A Combined Experimental and Theoretical Approach to the Kinetics of Magnetite Crystal Growth from Primary Particles

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Supplementary Information

Materials and Methods

Magnetite synthesis

Magnetite was synthesized with the modified co-precipitation method controlled by a titration system (Metrohm, 776 Dosimat and 719 S Titrino). Fe^{II}/Fe^{III}-chloride solution (1 M, $Fe^{II}:Fe^{III}$ = 1:2) was added with 1 µl/min to a total volume of 10 ml. The pH and the temperature were kept constant during the process (pH = 9 ± 0.4 with 1 M NaOH; Temperature = 5, 10, 15, 20, 25 ± 0.1 °C) and the solution was constantly stirred. All solutions were degased before using and the system was kept under nitrogen atmosphere during the synthesis. For sampling after every 60 minutes 60 µl were taken from the reactor and stored in the freezer until XRD analysis.

X-ray diffraction

The Material was dried on a Kapton thin film and measured in transmission with a 100 µm beam of the wavelength $\lambda \approx 0.82656$ Å at the µ-Spot beam line, BESSY II, Berlin. Fit2D and AutoFit were used for calculations. The size was determined with Scherrer analysis[1] by fitting the (311) peak with a pseudo-Voigt function. The peak width was corrected from instrumental peak broadening[2]:

$fwhm_{size} = \sqrt{fwhm_{exp}^2 - fwhm_{instr}^2}$	(Equation S1)

where $fwhm_{size}$ is the peak width caused by limited particle size, $fwhm_{exp}$ is the experimentally measured peak width and $fwhm_{instr}$ is the peak width caused by instrumental setup due to detector point spread and beam divergence. The mean particle diameter was calculated with:

$MD\ (nm) = \dfrac{2\pi}{fwhm_{size}\ (nm^{-1})}$	(Equation S2)

Transmission Electron Microscopy

Suspensions were measured with original concentration and without washing. The Transmission electron images were obtained with a Zeiss 912 Omega (MPIKG, Germany) to characterize the morphologies, structures and compositions of the nanoparticles.

Iron determination

The particulate iron was magnetically separated from the rest of the solution. The supernatant was measured by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) with an Optima 8000 DV.

Full Dataset

Table S1: Qadruplicated measurements at 5 °C plus averaged size development and standard deviation.

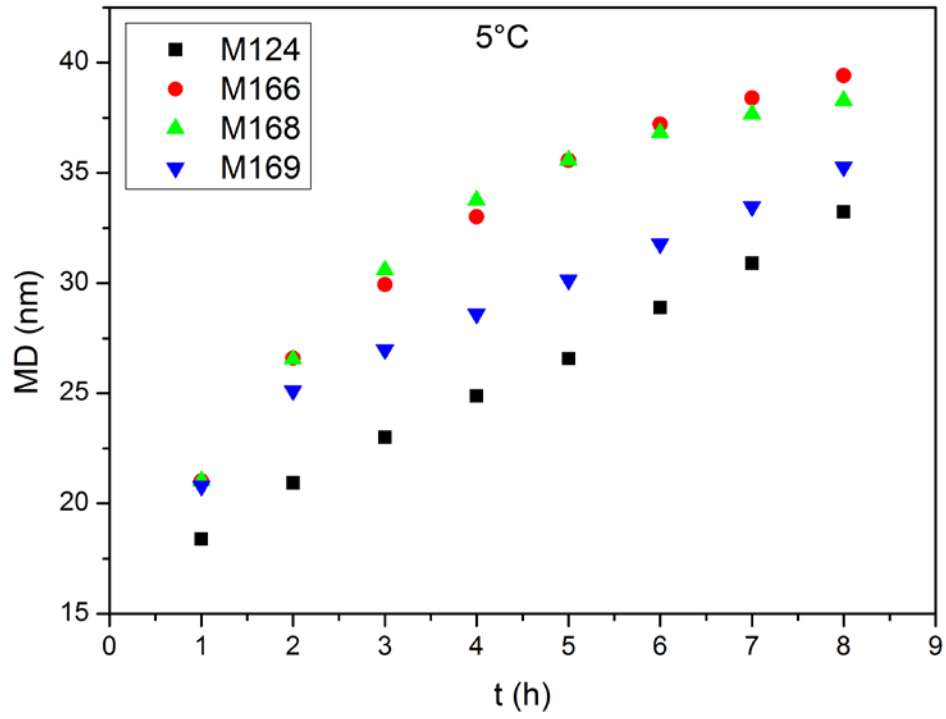| 5°C	M124	M166	M168	M169	Average		Standard deviation
Time (h)	**Mean particle diameter (nm)**						**(nm)**
1	18.4	21.0	21.0	20.8	20.3	±	1.3
2	20.9	26.6	26.5	25.1	24.8	±	2.7
3	23.0	29.9	30.6	27.0	27.6	±	3.5
4	24.9	33.0	33.8	28.6	30.1	±	4.1
5	26.6	35.6	35.6	30.2	32.0	±	4.4
6	28.9	37.2	36.8	31.8	33.7	±	4.0
7	30.9	38.4	37.7	33.5	35.1	±	3.6
8	33.2	39.4	38.3	35.3	36.6	±	2.8

Figure S1: The evolution of mean particle dimension as a function of time at 5 °C.

Table S2: Qadruplicated measurements at 10 °C plus averaged size development and standard deviation.

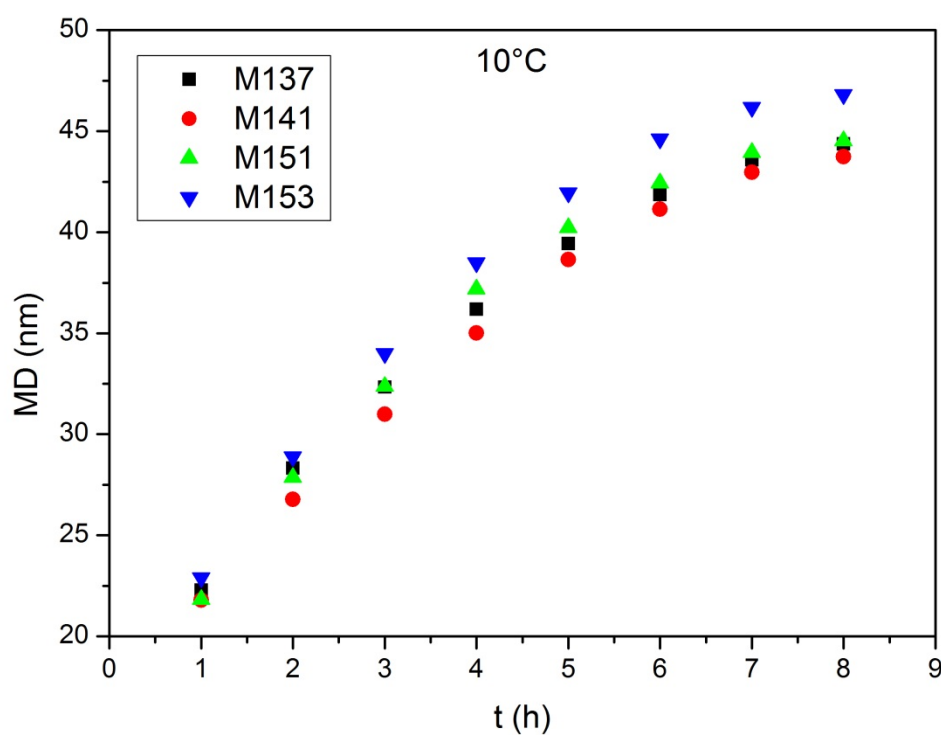| 10°C	M137	M141	M151	M153	Average		Standard deviation
Time (h)	**Mean particle diameter (nm)**						**(nm)**
1	22.3	21.8	21.8	22.9	22.2	±	0.5
2	28.3	26.8	27.9	28.9	28.0	±	0.9
3	32.3	31.0	32.4	34.0	32.4	±	1.2
4	36.2	35.0	37.2	38.5	36.7	±	1.5
5	39.4	38.7	40.2	41.9	40.1	±	1.4
6	41.9	41.2	42.4	44.6	42.5	±	1.5
7	43.6	43.0	43.9	46.2	44.2	±	1.4
8	44.4	43.7	44.5	46.8	44.9	±	1.3

Figure S2: The evolution of mean particle dimension as a function of time at 10 °C.

Table S3: Qadruplicated measurements at 15 °C plus averaged size development and standard deviation.

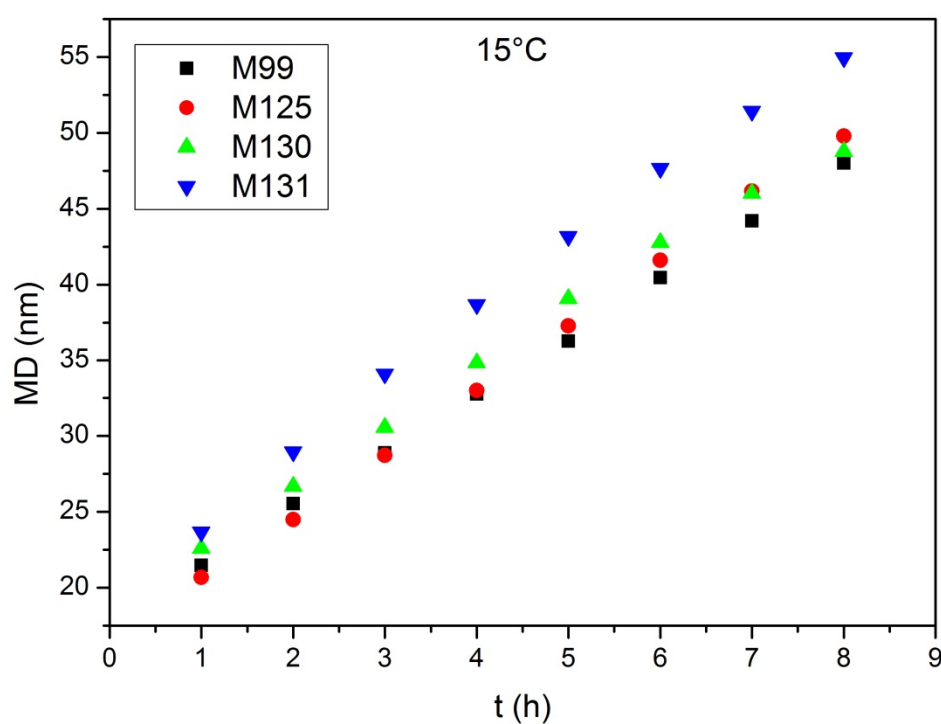| 15°C	M99	M125	M130	M131	Average		Standard deviation
Time (h)	Mean particle diameter (nm)						(nm)
1	21.5	20.7	22.6	23.7	22.1	±	1.3
2	25.6	24.5	26.7	29.0	26.4	±	1.9
3	28.9	28.7	30.6	34.1	30.6	±	2.5
4	32.8	33.0	34.9	38.7	34.8	±	2.7
5	36.3	37.3	39.1	43.2	39.0	±	3.0
6	40.5	41.6	42.8	47.7	43.1	±	3.2
7	44.2	46.2	46.0	51.4	47.0	±	3.1
8	48.0	49.8	48.8	55.0	50.4	±	3.1

Figure S3: The evolution of mean particle dimension as a function of time at 15 °C.

Table S4: Qadruplicated measurements at 20 °C plus averaged size development and standard deviation.

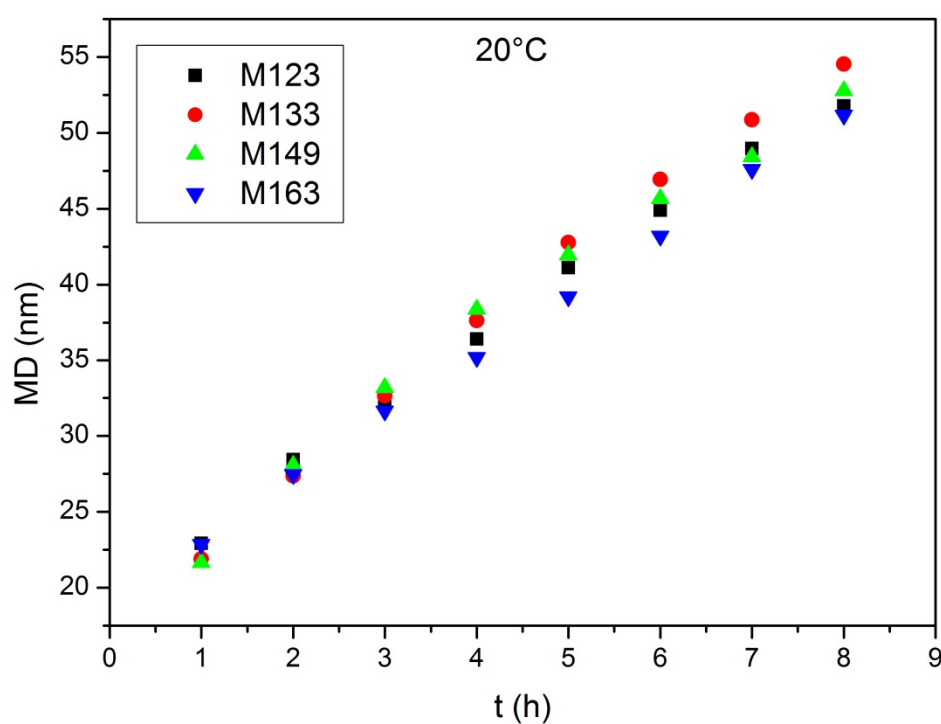| 20°C	M123	M133	M149	M163	Average		Standard deviation
Time (h)	**Mean particle diameter (nm)**						**(nm)**
1	22.9	21.9	21.7	22.8	23.1	±	2.2
2	28.5	27.4	28.1	27.5	28.6	±	2.2
3	32.3	32.7	33.2	31.6	33.2	±	2.4
4	36.4	37.6	38.4	35.2	37.6	±	2.8
5	41.1	42.8	42.0	39.2	41.8	±	3.1
6	44.9	46.9	45.7	43.2	45.8	±	3.5
7	49.0	50.9	48.4	47.6	49.4	±	3.5
8	51.8	54.5	52.8	51.2	52.9	±	3.7

Figure S4: The evolution of mean particle dimension as a function of time at 20 °C.

Table S5: Qadruplicated measurements at 25 °C plus averaged size development and standard deviation.

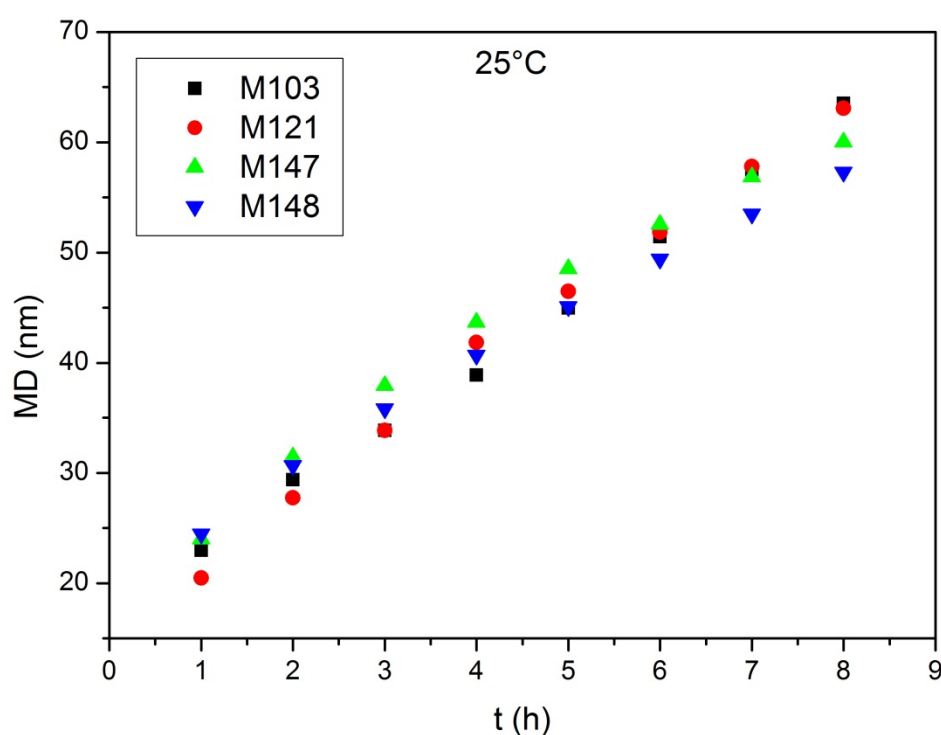| 25°C	M103	M121	M147	M148	Average		Standard deviation
Time (h)	**Mean particle diameter (nm)**						**(nm)**
1	23.0	20.5	24.0	24.5	23.0	±	1.8
2	29.4	27.7	31.4	30.7	29.8	±	1.6
3	33.9	33.9	38.0	35.8	35.4	±	2.0
4	38.9	41.9	43.7	40.7	41.3	±	2.0
5	45.0	46.5	48.5	45.1	46.3	±	1.7
6	51.4	51.9	52.6	49.4	51.3	±	1.4
7	57.5	57.8	56.9	53.5	56.4	±	2.0
8	63.5	63.1	60.0	57.3	61.0	±	2.9

Figure S5: The evolution of mean particle dimension as a function of time at 25 °C.

Supplementary Discussion

Particle size measurement

As explained above, the particle size is determined by the Scherrer equation using the peak

broadening of the X-ray data. However, the measured peak broadening is due to limited size but

potentially also to crystal perfection. Since we could not find any obvious mineral change, we assumed the measured peak broadening is mainly determined by the particle size.
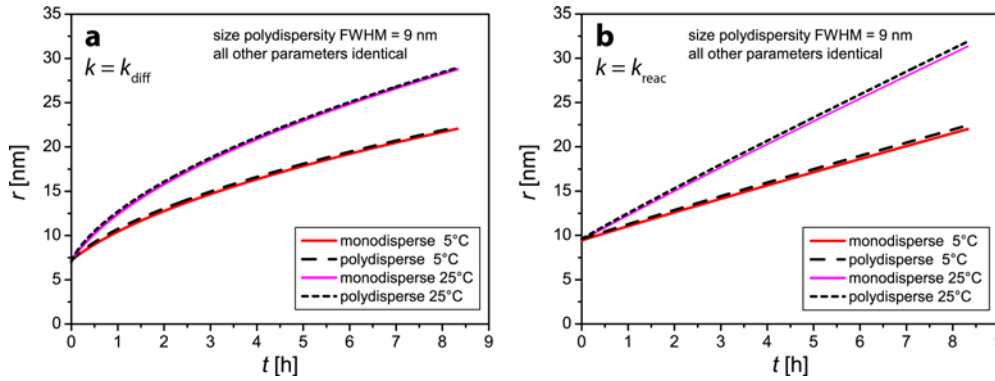
Effect of polydispersity

Figure S6: Influence of polydispersity in the magnetite particle initial radius on the modeled particle growth for diffusion limited (a) and reaction limited scenarios. It is seen that accounting for even pronounced polydispersity (FWHM = 9 nm) does not significantly affect the curves. As a consequence, the experimental data are reproduced for the virtually same model parameters irrespective of the polydispersity.

Calculation for magnetic separation

A permanent magnet is placed directly next to the approximately cylindrical particle container with radius a. The particle speed resulting from the gradient of the magnetic field strength in the container can be determined by linking the translational magnetic force with Stokes' friction force. It results a pellet formation time

$$t_0 = \frac{9\,\eta\,a}{2\,R^2\,M_S\,\mu_0\,\frac{\partial H}{\partial x}} \text{ (Equation S3)}$$

Thereby, M_S is the saturation magnetization of magnetite, μ_0 is the permeability of free space and $\frac{\partial H}{\partial x}$ is the gradient of the field strength along the axis of interest x. The gradient of the utilized cylindrical permanent magnet with a diameter of 10 mm, a length of 5 mm, a diametrical magnetization direction and a surface magnetic field strength of $1\ \text{T}\mu_0^{-1}$ is 35 MA m^{-2} and was

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determined numerically at a distance of 1.5 mm to the magnet. This value changes in space but can serve as an estimate for the gradient everywhere in the sample. With $a = 6$ mm and $R = 20$ nm for the particles of interest (40 nm), a pellet formation time of 6 minutes is found. For PPs, the time is about 1.5 days. Hence, after 10 minutes the pellet was extracted with a pipette in the experiment.

Full concentration calculations

Volume (in nm³) of one *PP* of radius R = 1 nm diameter:

$$V_{PP} = \frac{4}{3}\pi R^3 \approx 4$$

Assuming the *PP* is made of magnetite, we can calculate the amount of unit cells in such volume:

unit cells = V_{PP} / V$_{\text{unit cell}}$ ≈ 4 / 0.8397³ ≈ 7

There are 24 iron atoms per unit cells, thus we can calculate the number of iron atoms in a *PP*:

iron atoms in a *PP* ≈ 24 × 7 = 168

We exemplarily measured 3.6 mg Fe / L and can from this measure the molar concentration (in mol × L^{-1}), which is the mg/L concentration divided by the molecular mass of iron (55.85 g × mol^{-1}), we have:

[Fe] = 0.0036/55.85 ≈ 6,4 × 10^{-5} (in mol × L^{-1})

From this can we calculate [PP] (in number of particles per liter) assuming all the measured iron is obtained from the *PP* (N$_A$ is the Avogadro number):

[PP] = ([Fe] × N$_A$) / #iron atoms in a *PP* ≈ 2 × 10^{17} (in number of particles per liter)

SI References

(1) Patterson, A. L., The scherrer formula for x-ray particle size determination. *Physic. Rev.* **1939,** *56*, 978-982.

(2) Fischer, A.; Schmitz, M.; Aichmayer, B.; Fratzl, P.; Faivre, D., Structural purity of magnetite nanoparticles in magnetotactic bacteria. *J. R. Soc. Interface* **2011,** *8*, 1011-1018.