Goldschmidt 2022 Abstract
https://doi.org/10.46427/gold2022.10186

Evidence of the Impact of Substitutions in Goethite on Rare Earth Element Adsorption

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Since the 1980's the uses, and thus mining, of Rare Earth Elements (REE) have grown exponentially. This has led to questions about the impact of REE on the environment, and REE being designated emerging pollutants. Currently, knowledge about the behaviour of REE in the environment is still incomplete. For example, there are few studies on REE adsorption on iron (Fe) (oxy)hydroxides, which are considered key carriers of metal pollution, and on the other factors controlling this adsorption [1-4]. Knowing that in natural (oxy)hydroxides, Fe is frequently substituted by other elements in the environment in which they form, we were interested in the effect of these substitutions on the adsorption capacity of (oxy)hydroxides towards REE.

This study focusses on aluminium (Al, common in natural environments and easily substituted into Fe-oxyhydroxides) and gallium (Ga, chemical analogue to Al) substitutions in goethite (Goe), representative of commonly found Fe-(oxy)hydroxides whose well-defined structure allows for modelling of sorption and surface interactions. For this purpose, experiments of REE were conducted on pure and substituted goethites (Goe) with varying Al and Ga content.

A characterisation of these goethites, shows that the substitution does not affect the shape, size, and specific surface area significantly. Nevertheless, the REE adsorption patterns are affected by substitutions: 5% substitution decreases the sorption capacity of the goethite, and at 10% substitution the preferred adsorption of the mid and heavy REE diminishes, resulting in a 'flatter' pattern. Meanwhile, the Neodymium (Nd) L_3-edge EXAFS experiments show no modification of its binding mode to the Goe surfaces, forming corner sharing bidentate-binuclear complexes regardless of the substitution rate. However, TEM observations and Cerium (Ce) L_3-edge XANES experiments demonstrate that the Ga substitution favours a higher $Ce(IV)O_2$ adsorption, while the Al substitution favours Ce(III) adsorption compared to the pure Goe.

These results reveal the large impact of substitutions on the reactivity of goethite towards REE.

References:

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