

Supplementary Files

Optimisation of the Flame Spheroidisation Process for the Rapid Manufacture of Fe₃O₄-Based Porous and Dense Microspheres

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Effect of Fe₃O₄:CaCO₃ mass ratio

Structural analysis

Table S1. Generalised summary of unsieved flame spheroidised product proportions, as a function of precursor to porogen mass ratio. FS: flame spheroidised

Mass ratio Fe ₃ O ₄ :CaCO ₃	FS products (strong / medium / weak)				
	Fe ₃ O ₄	Fe ₂ O ₃	Ca ₂ Fe ₂ O ₅	CaCO ₃	CaO
3:1	m	s	m	w	-
1:1	m	s	s	s	-
1:3	w	m	s	m	s

Mineral composition reference and colour code

Table S2. Molar constituents (weight percentage) and mineral composition reference.

Mineral	Molar constituents (wt%)		Mineral reference (%)			
	CaO	Fe ₂ O ₃	Ca	Fe	O	C
Fe ₃ O ₄	N/A	N/A	0	72.4	27.6	0
Fe ₃ O ₄ with Ca	12	88	3.6	73.8	22.6	0
CFO-1	28.5	71.5	9.6	67.3	23.1	0
CFO-2	40.7	59.3	15.1	61.3	23.6	0
CFO-3 – Ca ₂ Fe ₂ O ₅	48.3	51.7	19.1	57	23.9	0
CFO-4	82.4	17.6	48.4	28.9	22.6	0
CaCO ₃	N/A	N/A	40	0	48	12



Figure S1. MLA mineral colour code as a function of excess (or deficit) Fe or Ca concentration.

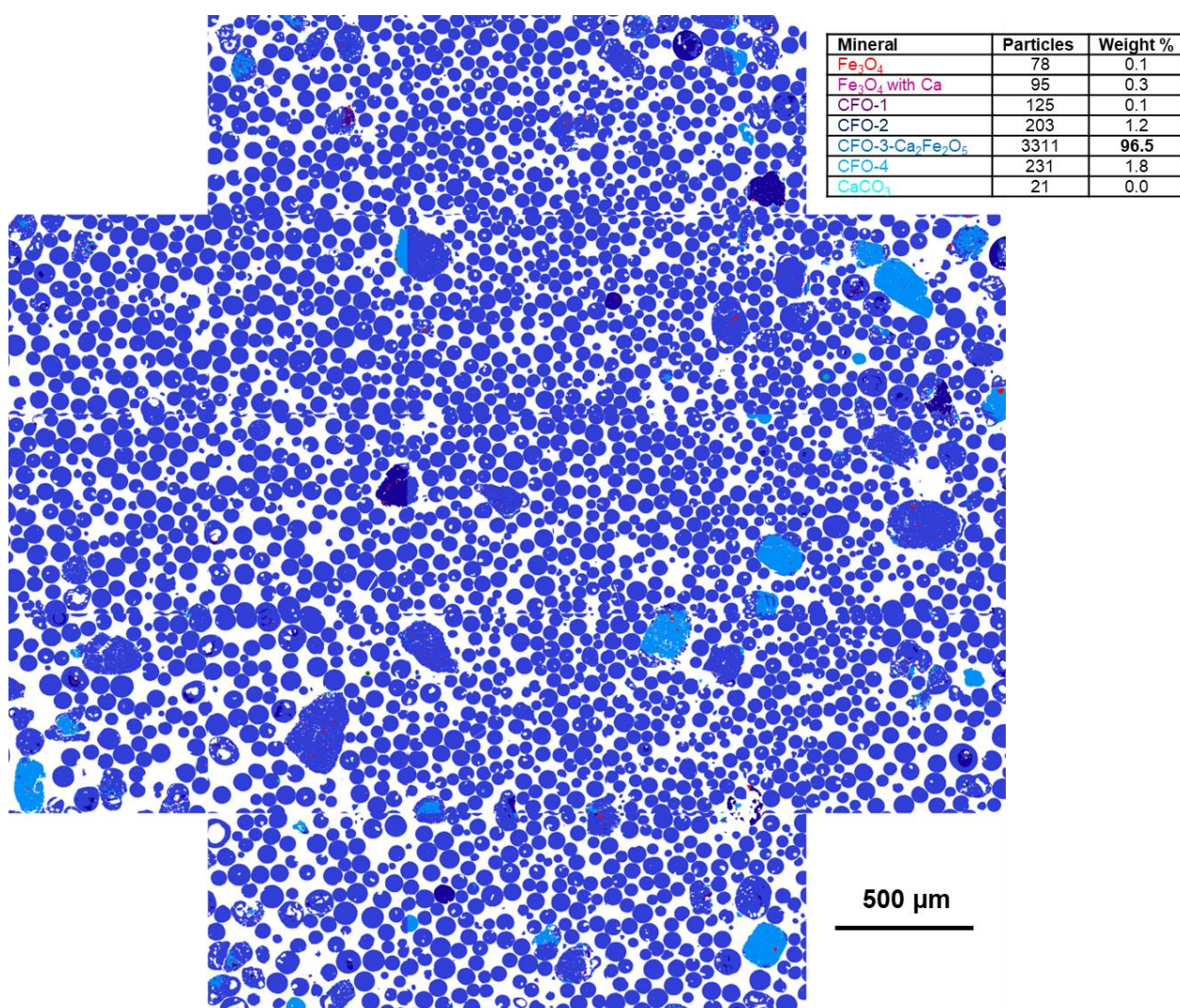


Figure S2. Full MLA compositional analysis and modal mineralogy of flame spheroidised Fe₃O₄:CaCO₃ (mass ratio 1:1; gas flow setting 2.5:2.5), following sieving and sectioning, demonstrating high levels of CFO-3-Ca₂Fe₂O₅.

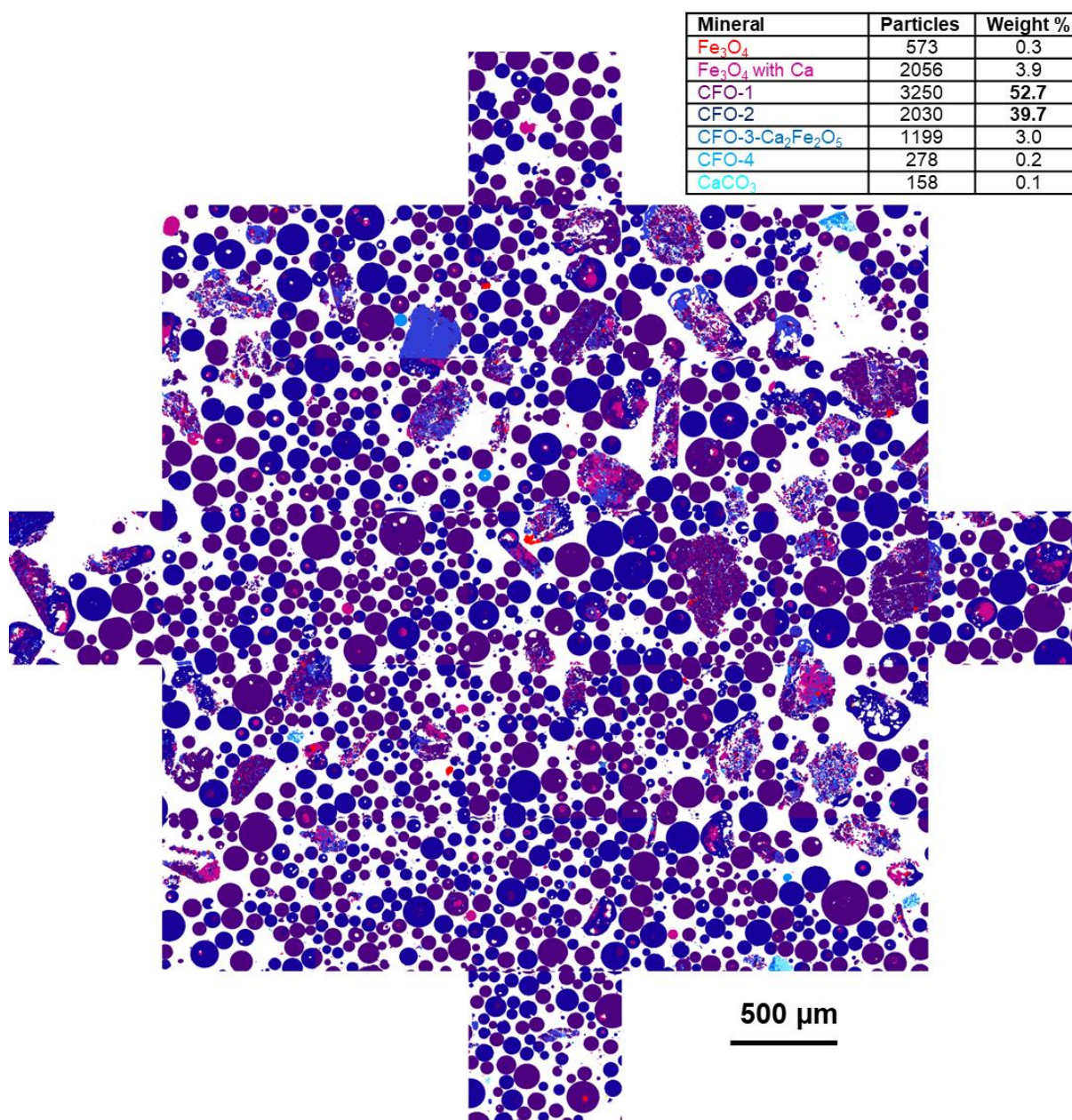


Figure S3. Full MLA compositional analysis and modal mineralogy of flame spheroidised Fe₃O₄:CaCO₃ (mass ratio 3:1; gas flow setting 2.5:2.5), following sieving and sectioning, demonstrating high levels of CFO-1 and CFO-2.

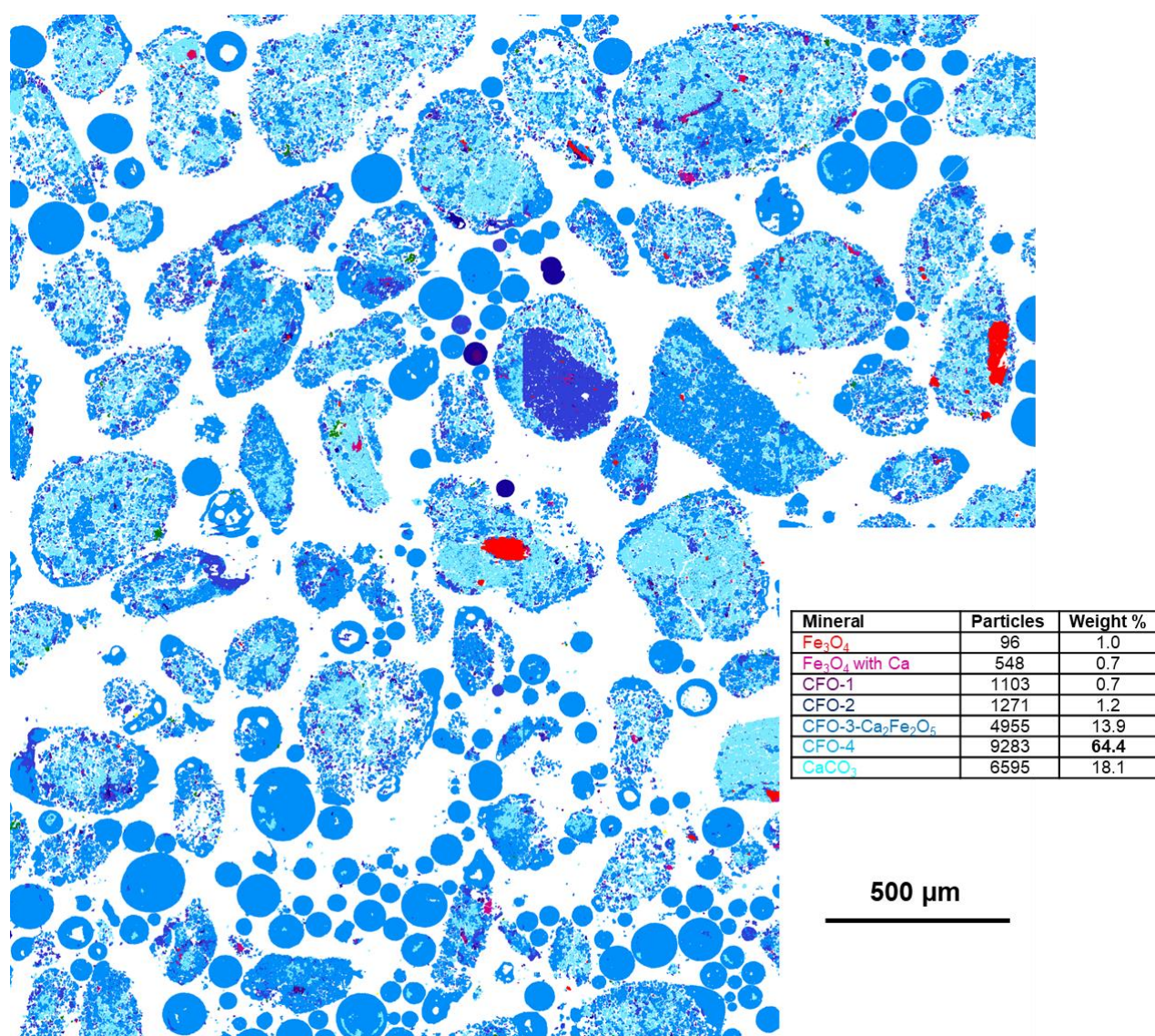


Figure S4. Full MLA compositional analysis and modal mineralogy of flame spheroidised Fe₃O₄:CaCO₃ (MR 1:3; GFS 2.5:2.5), following sieving and sectioning, demonstrating high levels of CFO-4.

Energy dispersive X-ray (EDS)

Complementary energy dispersive X-ray (EDX; BRUKER software, FEI Quanta 600; 20 kV; 12.9 mm working distance) analysis investigations were performed to appraise elemental distributions across sectioned $\text{Fe}_3\text{O}_4:\text{CaCO}_3$ (3:1, 1:1, 1:3) microspheres. Figure S5 presents BSE and elemental maps of the microsphere products, as a function of mass ratio. Table S3 highlights the molar concentrations of decomposed porogen, *i.e.*, CaO; and oxidised magnetite, Fe_2O_3 ; associated with the production of $\text{Ca}_2\text{Fe}_2\text{O}_5$, following $2\text{CaO} + \text{Fe}_2\text{O}_3 \rightarrow \text{Ca}_2\text{Fe}_2\text{O}_5$, in advance of droplet solidification.

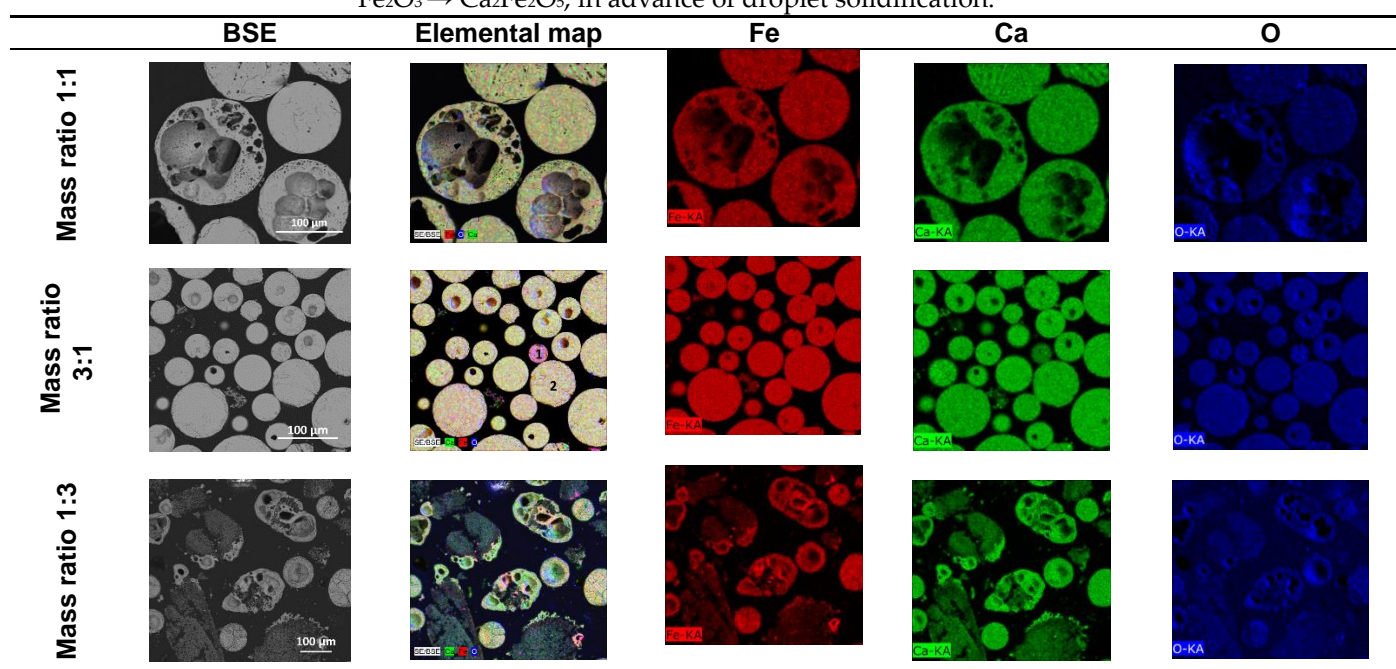


Figure S5. BSE images and elemental mappings showing iron, calcium and oxygen for flame spheroidised $\text{Fe}_3\text{O}_4:\text{CaCO}_3$ (mass ratios 3:1, 1:1, 1:3), following sieving and sectioning.

Table S3. EDS molar concentrations (wt%) and proposed equilibrium phases for flame spheroidised $\text{Fe}_3\text{O}_4:\text{CaCO}_3$ as a function of mass ratio.

$\text{Fe}_3\text{O}_4:\text{CaCO}_3$	CaO wt%	Fe_2O_3 wt%	Proposed phases
Mass ratio 1:1	66.06 ± 1.84	33.93 ± 1.84	CaO + $\text{Ca}_2\text{Fe}_2\text{O}_5$
Mass ratio 3:1	29.57 ± 2.10	70.42 ± 2.10	$\text{Ca}_2\text{Fe}_2\text{O}_5$ + CaFe_2O_4
	42.71 ± 1.54	57.28 ± 1.54	CaO + $\text{Ca}_2\text{Fe}_2\text{O}_5$
Mass ratio 1:3	77.34 ± 5.62	22.65 ± 5.62	CaO + $\text{Ca}_2\text{Fe}_2\text{O}_5$

Effect of gas flow setting

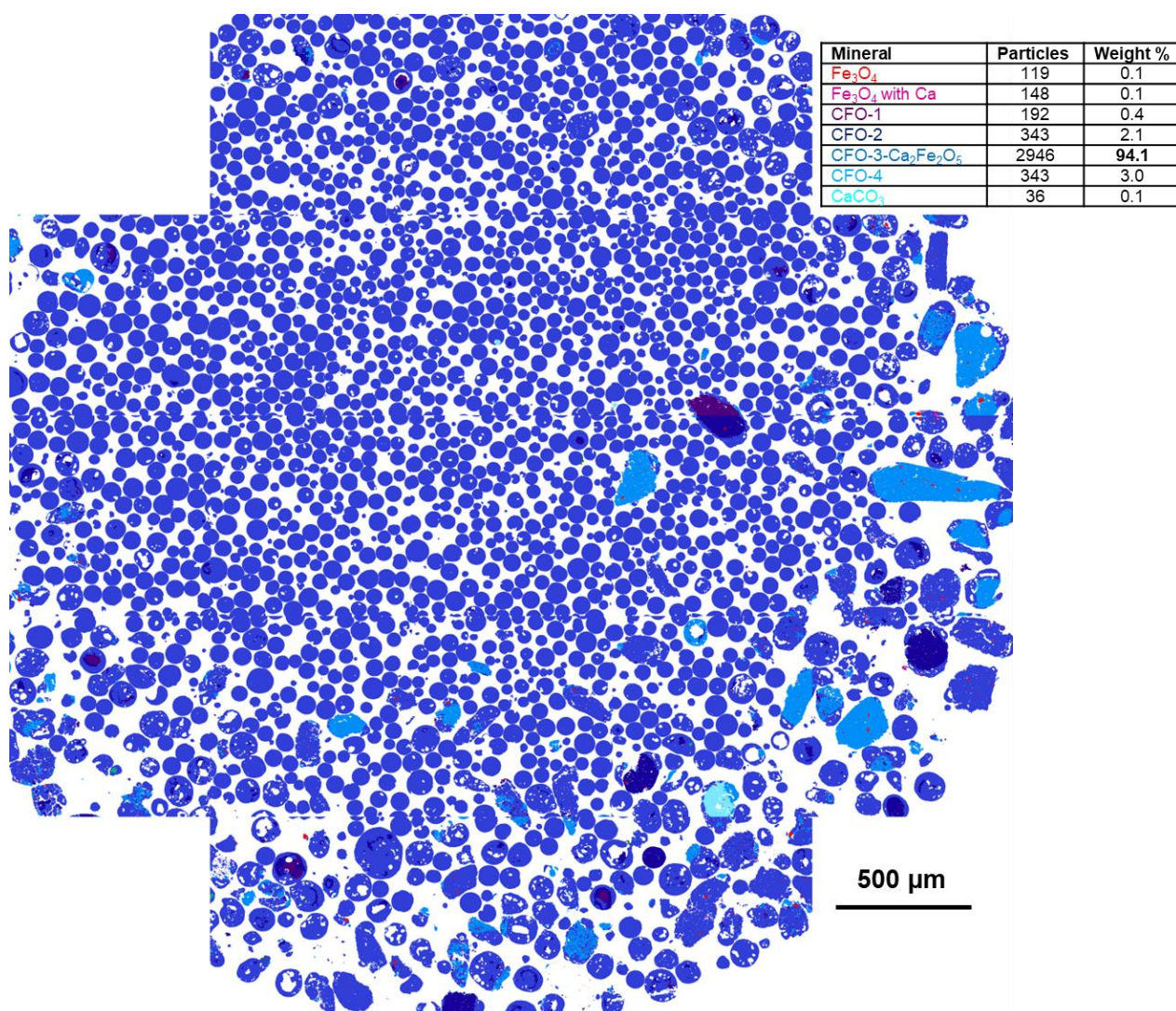


Figure S6. Full MLA compositional analysis and modal mineralogy of flame spheroidisation Fe₃O₄:CaCO₃ (mass ratio 1:1; gas flow setting 3:3), following sieving and sectioning, demonstrating high levels of CFO-3-Ca₂Fe₂O₅.

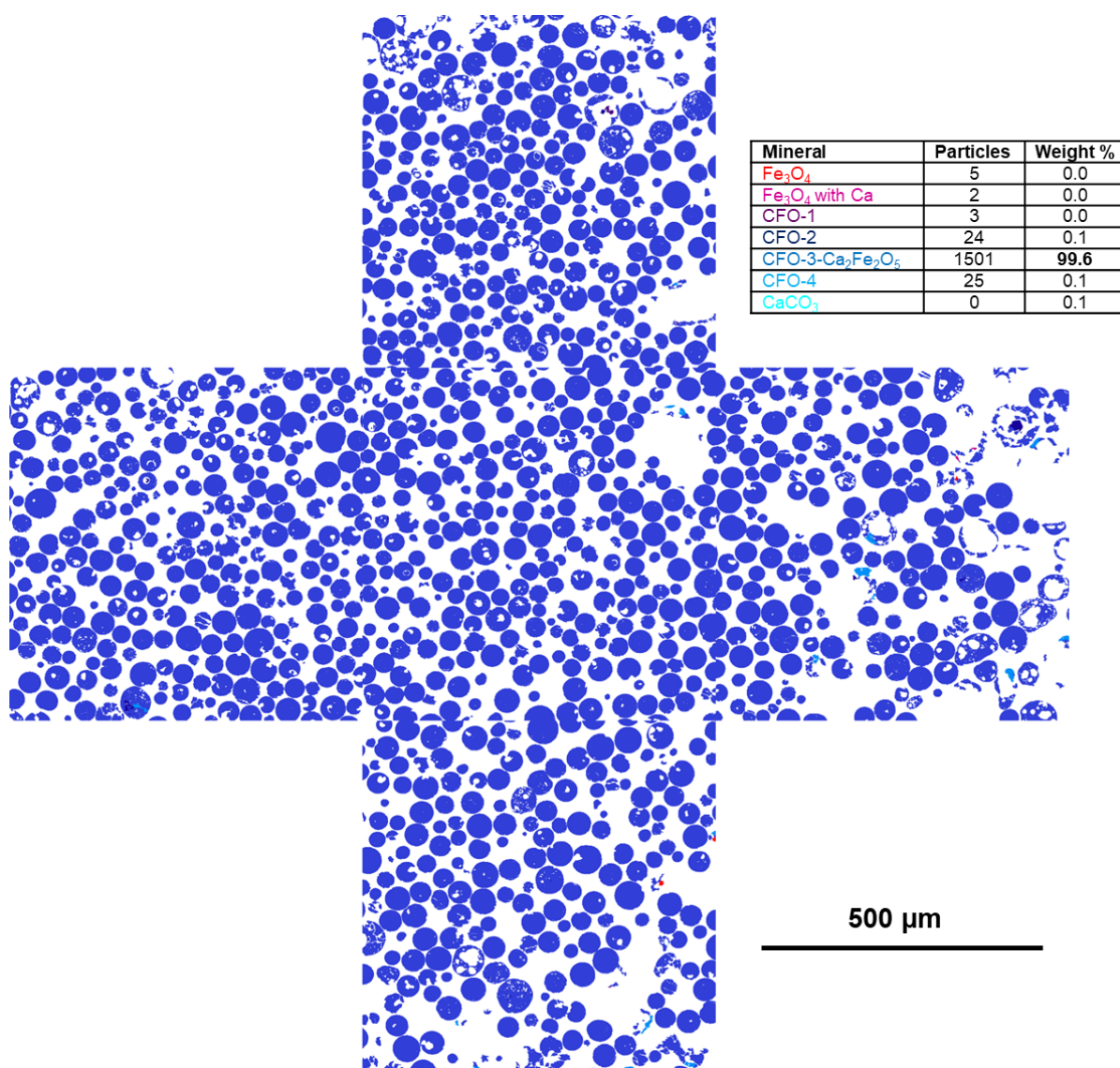


Figure S7. Full MLA compositional analysis and modal mineralogy of flame spheroidised Fe₃O₄:CaCO₃ (mass ratio 1:1; gas flow setting 2:2), following sieving and sectioning, demonstrating high levels of CFO-3-Ca₂Fe₂O₅.

Ca₂Fe₂O₅ microspheres (mass ratio 1:1; gas flow setting 2:2)

Induction heating – Std. errors

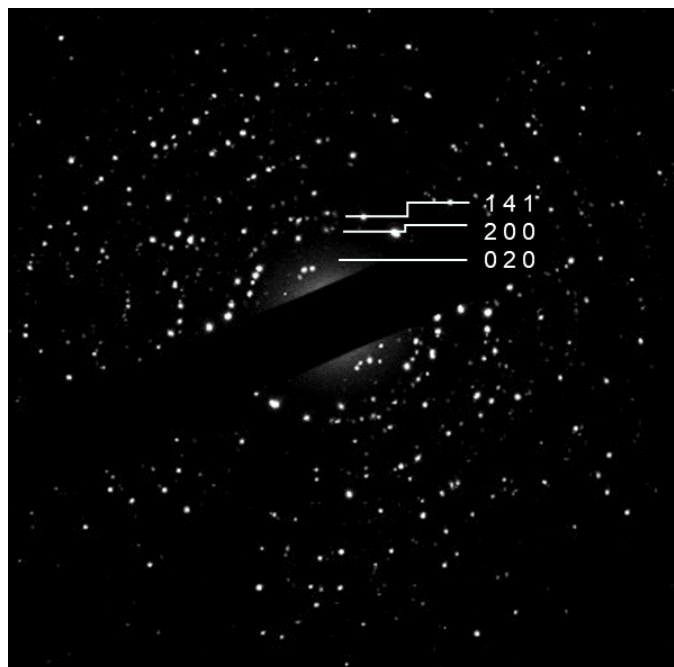
Table S4. Statistical analysis on induction heating experiments.

Std. Error	Ca ₂ Fe ₂ O ₅ microspheres	Fe ₃ O ₄ powder	CaCO ₃ porogen
Slope	0.006150	0.02827	0.0009041
Y-intercept	0.4288	1.971	0.06303

Diffraction contrast patterns

Compositionally uniform, flame spheroidised Fe₃O₄:CaCO₃ (MR-1:1; GFS 2:2), dominated by Ca₂Fe₂O₅ MS, was ground using a mortar and pestle, dispersed in suspension and deposited on to an amorphous holey carbon film on a Cu TEM support grid. Diffraction contrast imaging was performed using transmission electron microscopy (TEM) (JEOL 2100+ TEM; 200 kV; operational mode selected area electron diffraction (SAED)) for automated acquisition series (range of -40 to +40 degrees tilt). Stacked 120 tilted diffraction patterns were loaded and analysed using Crystallographic Tool Box (CrysTBox) software.

Figure S8 presents a cumulative selected area electron diffraction (SAED) pattern from fine-scale, $\text{Ca}_2\text{Fe}_2\text{O}_5$ microsphere fragments. Well defined rings are evident, indicative of a fine-grained polycrystalline material. Diffraction ring identification matched crystal planes - 0 2 0, 2 0 0, and 1 4 1- corresponding to $\text{Ca}_2\text{Fe}_2\text{O}_5$ crystal structure.



2-Theta	HKL
11.98	020
32.97	200
33.40	141

Figure S8. Cumulative selected area electron diffraction (SAED) pattern for 120 stacked tilted fields of view, corresponding to compositionally uniform, flame spheroidised $\text{Fe}_3\text{O}_4\text{:CaCO}_3$ (mass ratio 1:1; gas flow setting 2:2), i.e. $\text{Ca}_2\text{Fe}_2\text{O}_5$ microsphere fragments following grinding; Table comprising crystal planes and 2-Theta.