Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.19791

Evidence of the impact of Substitutions in Ferrihydrite on Rare Earth Element Adsorption

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The use of Rare Earth Elements (REE) in 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), and gallium (Ga, chemical analogue Al) as substitutes. Total REE and pure cerium (Ce) adsorption experiments were then performed.

The obtained REE patterns for pure end members (i.e. Fh, AlO(OH), and GaO(OH)) are all different. While the pure ferrihydrite is superimposable to the ones from previous studies [1-3], the aluminium and gallium substitution modify the pattern shape. Though gallium does not strongly affect the pattern shape, for the aluminium substitution there is a strong increase in Heavy REE enrichment with increasing aluminium content. This makes the pattern more closely resemble that of amorphous AlO(OH).

Furthermore, cerium adsorbed on the substituted ferrihydrite series exhibit variable Ce L_3-edge XANES spectra. While Ce(III) and Ce(IV) are both present, the Ce(III)/Ce(IV) ratio varies depending on the substituting metal, increasing with the aluminium substitution. 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 occurring Al-substitution can affect the reactivity of ferrihydrite towards REE in nature.

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