

Fe reduction and atom exchange rates during redox oscillation of Luquillo CZO forest soils

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The fate and bioavailability of carbon in soil undergoing frequent shifts in redox status are tightly coupled to iron cycling. We examined the influence of dynamic redox conditions on soils from the Bisley Site of the Luquillo Critical Zone Observatory in Puerto Rico. These soils contained ~2 g kg⁻¹ C and ~62 g kg⁻¹ Fe that resides predominately in a nano-crystalline Fe^{III} oxyhydroxide phase with an ⁵⁷Fe Mössbauer spectra most similar to nano-goethite. We conducted eight-week incubations of triplicate soil slurries subjected to 0 - 21% O₂ redox oscillations with a ratio of time under oxic to anoxic conditions of 1:6 at three frequencies (3.5-d, 7-d, and 14-d). HCl-extractable Fe^{II} was reduced to less than 30 mmol kg⁻¹ soil during all oxic cycles and increased to >140 mmol kg⁻¹ soil and included a significant contribution from Fe²⁺_(aq) during the reducing cycles. As the experiment progressed, the rate of Fe reduction increased, and the Fe^{II} concentration reached a plateau of ca. 160 mmol kg⁻¹ during each reducing cycle. This coincides with the amount of Fe extractable by citrate-ascorbate and the portion of Fe^{III} that magnetically orders between 77K and 13K in the Mössbauer spectra. By the end of the experiment newly precipitated Fe could be re-reduced in less than three days. Synthesis of this experimental data within our preliminary numerical model suggests temporal dynamics of Fe(II) can be explained by minor increases in the population of Fe reducers accompanied by progressive reductive dissolution of recalcitrant Fe(III) solid phases. To further constrain the rapid turnover of iron oxides, we probed the susceptibility of soil Fe phases toward Fe^{II}-facilitated atom exchange using isotopically-labeled Fe²⁺_(aq) coupled with a numerical model. We found that aqueous Fe atoms can be exchanged with both the labile (0.5 M HCl-extractable) and bulk (7M HCl-extractable) Fe pools, with turnover times on the order of hours and months, respectively.

Quadrupolar corrections and increased accuracy for non-bridging oxygen measurements in silicate glasses using ¹⁷O NMR

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Abstract

Oxygen-17 nuclear magnetic resonance (NMR) has been used to investigate glass and melt structure, providing useful insights. In particular, ¹⁷O NMR is being used to measure the non-bridging oxygen (NBO) content as a way to test structural models in a wide variety of glasses, especially metaluminous aluminosilicate glasses where NBO are present. Because of the importance of accurate measurements in these areas, we have synthesized a crystalline barium silicate, BaSiO₃, and a barium silicate glass, (BaO)_{0.43}(SiO₂)_{0.57}, in order to test the accuracy of this technique. These samples were chosen for the resolution between the NBO and BO components of the spectra, to reduce the sources of error introduced by overlapping. For the BaSiO₃, correcting the observed intensities for the quadrupolar effects as in Massiot et al., 1990¹, we measure an NBO content of 67.6% versus the known value of 67.7%. Applying the same correction technique to the glass gives a measured NBO content of 58.4% ± 0.7% versus the 55.5% ± 1.6% expected from stoichiometry (based on EMPA analysis). Comparison with the frequently used technique of sideband subtraction shows that this method offers a simple and robust correction, especially in glasses where estimates must be made for the asymmetry and average quadrupolar values. By improving our knowledge of the accuracy of this technique, we should be able to provide new insight into questions such as the presence of absence of measurable amounts of free oxide ions or oxygen triclusters in both simple silicate and more complex aluminosilicate glasses.

[1] Massiot et al. (1990) Journal of Magnetic Resonance **90** 231-232