Evidence of the impact of substitutions in ferrihydrite on rare earth element adsorption

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Résumé

The use of Rare Earth Elements (REE) in energy technology and other sectors has rapidly increased in the last few decades, and more REE are mined every year. This has led to concerns about their impact on the environment, and their designation as an emerging pollutant.

One of the factors controlling the fate of REE in the environment is adsorption on metal hydroxides. In nature, ferrihydrite (Fh), amorphous iron hydroxide with a high adsorption capacity, is ubiquitous and known to commonly contain metal substitutions. Though REE adsorption on Fh has been studied for its pure form (1-3), there is no study on the influence of substitutions on this adsorption.

For this purpose, a series of ferrihydrites were synthesized with varying contents (0 to 100%) of aluminium (Al, omnipresent and easily substituted into iron hydroxides) as substitutes. Total REE and pure cerium (Ce) and neodymium (Nd) adsorption experiments were then performed.

The obtained REE patterns are all different. While the pure ferrihydrite is superimposable to the ones from previous studies (1-3), the aluminium substitution modify the pattern shape and the ferrihydrite sorption capacity: Al-substituted ferrihydrites adsorb less REE but show a strong increase in heavy REE enrichment as compared to pure ferrihydrite. We demonstrated that these modifications are due to modification of the ferrihydrite size and shape leading to modifications of the distribution of the binding sites.

Furthermore, when looking at the redox of Ce adsorbed to ferrihydrites, Ce(III) and Ce(IV) are both present, but the Ce(III)/Ce(IV) ratio increases with the increasing aluminium substitution rate. These results contradict the usually assumed importance of Fe(III) redox reactivity as the main driver of Ce(III) oxidation, as oxidation is enhanced with higher redox-inert Al(III) content. With these results we show how strong the commonly naturally occurring Al-substitution can affect the reactivity of ferrihydrite towards REE.

References:

**Mots-Clés:** REE adsorption, Al substitution, ferrihydrite, speciation