

# Mechanistic insights into the formation of porous carbons from gelatin

## **Supporting information**

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## Experimental details

### Synthesis of Gels

A 10% w/v gelatin solution was prepared by adding gelatin (10 g, type A from porcine skin, Sigma Aldrich G2500) to deionised water (90 mL) and stirring at ~70 °C until a homogeneous solution was obtained. A 10% w/v iron nitrate solution was prepared by dissolving iron nitrate nonahydrate (10 g, Sigma Aldrich) in deionised water to give a total volume of 100 mL.

Gels were prepared by adding iron nitrate solution (40.4 mL, 0.01 moles of  $\text{Fe}(\text{NO}_3)_3$ ) to gelatin solution (20 g) with rapid stirring at 50-60 °C to give a viscous, red brown fluid. The mixture was stirred until homogeneous. The resulting sample could be cooled at room temperature to give a gel. For other metal nitrates, the samples were prepared in the same way, with volumes listed below in Table S1.

Samples with combinations of different metals were prepared at a constant ratio of 0.005 moles of metal per 1g of gelatin. These samples were prepared by pre-mixing the metal nitrate stock solutions and then adding to gelatin with fast stirring.

Samples of gelatin with nitric acid were prepared with the same concentration of  $\text{NO}_3^-$  as for the sample using  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . To achieve this, 3.3 mL of 1 mol/L nitric acid was added to 20 g of 10% w/v gelatin solution.

Samples of gelatin with HCl were prepared to examine the effect of pH without  $\text{NO}_3^-$  by adding 1M HCl to 20 g of 10% w/v gelatin solution until the pH was the same as the  $\text{HNO}_3$ /gelatin sample.

Metal salt	Volume of 10% w/v metal nitrate solution (mL)
Copper nitrate hemipentahydrate	23.30
Calcium nitrate tetrahydrate	23.60
Magnesium nitrate hexahydrate	25.60
Potassium nitrate	10.10
Sodium nitrate	8.50
Strontium nitrate	21.20
Cerium nitrate hexahydrate	43.40
Iron nitrate nonahydrate	40.40

**Table S1** Required volume of aqueous stock solution to be added to 20 g of 10% w/v gelatin solution for a range of metal nitrates.

### Synthesis of calcined foams

The gels were placed in an air oven at 70 °C to form either a foam (Fe/Cu) or a resin (other metals). The resulting solids/resins were transferred to cylindrical alumina crucibles with lids and calcined inside a metal retort in a muffle furnace with a continuous nitrogen flow to 800 °C with a ramp rate of 10 °C min<sup>-1</sup> and a 5 min hold. The samples were then cooled to room temperature before removing from the furnace. **Caution:** In the synthesis using iron and gelatin,  $\text{Fe}_3\text{C}$  is formed which reacts rapidly with air. It is important to cool completely to room temperature to avoid strongly exothermic reaction of iron carbide with air on removal of the sample. The slightly imperfect atmosphere of the

muffle furnace allows surface passivation of the Fe<sub>3</sub>C particles. **Caution:** All of the resins foam upon heating so only a small amount should be added to a crucible.

#### Determining the onset temperature of foaming

Gel samples prepared as above were placed in 100 mL beakers inside a vacuum oven retro fitted with a nitrogen feed, this was to prevent charring on top of the samples. Samples were dried at 70 °C overnight and the temperature then raised in 10 °C intervals with 3 hours hold at each interval to allow foaming to begin.

#### Thermogravimetric Analysis/Mass Spectrometry (TGA/MS)

Samples were run under argon instead of nitrogen (as in the standard synthesis) so that the carrier gas wouldn't overlap with peaks of interest in the mass spectrum. Dried iron nitrate/gelatin foam (~6 mg) was ground and placed in a dry alumina crucible and this was placed in the TGA chamber under flowing argon. The sample was heated at 10 °C min<sup>-1</sup> to 800 °C before cooling to room temperature. The exhaust gases pass through heated capillary tubes into a mass spectrometer. The mass spectrometer scanned through a predefined range of masses continuously. The TGA used was a Netzsch STA 449 F1 Jupiter and the mass spectrometer was a Netzsch QMS 403C Quadrupole Mass Spectrometer.

#### Bloom strength

20% w/v solutions of iron and magnesium nitrates were prepared by dissolving the solid in deionised water. Aliquots of the stock solution were diluted to 50 mL with water (Table S2). Gelatin solutions were prepared by dissolving 5g gelatin in 50 mL deionised water at 70 °C. The gelatin solution was then combined with the required metal nitrate solution, the mixture was stirred and cooled and then placed in a fridge overnight (~16 hours) to set. Samples were stored in a cool bag with ice blocks and removed one by one directly before gel strength was measured. These tests were carried out at Healan Ingredients. A 1/2 inch diameter plunger was pushed 20 mm into the samples with the instrument measuring the load as a function of distance. The first 4 mm of depression from the surface of a sample gives the bloom strength.

Molar ratio Mg:Fe	Moles of Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	Vol of 20% w/v Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O (mL)	Moles of Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Vol of 20% w/v Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (mL)
0 : 100	0.02500	50.50	-	-
0 : 50	0.01250	25.25	-	-
0 : 25	0.00625	12.63	-	-
0 : 10	0.00250	5.05	-	-
0 : 5	0.00125	2.53	-	-
0 : 2	0.00050	1.01	-	-
0 : 1	0.00025	0.51	-	-
100 : 0	0.00000	0.00	0.025	32.05
0 : 0	0.00000	0.00	0.000	0.000

**Table S2** Details of samples prepared for gel strength testing

## Rheology

Samples were prepared at the maximum possible concentration (maximum viable before it was impossible to homogenise the samples). This was in order to study the rheological properties of the iron/gelatin mixture as close as possible to the point at which foaming begins and the sample dries. Samples were prepared by adding aliquots (Table 2) of a 50% w/v  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solution to water to give a total volume of 10 mL. Gelatin (2 g) was then added and the samples were shaken then carefully heated in vials (to avoid loss of water) at 70 °C in an oven. Care must be taken to avoid bubbles through the resin.

Moles of Fe	Volume of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ stock (mL)	Volume of water (mL)
0.01	8.08	1.92
0.0075	6.06	3.94
0.005	4.04	5.96
0.0035	2.83	7.17
0.003	2.42	7.58
0.0025	2.02	7.98
0	0	10

**Table S3** Volumes of iron nitrate stock (50% w/v) and water for preparation of resins for rheological measurements.

For rheology experiments a cone and plate geometry was used. The cone had a 40 mm diameter and an incline of 2 ° and the plate was a 40 mm diameter sand blasted circle. The plate was heated to 50 °C to melt the gelatin and then cooled (25 °C) once the plate/cone were brought into working distance 1000 µm. The value of  $G_0$  (elastic modulus) was then measured at an oscillation frequency of 1 Hz in a strain sweep test from 0.1% to 50% percentage strain. This stress sweep was performed in order to determine the limit of the linear viscoelastic regime. The rest of the rheological measurements were frequency sweep tests with a strain of 2% maintained over the whole frequency range (0.01-100 Hz (rad/s)). The instrument used was a TA instruments AR G2.

### Circular Dichroism (CD)

Various cell lengths and concentrations were trialled, the data shown in this paper is for a 0.5 mm path length and 1% w/v gelatin. A gelatin stock (2% w/w) was prepared by adding gelatin (2 g, Sigma Aldrich, G2500) to 98 g of water with stirring and heating (70 °C). An aliquot (5 mL) of this was then mixed with portions of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  stock (1% w/v in deionised water) and deionised water (Table 3) to give a constant volume of 10 mL and a constant gelatin concentration across all samples. The samples were transferred to quartz cells and scanned from 400-200 nm at 200 nm/min. The instrument used was a Jasco J-810 spectropolarimeter.

<b>Vol of <math>\text{Fe}(\text{NO}_3)_3</math> stock (mL)</b>	<b>Volume of water (mL)</b>
<b>0.5</b>	4.5
<b>1</b>	4
<b>2</b>	3
<b>3</b>	2
<b>4</b>	1
<b>5</b>	0

**Table S4** List of samples prepared for circular dichroism.

## SANS

Metal nitrate stock solutions were prepared by dissolving 2 g of metal nitrate in D<sub>2</sub>O to give a total volume of 10 mL. To minimize incoherent scattering from H<sub>2</sub>O (and to ensure a constant background scattering), aliquots of H<sub>2</sub>O were added to samples to account for different levels of H<sub>2</sub>O being added via the hydrated metal salts. Samples were prepared by mixing metal nitrate stock solutions with H<sub>2</sub>O and then adding D<sub>2</sub>O to make up to a total volume of 10 mL. Full details are listed below in Tables 4-6. The solutions were heated in glass vials on a hot plate to ~50 °C, gelatin powder (0.5 g) was added and the mixture shaken on a vortex mixer. The capped vials were placed in an oven at 70 °C for the gelatin to dissolve. Care should be taken to avoid starting to decompose the gelatin and samples were left for a maximum of 60 minutes at 70 °C. The resulting mixtures were homogenized by vortex mixing and transferred to quartz sample cells before sealing and cooling to room temperature. **All samples were prepared to contain 0.005 moles of metal per 1 g of gelatin.**

Volume of Fe nitrate stock (mL)	Extra H <sub>2</sub> O required (mL)	Concentration of Fe(NO <sub>3</sub> ) <sub>3</sub> in final sample (mol/L)
5.05	0.000	0.250
3.79	0.101	0.188
2.53	0.203	0.125
1.26	0.304	0.063
0.76	0.344	0.038
0.51	0.365	0.025
0.25	0.385	0.013
0.10	0.397	0.005
0.05	0.401	0.003
0.00	0.405	0.000

**Table S5** Sample preparation details for samples of gelatin with various concentrations of iron nitrate.

Given that iron nitrate is provided as a nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), the addition of different amounts of this salt to gelatin in D<sub>2</sub>O would result in different H:D ratios in these systems. A higher H-content would lead to higher incoherent scattering (i.e. a higher background in the scattering pattern). In order to ensure a constant H:D ratio in all samples, the amount of H<sub>2</sub>O contributed by 100 mol% Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was calculated. Extra H<sub>2</sub>O was then added to samples of <100 mol% Fe, to make up the amount of H<sub>2</sub>O to a constant value.

Molar ratio Fe:Mg	Concentration of Fe(NO <sub>3</sub> ) <sub>3</sub> in final sample (mol/L)	Volume of Fe nitrate stock (mL)	Concentration of Mg(NO <sub>3</sub> ) <sub>2</sub> in final sample (mol/L)	Volume of Mg nitrate stock (mL)	Extra H <sub>2</sub> O required (mL)
100:0	0.250	5.05	0.000	0.00	0.000
75:25	0.188	3.79	0.063	0.80	0.034
50:50	0.125	2.53	0.125	1.60	0.068
25:75	0.063	1.26	0.188	2.40	0.101
10:90	0.025	0.51	0.225	2.88	0.122
5:95	0.013	0.25	0.238	3.04	0.128
2:98	0.005	0.10	0.245	3.14	0.132
1:99	0.003	0.05	0.248	3.17	0.134
0:100	0.000	0.00	0.250	3.20	0.135

**Table S6** Details for samples prepared from a combination of iron and magnesium nitrates with gelatin.

Metal salt	Molecular weight g/mol	Volume of metal nitrate stock (ml)	Extra H <sub>2</sub> O required (ml)
Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O	232.59	2.91	0.293
Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	434.22	5.43	0.135
NaNO <sub>3</sub>	84.99	1.06	0.405
KNO <sub>3</sub>	101.1	1.26	0.405
Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	297.49	3.72	0.135
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	236.15	2.95	0.225
LiNO <sub>3</sub>	68.95	0.86	0.405
Mn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	251	3.14	0.225
Sr(NO <sub>3</sub> ) <sub>2</sub>	211.63	2.65	0.405
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	256	3.20	0.135

**Table S7** Details for samples prepared from gelatin with various metal nitrates

SANS measurements were carried out at the ISIS Neutron and Muon source, Rutherford Appleton Laboratory, UK on SANS2D. Samples were housed in Hellma cells with a path length of 2 mm and a thermostated sample changer provided temperature control. A beam width of 8 mm was used, providing a detectable Q range of order 0.001 – 1 Å<sup>-1</sup>. Absolute intensities for I(Q) (in Å<sup>-1</sup>) were determined by calibrating the received signal for a polymer standard and correcting for sample transmission and solvent (D<sub>2</sub>O doped with H<sub>2</sub>O) background.

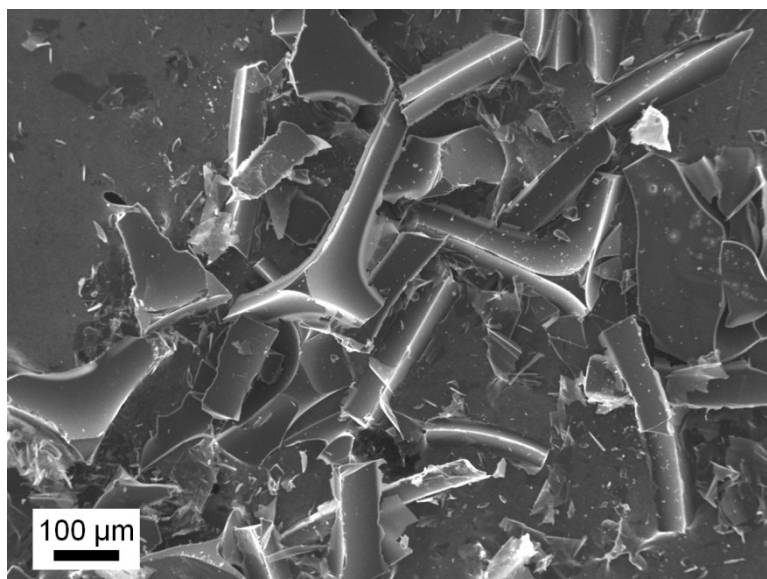
Scattering from the metal nitrate/gelatin mixtures was modelled using IGOR PRO software. The model used was a modified correlation length function (Equation S1), which consists of the following parameters. C is the scale factor, B is the (Q-independent) incoherent background level,  $\xi$  is a correlation length, m is the high-Q Porod exponent and s is the low-Q Porod exponent (sometime referred to as the “dimensionality factor”) representing structure anisotropy (s=1 for elongated rod-like structures and s=0 for isotropic globular structures).

$$I(Q) = \frac{1}{Q^s} \frac{C}{1 + (Q\xi)^m} + B \quad \text{Equation S1}$$

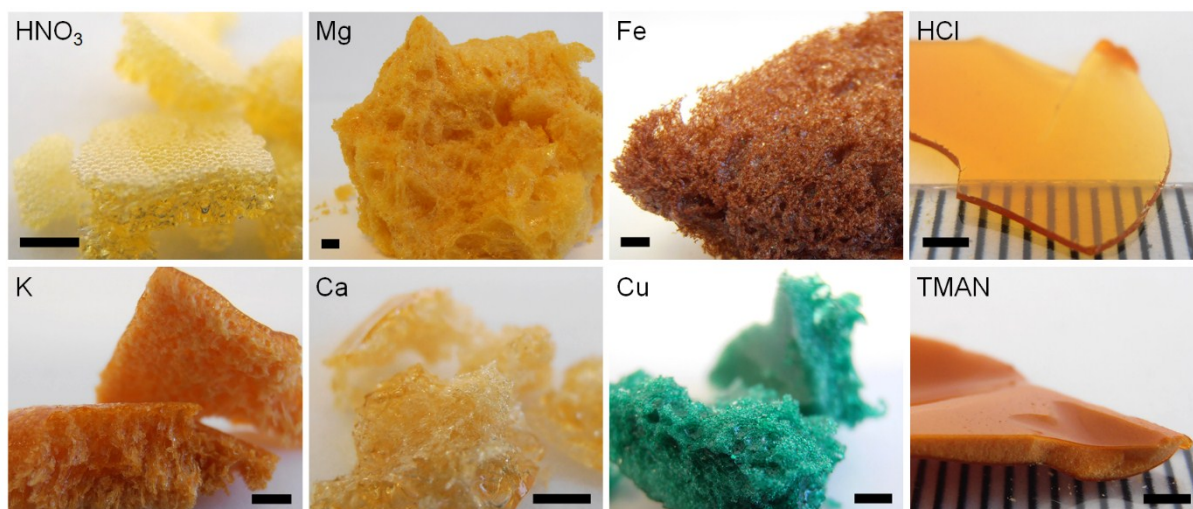
Modelling was restricted to the region  $Q > 0.008 \text{ Å}^{-1}$  as the low Q Porod region contained so few data points. It was possible to fit the data by incorporating a second power law to account for the low Q Porod region. However, this has a negligible effect on the values for correlation length and therefore does not affect the conclusions of this work.

## Results and Discussion

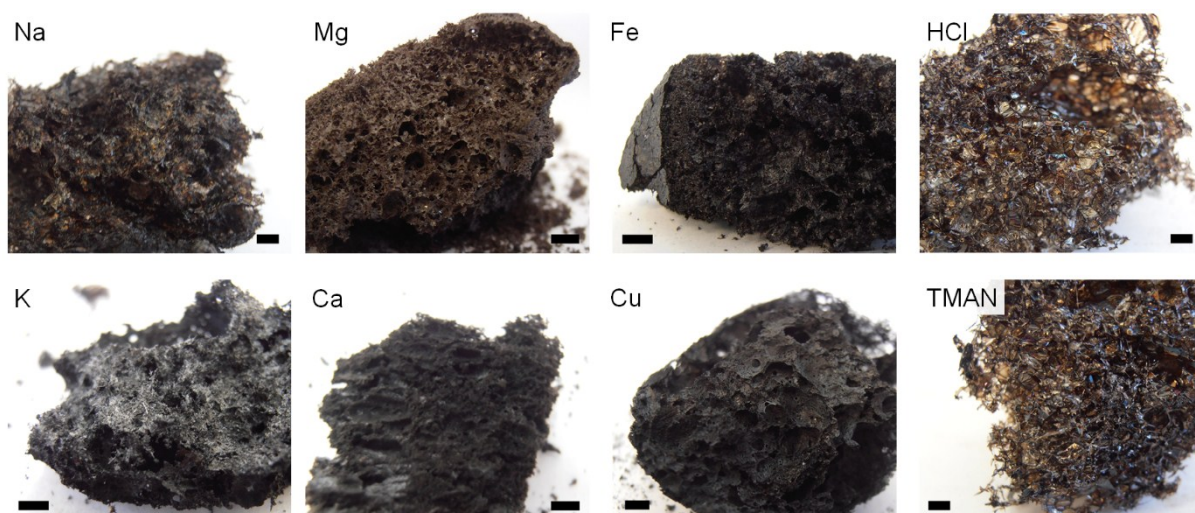
### Observations of foam structure



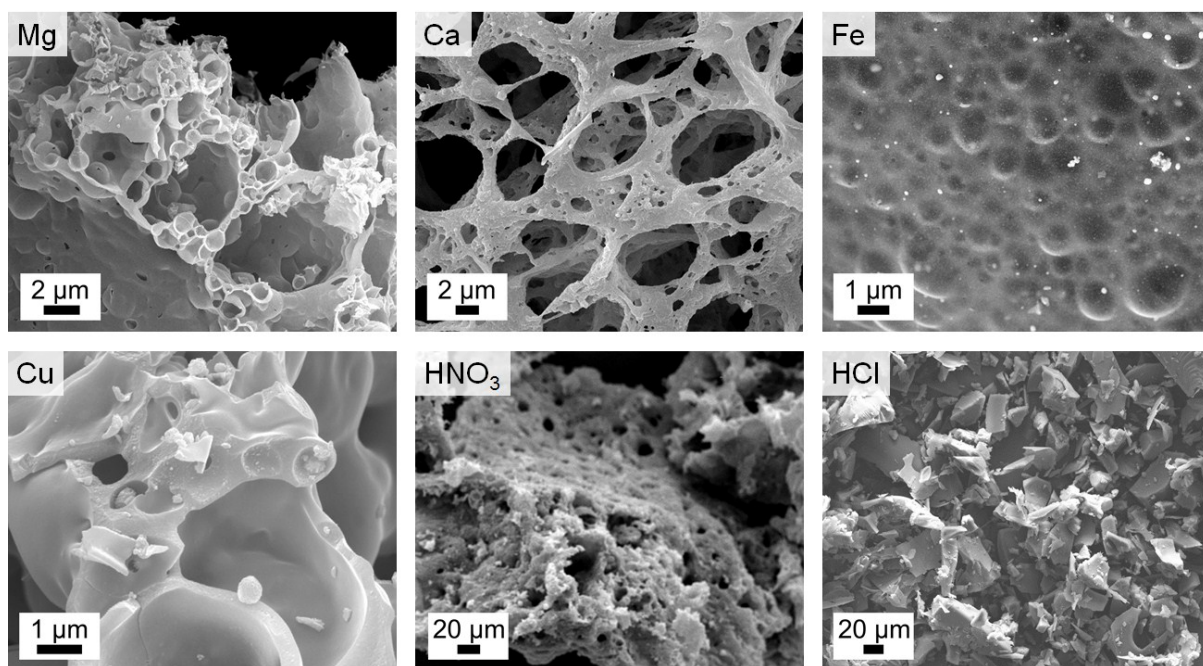
**Figure S1** SEM image of a sample prepared by heating gelatin to 800 °C under nitrogen



**Figure S2** Images of metal nitrate/gelatin foams after drying at various temperatures from 70-160°C as detailed in Table 1 in the main paper. Scale bars = 2 mm

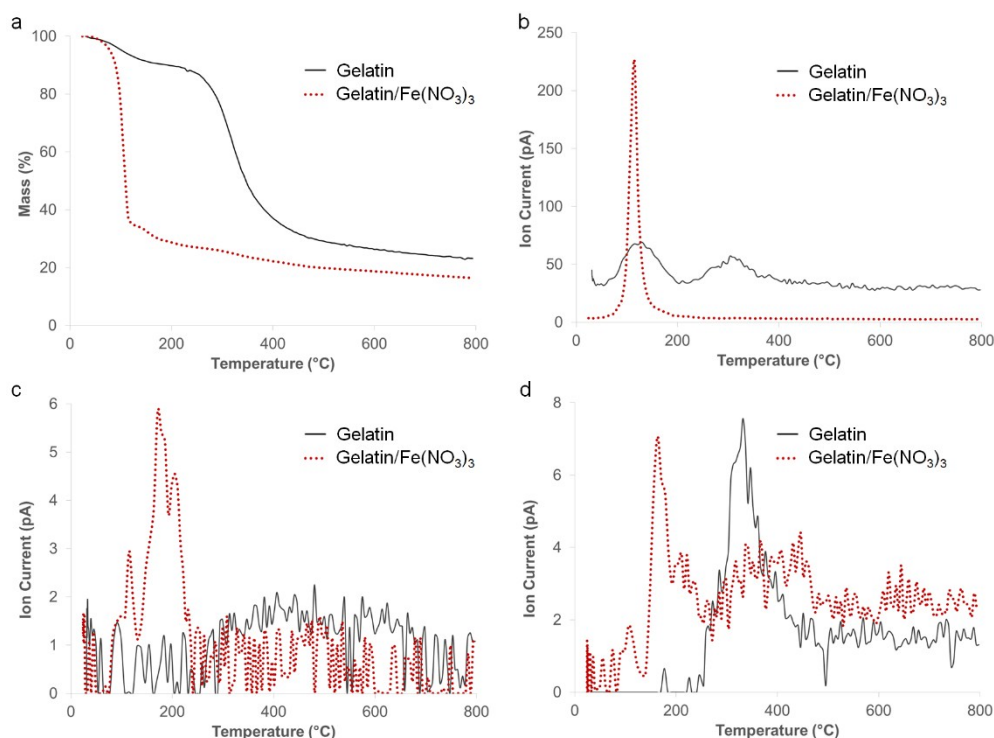


**Figure S3** Images of metal nitrate/gelatin foams after calcination to 800 °C Scale bars = 2 mm



**Figure S4** SEM images of samples prepared using various metal nitrates with gelatin as well as  $\text{HNO}_3$  and  $\text{HCl}$  with gelatin.

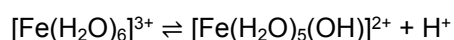
## TGA-MS (Thermogravimetric analysis – mass spectrometry)



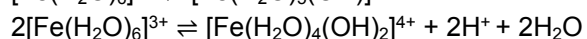
**Figure S5** a) TGA data showing the % mass loss from a sample of gelatin as well as a sample of gelatin with iron nitrate. Mass spectrometry data for the resulting exhaust gases from TGA showing peaks for  $m/z =$  b) 18, c) 30 and d) 44.

## Attempt to evaluate iron binding with UV-Visible spectroscopy

For solutions of constant iron nitrate concentration, an increasing gelatin concentration was observed to produce a progressively darker red-brown colour that can be followed graphically using UV-Vis spectroscopy. We previously proposed this was an indication of the changing coordination environment of the Fe<sup>3+</sup>, i.e. evidence for binding of iron to gelatin. However, it is also possible that hydrolysis reactions are occurring in the solution, producing iron-hydroxo species that are known to be a dark red colour. Two of these possible reactions are shown in Equations 2 and 3. Given the acidic nature of iron nitrate solutions, it is unlikely that hydrolysis of the Fe aqua species occurs in water. However, gelatin is a polyampholyte and could act as a buffer, driving the equilibrium to the right and forming the iron hydroxo species.

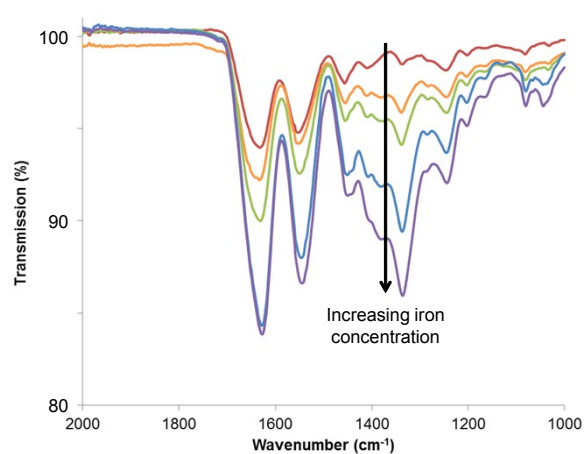


Equation S2

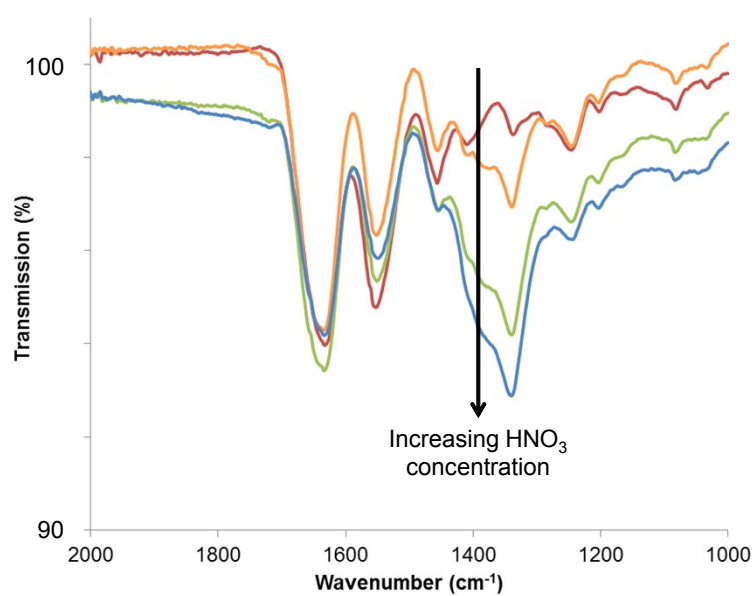


Equation S3

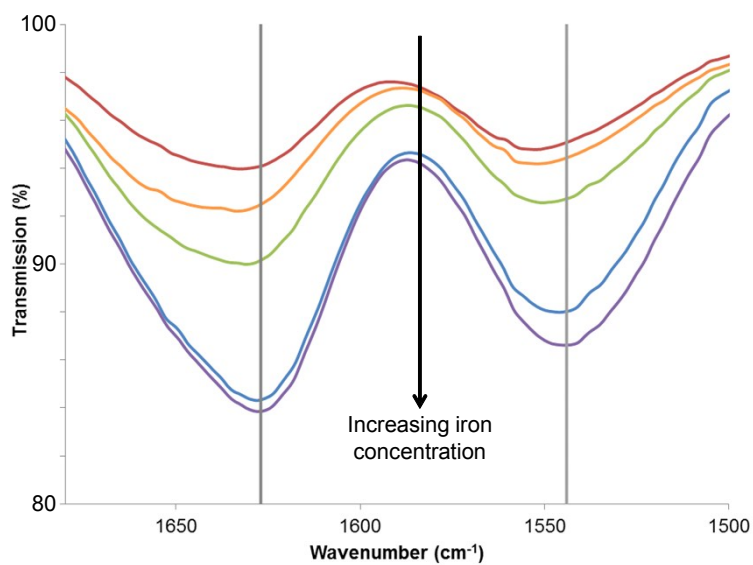
### Infra-red absorption spectroscopy of iron



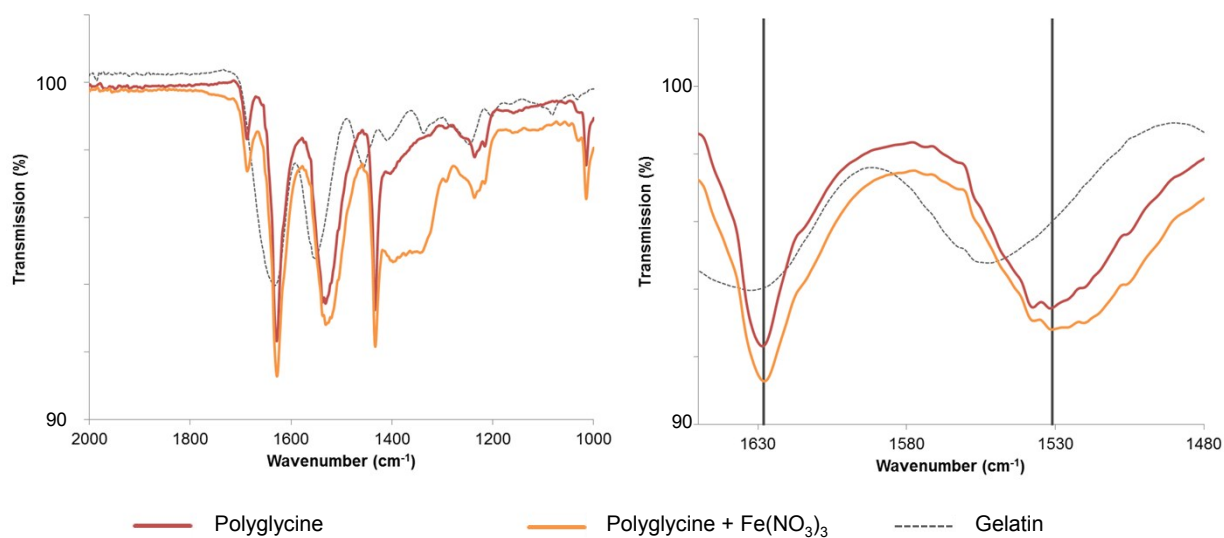
**Figure S6** IR spectra of samples of iron nitrate and gelatin with an increasing Fe:gelatin ratio.



**Figure S7** IR spectra of samples of  $\text{HNO}_3$  and gelatin with an increasing  $\text{HNO}_3$ :gelatin ratio.

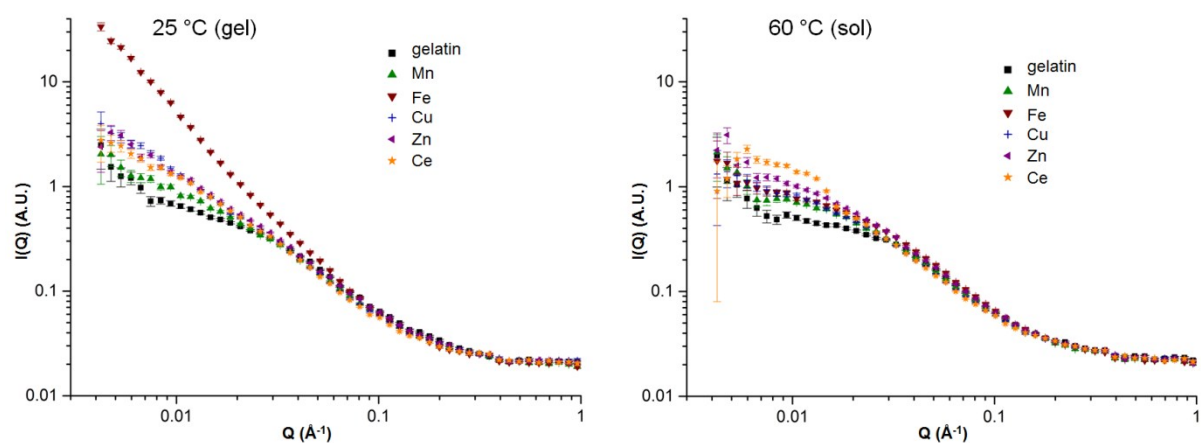


**Figure S8** IR spectra of samples of iron nitrate and gelatin with an increasing Fe:gelatin ratio.

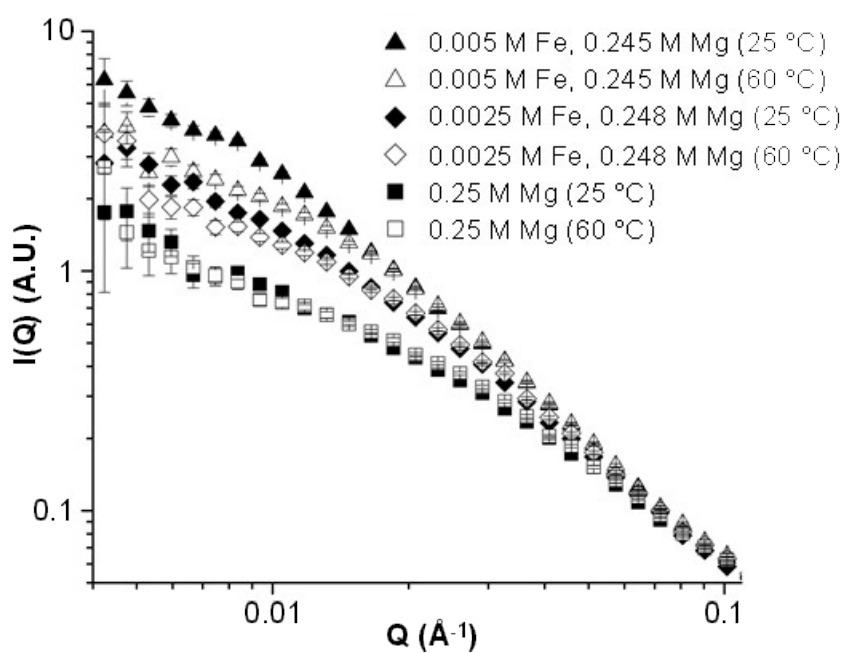


**Figure S9** IR spectra of polyglycine before and after soaking in Fe(NO<sub>3</sub>)<sub>3</sub> as well as a reference spectra for pure gelatin.

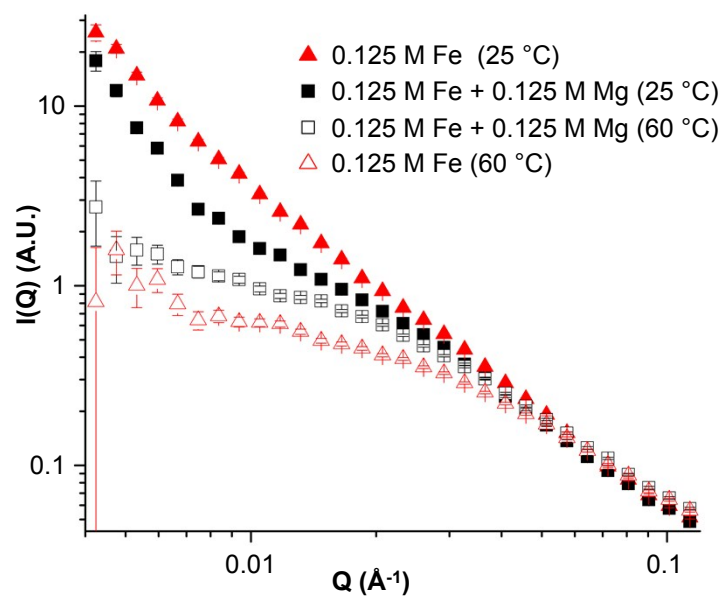
## SANS of gelatin with various metal nitrates



**Figure S10** SANS data for gelatin with various metal nitrate salts at 25 °C and 60 °C. In this and the subsequent figures, statistical error bars are smaller than the plotting symbols.



**Figure S11** SANS data for samples of gelatin with small amounts of iron nitrate combined with magnesium nitrate at 25 °C and 60 °C.



**Figure S12** SANS data for samples of gelatin with 0.125 mol/L iron nitrate (both with and without magnesium nitrate) at 25 °C and 60 °C.

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