, the experimentally determined D^X plotted against their
28
29 163 cation radius were close to the predicted values calculated from Eq. 2 (Fig. 1). This shows that
30 164 the incorporation of most trace and minor elements into abiotic magnetite can be predicted by
31
32 165 a lattice strain model. The strain-compensated $D_n^{0(M)}$ extracted from Fig. 1 and represented
33
34 166 against ionic charge also followed the expected parabolic trend (Fig. 2) (Eq. 3). The maximum
35 167 $D_n^{0(M)}$ corresponding to $D^{00(M)}$ was observed for a cation charge of +2.7, almost identical to the
36
37 168 bulk Fe valence in magnetite (+2.67). Overall, the distribution of D^X values determined
38
39 169 experimentally in abiotic precipitation followed a lattice strain model, demonstrating that cation
40
41 170 radius and valence control the incorporation of trace and minor elements in abiotic magnetite.
42
43 171 However, a few exceptions were observed: Cr(II), Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and
44 172 Zn(II) (grey circles in Fig. 1), which all belong to the first series of transition metals (3d metals)
45 173 also containing Fe, showed higher D^X than expected from their radii and valence. Such
46
47 174 preferential incorporation cannot be explained by potential co-precipitation of distinct
48
49 175 (oxyhydr)oxides phases as shown by X-ray diffraction and electron microscopy performed on
50 176 the samples used for the determination of D^X .¹⁰

51 177 Next, we consider the partition coefficients of trace and minor elements between the
52
53 178 biological magnetite and the growth medium, which shows a distinct picture from abiotic
54 179 results (Fig. 1). D^X values were consistently lower than those predicted from a lattice strain
55
56 180 model (Eq. 2). Such depletion corresponds to a factor of $\sim 5 \times 10^1$ [Cs(I)] up to $\sim 9 \times 10^7$ [La(III)].
57
58 181 The range of variation for D^X was also narrower in the case of biological magnetite, with most
59
60

1
2
3
4 182 values ranging between 10^{-1} and 10^2 , compared to the D^X variation in abiotic magnetite of 7
5 183 orders of magnitude (Rb to Bi). Finally, the distribution of partition coefficients could not be
6
7 184 modeled by the lattice strain theory using Eq. 2, showing that crystal-chemical parameters
8
9 185 cannot explain the partitioning of trace and minor elements between AMB-1 magnetite and the
10 186 external growth medium.

11 187

12 188 **Biological control over element transfer to magnetosomes in magnetotactic bacteria**

13
14 189 Our work aims at understanding the mechanisms controlling the incorporation of cations
15
16 190 distinct from Fe into magnetite. It demonstrates that partitioning of trace and minor elements
17 191 between abiotic magnetite and surrounding solution is controlled by cation radius and valence
18 192 (with the exception of the first series of transition metals, see below for details). The biological
19 193 case showed a distinct picture as the distribution of D^X could not be modeled from lattice strain.
20 194 MTB selectively incorporate Fe into the intracellular medium, and sequester it in magnetosome
21 195 for magnetite formation thus excluding distinct trace and minor elements that cannot substitute
22 196 with Fe for their incorporation into magnetite. The low partition coefficients and low variation
23
24 197 of D^X in the biological conditions are in line with the proposed hypothesis of Fe biopurification
25 198 during magnetite formation, establishing the chemical purity of magnetite as a signature of
26 199 MTB activity.

27
28 200 MTB precipitate magnetite in lipid vesicles (*i.e.*, the intramagnetosomal environment),
29 201 which are physically separated from the extracellular medium. They create local specific
30 202 intracellular environments in magnetosomes with defined chemical conditions (pH, redox
31 203 potential etc.) that allow magnetite formation.¹⁶ The variability induced by MTB on trace and
32 204 minor element partitioning could arise from the homeostasis of chemical conditions in the
33 205 intracellular environment, which are distinct from the external solution and maintained by the
34 206 metabolic activity of the bacteria.^{16–18} These chemical conditions control the cation valence and
35 207 speciation (and thus its size) in solution, which may in turn shift element partitioning (Eqs 2
36 208 and 3, Figs. 1 and 2). However, the variability of cation size and valence evidenced by XAS
37 209 measurements (see below) is too low to account for the decrease of D^X in the biological
38 210 conditions (up to 7 orders of magnitude, see Fig. 1).

39 211 Although not demonstrated, the lower levels of doped cations in biological magnetite were
40 212 discussed as being caused by active and selective Fe incorporation into magnetosomes that
41 213 excludes distinct elements.¹⁰ A notable difference between both conditions of magnetite
42 214 precipitation is the decrease of partition coefficients in bacterial cultures as all elements showed
43 215 lower D^X values than those predicted from the lattice strain theory (Fig. 1). The range of

1
2
3
4 216 partition coefficients was also narrower in AMB-1 cultures compared to abiotic magnetite (Fig.
5 217 1). Consequently, the enrichment of trace elements in AMB-1 magnetite quantified by the ratio
6
7 218 of measured D^X normalized to D^X values predicted from the lattice strain theory decreases
8 219 linearly with the increase of cation radius, down to the ideal size ($r_n^{0(M)}$) that is associated with
9 220 the maximum D^X (Fig. 3). Enrichment of doping elements in MTB magnetite then increases
10 221 again for cation radii higher than $r_n^{0(M)}$ (Figs. 3A and 3D). Accordingly, the depletion of trace
11 222 and minor elements from MTB magnetite is higher for elements showing high affinity for
12 223 magnetite, and minimal for cations with the lowest abiotic D^X (Fig. 3). This illustrates a
13 224 screening effect induced by the bacterial membranes that limits the transfer of cations distinct
14 225 from Fe from the external solution to the location of magnetite formation regardless of the
15 226 cation size and valence. Silver was one exception to this picture, as it was more enriched in
16 227 AMB-1 magnetite than the rest of the monovalent elements (Fig. 3A). This could reflect the
17 228 antimicrobial properties of Ag(I) ¹⁹ and its sequestration into magnetite for detoxification as
18 229 previously proposed for toxic cations.²⁰ Alternatively, such preferential inclusion of Ag in
19 230 AMB-1 could arise from passive diffusion between the external solution and the intracellular
20 231 medium.
21
22 232

23 233 **Investigating the crystal-chemical properties of trace and minor elements belonging to the first** 24 234 **series of transition metals**

25 235 We show in Fig. 1 that elements from the first series of transition metals (Cr, Mn, Co, Ni,
26 236 Cu and Zn) behave in a distinct manner from other metal groups: their partitioning could not
27 237 be explained from the lattice strain theory with D^X values higher than those predicted. Such
28 238 enhanced incorporation was not evidenced in the case of biological magnetite produced by
29 239 AMB-1. To ensure that these observations are real and were not generated by specific
30 240 precipitation conditions or bacterial strain, we performed additional magnetite syntheses with
31 241 a mixture of Co, Mn and Zn using distinct protocols and bacterial strain. The choice of metals
32 242 is made by their frequent use as dopants to tune magnetic properties of magnetite.^{8,9,21} First,
33 243 abiotic magnetite nanoparticles were synthesized using a titration device (see Materials and
34 244 Methods) following a well-established protocol to produce highly pure magnetite.^{22–24} Using
35 245 this device, the pH of the precipitation solution is kept constant over magnetite precipitation by
36 246 adding NaOH solution, and the Fe, Co, Mn and Zn mixture is progressively added to the
37 247 precipitation solution. In addition, the magnetotactic strain *Magnetospirillum gryphiswaldense*
38 248 MSR-1 was cultivated with the same Co, Mn and Zn mixture at the same concentration (see
39 249 Materials and Methods). Three replicates were prepared for each condition.
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 250 Fig. 4 shows representative transmission electron microscopy images of biological
5 251 magnetite synthesized by MTB (Figs. 4A and 4B) and abiotic magnetite nanoparticles
6
7 252 synthesized via co-precipitation of Fe(II) and Fe(III) (Fig. 4C). To confirm the crystal phase
8
9 253 purity of magnetite, both samples were characterized with X-ray diffraction (XRD) as presented
10 254 in Fig. 5A (see Fig. S1 for XRD comparison of AMB-1 and MSR-1). X-ray diffraction showed
11
12 255 similar peaks for all samples which are consistent with magnetite as the sole crystal phase
13
14 256 contained in the samples. We note the abiotic sample has broader peaks due to the smaller and
15 257 more dispersed crystallite sizes. Due to the nature of the co-precipitation synthesis, which does
16
17 258 not use any surface protecting ligands, the aggregation of nanoparticles is inevitable (Fig. 4C)
18
19 259 and thus renders it difficult to measure individual particle sizes. Therefore, XRD measurement
20 260 and peak refinement yielded mean crystal sizes of about 12 and 32 nm for abiotic and biological
21
22 261 magnetite, respectively (Table S3), though the range of particle sizes is wider in the case of
23
24 262 biological formation. The oxidation state and coordination of Fe, Mn, Co and Zn in magnetite
25 263 was determined using X-ray absorption spectroscopy (XAS). Iron K-edge XAS spectra in Figs.
26
27 264 5B and 5C, presented as k -space and R-space, show corresponding post-edge XAFS oscillations
28
29 265 that overall match in phase, though small deviations are noticed for the abiotic sample. We
30 266 attribute this to the high amount of small nanoparticles in the synthetic product (see Fig. 4C)
31
32 267 where higher surface area to volume can shift the average scattering distances for Fe-O and Fe-
33
34 268 Fe bonds. This difference is reflected in the EXAFS refinement of the abiotic sample (see. Fig.
35 269 S2 and Table S4) where the bond distances are slightly longer and the Fe-O scattering
36
37 270 contributions in R-space are more dominant, again reflecting the smaller particle sizes.

38
39 271 In both abiotic and MSR-1 cases, the magnetite samples were recovered and purified (see
40 272 Materials and Methods), and their content in Fe, Co, Mn and Zn was measured using HR-ICP-
41
42 273 MS. D^X coefficients were then determined by also analyzing the residual solution corresponding
43
44 274 to the precipitation solution or MSR-1 growth medium. These results, given in Table S6,
45 275 confirm our previous findings with D^X values highly similar or identical to those previously
46
47 276 obtained within analytical uncertainties (Fig. 1). They further demonstrate enhanced
48
49 277 incorporation of Co, Mn and Zn in magnetite and suggest that bacterial element screening is
50 278 universal to MTB and not specific to strain type. Indeed, incorporation of Co, Cu, Mn, Ni and
51
52 279 Zn occurs at thermodynamic equilibrium.¹⁶ Consequently, trace and minor element
53
54 280 incorporation do not occur at thermodynamic equilibrium in MTB, which further points to the
55 281 biological control exerted by the bacteria over element transfer from the external solution to
56
57 282 magnetite. We demonstrate below that crystal-chemical mechanisms specifically stabilizing 3d
58
59 283 metals in the magnetite lattice correspond to crystal field effects.

1
2
3
4 284
5 285 **Crystal field constraints on element incorporation into magnetite and coordination of 3d metals**
6
7 286 **in magnetite**

8
9 287 Elements from the first series of transition metals, including Fe, possess unfilled 3d orbitals
10 288 in at least one of their oxidation states.²⁵ The two sets of 3d orbitals, namely t_{2g} (*i.e.*, d_{xy} , d_{xz} ,
11 289 d_{yz}) and e_g (*i.e.*, d_{z^2} and $d_{x^2-y^2}$), have different geometries with the electronegative charge
12 290 pointing in distinct directions. In octahedral configuration, electrons from e_g orbitals directly
13 291 face the negatively charged oxygen, which maximizes the electric repulsion and thus
14 292 corresponds to more energetic configurations.²⁵ The opposite case is observed in tetrahedral
15 293 coordination. The origin and consequences of these electrostatic interactions on the energy
16 294 levels of 3d orbitals is described by the crystal field theory.²⁵ For each element of a given
17 295 valence, the crystal field stabilization energy (CFSE) was documented by McClure in
18 296 octahedral and tetrahedral coordination.²⁶ The partitioning of Cr(II), Cr(III), Mn(II), Co(II),
19 297 Ni(II), Cu(II) and Zn(II) during abiotic magnetite precipitation was modeled from their CFSE
20 298 (values taken from McClure²⁶) for both coordination configurations (Fig. S3). No clear
21 299 correlation between $\log D^X$ and CFSE values was observed, suggesting that coordination and/or
22 300 valence of doping elements are not as expected. This needed to be confirmed to determine
23 301 whether crystal field effects control the incorporation of 3d metals in magnetite.

24 302 We determined the coordination and valence of Co, Mn and Zn using XAS in both abiotic
25 303 and biological magnetite. The X-ray absorption near-edge structure (XANES) spectra along
26 304 with references are presented in Fig. 6. Abiotic syntheses and MSR-1 cultures were performed
27 305 in the presence of Co(II), Mn(II) and Zn(II) under the same experimental mixed-doping
28 306 conditions. The coordination of Co, Mn and Zn has already been extensively characterized in
29 307 abiotic magnetite as well as in biological magnetite produced by AMB-1 and MSR-1.^{21,27-31}
30 308 Therefore, this work aimed to concomitantly determine Co, Mn and Zn local structure and
31 309 partition coefficients, and establish whether their incorporation can be explained by the energy
32 310 level of their unfilled 3d orbitals. MSR-1 was selected for these additional experimental
33 311 characterizations in order to further assess the specific behaviors of Co, Mn and Zn in MTB
34 312 and evaluate their biological relevance. The D^X values corresponding to abiotic precipitation
35 313 were similar to those previously obtained (see Fig. S4, Tables S1 and S6), but D^X values
36 314 obtained from MSR-1 were higher than those initially obtained from AMB-1 (Fig. S4, Tables
37 315 S2 and S6). Such discrepancy can be explained by the magnetite yield and intracellular Fe
38 316 content in the two strains, as MSR-1 is known to incorporate more iron than AMB-1 under
39 317 standard growth conditions used in the present contribution.³² An increased mass of magnetite
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 318 increases the total mass of trace elements contained in magnetite, which in turn decreases the
5 319 concentrations of trace elements in the residual medium and lead to an increase of D^X . We thus
6
7 320 calculated partition coefficients of Mn, Co and Zn normalized to Fe ($D^{X/Fe}$) to compare values
8
9 321 obtained from AMB-1 and MSR-1, and obtained similar results in both strains (Table S7)
10 322 demonstrating that Co, Mn and Zn are highly similarly processed in AMB-1 and MSR-1.

11
12 323 Abiotic and biological magnetite samples were measured with XAS in powdered form at the
13
14 324 respective dopant K-edges to confirm the valence and site occupancy of doped metals in
15 325 magnetite. Due to the dopant-level concentration of each metal in magnetite, fluorescence
16
17 326 detection was employed to collect XAS spectra. In the case of Co for abiotic magnetite
18
19 327 nanoparticles, the fluorescence signal was too weak to collect usable spectra, which is
20 328 understandable given the ten-fold lower Co concentration abiotic in magnetite relative to Mn
21
22 329 and Zn (see Table S6). Nevertheless, from similar previous characterizations of Co-ferrite
23
24 330 nanoparticles ($\text{Co}_x\text{Fe}_{3-x}\text{O}_4$) prepared via different synthetic methods, Co is well known to
25 331 occupy mainly octahedral sites^{33,34} and was used forth in the CFSE calculation.

26
27 332 K-edge XAS for Mn-doped abiotic magnetite (Fig. 6A) has near-edge structural features that
28
29 333 resemble a $\text{Mn}_{0.5}\text{Fe}_{2.5}\text{O}_4$ reference (where Mn is a mixture of Mn(II) located in tetrahedral sites
30 334 and Mn(III) in octahedral sites).³⁵⁻³⁷ Comparison with Mn-based oxides shows an oxidation
31
32 335 state between Mn(II) and Mn(III) but closer to MnO. This is reflected by the position of the
33
34 336 main rising edge (Fig. S5). Weaker pre-edge and post-edge features (6562 eV) potentially
35 337 originate from the dilute and mixed nature of the dopant metal in the magnetite lattice compared
36
37 338 to the Mn-ferrite reference. Interestingly, it was found that Mn K-edge XANES of our sample
38
39 339 well matched Mn-ferrite nanocrystals prepared in the stoichiometry of the mineral jacobsite
40 340 (MnFe_2O_4).³⁸ This reference (called MnFe_2O_4) is included for comparison in Fig. 6A. Here,
41
42 341 similar edge position and near-edge features confirms comparable local environments for Mn,
43
44 342 which was ascribed to be partially oxidized Mn(II) in 80% tetrahedral sites (*i.e.*, having 0.2
45 343 degree of inversion). Since the extended X-ray absorption fine structure (EXAFS) region is too
46
47 344 noisy to fit scattering paths for structural information, *ab initio* simulations of the Mn K-edge
48
49 345 XANES for tetrahedral and octahedral Mn substitutions in magnetite (Fig. S6) provided another
50 346 perspective. The relative energy positions of near-edge absorption features for $\text{Mn}_{0.5}\text{Fe}_{2.5}\text{O}_4$ and
51
52 347 MnFe_2O_4 references match better with tetrahedral coordination from the simulated XANES.

53
54 348 Zinc K-edge XANES for Zn-doped abiotic magnetite (Fig. 6C) has poorly defined near-
55 349 edge features and very weak EXAFS. When compared with a Zn-ferrite reference, known to
56
57 350 have a normal spinel crystal structure with Zn(II) occupying tetrahedral sites, the width and
58
59 351 positioning of the XANES aligns well but clear near-edge features are less apparent.
60

1
2
3
4 352 Additionally, an unexpected near-edge feature that did not match with any of our reference
5 353 materials. Based on the energy position of this feature, Zn metal contamination from the sample
6
7 354 holder is suspected. Indeed, linear combination fitting revealed a best fit of 39% Zn metal, 36%
8
9 355 Zn(II)-histadine complex and 25% ZnFe_2O_4 with R-factor = 0.0076. Without contribution from
10 356 the sample holder, this translates to 59% Zn(II)-histadine and 41% ZnFe_2O_4 . We note that
11
12 357 histadine residues were not present in the reaction mixture. Nevertheless, due to the similarity
13
14 358 in electronic structure of N and O, and their photoelectron backscattering properties, we
15 359 attribute a portion of the Zn cations to be in molecular complex-like environments while the
16
17 360 remaining Zn cations incorporate into magnetite as Zn-ferrite spinel.

18
19 361 Higher quality data was obtained for biological magnetite since dopants were found to be in
20 362 higher concentration than in the abiotic samples, at least partially due to the high initial
21
22 363 concentrations used in the bacterial growth media (Table S6). Cobalt K-edge XANES for Co-
23
24 364 doped biological magnetite highly resembles that of a CoFe_2O_4 reference (Fig. 6B and Fig. S7),
25 365 given the identical energies of distinctive near-edge features. From known crystal structure of
26
27 366 Co-ferrite nanoparticles,^{39,40} Co mainly occupies octahedral sites in magnetite in line with
28
29 367 previous work on both AMB-1 and MSR-1 strains.^{27,30,31} Manganese K-edge XANES of Mn-
30 368 doped biological magnetite is again similar to the $\text{Mn}_{0.5}\text{Fe}_{2.5}\text{O}_4$ reference (Fig. 6A), with peak
31
32 369 positions and their relative intensities even more comparable. The higher data quality for this
33
34 370 sample afforded supplemental EXAFS information and a well-resolved pre-edge region.
35 371 EXAFS fitting yielded a Mn-O coordination number of 4.1 ± 0.6 and a bond distance of $202 \pm$
36 372 2 pm (Fig. S8 and Table S8), both suggesting a tetrahedral environment for Mn dopants is likely,
37
38 373 consistent with another recent study.²⁸ Nevertheless, a small contribution of Mn-Fe single
39 374 scattering from Mn in octahedral sites (coordination number of 1.9 ± 0.6 and bond distance 296
40 375 ± 2 pm] was found to complete EXAFS fitting of Mn-O and Mn-Fe (coordination number of
41
42 376 15 ± 2 and bond distance 352 ± 5 pm) scattering from Mn in tetrahedral sites. This further
43
44 377 confirms a partial +3 valence state of the dopant and moreover, mainly tetrahedral coordination
45 378 of Mn.
46
47
48

49 379 Distinct Zn K-edge XANES features are more prominent for Zn-doped biological magnetite
50 380 than that for the abiotic case, with near-edge features resembling a Zn-ferrite reference material
51
52 381 (Fig. 6C). From linear combination fitting, we obtain a best fit of 64% ZnFe_2O_4 , 18% Zn-citrate
53
54 382 and 18% Zn metal (sample holder contamination) with R-factor = 0.0026 (Fig. S9). The smaller
55 383 contribution from Zn-citrate could suggest partial octahedral coordination in addition to the
56
57 384 tetrahedral coordination expected from Zn-ferrite. However, EXAFS fitting of Zn-O path
58
59 385 yielded a coordination number of 4 ± 1 and bond distance of 205 ± 2 pm confirming Zn mainly
60

1
2
3
4 386 occupy tetrahedral sites (Fig. S8 and Table S8). In our case, we note a high incorporation of Zn
5 387 into MSR-1 magnetite as ZnFe_2O_4 from doping bacteria growth media with Zn(II), whereas
6
7 388 another study found more ZnO than ZnFe_2O_4 .²⁸

8
9 389 Using the experimentally determined coordination and valence of Mn, Co and Zn, a
10 390 corrected CFSE was calculated. As mentioned above, Mn in abiotic magnetite showed mixed
11
12 391 +2/+3 valence. The rising edge position (determined from the first derivative maximum of the
13
14 392 main absorption edge) was shifted towards higher values when compared to $\text{Mn}_{0.5}\text{Fe}_{2.5}\text{O}_4$. This
15 393 indicates more oxidized Mn in the abiotic magnetite samples than in the measured Mn-ferrite
16
17 394 reference, which has been shown to contain 25% Mn(III) and 75% Mn(II),^{35-37,41} while the
18
19 395 biological magnetite overlapped the Mn-ferrite reference which suggests a similar valence for
20 396 Mn. Therefore, based on the shift of the absorption edge position, the Mn(III) / Mn_{total} ratios in
21
22 397 the abiotic and biologic magnetite were taken as 0.3 (*i.e.*, higher than Mn-ferrite reference) and
23
24 398 0.25 (*i.e.*, similar to Mn-ferrite reference), respectively. Zinc coordination was considered to be
25 399 60% octahedral/40% tetrahedral in the abiotic magnetite, and 20% octahedral/80% tetrahedral
26
27 400 in the biological nanoparticles based on the fitting results. Finally, Co was considered to mainly
28
29 401 occupy octahedral sites based on the extensive literature^{42,43} that is consistent with present Co-
30 402 doped MSR-1 magnetite. Measured partition coefficients represented against XAS-corrected
31
32 403 CFSE are shown in Fig. 7. In the abiotic case, $\log D^X$ values showed a weak linear relationship
33
34 404 with CFSE (correlation coefficient of 0.87), while biological $\log D^X$ showed almost constant
35 405 values with no correlation with CFSE (correlation coefficient of 0.006) (Fig. 7A). To take into
36
37 406 account crystal field controls independently of lattice strain mechanisms, the measured partition
38
39 407 coefficients in abiotic nanoparticles were normalized to the D^X predicted from lattice strain
40 408 theory (Eq. 2 and Fig. 1). The results are presented in Fig. 7B and show a stronger linear
41
42 409 correlation between the trace element stabilization and the corrected CFSE (correlation
43
44 410 coefficient of 0.99). Our results thus demonstrate the importance of taking into account the
45 411 actual coordination of trace 3d metals in magnetite since their incorporation is controlled by
46
47 412 crystal field mechanisms.

48
49 413

51 414 **Conclusion**

52 415 The present contribution establishes an experimental and theoretical framework that can
53
54 416 predict the behavior of trace and minor cations during synthetic magnetite formation based on
55
56 417 their size, valence and unfilled 3d orbitals. It also helps elucidate the screening effect MTB
57 418 have on biological magnetite formation. Beyond the geobiological interests for the
58
59 419 identification of ancient terrestrial and extra-terrestrial life, our work has significant
60

1
2
3
4 420 implications for nanotechnological applications of biological and/or abiotic nanoparticles of
5 421 magnetite. Deliberate doping of trace and minor elements has been carried out to optimize
6
7 422 magnetite nanoparticle composition for dedicated applications, including doping of Co and Zn
8
9 423 that increase the efficiency of magnetite's magnetic properties for cancer treatment using
10 424 hyperthermia,^{8,9,44} as well as its capacity of organic pollutant remediation and (bio)remediation
11
12 425 of contaminated water.⁴⁵⁻⁴⁷ The appropriateness of doped magnetite nanomaterials with tailored
13
14 426 properties (*e.g.*, magnetism) for future applications will be further evaluated with our
15 427 methodology by identifying the different outcomes of dopant composition via abiotic or
16
17 428 biological synthesis.
18

19 429

20 430 **Materials and Methods**

21 431 **Magnetite abiotic synthesis**

22
23
24 432 Production of abiotic magnetite nanoparticles was performed using a titration device as
25
26 433 already described.⁴⁸ An Fe chloride mixture ($[\text{Fe(II)Cl}_2] = 0.33 \text{ M}$ and $[\text{Fe(III)Cl}_3] = 0.66 \text{ M}$)
27 434 was added to a NaOH solution (pH = 11) at room-temperature. The decrease of pH associated
28
29 435 with the release of protons during magnetite precipitation was compensated by adding
30
31 436 additional NaOH solution (1 M) to keep the pH constant throughout the experiment. All doping
32 437 elements were mixed in the Fe solution and added at similar concentrations (100 ppb for each
33
34 438 element from dissolution of chloride salts purchased from Sigma-Aldrich). The Fe mixture,
35
36 439 NaOH solution, and the magnetite precipitation solution were kept under constant anoxic
37 440 conditions by flushing N_2 to prevent Fe(II) oxidation. Magnetite samples were then recovered
38
39 441 by centrifugation (8 000 rpm for 15 min), rinsed two times with Milli-Q water and dried in a
40
41 442 desiccator. All samples were kept under anoxic conditions before XAS analyses. Electron
42 443 microscopy revealed nanoparticles with size and shape similar to previous works using the same
43
44 444 co-precipitation method for magnetite production.^{10,22}
45

46 445

47 446 **Bacterial cultures and magnetite purification**

48
49 447 Procedures for AMB-1 cultivation are detailed in previous work.¹⁰ Two culturing methods
50
51 448 were used for AMB-1 (batch and fermentor cultures) to assess the biological variability induced
52 449 by different culture conditions. The size of nanoparticles produced by MSR-1 is in the range of
53
54 450 published works on both AMB-1 and MSR-1 strains.⁴⁹⁻⁵¹ MSR-1 magnetite observed with
55
56 451 electron microscopy was similar in size (Table S3) and shape to standard MSR-1 cultures as
57 452 previously observed.³² Because MTB magnetite is strongly depleted in dopant elements
58
59 453 compared to its abiotic counterpart,¹⁰ Mn, Co and Zn were added at higher concentration to
60

1
2
3
4 454 maximize their incorporation into MSR-1 magnetite for XAS measurements (see Fig. S10 for
5 455 doping trials with Cu and Ni). Doping elements were added at similar concentrations (33 μM
6
7 456 for each element in the mixed-element condition, and 100 μM for single-doped samples from
8
9 457 dissolution of chloride salts purchased from Sigma-Aldrich) in MSR-1 growth medium. They
10 458 did not induce toxicity for the bacteria, as shown by similar cell densities in doped cultures
11
12 459 when compared to bacteria cultivated with no doping elements (Table S9). MSR-1 magnetite
13
14 460 was then extracted for XAS and HR-ICP-MS analyses: MSR-1 bacteria were lysed using a
15 461 French Press (3 runs at 7 000 kPa), recovered with a magnet, and purified with an EDTA-
16
17 462 Triton-SDS preparation following a previously described procedure.¹⁰ Complete removal of the
18
19 463 magnetosome membrane using this protocol was previously confirmed from electron
20 464 microscopy (no membrane features after purification) and energy dispersive X-ray
21
22 465 spectroscopy (no detectable phosphorous and nitrogen after purification, which are elements
23
24 466 contained in organic matter and absent from magnetite). This was also confirmed for our
25 467 biological magnetite samples, which showed no residual membrane after purification (Fig. 4).
26
27 468 Finally, all magnetite samples were leached using an EDTA solution for 20 minutes to remove
28
29 469 elements adsorbed on the magnetite surface but not incorporated into the crystal lattice.¹⁰ Such
30 470 methodology was shown not to dissolve magnetite.¹⁰ The partition coefficients normalized to
31
32 471 iron obtained in this work were identical (within analytical uncertainty) to the ones previously
33
34 472 obtained in the initial study establishing the purification protocol, further demonstrating that
35 473 magnetite samples were efficiently purified.¹⁰

36 474

39 475 **Transmission electron microscopy**

40 476 Abiotic magnetite nanoparticles and MSR-1 bacteria were deposited on carbon-coated
41
42 477 copper grids for electron microscopy characterizations. MSR-1 grids were rinsed using Milli-
43
44 478 Q water to remove salts precipitated from the growth medium. Samples were then observed
45 479 with a FEI Tecnai G2 Biotwin microscope operating at 100 kV. The size of magnetite particles
46
47 480 produced by MSR-1 was measured with the ImageJ software. The size of abiotic magnetite
48
49 481 nanoparticles could not be measured reliably from electron microscopy due to agglomeration,
50 482 and was instead determined from X-ray diffraction (see below).

51 483

54 484 **Selection of trace and minor elements**

55 485 Four elements (B, Ca, K, Mg) from the initial work¹⁰ were excluded for the present work: B
56
57 486 and K are contained in the glassware (borosilicates) used for the preparation and storage of
58
59
60

487 samples, and thus contaminate the magnetite and solution samples, while only one replicate
488 could be obtained in the case of Ca and Mg.

489

490 **Determination of element oxidation state in solution and magnetite**

491 The oxidation state of all doping trace and minor elements in precipitation solutions was
492 determined at the pH / E_h conditions representative of the abiotic precipitation solution and the
493 proposed magnetosome internal solution¹⁸ with the geochemical code CHESS⁵² using the
494 THERMODDEM⁵³ database. Because Fe(II) is found in octahedral sites in magnetite, all
495 divalent cations were considered as occupying octahedral sites in magnetite. Similarly, half of
496 Fe(III) is present in octahedral sites magnetite, the other half being contained in tetrahedral sites.
497 We thus considered trivalent cations to be incorporated in both 6- (50%) and 4-coordination
498 (50%).

499

500 **Prediction of trace and minor element partition coefficients from lattice strain theory**

501 The distribution of D^X values for an isoivalent series of elements can be described by ref.¹⁵:

502

$$503 \quad D^X = D_{n+}^{0(M)} \times \exp\left\{ \frac{-4\pi N E^M \left[\frac{1}{A} r^{0(M)} (r^X - r^{0(M)})^2 + \frac{1}{3} (r^X - r^{0(M)})^3 \right]}{RT} \right\} \quad (2)$$

504

505 With $D_{n+}^{0(M)}$ the partition coefficient for a fictive element with $r^X = r^{0(M)}$ and causing no elastic

506 strain (*i.e.* strain-compensated D^X), E_{n+}^M the lattice strain parameter describing the Young's

507 Modulus (in GPa) of the site M, N_A the Avogadro's number, R the perfect gas constant, and T

508 the temperature in Kelvin. Similarly, heterovalent cation substitution entail excess electric

509 charge accommodated by the crystal lattice that will also translate into a penalty in energy for
510 element incorporation¹⁵:

511

$$512 \quad D_{n+}^{0(M)} = D^{00(M)} \times \exp\left\{ \frac{-N_A e^2 (Z^X - Z^{0(M)})^2}{(2\varepsilon\rho RT)} \right\} \quad (3)$$

513

514 Where $D^{00(M)}$ is the strain-compensated partition coefficient for a fictive ion causing no
515 electrostatic charging (*i.e.*, homovalent substitution), e the electron charge, ρ the radius of the

516 region over which the excess charge is distributed, ε the dielectric constant of that region, and

517 Z^X and $Z^{0(M)}$ the ionic charge and the optimum ionic charge at the site M, respectively.

518 The parameters used for the calculation of predicted partition coefficients using Eq. 2 ($D_{n+}^{0(M)}$,
519 $r_{n+}^{0(M)}$, and E_{n+}^M) are given in Table S5. Selected Young's modulus range between 90 and 1430

1
2
3
4 520 GPa , which is in good agreement with the range of published values for macrocrystals and
5 521 nanoparticles of magnetite.⁵⁴⁻⁵⁶ Higher variability in n_+ than that observed here for magnetite
6 E^M

7 522 has already been reported in many mineral phases, including plagioclase, diopside, augite,
8 523 anorthite, albite, diopside or fluorite.^{57,58} Such variability is related to the ion charge and the
9 524 cation – oxygen distance.¹⁵ In the case of magnetite, it can also be explained by the variability
10 525 induced by the two lattice sites under consideration (tetrahedral and octahedral). For Eq. 3, a
11 526 dielectric constant (ϵ) of 55 and a lattice region with a radius (ρ) of 9 nm were considered. Such
12 527 values correspond to published ϵ for magnetite.^{59,60} Due to the agglomerated nature of abiotic
13 528 magnetite samples, it was impossible to assess the particle size from electron microscopy. XRD
14 529 peak fitting indicated a mean radius of 6 nm for abiotic nanoparticles. However it is known to
15 530 generate lower (up to 50 %) values than direct observation from electron microscopy.²² Given
16 531 the discrepancy between these two techniques, we consider our theoretical value of 9 nm to be
17 532 compatible with the size of our abiotic magnetite samples.

18 533 We note that the partition coefficient D^X is expressed differently from other publications of
19 534 our group.^{10,16} Specifically, it is not normalized to iron (except for the AMB-1/MSR-1
20 535 comparison, see section “Crystal field constraints on element incorporation into magnetite and
21 536 coordination of 3d metals in magnetite” for details) to determine the values of $D_{n+}^{0(M)}$ and $D^{00(M)}$
22 537 coefficients).

23
24 538

25 539 **Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) analyses**

26 540 The concentrations of Fe, Mn, Co and Zn in the abiotic and MSR-1 magnetite nanoparticles
27 541 (samples only from the metal mixture culture were used), in the residual precipitation solution
28 542 and in the residual bacterial growth media were determined using a Perkin Elmer NexIon 300X
29 543 mass spectrometer (collision mode configuration with a Rh103 internal standard) at the *Centre*
30 544 *Européen de Recherche et d’Enseignement en Géosciences de l’Environnement* (CEREGE
31 545 Aix-en-Provence, France). Three replicates were performed for each experimental condition.
32 546

33 547 **X-ray diffraction (XRD)**

34 548 X-ray diffraction measurements were performed at the μ Spot beamline at the BESSY II facility
35 549 (Helmholtz Zentrum für Materialien und Energie, Berlin, Germany).⁶¹ Measurements were
36 550 carried out using a B4C/Mo Multilayer (2 nm period) monochromator and an energy of 15 keV.
37 551 A sequence of pinholes was used to select 100x100 μm^2 spot size. The data was normalized on
38 552 primary beam intensity and the background was subtracted. Transmission through the sample
39 553 was calculated from an X-ray fluorescence signal collected from a lead beamstop using
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 554 RAYSPEC Sirius SD-E65133-BE-INC detector equipped with an 8 μm beryllium window,
5 555 where the primary beam intensity was monitored using an ion chamber. Diffraction data were
6 556 collected by an Eiger 9M detector with $75 \times 75 \mu\text{m}^2$ pixel area. Further data processing and
7 557 reduction was done using the directly programmable data analysis kit (DPDAK).⁶² Diffraction
8 558 patterns were radially integrated and the scattered intensity $I(Q)$ was calculated as a function of
9 559 the momentum transfer Q , defined as

$$Q = \frac{2\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (4)$$

13 560
14 561
15 562
16 563 with λ and θ the photon wavelength and the scattering angle, respectively. Sample to detector
17 564 distance was set to 189 mm and calibrated by using quartz powder (NIST, standard reference
18 565 material 1878a). Determination of peak position and particle size was performed following
19 566 established methodology with an in-house python-based script exploiting Scipy library. Fits
20 567 were performed by assuming a Lorentzian distribution and by taking into account experimental
21 568 errors and instrumental broadening (Fig. S11).

30 570 **X-ray Absorption Spectroscopy (XAS)**

31 571 The abiotic and biological magnetite samples were measured under cryogenic conditions in
32 572 powdered form. To prepare the samples for measurement, the purified abiotic and biological
33 573 magnetite nanoparticles were spread onto Kapton tape and folded to seal the sample. The
34 574 samples were kept frozen during storage, shipment and measurement. Principal data was
35 575 collected at the I20-Scanning beamline (Diamond Light Source, Didcot, UK). Preliminary XAS
36 576 data (additional Fe, Ni and Cu K-edge spectra) was collected at the Sector BM-20 beamline
37 577 (Advanced Photon Source, Argonne National Laboratory, IL, USA). Additional reference
38 578 materials were acquired and energy calibrated for comparison with abiotic and biological
39 579 samples. Due to the dilute nature of dopant metals, fluorescence detection was employed to
40 580 collect XAS spectra. Several scans were collected and averaged to produce the spectra
41 581 presented in this work. XAS of reference foils for Mn, Co and Zn were simultaneously collected
42 582 downstream via ionization chambers for energy calibration. Athena and WinXAS programs
43 583 were used for background subtraction, energy calibration, normalization and transformation to
44 584 FT-EXAFS spectra. Athena was implemented for linear combination fitting and WinXAS for
45 585 refined EXAFS fitting. The computational package FEFF8.2 was employed to simulate
46 586 scattering paths for EXAFS fitting and to simulate Mn K-edge XANES of Mn in octahedral
47 587 and tetrahedral lattice sites in magnetite. Reported errors in EXAFS fitting results were
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 588 computed from off-diagonal elements of the correlation matrix, which were weighted by the
5 589 square root of the reduced chi-squared values obtained from each simulated fit. The amount of
6
7 590 experimental noise was also taken into consideration for each Fourier transformed R-space
8
9 591 spectrum from 15-25 Å.
10 592

11 593 **Acknowledgements**

12
13
14 594 MA is supported by a grant through the *Fondation pour la Recherche Médicale*
15 595 (ARF201909009123). DMC acknowledges research funding through a European Union Marie-
16 596 Skłodowska Curie Action International Fellowship (MSCA-IF Project 797431:
17
18 597 BioNanoMagnets) and from a CNRS starting grant. CLS@APS facilities (Sector 20-BM) at the
19 598 Advanced Photon Source (APS) are supported by the U.S. Department of Energy (DOE),
20 599 NSERC Canada, the University of Washington, the Canadian Light Source (CLS), and the APS.
21
22 600 Use of the APS is supported by the DOE under Contract No. DE-AC02-06CH11357. We
23
24 601 acknowledge Diamond Light Source for beamtime on I20-scanning under proposal SP25495.
25 602 We thank beamline scientists Michael Pape (APS) for technical assistance during beamtimes.
26
27 603 The groups of Thomas N. Stokes, Daniela Carta, Alicia Muela and M. Luisa Fdez-Gubieda are
28
29 604 thanked for sharing XAS data on ferrite references. We thank Bernard Angeletti and Jean-Paul
30 605 Ambrosi from the *Centre Européen de Recherche et d'Enseignement des Géosciences de*
31
32 606 *l'Environnement* (Aix-en-Provence, France) for assistance with the mass spectrometry
33
34 607 measurements. We thank Lucas Kuhrts for providing additional reference XRD diffractogram
35 608 of magnetite and Paul N. Duchesne for constructive feedback and comments on the manuscript.
36
37 609
38
39
40

41 610 **Associated Content**

42
43 611 Supporting Information is available free of charge at [https://](https://pubs.acs.org/doi/10.1021/acsnano...)
44 612 pubs.acs.org/doi/10.1021/acsnano... The file contains additional X-ray diffraction and X-ray
45 613 absorption spectroscopy data for abiotic and biological magnetite samples, plots and tabulated
46 614 values of calculated partition coefficients, massic concentration of elements from ICP-MS
47 615 measurements, particle size measurements, EXAFS fitting results, ideal radii and Young's
48 616 modulus values for lattice strain calculations and results from dopant metal tolerance study.

49 617 This manuscript was initially deposited on a pre-print server and can be found with the
50 618 following information: Matthieu Amor, Damien Faivre, Daniel M. Chevrier, Crystal-chemical
51 619 and biological controls of trace and minor element incorporation into magnetite nanocrystals.
52
53 620 2021, ChemRxiv. [https://chemrxiv.org/engage/chemrxiv/article-](https://chemrxiv.org/engage/chemrxiv/article-details/6177bd06913a742b636afc83)
54 621 [details/6177bd06913a742b636afc83](https://chemrxiv.org/engage/chemrxiv/article-details/6177bd06913a742b636afc83) (accessed December 16, 2022).
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

622

623 **References**

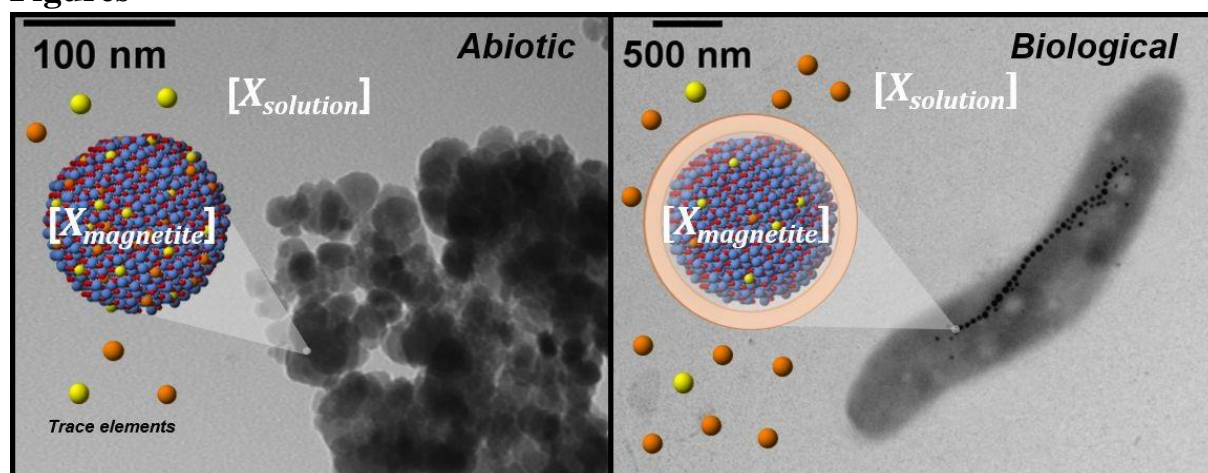
- 624 (1) Usman, M.; Byrne, J. M.; Chaudhary, A.; Orsetti, S.; Hanna, K.; Ruby, C.; Kappler,
625 A.; Haderlein, S. B. Magnetite and Green Rust: Synthesis, Properties, and Environmental
626 Applications of Mixed-Valent Iron Minerals. *Chem. Rev.* **2018**, *118* (7), 3251–3304.
627 <https://doi.org/10.1021/acs.chemrev.7b00224>.
- 628 (2) Uebe, R.; Schüler, D. Magnetosome Biogenesis in Magnetotactic Bacteria. *Nat. Rev.*
629 *Microbiol.* **2016**, *14* (10), 621–637. <https://doi.org/10.1038/nrmicro.2016.99>.
- 630 (3) Lin, W.; Paterson, G. A.; Zhu, Q.; Wang, Y.; Kopylova, E.; Li, Y.; Knight, R.;
631 Bazylinski, D. A.; Zhu, R.; Kirschvink, J. L.; Pan, Y. Origin of Microbial Biomineralization
632 and Magnetotaxis during the Archean. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114* (9), 2171–
633 2176. <https://doi.org/10.1073/pnas.1614654114>.
- 634 (4) Amor, M.; Mathon, F. P.; Monteil, C. L.; Busigny, V.; Lefevre, C. T. Iron-
635 Biomineralizing Organelle in Magnetotactic Bacteria: Function, Synthesis and Preservation in
636 Ancient Rock Samples. *Environ. Microbiol.* **2020**, *22* (9), 3611–3632.
637 <https://doi.org/10.1111/1462-2920.15098>.
- 638 (5) Plan Sangnier, A.; Preveral, S.; Curcio, A.; K A Silva, A.; Lefèvre, C. T.; Pignol, D.;
639 Lalatonne, Y.; Wilhelm, C. Targeted Thermal Therapy with Genetically Engineered
640 Magnetite Magnetosomes@RGD: Photothermia Is Far More Efficient than Magnetic
641 Hyperthermia. *J Control Release* **2018**, *279*, 271–281.
642 <https://doi.org/10.1016/j.jconrel.2018.04.036>.
- 643 (6) Felfoul, O.; Mohammadi, M.; Taherkhani, S.; de Lanauze, D.; Xu, Y. Z.; Loghin, D.;
644 Essa, S.; Jancik, S.; Houle, D.; Lafleur, M.; Gaboury, L.; Tabrizian, M.; Kaou, N.; Atkin, M.;
645 Vuong, T.; Batist, G.; Beauchemin, N.; Radzioch, D.; Martel, S. Magneto-Aerotactic Bacteria
646 Deliver Drug-Containing Nanoliposomes to Tumour Hypoxic Regions. *Nat. Nanotechnol.*
647 **2016**, *11* (11), 941–947. <https://doi.org/10.1038/NNANO.2016.137>.
- 648 (7) Zingsem, B. W.; Feggeler, T.; Terwey, A.; Ghaisari, S.; Spoddig, D.; Faivre, D.;
649 Meckenstock, R.; Farle, M.; Winklhofer, M. Biologically Encoded Magnonics. *Nature*
650 *Communications* **2019**, *10* (1), 4345. <https://doi.org/10.1038/s41467-019-12219-0>.
- 651 (8) Byrne, J. M.; Coker, V. S.; Moise, S.; Wincott, P. L.; Vaughan, D. J.; Tuna, F.;
652 Arenholz, E.; van der Laan, G.; Pattrick, R. A. D.; Lloyd, J. R.; Telling, N. D. Controlled
653 Cobalt Doping in Biogenic Magnetite Nanoparticles. *Journal of The Royal Society Interface*
654 **2013**, *10* (83), 20130134. <https://doi.org/10.1098/rsif.2013.0134>.
- 655 (9) Byrne, J. M.; Coker, V. S.; Cespedes, E.; Wincott, P. L.; Vaughan, D. J.; Pattrick, R.
656 A. D.; Laan, G. van der; Arenholz, E.; Tuna, F.; Bencsik, M.; Lloyd, J. R.; Telling, N. D.
657 Biosynthesis of Zinc Substituted Magnetite Nanoparticles with Enhanced Magnetic
658 Properties. *Advanced Functional Materials* **2014**, *24* (17), 2518–2529.
659 <https://doi.org/10.1002/adfm.201303230>.
- 660 (10) Amor, M.; Busigny, V.; Durand-Dubief, M.; Tharaud, M.; Ona-Nguema, G.; Gélabert,
661 A.; Alphandéry, E.; Menguy, N.; Benedetti, M. F.; Chebbi, I.; Guyot, F. Chemical Signature
662 of Magnetotactic Bacteria. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (6), 1699–1703.
663 <https://doi.org/10.1073/pnas.1414112112>.
- 664 (11) Thomas-Keprta, K. L.; Bazylinski, D. A.; Kirschvink, J. L.; Clemett, S. J.; McKay, D.
665 S.; Wentworth, S. J.; Vali, H.; Gibson, E. K.; Romanek, C. S. Elongated Prismatic Magnetite
666 Crystals in ALH84001 Carbonate Globules: Potential Martian Magnetofossils. *Geochim.*
667 *Cosmochim. Acta* **2000**, *64* (23), 4049–4081. [https://doi.org/10.1016/S0016-7037\(00\)00481-](https://doi.org/10.1016/S0016-7037(00)00481-6)
668 6.
- 669 (12) Thomas-Keprta, K. L.; Clemett, S. J.; McKay, D. S.; Gibson, E. K.; Wentworth, S. J.
670 Origins of Magnetite Nanocrystals in Martian Meteorite ALH84001. *Geochim. Cosmochim.*

- 1
2
3 671 *Acta* **2009**, *73* (21), 6631–6677. <https://doi.org/10.1016/j.gca.2009.05.064>.
- 4 672 (13) Golden, D. C.; Ming, D. W.; Schwandt, C. S.; Lauer, H. V.; Socki, R. A.; Morris, R.
5 673 V.; Lofgren, G. E.; McKay, G. A. A Simple Inorganic Process for Formation of Carbonates,
6 674 Magnetite, and Sulfides in Martian Meteorite ALH84001. *Am. Miner.* **2001**, *86* (3), 370–375.
- 7 675 (14) Jimenez-Lopez, C.; Rodriguez-Navarro, C.; Rodriguez-Navarro, A.; Perez-Gonzalez,
8 676 T.; Bazylinski, D. A.; Lauer, H. V.; Romanek, C. S. Signatures in Magnetites Formed by
9 677 (Ca,Mg,Fe)CO₃ Thermal Decomposition: Terrestrial and Extraterrestrial Implications.
10 678 *Geochim. Cosmochim. Acta* **2012**, *87*, 69–80. <https://doi.org/10.1016/j.gca.2012.03.028>.
- 11 679 (15) Blundy, J.; Wood, B. Partitioning of Trace Elements between Crystals and Melts.
12 680 *Earth Planet. Sci. Lett.* **2003**, *210* (3–4), 383–397. <https://doi.org/10.1016/S0012->
13 681 821X(03)00129-8.
- 14 682 (16) Amor, M.; Faivre, D.; Corvisier, J.; Tharaud, M.; Busigny, V.; Komeili, A.; Guyot, F.
15 683 Defining Local Chemical Conditions in Magnetosomes of Magnetotactic Bacteria. *J. Phys.*
16 684 *Chem. B* **2022**, *126* (14), 2677–2687. <https://doi.org/10.1021/acs.jpcc.2c00752>.
- 17 685 (17) Ona-Nguema, G.; Morin, G.; Wang, Y.; Foster, A. L.; Juillot, F.; Calas, G.; Brown, G.
18 686 E. XANES Evidence for Rapid Arsenic(III) Oxidation at Magnetite and Ferrihydrite Surfaces
19 687 by Dissolved O₂ via Fe²⁺-Mediated Reactions. *Environ. Sci. Technol.* **2010**, *44* (14), 5416–
20 688 5422. <https://doi.org/10.1021/es1000616>.
- 21 689 (18) Eguchi, Y.; Fukumori, Y.; Taoka, A. Measuring Magnetosomal PH of the
22 690 Magnetotactic Bacterium *Magnetospirillum Magneticum* AMB-1 Using PH-Sensitive
23 691 Fluorescent Proteins. *Biosci. Biotechnol. Biochem.* **2018**, *82* (7), 1243–1251.
24 692 <https://doi.org/10.1080/09168451.2018.1451739>.
- 25 693 (19) Hsueh, Y.-H.; Lin, K.-S.; Ke, W.-J.; Hsieh, C.-T.; Chiang, C.-L.; Tzou, D.-Y.; Liu, S.-
26 694 T. The Antimicrobial Properties of Silver Nanoparticles in *Bacillus Subtilis* Are Mediated by
27 695 Released Ag⁺ Ions. *PLOS ONE* **2015**, *10* (12), e0144306.
28 696 <https://doi.org/10.1371/journal.pone.0144306>.
- 29 697 (20) Komeili, A. Molecular Mechanisms of Compartmentalization and Biomineralization
30 698 in Magnetotactic Bacteria. *Fems Microbiol. Rev.* **2012**, *36* (1), 232–255.
31 699 <https://doi.org/10.1111/j.1574-6976.2011.00315.x>.
- 32 700 (21) Marcano, L.; Orue, I.; García-Prieto, A.; Abrudan, R.; Alonso, J.; Fernández Barquín,
33 701 L.; Valencia, S.; Muela, A.; Fdez-Gubieda, M. L. Controlled Magnetic Anisotropy in Single
34 702 Domain Mn-Doped Biosynthesized Nanoparticles. *J. Phys. Chem. C* **2020**, *124* (41), 22827–
35 703 22838. <https://doi.org/10.1021/acs.jpcc.0c07018>.
- 36 704 (22) Kuhrts, L.; Macías-Sánchez, E.; Tarakina, N. V.; Hirt, A. M.; Faivre, D. Shaping
37 705 Magnetite with Poly-L-Arginine and PH: From Small Single Crystals to Large Mesocrystals.
38 706 *J. Phys. Chem. Lett.* **2019**, *10* (18), 5514–5518. <https://doi.org/10.1021/acs.jpcclett.9b01771>.
- 39 707 (23) Kuhrts, L.; Prévost, S.; Chevrier, D. M.; Pekker, P.; Spaeker, O.; Eglseder, M.;
40 708 Baumgartner, J.; Pósfai, M.; Faivre, D. Wettability of Magnetite Nanoparticles Guides
41 709 Growth from Stabilized Amorphous Ferrihydrite. *J. Am. Chem. Soc.* **2021**, *143* (29), 10963–
42 710 10969. <https://doi.org/10.1021/jacs.1c02687>.
- 43 711 (24) Baumgartner, J.; Bertinetti, L.; Widdrat, M.; Hirt, A. M.; Faivre, D. Formation of
44 712 Magnetite Nanoparticles at Low Temperature: From Superparamagnetic to Stable Single
45 713 Domain Particles. *PLOS ONE* **2013**, *8* (3), e57070.
46 714 <https://doi.org/10.1371/journal.pone.0057070>.
- 47 715 (25) Burns, R. G. *Mineralogical Applications of Crystal Field Theory*; Cambridge
48 716 University Press, 1993.
- 49 717 (26) McClure, D. S. The Distribution of Transition Metal Cations in Spinel. *Journal of*
50 718 *Physics and Chemistry of Solids* **1957**, *3* (3), 311–317. <https://doi.org/10.1016/0022->
51 719 3697(57)90034-3.
- 52 720 (27) Marcano, L.; Muñoz, D.; Martín-Rodríguez, R.; Orue, I.; Alonso, J.; García-Prieto, A.;

- 1
2
3 721 Serrano, A.; Valencia, S.; Abrudan, R.; Fernández Barquín, L.; García-Arribas, A.; Muela,
4 722 A.; Fdez-Gubieda, M. L. Magnetic Study of Co-Doped Magnetosome Chains. *J. Phys. Chem.*
5 723 *C* **2018**, *122* (13), 7541–7550. <https://doi.org/10.1021/acs.jpcc.8b01187>.
6 724 (28) Muñoz, D.; Marcano, L.; Martín-Rodríguez, R.; Simonelli, L.; Serrano, A.; García-
7 725 Prieto, A.; Fdez-Gubieda, M. L.; Muela, A. Magnetosomes Could Be Protective Shields
8 726 against Metal Stress in Magnetotactic Bacteria. *Sci Rep* **2020**, *10* (1), 11430.
9 727 <https://doi.org/10.1038/s41598-020-68183-z>.
10 728 (29) Prozorov, T.; Perez-Gonzalez, T.; Valverde-Tercedor, C.; Jimenez-Lopez, C.; Yebra-
11 729 Rodriguez, A.; Körnig, A.; Faivre, D.; Mallapragada, S. K.; Howse, P. A.; Bazylnski, D. A.;
12 730 Prozorov, R. Manganese Incorporation into the Magnetosome Magnetite: Magnetic Signature
13 731 of Doping. *Eur. J. Mineral.* **2014**, *26* (4), 457–471. [https://doi.org/10.1127/0935-](https://doi.org/10.1127/0935-1221/2014/0026-2388)
14 732 [1221/2014/0026-2388](https://doi.org/10.1127/0935-1221/2014/0026-2388).
15 733 (30) Staniland, S.; Williams, W.; Telling, N.; Van der Laan, G.; Harrison, A.; Ward, B.
16 734 Controlled Cobalt Doping of Magnetosomes in Vivo. *Nat. Nanotechnol.* **2008**, *3* (3), 158–
17 735 162. <https://doi.org/10.1038/nnano.2008.35>.
18 736 (31) Li, J.; Menguy, N.; Arrio, M.-A.; Sainctavit, P.; Juhin, A.; Wang, Y.; Chen, H.;
19 737 Bunau, O.; Otero, E.; Ohresser, P.; Pan, Y. Controlled Cobalt Doping in the Spinel Structure
20 738 of Magnetosome Magnetite: New Evidences from Element- and Site-Specific X-Ray
21 739 Magnetic Circular Dichroism Analyses. *J. R. Soc. Interface* **2016**, *13* (121), 20160355.
22 740 <https://doi.org/10.1098/rsif.2016.0355>.
23 741 (32) Heyen, U.; Schuler, D. Growth and Magnetosome Formation by Microaerophilic
24 742 Magnetospirillum Strains in an Oxygen-Controlled Fermentor. *Appl. Microbiol. Biotechnol.*
25 743 **2003**, *61* (5–6), 536–544. <https://doi.org/10.1007/s00253-002-1219-x>.
26 744 (33) Tsvetkov, M.; Milanova, M.; Ivanova, I.; Neov, D.; Cherkezova-Zheleva, Z.;
27 745 Zaharieva, J.; Abrashev, M. Phase Composition and Crystal Structure Determination of
28 746 Cobalt Ferrite, Modified with Ce, Nd and Dy Ions by X-Ray and Neutron Diffraction. *Journal*
29 747 *of Molecular Structure* **2019**, *1179*, 233–241. <https://doi.org/10.1016/j.molstruc.2018.07.083>.
30 748 (34) Amiri, S.; Shokrollahi, H. The Role of Cobalt Ferrite Magnetic Nanoparticles in
31 749 Medical Science. *Materials Science and Engineering: C* **2013**, *33* (1), 1–8.
32 750 <https://doi.org/10.1016/j.msec.2012.09.003>.
33 751 (35) Mazarío, E.; Mayoral, A.; Salas, E.; Menéndez, N.; Herrasti, P.; Sánchez-Marcos, J.
34 752 Synthesis and Characterization of Manganese Ferrite Nanoparticles Obtained by
35 753 Electrochemical/Chemical Method. *Mater. Des.* **2016**, *111*, 646–650.
36 754 <https://doi.org/10.1016/j.matdes.2016.09.031>.
37 755 (36) Stokes, T. N.; Bromiley, G. D.; Gatta, G. D.; Rotiroti, N.; Potts, N. J.; Saunders, K.
38 756 Cation Distribution and Valence in Synthetic Al–Mn–O and Fe–Mn–O Spinel Structures under Varying
39 757 Conditions. *Mineralogical Magazine* **2018**, *82* (4), 975–992.
40 758 <https://doi.org/10.1180/mgm.2018.109>.
41 759 (37) Liang, X.; Zhong, Y.; Zhu, S.; He, H.; Yuan, P.; Zhu, J.; Jiang, Z. The Valence and
42 760 Site Occupancy of Substituting Metals in Magnetite Spinel Structure Fe₃–xM_xO₄ (M = Cr,
43 761 Mn, Co and Ni) and Their Influence on Thermal Stability: An XANES and TG-DSC
44 762 Investigation. *Solid State Sci.* **2013**, *15*, 115–122.
45 763 <https://doi.org/10.1016/j.solidstatesciences.2012.10.005>.
46 764 (38) Carta, D.; Casula, M. F.; Falqui, A.; Loche, D.; Mountjoy, G.; Sangregorio, C.;
47 765 Corrias, A. A Structural and Magnetic Investigation of the Inversion Degree in Ferrite
48 766 Nanocrystals MFe₂O₄ (M = Mn, Co, Ni). *J. Phys. Chem. C* **2009**, *113* (20), 8606–8615.
49 767 <https://doi.org/10.1021/jp901077c>.
50 768 (39) Swatsitang, E.; Phokha, S.; Hunpratub, S.; Usher, B.; Bootchanont, A.; Maensiri, S.;
51 769 Chindaprasirt, P. Characterization and Magnetic Properties of Cobalt Ferrite Nanoparticles.
52 770 *Journal of Alloys and Compounds* **2016**, *664*, 792–797.

- 1
2
3 771 <https://doi.org/10.1016/j.jallcom.2015.12.230>.
- 4 772 (40) Nakagomi, F.; da Silva, S. W.; Garg, V. K.; Oliveira, A. C.; Morais, P. C.; Franco
5 773 Júnior, A.; Lima, E. C. D. The Influence of Cobalt Population on the Structural Properties of
6 774 $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$. *Journal of Applied Physics* **2007**, *101* (9), 09M514.
7 775 <https://doi.org/10.1063/1.2712821>.
- 8 776 (41) Carta, D.; Casula, M. F.; Floris, P.; Falqui, A.; Mountjoy, G.; Boni, A.; Sangregorio,
9 777 C.; Corrias, A. Synthesis and Microstructure of Manganese Ferrite Colloidal Nanocrystals.
10 778 *Phys. Chem. Chem. Phys.* **2010**, *12* (19), 5074–5083. <https://doi.org/10.1039/B922646J>.
- 11 779 (42) Toksha, B. G.; Shirsath, S. E.; Mane, M. L.; Patange, S. M.; Jadhav, S. S.; Jadhav, K.
12 780 M. Autocombustion High-Temperature Synthesis, Structural, and Magnetic Properties of
13 781 $\text{Co}_x\text{Fe}_{2-x}\text{O}_4$ ($0 \leq x \leq 1.0$). *J. Phys. Chem. C* **2011**, *115* (43), 20905–20912.
14 782 <https://doi.org/10.1021/jp205572m>.
- 15 783 (43) Giri, A. K.; Kirkpatrick, E. M.; Moongkhamklang, P.; Majetich, S. A.; Harris, V. G.
16 784 Photomagnetism and Structure in Cobalt Ferrite Nanoparticles. *Appl. Phys. Lett.* **2002**, *80*
17 785 (13), 2341–2343. <https://doi.org/10.1063/1.1464661>.
- 18 786 (44) Alphantery, E.; Carvallo, C.; Menguy, N.; Chebbi, I. Chains of Cobalt Doped
19 787 Magnetosomes Extracted from AMB-1 Magnetotactic Bacteria for Application in Alternative
20 788 Magnetic Field Cancer Therapy. *J. Phys. Chem. C* **2011**, *115* (24), 11920–11924.
21 789 <https://doi.org/10.1021/jp201274g>.
- 22 790 (45) Fazli, A.; Khataee, A.; Brigante, M.; Mailhot, G. Cubic Cobalt and Zinc Co-Doped
23 791 Magnetite Nanoparticles for Persulfate and Hydrogen Peroxide Activation towards the
24 792 Effective Photodegradation of Sulfalene. *Chem. Eng. J.* **2021**, *404*, 126391.
25 793 <https://doi.org/10.1016/j.cej.2020.126391>.
- 26 794 (46) Huber, F.; Schild, D.; Vitova, T.; Rothe, J.; Kirsch, R.; Schaefer, T. U(VI) Removal
27 795 Kinetics in Presence of Synthetic Magnetite Nanoparticles. *Geochim. Cosmochim. Acta* **2012**,
28 796 *96*, 154–173. <https://doi.org/10.1016/j.gca.2012.07.019>.
- 29 797 (47) Crean, D. E.; Coker, V. S.; van der Laan, G.; Lloyd, J. R. Engineering Biogenic
30 798 Magnetite for Sustained Cr(VI) Remediation in Flow-through Systems. *Environ. Sci. Technol.*
31 799 **2012**, *46* (6), 3352–3359. <https://doi.org/10.1021/es2037146>.
- 32 800 (48) Baumgartner, J.; Carillo, M. A.; Eckes, K. M.; Werner, P.; Faivre, D. Biomimetic
33 801 Magnetite Formation: From Biocombinatorial Approaches to Mineralization Effects.
34 802 *Langmuir* **2014**, *30* (8), 2129–2136. <https://doi.org/10.1021/la404290c>.
- 35 803 (49) Olszewska-Widdrat, A.; Schiro, G.; Reichel, V. E.; Faivre, D. Reducing Conditions
36 804 Favor Magnetosome Production in *Magnetospirillum Magneticum* AMB-1. *Front. Microbiol.*
37 805 **2019**, *10*, 582. <https://doi.org/10.3389/fmicb.2019.00582>.
- 38 806 (50) Amor, M.; Ceballos, A.; Wan, J.; Simon, C. P.; Aron, A. T.; Chang, C. J.; Hellman, F.;
39 807 Komeili, A. Magnetotactic Bacteria Accumulate a Large Pool of Iron Distinct from Their
40 808 Magnetite Crystals. *Appl. Environ. Microbiol.* **2020**, *86* (22), e01278-20.
41 809 <https://doi.org/10.1128/AEM.01278-20>.
- 42 810 (51) Lohße, A.; Borg, S.; Raschdorf, O.; Kolinko, I.; Tompa, É.; Pósfai, M.; Faivre, D.;
43 811 Baumgartner, J.; Schüler, D. Genetic Dissection of the MamAB and Mms6 Operons Reveals
44 812 a Gene Set Essential for Magnetosome Biogenesis in *Magnetospirillum Gryphiswaldense*. *J*
45 813 *Bacteriol* **2014**, *196* (14), 2658–2669. <https://doi.org/10.1128/JB.01716-14>.
- 46 814 (52) Van der Lee, J.; De Windt, L. CHESS Tutorial and Cookbook. Updated for Version
47 815 3.0, Manual Nr. LHM/RD/02/13.; Paris, 2002; p 116.
- 48 816 (53) Blanc, P.; Lassin, A.; Piantone, P.; Azaroual, M.; Jacquemet, M.; Fabbri, A.; Gaucher,
49 817 E. C. Thermoddem: A Geochemical Database Focused on Low Temperature Water/Rock
50 818 Interactions and Waste Materials. *Appl. Geochem.* **2012**, *27* (10), 2107–2116.
51 819 <https://doi.org/10.1016/j.apgeochem.2012.06.002>.
- 52 820 (54) Chicot, D.; Mendoza, J.; Zaoui, A.; Louis, G.; Lepingle, V.; Roudet, F.; Lesage, J.

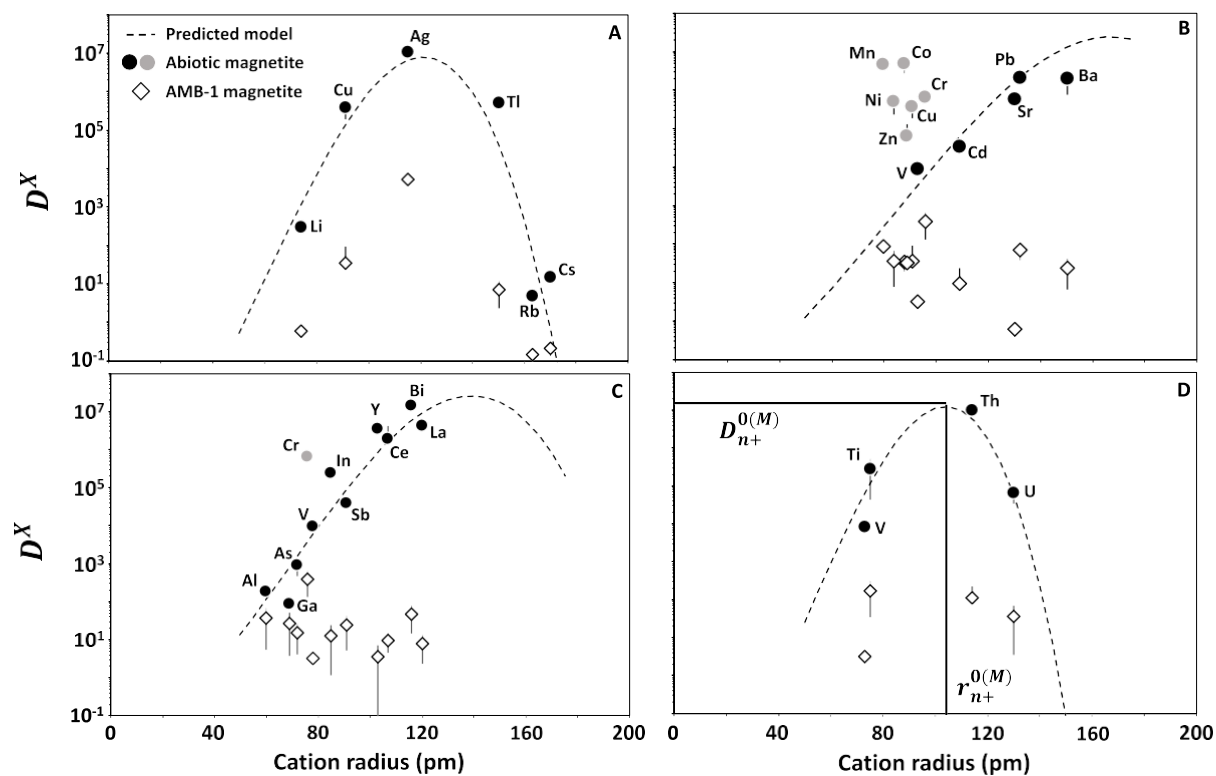
- 1
2
3 821 Mechanical Properties of Magnetite (Fe₃O₄), Hematite (Alpha-Fe₂O₃) and Goethite (Alpha-
4 822 FeO Center Dot OH) by Instrumented Indentation and Molecular Dynamics Analysis. *Mater.*
5 823 *Chem. Phys.* **2011**, *129* (3), 862–870. <https://doi.org/10.1016/j.matchemphys.2011.05.056>.
6 824 (55) Fine, M. E.; Kenney, N. T. Moduli and Internal Friction of Magnetite as Affected by
7 825 the Low-Temperature Transformation. *Phys. Rev.* **1954**, *94* (6), 1573–1576.
8 826 <https://doi.org/10.1103/PhysRev.94.1573>.
9 827 (56) Gholizadeh, A. A Comparative Study of Physical Properties in Fe₃O₄ Nanoparticles
10 828 Prepared by Coprecipitation and Citrate Methods. *J. Am. Ceram. Soc.* **2017**, *100* (8), 3577–
11 829 3588. <https://doi.org/10.1111/jace.14896>.
12 830 (57) Blundy, J.; Wood, B. Prediction of Crystal-Melt Partition-Coefficients from
13 831 Elastic-Moduli. *Nature* **1994**, *372* (6505), 452–454. <https://doi.org/10.1038/372452a0>.
14 832 (58) van Hinsberg, V. J.; Migdisov, A. A.; Williams-Jones, A. E. Reading the Mineral
15 833 Record of Fluid Composition from Element Partitioning. *Geology* **2010**, *38* (9), 847–850.
16 834 <https://doi.org/10.1130/G31112.1>.
17 835 (59) Pimenov, A.; Tachos, S.; Rudolf, T.; Loidl, A.; Schrupp, D.; Sing, M.; Claessen, R.;
18 836 Brabers, V. A. M. Terahertz Conductivity at the Verwey Transition in Magnetite. *Phys. Rev.*
19 837 *B* **2005**, *72* (3), 035131. <https://doi.org/10.1103/PhysRevB.72.035131>.
20 838 (60) Zulfiqar; Afzal, S.; Khan, R.; Zeb, T.; Rahman, M. ur; Burhanullah; Ali, S.; Khan, G.;
21 839 Rahman, Z. ur; Hussain, A. Structural, Optical, Dielectric and Magnetic Properties of PVP
22 840 Coated Magnetite (Fe₃O₄) Nanoparticles. *J Mater Sci: Mater Electron* **2018**, *29* (23), 20040–
23 841 20050. <https://doi.org/10.1007/s10854-018-0134-6>.
24 842 (61) Zizak, I. The MySpot Beamline at BESSY II. *Journal of large-scale research facilities*
25 843 *JLSRF* **2016**, *2* (0), 102. <https://doi.org/10.17815/jlsrf-2-113>.
26 844 (62) Benecke, G.; Wagermaier, W.; Li, C.; Schwartzkopf, M.; Flucke, G.; Hoerth, R.;
27 845 Zizak, I.; Burghammer, M.; Metwalli, E.; Müller-Buschbaum, P.; Trebbin, M.; Förster, S.;
28 846 Paris, O.; Roth, S. V.; Fratzl, P. A Customizable Software for Fast Reduction and Analysis of
29 847 Large X-Ray Scattering Data Sets: Applications of the New DPDAK Package to Small-Angle
30 848 X-Ray Scattering and Grazing-Incidence Small-Angle X-Ray Scattering. *J Appl Cryst* **2014**,
31 849 *47* (5), 1797–1803. <https://doi.org/10.1107/S1600576714019773>.
32 850 (63) Shannon, R. D.; Prewitt, C. T. Effective Ionic Radii in Oxides and Fluorides. *Acta*
33 851 *Crystallographica Section B* **1969**, *25* (5), 925–946.
34 852 <https://doi.org/10.1107/S0567740869003220>.
35 853 (64) Fischer, A.; Schmitz, M.; Aichmayer, B.; Fratzl, P.; Faivre, D. Structural Purity of
36 854 Magnetite Nanoparticles in Magnetotactic Bacteria. *J. R. Soc. Interface* **2011**, *8* (60), 1011–
37 855 1018. <https://doi.org/10.1098/rsif.2010.0576>.
38
39
40
41
42
43
44 856
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

857 **Figures**

858
859 **Scheme 1.** Illustration of trace and minor elements analyzed in abiotic and biological magnetite.

860 $[X_{magnetite}]$ refers to element concentration in magnetite, and $[X_{solution}]$ indicates the element
861 concentration in the residual solution and residual growth medium in the case of abiotic and
862 biological magnetite formation, respectively.

863



864

865

866 **Figure 1.** Partition coefficients (D^X) of (A) monovalent, (B) divalent, (C) trivalent and (D)

867 tetravalent cations in the case of abiotic (black and grey circles) and biological (AMB-1, open

868 diamonds) magnetite. Dashed line indicate the predicted values of D^X based on a lattice strain

869 model (Eq. 2). Grey symbols point to 3d metals [Co(II), Cr(II), Cr(III), Cu(II), Mn(II), Ni(II),

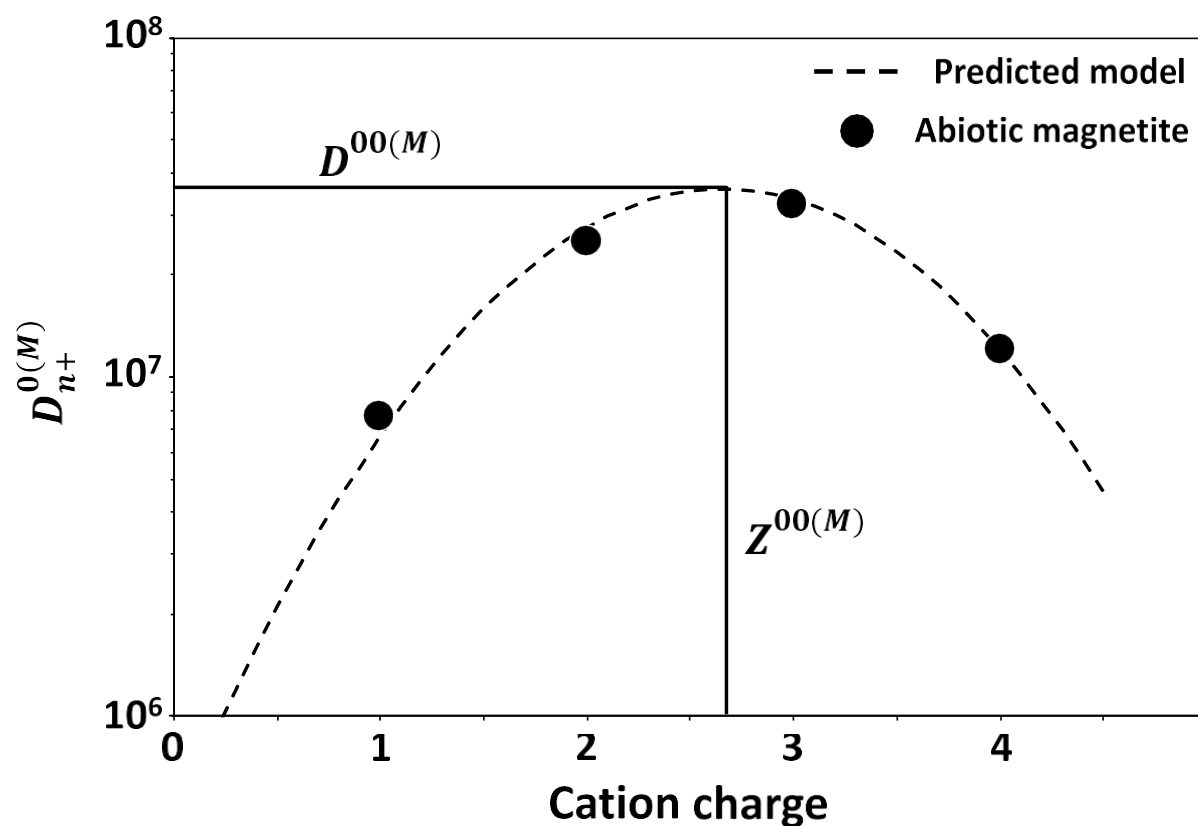
870 Zn(II)] showing variations from the predicted values in the abiotic precipitation of magnetite.

871 Cation radius taken from Shannon and Prewitt and summarized in Table S10⁶³. Black lines in

872 (D) indicate the position of ideal cation radius ($r_{n+}^{0(M)}$) and strain-compensated partition

873 coefficient ($D_{n+}^{0(M)}$).

874

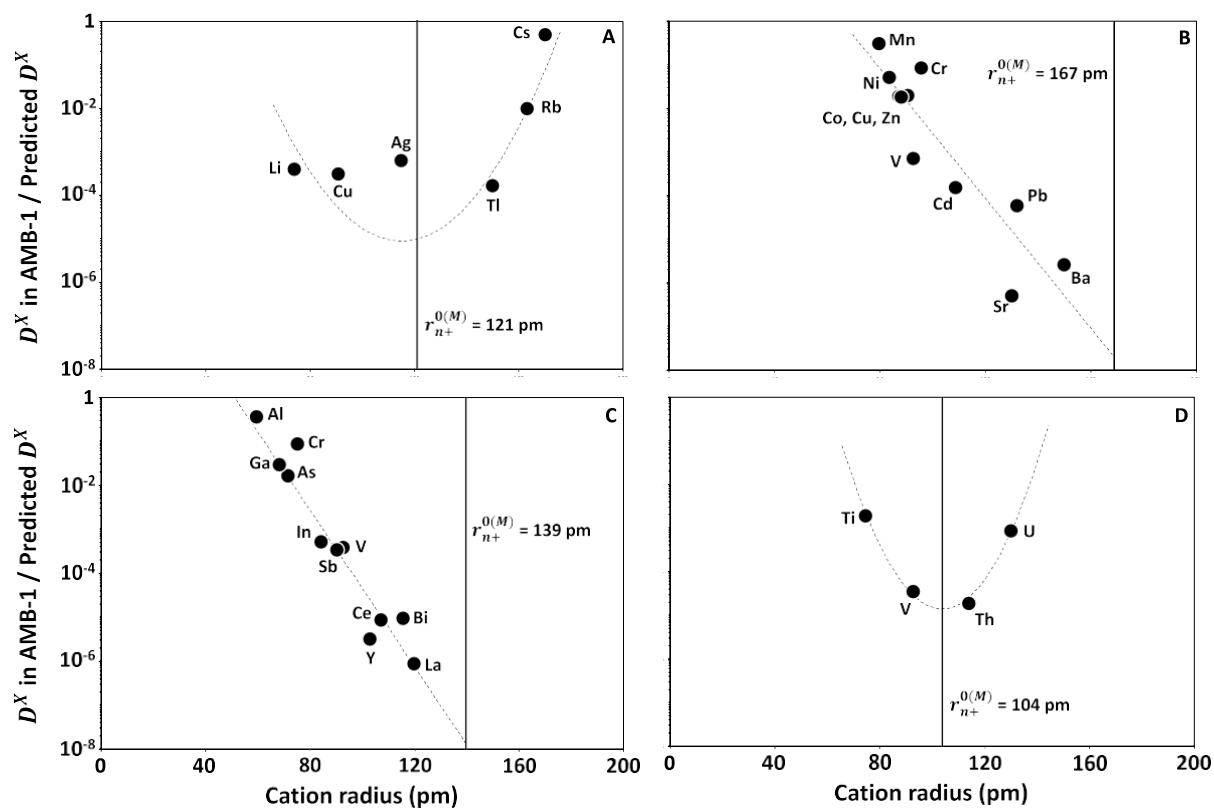


875

876

877 **Figure 2.** Strain-compensated partition coefficients ($D_{n+}^{0(M)}$) for each element valence extracted
 878 from Figs. 3A to 3D. The predicted model was calculated using Eq. 3 and considering published
 879 values of magnetite's dielectric constant of 55 and a lattice region with a radius of 9 nm (see
 880 Materials and Methods). Black lines indicate the position of ideal charge ($Z^{00(M)}$) and strain-
 881 compensated partition coefficient causing no electrostatic charging ($D^{00(M)}$).

882



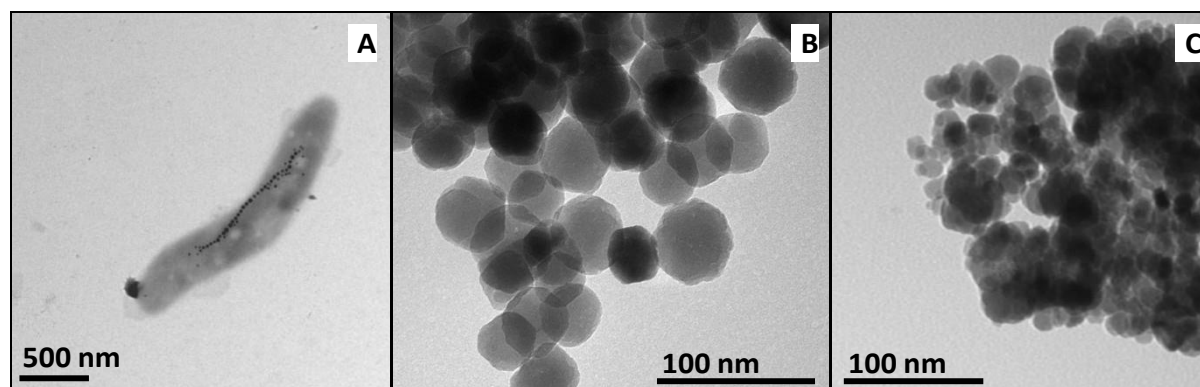
883

884

885 **Figure 3.** Biological D^X obtained from AMB-1 cultures normalized to the D^X predicted from
 886 lattice strain theory (Eq. 2) in the case of (A) monovalent, (B) divalent, (C) trivalent and (D)
 887 tetravalent elements. $r_{n+}^{0(M)}$ values reported here are extracted from Fig. 3 and Table S5.

888

889



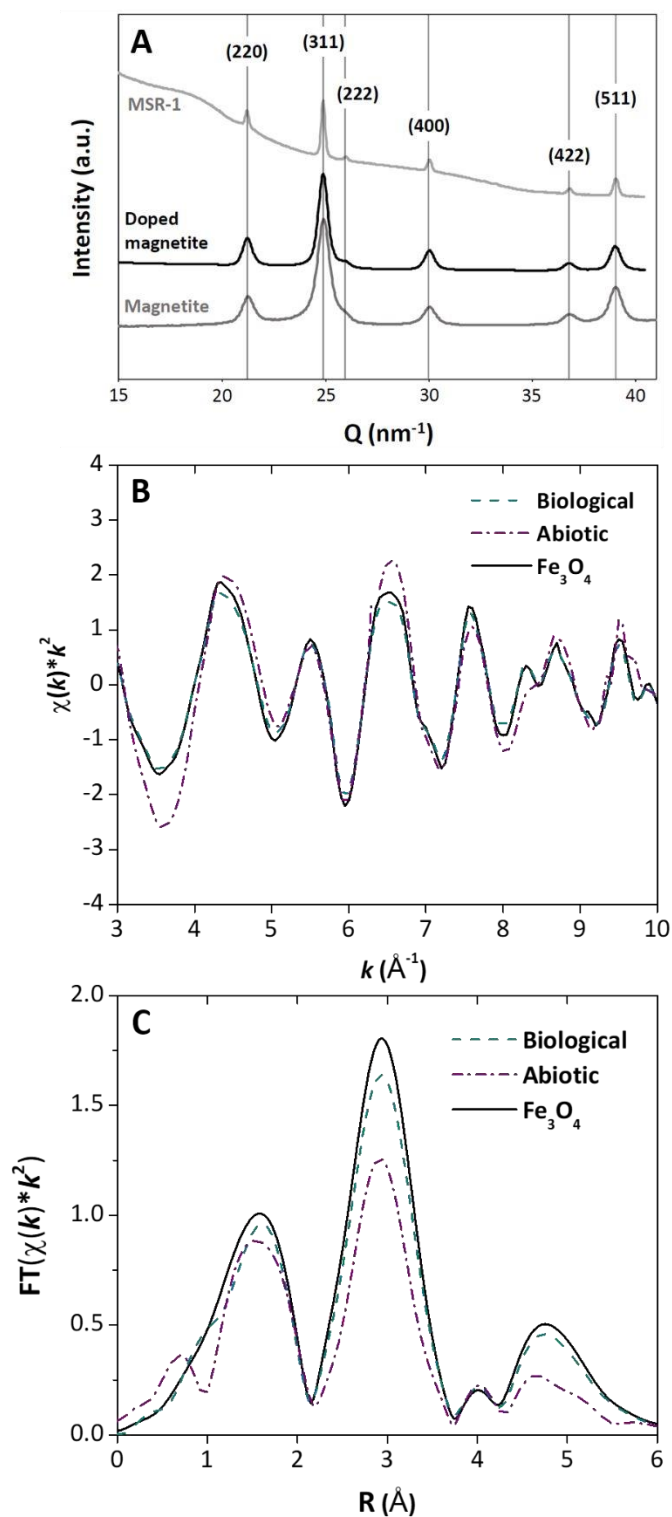
890

891

892 **Figure 4.** Transmission electron microscopy images of (A) MSR-1 bacteria containing
893 magnetite nanoparticles, (B) biological magnetite nanoparticles extracted from MSR-1 and
894 purified (see Materials and Methods), and (C) abiotic magnetite nanoparticles.

895

896



897

898 **Figure 5.** (A) X-ray diffractograms of doped abiotic and biological magnetite. An additional

899 undoped abiotic magnetite reference is given for comparison. Abiotic magnetite shows all peaks

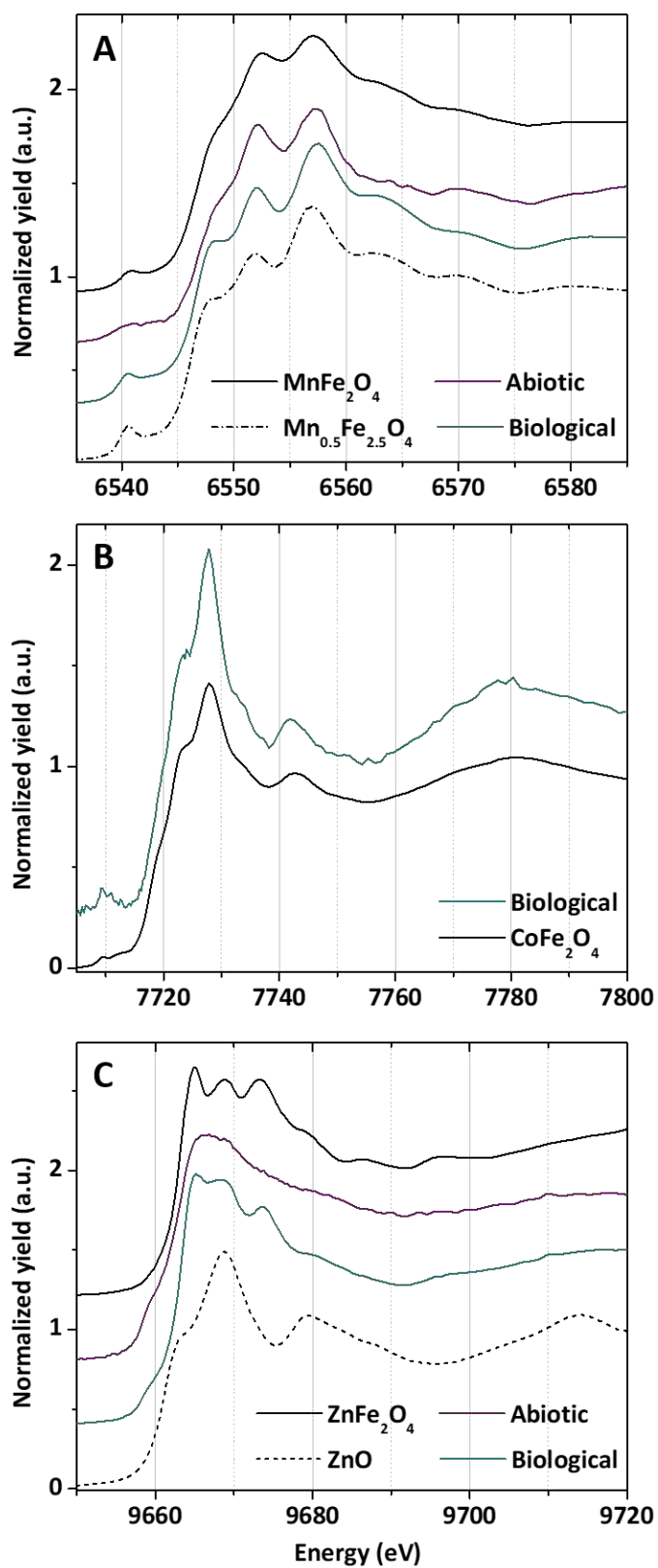
900 typical of magnetite⁶⁴. The broader peaks for abiotic magnetite can be explained by smaller

58

59

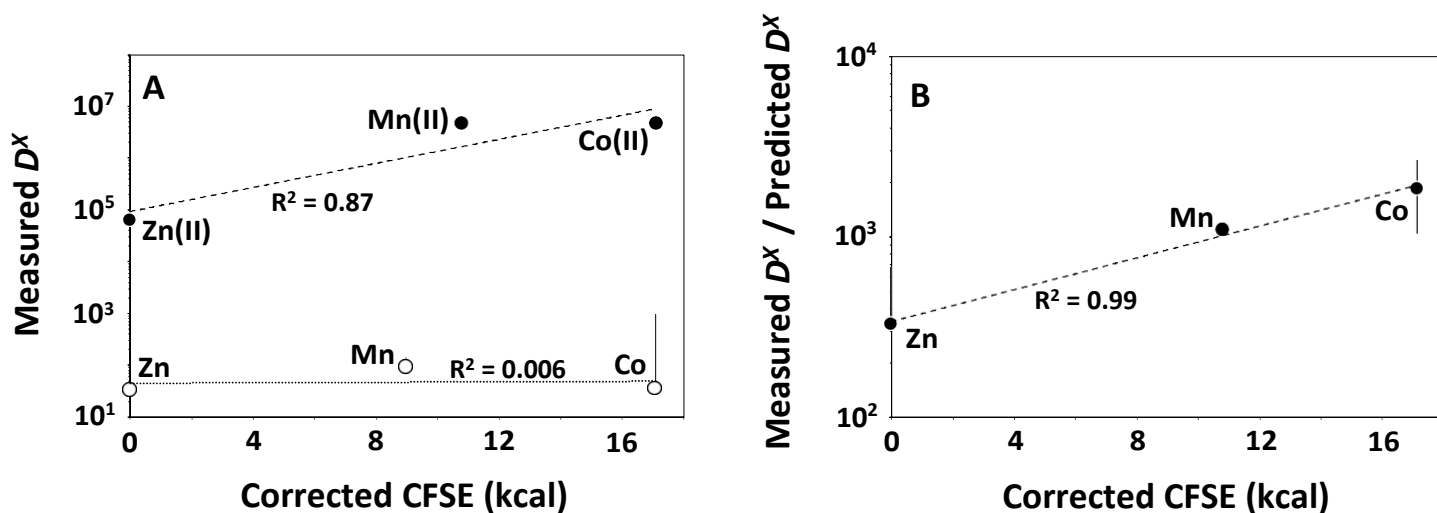
60

1
2
3
4 901 particles (see supplementary text). Fe K-edge XAS presented in the form of (B) k -space and
5 902 (C) R-space spectra for magnetite reference, biological magnetite and abiotic magnetite.
6
7 903
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



904

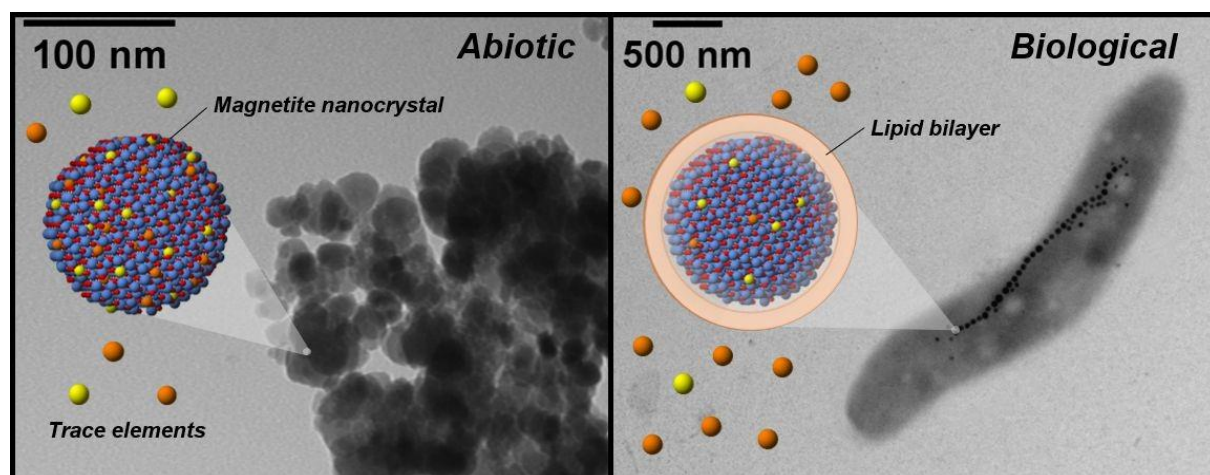
905



906 **Figure 6.** X-ray absorption near edge structure (XANES) of doped abiotic and biological
 907 magnetite nanoparticles with reference materials at (A) Mn K-edge (inset, pre-edge region), (B)
 908 Co K-edge and (C) Zn K-edge.

909
 910 **Figure 7.** (A) Partition coefficients (D^x) and (B) ratio of measured partition coefficients and
 911 partition coefficients predicted from a lattice strain theory (Eq. 2) of Mn, Co and Zn represented
 912 against their XAS-corrected Crystal Field Stabilization Energy (CFSE). Black and open
 913 symbols represent abiotic and biological conditions, respectively.

914
 915



916

917 **ToC Image.**

918

919