Supporting Information for

2	Direct and Indirect Nucleation of Magnetite Nanoparticles from
3	Solution Revealed by Time-Resolved Raman Spectroscopy
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17 Table S1. Summary of identified iron phases (solids and ions) peaks in time-resolved Raman spectroscopy

18 measurements. These identifications are supported by studies that used ex-situ or in-situ Raman

19 spectroscopy.

Solid phase/ aqueous	Formula	The strongest band in	Ref.
specie		Raman (cm ⁻¹)	
Ferric chloride ion A	trans- $[FeCl_2(H_2O)_4]^+$	315	This study
		315-316	Murata et al., 1988
		314-315	Kanno and Hiraishi,
			1982
		315	
			Scholten et al., 2019
Ferric chloride ion B	$[FeCl(H_2O)_5]^{2+}$	485 (broad medium band)	This study
		485 (solutions in glassy	Kanno and Hiraishi,
		state)	1982
Green rust		500-503	This study
	Fe ^{II} Fe ^{III} (OH) ₅	518	Trolard et al., 1996
	Not reported	528	Watanabe et al.,
			2008
	$[Fe(II)_4Fe(III)_2(OH)_{12}][CO_3.2H_2O]$	509, 511	Legrand et al., 2001
	Or FeII/FeIII =1 (more stable)		
	Not reported	506	Li and Hihara, 2012
	$[Fe(II)_4Fe(III)_2(OH)_{12}][SO_4.8H_2O]$	505-507	Langumier et al.,
			2009
	$[Fe(II)_3Fe(III)(OH)_8][Cl.nH_2O]$	505	Cambier et al., 2014
Magnetite	Fe_3O_4 or $FeO.Fe_2O_3$	670-673	This study
		670	Hanesch, 2008
		660 or 676	Watanabe et al.,
			2008
Molecular water	Bending O-H mode in aqueous	1645-1650	This study
	systems		
	In liquid phase	1650	Seki et al., 2020
	In gas phase	1590	Seki et al., 2020

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Figure S1: Time-lapse spectra for iron solution addition into NaOH solution at two different addition rates; 2.3 ml/minute (experiment 1) on the left and 12 ml/minute (experiment 2) on the right. Direct nucleation of magnetite peaking at 673 cm⁻¹ is detected in the Raman spectra. Temporal decrease of the bending of molecular water peaking at 1645 cm⁻¹ in the dispersed suspensions reveals a change from hydrophilic to hydrophobic in the system.

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Figure S2: (Left) Time-lapse spectra for iron solution addition into NaOH solution. Alkaline solution heated at 90°C and addition rate of iron solution of 2.3 ml/minute (experiment 3). Here, the addition of iron solution produces a small temperature variation (< 2°C). A temporal decrease of the bending of molecular water peaking at 1645 cm⁻¹ in the dispersed suspensions reveals a change from hydrophilic to hydrophobic in the system. (Right) Zoom on the magnetite temporal behavior monitored by the intensity of the strongest Raman signature peaking at 670 cm⁻¹. Similar to experiments 1 and 2, direct nucleation of magnetite is only detected in the Raman spectra.

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Figure S3: (Left) Time-lapse spectra for iron solution addition into NaOH solution. Here, the effect of citric acid is assessed and this compound was initially added into alkaline solution. The iron solution is here added at 12 ml/minute (experiment 4). The temporal decrease of bending of molecular water peaking at 1645 cm⁻¹ in the dispersed suspensions reveals a change from hydrophilic to hydrophobic in the system. (Right) Zoom on the magnetite temporal behavior measured by the intensity for the strongest Raman signature peaking at 671 cm⁻¹. Similar to experiments 1, 2 and 3, direct nucleation of magnetite is only detected in the Raman spectra.



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Figure S4: Time-lapse spectra for NaOH solution addition into mixed-valent iron solution (addition 55 rate = 12 ml/minute, room T~26°C and initial pH~1) (experiment 8). Indirect nucleation of 56 magnetite peaking at 671 cm⁻¹ is detected in the Raman spectra. Here, green rust peaking at 500 57 cm⁻¹ is mainly a transient phase. The initial hydration state of mixed-valent iron solution is 58 characterized by a Raman signature peaking at 315 cm⁻¹ and a broad band peaking at 485cm¹, both 59 assigned to ferric species (see Table S1 and Figure S5). The temporal decrease of bending of 60 molecular water peaking at 1645 cm⁻¹ in the dispersed suspensions reveals a change from 61 62 hydrophilic to hydrophobic in the system.



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Figure S5: Raman spectra of the initial iron solutions show the speciation chemistry of single
ferrous iron solution (blue spectrum), single ferric solution (red spectrum) and mixed-valent iron
solution (black spectrum).



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Figure S6: Kinetics behavior during the direct formation of magnetite at 90°C from the integrated peak surfaces versus time (experiment 3). Inset graph shows the nucleation time and the fast hyperbolic kinetic step; this latter is directly correlated with a change from hydrophilic to hydrophobic in the suspension. For longer reaction times, a slow kinetics step is measured and, after 24h of reaction, a decrease of the Raman signal is detected, probably related to a dissolution processes (see also Figure 4 in the main text).



Figure S7: Kinetics behavior of direct magnetite formation at room temperature in the presence of citric acid from integrated peak surface areas versus time (experiment 4). Inset graph shows the nucleation time and the fast hyperbolic kinetics step; this latter is directly correlated to a change from hydrophilic to hydrophobic in the suspension. For longer reaction times, a slow kinetics step is measured until the end of experiment, the slow progressive increase of Raman intensity is related to the formation of magnetite residual colloidal particles (see also Figure 5 in the main text).



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Figure S8: Formation of ferric hydroxide gel showing two weak broad-bands from our Raman measurements in reference-experiment 9 (Table 1). Based on these results, the reaction 3 is also proposed during the olation process for indirect nucleation of magnetite (reactions 2 to 4 in the main text).



Figure S9: FESEM image at high magnification without metallic coating of the magnetite
recovered at the end of experiment 1. Magnetite nanoparticles with crystal size, 5<z<16nm and
low agglomeration state.



Figure S10: FESEM image at high magnification without metallic coating of magnetite recovered
at the end of experiment 2. Magnetite nanoparticles have crystal size, 5<z<20nm and low
agglomeration state.

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Figure S11: FESEM image at high magnification without metallic coating of magnetite recovered at the end of experiment 8. Magnetite nanoparticles have crystal size, 10<z<25nm and high agglomeration state.



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Figure S12: X-ray diffraction (XRD) patterns for four selected powdered magnetite samples; recovered from experiments 1, 2, 7 and 8 (Table 1). Coherent domain average size of magnetite crystals for selected samples are determined from Rietveld refinement of XRD patterns and the obtained values are displayed in Table 1.

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Figure S13. Temporal behavior of FWHM parameter for direct and indirect nucleation of magnetite including six selected experiments (Table 1). Assuming that the crystal size is proportional to 1/FWHM, smaller particles of magnetite are obtained from a direct nucleation process (see also FESEM images in Figures S9 and S11 and Rietveld results summarized in Table 1).



