

## SAMPLING

Sampling was conducted at a deep-water station (2°28.00 S, and 121°17.00 E) in February 2009. Water samples were collected by pumping through 1 cm internal diameter plastic tubing. The depth of the pump inlet was set using a CTD (Sea and Sun Technology) equipped with a temperature probe, conductivity probe, turbidity probe, and an oxyguard oxygen probe. The multiparameter probe was interfaced to a computer at the surface using a hydrowire. This allowed real-time positioning of the pump inlet with a vertical accuracy of 0.1 m and a between-cast precision of 0.25 m. The tubing was flushed with at least three times the volume (12 L) contained within the tubing using a diaphragm pump. Following the flushing period, water was pumped for sampling with a peristaltic pump (Masterflex L/S computerized drive model number 7523-60) through a combination of tygon and marprene tubing.

Water column particulate matter was collected by filtering 10-20 L of water through 0.2 µm polycarbonate filters housed on an in-line filtration device (preventing contact with the atmosphere). While filtering on board the research vessel, this device was kept in a glove bag under a nitrogen atmosphere. Filters for X-ray Absorption Structure (XAS) were removed from the filtration device, folded, and sealed in kapton tape (serving as an additional oxygen barrier that is virtually transparent to X-rays) while under N<sub>2</sub>. Filters for synchrotron-based analyses were stored in nitrogen-filled glass vials at -20°C until analysis. Filters for SEM, TEM and geochemical analyses were stored refrigerated in serum bottles sealed under N<sub>2</sub> with butyl rubber stoppers.

## GEOCHEMICAL ANALYSES

Dissolved Fe was measured by ICP-OES (Perkin Elmer Optima 5300DV). The ΣCO<sub>2</sub> was measured by the Flow Injection method (Hall and Aller, 1992) and pH measured as previously described (Crowe et al., 2011). The 0.5 N HCl leachable Ni content of particulate material was determined by ICP-OES (Perkin Elmer Optima 5300DV) after a 1 hr leach at room-temperature. Nickel in the dissolved phase was determined via ICP-MS (Table DR1).

Iron speciation (Table DR2) was determined via a modified version of the sequential extraction technique of Poulton and Canfield (2005), which extracts different, operationally defined Fe pools. In the first step, samples were subjected to a 0.5 N HCl extraction for 1 hr (Thamdrup et al., 1994), to remove poorly crystalline hydrous ferric oxides (Fe(III)<sub>HFO</sub>) plus any reduced Fe(II) associated with particle surfaces, GR or FeS (Fe(II)<sub>red</sub>). Fe(II) in this fraction was measured using the ferrozine assay (Viollier et al., 2000). Crystalline ferric (oxyhydr)oxides such as goethite and hematite (Fe<sub>ox</sub>) were determined via a 2 h sodium dithionite extraction. Magnetite (Fe<sub>mag</sub>) was determined via a 6 h sodium oxalate extraction. Total Fe in each extract was determined via AAS, with a RSD of <5% for all steps. These minerals define an Fe pool which is considered 'highly reactive' (Fe<sub>HR</sub>) during sedimentation and diagenesis (Poulton et al.,

2004). Pyrite and acid volatile sulfides ( $\text{Fe}_{\text{py}}$ ) were determined on deposited sediment via the chromous chloride distillation technique of Canfield et al. (1986). The highly reactive pool was determined as,  $\text{Fe}_{\text{HR}} = \text{Fe(II)}_{\text{red}} + \text{Fe(III)}_{\text{HFO}} + \text{Fe}_{\text{ox}} + \text{Fe}_{\text{mag}} + \text{Fe}_{\text{py}}$ .

## MICROSCOPY

Scanning electron microscopy (SEM) was conducted on filters that were stub-mounted and gold-sputter coated for 1.5 minutes. Images were acquired using a Leo 1550 scanning electron microscope operated at an accelerating voltage of 20 kV with an energy dispersive spectrometer (EDS) for elemental analysis.

For transmission electron microscopy (TEM), particles on the filters (stored in anoxic jars until analysis) were resuspended in deoxygenated ultrapure water using a vortex mixer in an anoxic glove-box ( $<2$  ppm  $\text{O}_2$ ). A drop of particle suspension was deposited onto a holey carbon Cu TEM grid and left to dry at room temperature under anoxic conditions. Using an anoxic transfer chamber the TEM grids were loaded and imaged with a FEI CM200 TEM equipped with a field-emission gun operated at an acceleration voltage of 200 kV. Selected area electron diffraction (SAED) patterns were obtained with the smallest selected-area aperture available (180 nm  $\varnothing$ ). The camera length used for d-spacing calculations was 23.9 mm. The exposure times of the films were typically 20 s with the beam-blocker and 0.2 s without the beam-blocker. The distances in millimeters (from the center to individual rings) were measured directly on the photographic negative exposed during the diffraction recording. The radius of each ring/dot was then normalized to the camera length in order to obtain the d-spacing. Energy dispersive X-ray spectroscopy (EDS) analyses were performed on particles using a UTW ISIS analyzer (Oxford Instruments, United Kingdom).

Synchrotron X-ray spectroscopic analyses of particulates were performed at the Advanced Photon Source (APS) at Argonne National Laboratory (Illinois).  $\mu\text{XRF}$  fluorescence ( $\mu\text{XRF}$ ) maps and  $\mu\text{XRD}$  patterns were collected on beamline 20-BM-B (PNC-CAT). Filters were subsampled, mounted particle-side down on Kapton<sup>®</sup> film and sealed in Kapton<sup>®</sup> tape under an  $\text{N}_2$  atmosphere. The filter sample was mounted in a vertical plastic sample holder oriented at  $45^\circ$  to the beam in the horizontal plane. The incident X-ray beam was focused using a pair of Kirkpatrick-Baez mirrors, and a monochromatic incident beam was achieved using a Si(111) double crystal monochromator.  $\mu\text{XRF}$  elemental maps were collected with monochromatic incident X-rays (Si(111)) tuned to 14,000 eV ( $\lambda = 0.88550$  Å) and focused to a spot size of  $5 \times 5$   $\mu\text{m}$ . The sample was rastered through the focussed X-ray beam in 5  $\mu\text{m}$  steps with a count time of 1 s per step. The emitted fluorescence X-rays (Fe  $\text{K}\alpha$ , Ni  $\text{K}\alpha$ ) were collected simultaneously with a 13 element Germanium detector (Canberra). On selected areas of the  $\mu\text{XRF}$  maps, where Fe fluorescence counts were high,  $\mu\text{XRD}$  patterns were collected onto an image plate in transmission geometry with the incident X-ray beam energy tuned to 14,000 eV. The resulting 2D images were processed in the computer program, FIT2D, to produce 1D diffraction patterns for peak identification. Raw fluorescence intensity counts for Fe and Ni were calibrated to moles by integrating the raw intensity counts, less the average blank, in a given area and dividing by the concentration of Fe or Ni per given filter area as determined by total digestions.

## SATURATION STATE CALCULATIONS

Saturation indices were calculated for the relevant mineral and amorphous species as:

$$SI = -\log \frac{IAP}{K_{sp}}$$

where IAP is the ion activity product for the relevant mineral phase and  $K_{sp}$  is its corresponding solubility product. Saturation indices greater than 0 indicate supersaturation, whereas those less than 0 indicate undersaturation with respect to a given mineral phase. Solubility products for magnetite and siderite were gleaned from the MINTEQA database, those for green rust 1 ( $\text{CO}_3^{2-}$ ) were obtained from Drissi et al. (1995), and amorphous FeS from Theberge and Luther (1997). The redox potential (pe) of Lake Matano waters was calculated from the Fe(II)/Fe(III) couple relative to the solubility product of amorphous  $\text{Fe}(\text{OH})_3$  using measured concentrations of  $\text{Fe}(\text{II})_{\text{aq}}$ .

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**Table DR1. Ni data used to calculate distribution coefficients ( $K_D$ ).**

Depth (m)	Particulate Ni/Fe (0.5 N HCl)	Ni <sub>aq</sub> (nM)	$K_D$
118.5	0.02	31	$6.45 \times 10^{-4}$
129	0.09	50	$1.8 \times 10^{-3}$

**Table DR2. Water column iron speciation results (% of Fe<sub>HR</sub>).**

Depth (m)	Fe(II) <sub>red</sub>	Fe(III) <sub>HFO</sub>	Fe <sub>ox</sub>	Fe <sub>mag</sub>
117	2.4	60.3	31.6	5.7
118.5	0.9	61.1	30.9	7.1
120.5	36.0	26.5	31.4	6.1
122.5	35.1	18.5	39.3	7.1
124.5	43.2	6.2	40.9	9.7
129	62.7	5.9	24.4	7.0
131	54.8	6.4	30.6	8.2