Characterization of Nano-crystalline Fe in basaltic soils

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We used room temperature (RT, 22°C) and liquid helium temperature (LHeT, 4.2 K) ^{57}Fe Mössbauer (MB) spectroscopy, X-ray diffraction and selective chemical extractions to characterize the nano-crystalline Fe components of basaltic soils in the Hawaiian islands. We analyzed soils from surface and subsurface horizons along age and climate gradients ranging from 0.3 to 4, 100 ka and 1, 800 to 4, 000 mm mean annual precipitation. The Mössbauer quadrapole splitting (QSDs) and hyperfine field (HFDs) distributions were compared with those of nano and microcrystalline hematite, goethite, ferrihydrite and lepidocrocite standards.

Where present, bulk high-crystallinity goethite and hematite can be clearly identified from their XRD patterns and are also observed in the MB spectra. Here we focus instead on nano-crystalline phases that are difficult to discern in the X-ray difractograms. These phases are readily resolved in LHeT Mössbauer spectra when they magnetically order and exhibit hyperfine field parameters consistent with microcrystalline hematite, and admixtures of nano-goethite, lepidocrocite and ferrihydrite in varying proportions across the age and climate gradients. In general, the nano-crystalline Fe phases observed in these soils exhibit lower hyperfine fields (Bhf) and greater line-broadening (reported as the standard deviation of the hyperfine field, σ_{HFD}) than synthetic standards, suggesting even lower-crystallinity likely arising from substitutional or other defects and from nanometric particle or coherent-region sizes.

Comparison of spectroscopic data with standard selective chemical extractions also yields interesting results. The abundance of acid-ammonium oxalate (AAO) extractable Fe correlated well with the amount of the most disordered end-member nano-crystalline Fe phase in the MBS. However, there was no correlation between Na-pyrophosphate (Na-Pyro) extractable Fe and the portion of the MB spectra in which organically-complexed Fe should be resolved. Thus, the Na-Pyro extract generally overpredicted the amount of Fe complexed by organic matter at the molecular scale. Instead, our MBS results suggest Fe extracted by Na-pyro from these soils is primarily present as nanoscale Fe-(oxyhydr)oxides rather than monomeric Fe organic complexes.

Sulfur cycling in an Early to Middle Ordovician greenhouse climate

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The Ordovician represents a time of pronounced increase in biodiversification as well as a drastic shift from global greenhouse to icehouse climates. Since carbon and sulfur isotopes are recorded via C_{org} burial, bacterial sulfate reduction (BSR) and pyrite burial, reconstructing marine C and S chemostratigraphic profiles from the Early to Mid-Ord can help constrain changes in the marine environment preceeding and during these events. Here, we present $\delta^{13}C_{carb}$ and $\delta^{34}S_{CAS}$ profiles for Early to Mid-Ord carbonates in the Argentine Precordillera, La Silla (LSF), San Juan (SJF), Gualcamayo (GF), Las Chacritas and Aguaditas Fms (AF) and Western Newfoundland, Table Head Gp (THG).

$\delta^{13}C_{carb}$ profiles are in good agreement with published global and regional $\delta^{13}C$ curves that show relatively stable isotopic compositions commonly associated with greenhouse climates [1, 2]. $\delta^{34}S_{CAS}$ profiles show short-term variation (6‰ over 10-30m) superimposed over longer-term variation (9‰ over 100m). Longer-term $\delta^{34}S$ variation is sympathetic to changes in $\delta^{13}C$, where $\delta^{34}S$ enrichment corresponds to $\delta^{13}C$ enrichment, indicating long-term changes in the burial of pyrite and C_{org}. Similarity in duration and magnitude of short-term $\delta^{34}S$ variation in lithologically homogeneous (THG) and heterogeneous (LSF, SJF) sections suggests $\delta^{34}S$ represents an oceanographic signal. Changes in the extent of BSR and S-reoxidation are related to C_{org} availabilty, reactive Fe, and the extent of bottom-water oxygenation. C_{org} and reactive Fe concentrations in the AF, GF and THG indicate both were abundant and, thus, non-limiting for BSR. Short-term $\delta^{34}S$ variation likely reflects a dynamic marine oxycline, which would affect the extent of oxygenated marine substrate and the balance of pyrite burial and S-reoxidation. The preservation of short-term changes in the overlying, well-mixed water column suggests overall low marine SO_4 concentrations, that are similar to or smaller than those estimated by [3]. In support of this observation, the deep-water AF records average $\delta^{34}S$ values that are depleted 6‰ relative to shallower-water strata of the SJF, suggesting limited delivery of SO_4 to deep water and reduced $\Delta^{34}S_{CAS-PY}$ under SO_4-limited conditions.

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