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Reduction of Copper by Structural Fe(II) in Clay Minerals under Reducing Environments

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Previous studies have investigated the redox properties of structural iron in clay minerals, reporting standard redox potentials (Eh0) ranging from -0.17 to +0.02 V vs. SHE [1]. Given that the Eh0 for Cu^{2+} reduction is approximately +0.2 V vs. SHE, structural Fe(II) is thermodynamically capable of reducing Cu^{2+}. While the reduction of Cu^{2+} by aqueous iron or iron oxides has been extensively studied[2][3], its interaction with structural iron in clay minerals remains less explored.

In natural geological settings, divalent copper ions (Cu^{2+}), leached by meteoric water and surface oxidation, infiltrate deeper into the subsurface. As depth increases, the environment becomes strongly reducing with severely restricted oxygen availability. Here, these ions encounter clay minerals containing structural iron in its reduced state. Because clay mineral surfaces carry a negative charge, Cu^{2+} can be readily adsorbed onto them, leading to the expectation that structural ferrous iron in clay minerals could reduce Cu^{2+} to Cu^{+}. In this study, we conducted a series of experiments using absorption photometry and X-ray absorption fine structure (XAFS) spectroscopy to investigate this reduction process.

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[3] White, A. F., & Peterson, M. L. (1996). *Geochimica et Cosmochimica Acta, 60*(20), 3799–3814.