Electronic Annex EA-2

SEM AND TEM IMAGES OF SOLID RUN PRODUCTS

“Experimental constraints on Fe isotope fractionation during magnetite and Fe carbonate formation coupled to dissimilatory hydrous ferric oxide reduction”
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Fig. EA-2-1. Scanning electron microscope images of Fe carbonate produced in experiments with Shewanella putrefaciens strain CN32 (Experiment 1).

Large and detailed views of siderite crystals formed in Ca-free experiment (1A). The rounded crystal form and evidence for surface dissolution features suggest that after the ca. 500 d incubation period, dissolution (and possible re-precipitation) of the crystals occurred. Energy-dispersive spectra show that all crystals are pure siderite, and this is confirmed by XRD spectra on bulk samples.
Fig. EA-2-2. Scanning electron microscope images of Fe carbonate produced in experiments with *Shewanella putrefaciens* strain CN32 (Experiment 1).

Large and detailed views of siderite crystals formed in Ca-bearing experiment (1B). As in Experiment 1A, the rounded crystal form and evidence for surface dissolution features suggest that after the ca. 500 d incubation period, dissolution (and possible re-precipitation) of the crystals occurred. Energy-dispersive spectra show that all crystals are Ca-bearing siderites, where stoichiometries vary from $\text{Ca}_{0.12}\text{Fe}_{0.88}\text{CO}_3$ to $\text{Ca}_{0.15}\text{Fe}_{0.85}\text{CO}_3$; this is confirmed by XRD spectra and AA on bulk-samples.
Fig. EA-2-3. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Geobacter sulfurreducens* of Experiment 2.

Large and detailed views of sample after 4 d of incubation. Sample appears to be entirely unreacted HFO, which is confirmed by XRD spectra, and ferric:ferrous ratios of the solids.
Fig. EA-2-4. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Geobacter sulfurreducens* of Experiment 2.

Large and detailed views of sample after 8 d of incubation. SEM images show first appearance of tabular lepidocrocite (γFeO*OH), and XRD spectra on this sample confirms the presence of γFeO*OH. Ferric:ferrous ratios of the solids indicate that no significant magnetite exists in this sample.
Fig. EA-2-5. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Geobacter sulfurreducens* of Experiment 2.

Large and detailed views of sample after 16 d of incubation. Sample appears to be dominated by tabular lepidocrocite (γFeO*OH), which is confirmed by XRD spectra. Ferric:ferrous ratios of the solids indicate virtually no conversion to magnetite, and XRD spectra do not show the presence of magnetite.
Fig. EA-2-6. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Geobacter sulfurreducens* of Experiment 2.

Large and detailed views of sample after 21 d of incubation. SEM images show that most of the tabular lepidocrocite (γFeO*OH) has been lost, and XRD spectra on this sample does not show evidence for γFeO*OH. A few remnant tabular lepidocrocite crystals remain (detail). Ferric:ferrous ratios of the solids indicate that over half of the solid has been converted to magnetite, and this is confirmed by strong magnetite XRD spectra in this sample. Therefore, the majority of fine-grained material in the sample is interpreted to be fine-grained magnetite.
Fig. EA-2-7. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Geobacter sulfurreducens* of Experiment 2.

Large and detailed views of sample after 99 d of incubation. Sample appears to be dominated by fine-grained magnetite, which is confirmed by XRD spectra. Ferric:ferrous ratios of the solids indicate that the sample is entirely magnetite. Euhedral magnetite observed in Experiment 4 is not seen; large forms in the images are likely to be clumped fine-grained magnetite.
Fig. EA-2-8. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Shewanella algae* of Experiment 3.

Large and detailed views of sample after 8 d of incubation. Sample appears to be entirely unreacted HFO, which is confirmed by XRD spectra, and ferric:ferrous ratios of the solids.
Fig. EA-2-9. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Shewanella algae* of Experiment 3.

Large and detailed views of sample after 16 d of incubation. XRD spectra on this sample indicate the presence of magnetite. Ferric:ferrous ratios of the solids indicate some conversion of HFO to magnetite, although the proportion of magnetite is still small.
Fig. EA-2-10. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Shewanella algae* of Experiment 3.

Large and detailed views of sample after 99 d of incubation. Sample consists of aggregates of fine-grained magnetite, as confirmed by XRD spectra and ferric:ferrous ratios of the solids. Note that strong magnetite peaks in XRD spectra are shown in earlier time samples. Ferric:ferrous ratios of this sample suggest that the solid is 100% magnetite.
Fig.  EA-2-11. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Geobacter sulfurreducens* of Experiment 4.

Sample after 22 d of incubation. Large and detailed views of magnetite crystals illustrating large (ca. 1 µm) euhedral magnetite crystals, in addition to fine-grained material. Energy-dispersive spectra obtained on the large crystals are consistent with magnetite, and this interpretation is supported by XRD data on bulk samples.
Fig. EA-2-12. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Geobacter sulfurreducens* of Experiment 4.

Large and detailed views of sample after 164 d of incubation. The large magnetite crystals observed are similar in size as those observed earlier in the experiment. The proportion of fine-grained material has markedly decreased in the long-term experiment.
Large and detailed views of sample after 4 d of incubation. The morphology of the vast majority of grains in the fine-grained material indicates that it is dominated by magnetite, and electron diffraction patterns support this conclusion. Detail of ca. 20 nm-sized magnetite crystal illustrating lattice fringes shown in inset in lower left. However, long-bladed crystals match the morphology for ferric oxyhydroxide minerals such as goethite (see detailed inset in upper left), which is interpreted to reflect partial re-crystallization of HFO early in the experiment. The presence of un-reduced ferric oxyhydroxide in the early parts of the experiment is supported by the ferric:ferrous ratios determined for the bulk solid material from this sample.
Fig. EA-2-14. Transmission electron microscope images of fine-grained solid products observed in SEM images of Experiment 4.

Large and detailed views of sample after 164 d of incubation. All of the fine-grained material appears to have the morphology of magnetite, and this interpretation is consistent with electron diffraction patterns. None of the long-bladed ferric oxyhydroxide crystals observed in the 4 d sample were found in this sample.
Fig. EA-2-15. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Geobacter sulfurreducens* of Experiment 5.

Large and detailed views of sample after 2 d of incubation. Early siderite formation consists of globules, which we have observed in rapid precipitation experiments in abiologic systems (Wiesli et al., 2004).
Fig. EA-2-16. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Geobacter sulfurreducens* of Experiment 5.

Large and detailed views of sample after 7 d of incubation. SEM images show that the carbonate globules that are common in the 2 d sample have extensively re-crystallized to rhombohedral siderite.
Fig.  EA-2-17. Scanning electron microscope images of solid products produced by dissimilatory reduction of HFO by *Geobacter sulfurreducens* of Experiment 5.

Large and detailed views of sample after 27 d of incubation. Siderite consists exclusively as rhombohedral shapes, with small crystals scattered on the surfaces. Magnetite appears to be largely fine-grained.