

Crystal growth and aggregation in suspensions of δ -MnO₂ nanoparticles:

Implications for surface reactivity

Electronic Supplementary Information

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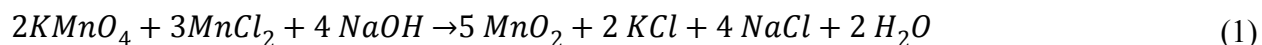
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Keywords

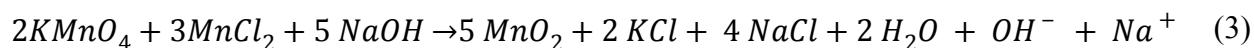
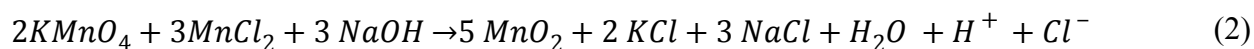
Surface reactivity, birnessite, δ -MnO₂ nanoparticles, specific surface area, aggregation

Mineral synthesis protocol

The synthesis of δ -MnO₂ occurs by mixing potassium permanganate and manganese chloride in the presence of sodium hydroxide according to the following reaction:



where NaOH is used to neutralize the acid formed during the reaction and to enhance the kinetics of Mn(II) oxidation. Equation 1 describes the stoichiometry for the reaction when a 0.5 M NaOH solution is used. However, in this study we used varying stoichiometries for NaOH, which would make the reactions the following whether 0.4 M or 0.6 M of NaOH were used, respectively:



The two most cited protocols Murray and coauthors¹ and Villalobos and coauthors² use either 4 or 5 moles of NaOH. The synthesis protocol used in this study follows closely that described by Villalobos and coauthors,² except where noted in italics:

1. Solutions of *300 ml* of 0.2 M KMnO₄, *300 ml of* 0.3 M MnCl₂ and *340 ml of 0.3, 0.4 and 0.5 M* NaOH were prepared separately in volumetric flasks to yield a 2:3:4, 2:3:5, 2:3:6 mole ratio of Mn(VII):Mn(II):NaOH, respectively (leading to the A, B and C sample series, respectively).
2. The KMnO₄ solution was added to the NaOH solution *in a wide neck 1 L Erlenmeyer flask* at a rate of 256 ml/min (5 min total time) *using a Cole-parmer Masterflex peristaltic pump and Tygon[®] tubing (Figure S1)* under vigorous stirring *with an overhead paddle stirrer set at 500 rpm and equipped with a BOLA PTFE-coated 4-blade stirrer shaft.*

3. The MnCl_2 solution was added to the $\text{KMnO}_4 + \text{NaOH}$ mixture at rates of 16, 36, and 72 ml/min (leading to the 1, 2, and 3 sample subseries, respectively) under vigorous stirring as described in step 2.
4. The suspension was allowed to settle for 30 minutes. The supernatant (100-200 ml) was syphoned to reduce the washing volume.
5. The suspension obtained in Step 4 was centrifuged at 27500 relative centrifugal force (RCF) for 20 minutes at 25° C in 250 ml polypropylene co-polymer (PPCO) bottles. The supernatant was discarded after centrifugation.
6. The mineral paste was resuspended in 1 M NaCl, washed by shaking for 1 hour and centrifuged (27500 RCF, 20 min, 25°C). The supernatant was discarded *after measuring its pH and electrical conductivity with Merck Millipore pH paper (1 pH unit precision) and a Mettler EL30 conductivity meter, respectively*. This washing procedure was repeated four more times, with washing times that ranged from 1 hour to overnight. This step exchanges K^+ for Na^+ as the interlayer counter ion.
7. The mineral paste was washed as described in Step 5, but using MQ water instead of NaCl *until the electrical conductivity of the supernatant was below 10 $\mu\text{S cm}^{-1}$* . The washing times ranged from 1 hour to overnight. This step removes all Na from the supernatant.
8. The final product was divided into 2 aliquots: one was kept in suspension *at the final washing pH value* and the other was freeze-dried.

Average Mn oxidation number potentiometric titration

The average Mn oxidation number of the samples was obtained through potentiometric titration, as described in Gaillot and coauthors, ³, Grangeon and coauthors, ⁴, Gaillot and

coauthors.⁵ Briefly, 15 mg of δ -MnO₂ were dissolved in a 0.01 M Mohr's salt [(NH₄)₂Fe(SO₄)₂•6H₂O] solution and residual Fe(II) was titrated with 0.01 M KMnO₄. A parallel Mohr's salt solution, to which no mineral was added but whose mass was matched gravimetrically on an analytical balance (\pm 0.001 g precision), was also titrated with 0.01 M KMnO₄. The difference in the volume of KMnO₄ used in these two titrations thus provided the amount of Fe(II) required to reductively dissolve the mineral. The amount of Mn(II) generated by reductive dissolution of the mineral was back titrated with 0.02 M KMnO₄ to Mn(III), which was trapped by complexation with excess sodium pyrophosphate (Na₄P₂O₇, abbreviated hereafter as PP).⁶⁻⁸ The accuracy of this method was assessed by AMON determinations of MnCl₂, Mn(III)-acetate powder and pyrolusite (β -MnO₂, 99.99 % trace metals basis).

Extraction of Mn(III) by sodium pyrophosphate and method validation.

The amount of Mn(III) present in the mineral was determined by complexation with sodium pyrophosphate, as described in Kostka and coauthors⁷, Klewicki and coauthors,⁹ Wang and coauthors¹⁰. Briefly, 5 mg of dry sample were equilibrated in excess PP with a 20:1 PP:Mn ratio (50 ml of 20 mM PP at pH 6.5) for 48 hours in polypropylene centrifuge tubes in the dark. Pyrophosphate is a redox-inert chelator,¹¹ thus no Mn(III) should be generated by reduction of Mn(IV) during the extraction. The absorbance of a filtered aliquot was measured at 254 nm ($\epsilon = 6562 \text{ M cm}^{-1} \text{ L}^{-1}$) in a 1 cm path length quartz cuvette using a 20 mM PP solution as a blank. To obtain the mole fraction of Mn(III), the Mn(III) concentration measured spectrophotometrically was divided by the total Mn concentration in the suspension, as measured by ICP-OES analysis of an acid-digested suspension aliquot. All measurements were conducted in triplicate.

The PP extraction method was validated through AMON measurements of two well-defined Mn oxide phases under the assumption that each mineral consisted exclusively of Mn(III) and Mn(IV). For triclinic birnessite [$\text{Na}_{0.25}\text{Mn(III)}_{0.16}\text{Mn(IV)}_{0.84}\text{O}_2 \cdot 0.66 \text{H}_2\text{O}$], we found 15 ± 0.5 % PP-extractable Mn(III) and an AMON value of 3.84 ± 0.05 , which corresponds to 16 ± 5 % Mn(III). For K-birnessite [$\text{K}_{0.265}\text{Mn(III)}_{0.10}(\text{Mn(IV)})_{0.825}\text{Vac}_{0.175}\text{O}_2 \cdot 0.68 \text{H}_2\text{O}$], we found 10.3 ± 0.5 % extractable Mn(III) and an AMON value of 3.90 ± 0.01 , which corresponds to 10 ± 1 % Mn(III).¹² These independent measurements of Mn(III) are in excellent agreement, and demonstrate that PP is able to extract both surface-sorbed Mn(III) and “bulk” Mn(III). Furthermore, the uncertainty on Mn(III) content as extracted by PP is generally lower than that determined by the potentiometric titration method.

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ESI Figures

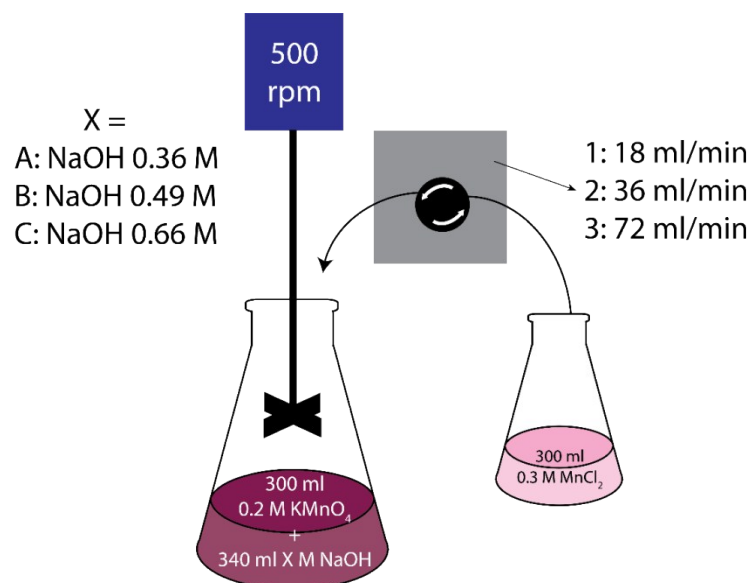


Figure S1: Schematic of the synthesis procedure and legend for sample names as a function of the parameters that were varied during the synthesis of the different samples.

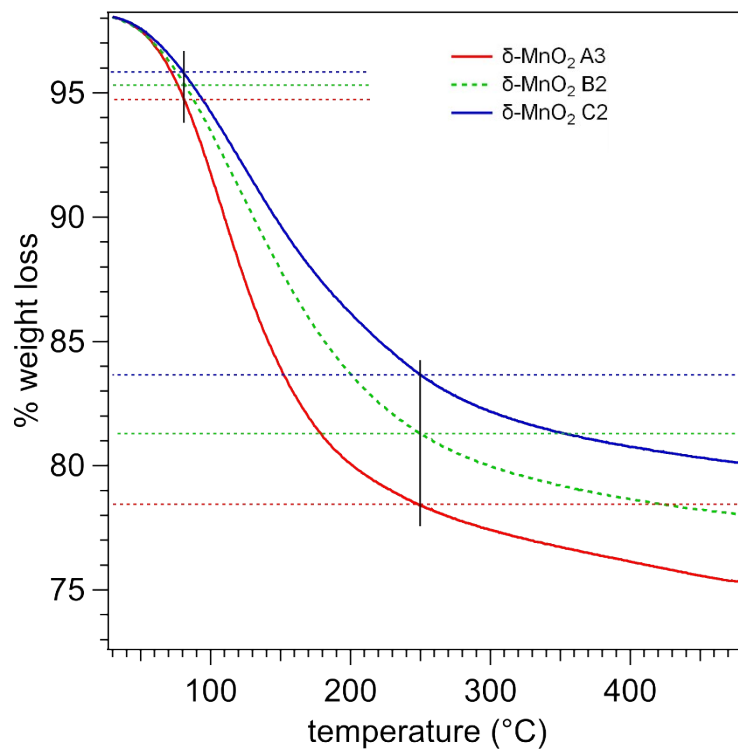


Figure S2: Thermogravimetric analysis weight loss curves normalized to sample weight at room temperature. The horizontal lines indicate the temperatures at which strongly bound water is lost.

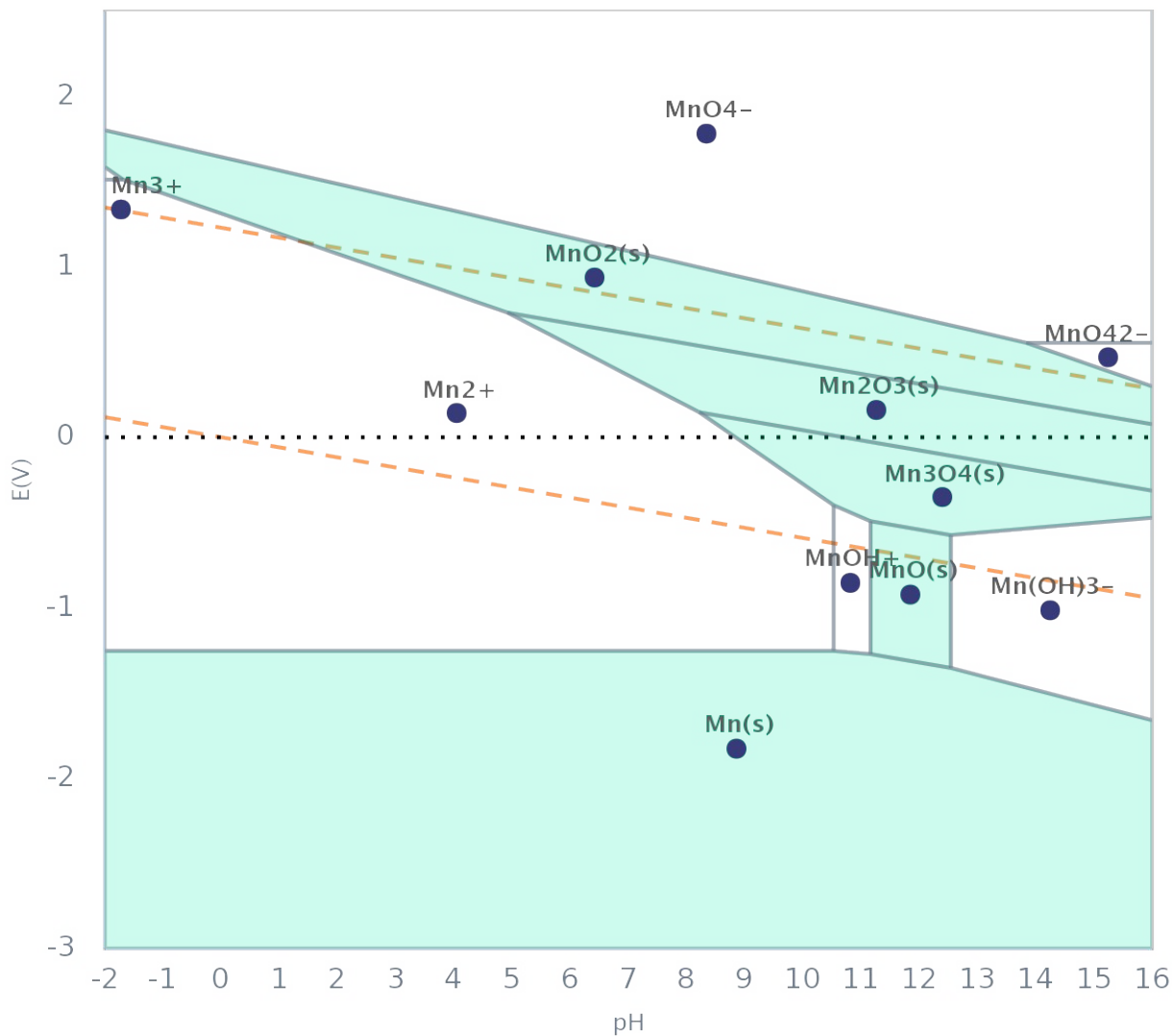


Figure S3: Eh-pH diagram showing the thermodynamic stability of MnO₂ and water as a function of pH calculated on the materials project website (www.materialsproject.org¹³) for a Mn concentration on the order of 100 millimoles per liter. The lower dashed line indicates the stability of water against reduction, the upper one its stability against oxidation.

ESI Tables

Table S1: Additional parameters obtained from refinement of powder XRD patterns.

Sample name	Na/Mn [%] from XRD	H₂O [wt %] from XRD
δ -MnO ₂ _A1		
δ -MnO ₂ _A2		
δ -MnO ₂ _A3	15.5	18.7
δ -MnO ₂ _A3b		
δ -MnO ₂ _B2	28.4	18.9
δ -MnO ₂ _B3		
δ -MnO ₂ _C2	32.8	18.3

Table S2: atomic coordinates and site occupancies of synthesized δ -MnO₂ samples.

Atom	δ -MnO ₂ _A3				δ -MnO ₂ _B2				δ -MnO ₂ _C2			
	Coordinates			Occ.	Coordinates			Occ.	Coordinates			Occ.
x	y	z	x		y	z	x		y	z		
^E Mn (Mn1)	0	0	0	0.92	0	0	0	0.90	0	0	0	0.89
O _{Mn1} (O1)	0.333	0	0.139	2.00	0.333	0	0.139	2.00	0.333	0	0.139	2.00
^{TC} Mn (Mn2)	0	0	0.292	0.05	0	0	0.292	0.05	0	0	0.292	0.06
O _{Mn2} (O2)	-0.333	0	0.451	0.15	-0.333	0	0.451	0.15	-0.333	0	0.451	0.18
Na ⁺	0.190	0	0.500	0.15	0.170	0	0.500	0.27	0.176	0	0.500	0.31
O _{Na+} (O3) ¹	0.190	0	0.500	0.45	0.170	0	0.500	0.81	0.176	0	0.500	0.94
H ₂ O (O4) ¹	-0.520	0	0.500	0.72	-0.400	0	0.500	0.39	-0.400	0	0.500	0.24

Notes: the C2/m space group (#12) may be used to represent the structure model. However, equivalent positions from adjacent layers must not be generated, as δ -MnO₂ only has 2D periodicity. Occupancies are given per octahedral layer site (i.e. per half unit cell) and as the sum of $(x, 0, z)$ and $(-x, 0, -z)$ sites. Debye–Waller factors were fixed to 0.5 Å² for Mn1, 1 Å² for O1 and Mn2, and 2 Å² for all other atoms.

¹Additional equivalent positions are generated at $(-x/2, 3x/2, z)$, $(-x/2, -3x/2, z)$, $(-x, 0, -z)$, $(x/2, -3x/2, -z)$, $(x/2, -3x/2, -z)$, site occupancy being given as the sum of all positions.