Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.16428

Effect of the crystallochemistry on (bio)weathering of Fe-rich clays: an experimental study using model system

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Clay minerals are ubiquitous in the environment and one of the most reactive solid phases which control the availability of metallic elements such as iron. The weathering process of clay minerals in natural environment depends on (bio)physicochemical conditions and crystallographic properties[1] of minerals. However, understanding the crystallochemistry effects on bio-weathering processes remain challenging due to the high heterogeneity of natural samples. The objective of this study was to examine the mobilization of iron from two different Fe-rich clays, by bacteria (*Pseudomonas* sp. and *Mycolicibacterium* sp.). Synthetic clays were used to overcome the complexity of natural samples, distinguishing by the chemistry and the location of isomorphic substitutions: $Si_{6.86}Fe^{3+}_{1.14})(Fe^{3+}_{4})O_{20}(OH)_4Na_{1.14}$, $(Si_{7.4}Fe^{3+}_{0.6})(Fe^{3+}_{3.4}Mg_{0.6})O_{20}(OH)_4Na_{1.2}$.

To avoid aggregation, synthetic Fe-rich clays (<100 nm) were embedded in a porous silica gel[2] and submitted to controlled biotic and abiotic conditions on a pH range from 2 to 6. All experiments were conducted under aerobic condition, at 20°C under stirring for 9-days with regular monitoring of bacterial growth, pH, and solubilized iron concentration (< 0.2 µm). At the end of incubation, the silica gel was treated with hydroxylamine to evaluate the amount of iron precipitated or adsorbed onto mineral surfaces, which represents potentially available Fe. The results demonstrate that regardless of the crystallochemistry of studied clays, the acidification, and the presence of organic exudates in growth medium were observed in biotic incubations. For both clays, the release of iron was systematically higher in the presence of bacteria compared to the abiotic condition at similar pH values. It indicates that iron complexation by bacterial exudates, in addition to acidification, significantly operated in Fe solubilization. However, the amount of iron solubilized by hydroxylamine depended mainly on the medium acidity suggesting that bacterially produced exudates did not impact the precipitation/adsorption of Fe. Overall, the intensity of minerals bio-weathering varied depending on the clays/bacteria pairs tested, meaning that the mobilization of iron depended on the crystallochemistry of the mineral as well as the specific microbial activity associated with this mineral.

[1] Grybos, Masson, Gorgeon et al. (2022), *Minerals 12*(7), 812.

[2] Parrello, Zegeye, Mustin et al. (2016), *Frontiers in microbiology* 7, 423.