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Gallium Crystal Chemistry in Synthetic Goethites

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ABSTRACT

The distribution of Ga and Al atoms within the octahedral sheets of synthetic goethites has been investigated by XRD and Ga K-edge XANES and EXAFS spectroscopies. XRD results indicate a solid solution between goethite (αFeOOH) and GaGoe4 (40 mol% of Ga). The XANES data indicate the presence of ^{67}Ga in the solid solution. The fitting procedures for EXAFS spectra show no evidence of preferential octahedral site substitutions for Ga.

1. INTRODUCTION

It is well known that gallium and aluminium should present a similar behaviour (Ga extraction from bauxites). Hieronymus *et al.* (1990) [1] showed that in case of classical ferralitic alteration, Al and Ga are strongly bound and present a positive correlation. But this correlation is reversed when additional leaching of Al and/or Fe are superimposed and a positive correlation between Ga and Fe is noted, with a Ga retention or mobilisation by iron oxides and hydroxides. The difference between the ionic radii of Ga and Fe is much smaller (0.61 vs 0.63 Å) than between Fe and Al (0.53 Å), so that a similar change in the unit cell parameters will also be expected. Goethite has a great potential for isomorphic substitution of Fe by other metals like Al, Cd, Co, Cu, Ge, Mn, Ni, Pb, Ti, V and Zn [2, 3]. In particular, substitutions of Fe by Mn, Cd, Co, Cr, Cu, Ni, Pb, and Zn have been well established using X-ray diffraction data, chemical and DTA-DGA analyses, infrared and Mössbauer spectroscopies [4, 5]. The aim of the present study was to synthesize goethites in presence of Ga in order to evidence the incorporation of Ga into the goethite structure. The understanding of substitution mechanisms should permit to investigate laterite development for the revalorisation of Al (-Fe) ore deposits.

2. RESULTS

2.1 XRD

Sample	Start mol %Ga	a in Å	b in Å	c in Å	%Occ. Fe	MCD a	MCD b	MCD c	cell volume	XRD mol %Ga
GaOOH	100	4.516	9.779	2.966					130.98	
GaGoe4	38.00	4.586	9.883	3.008	0.471	271	397	438	136.33	40
GaGoe3	20.00	4.601	9.910	3.015	0.450	293	442	511	137.47	25
GaGoe2	8.00	4.614	9.934	3.021	0.427	152	259	293	138.47	10
Goethite	0	4.605	9.952	3.020					138.40	

Table 1 : XRD results MCD : Mean coherent domain (Å).

XRD results obtained using Rietveld refinement, indicate a replacement of Fe^{3+} (0.63 Å) by Ga^{3+} (0.61 Å), inducing a decreases of the unit cell volume (Tab. 1) that is unambiguously observed by a decreasing of a, b, and c cell parameters. These results presenting a linearly constant evolution between the two end-members (Goethite and GaOOH) can be explained by assuming Fe/Ga substitutions as well as Fe/Al substitutions [7]. However chemistry of start products with Ga amount ranging from 45 to 95 mol % gives a mixing of two phases : Goethite and GaOOH. Similar observations have been noted in the Fe/Al system [5]. Nevertheless, a solid solution was obtained between goethite and GaGoe4 (40 mol% of Ga).

2.2 XANES and EXAFS data

The experiments were run at the French synchrotron facility (LURE, Orsay), on the D44 station. The DCI storage ring was operated at 1.85 GeV and 200 mA. A Si (311) double-crystal was used to monochromatize the X-ray beam. The XANES and EXAFS spectra at the Ga-K edge were collected in transmission mode at room temperature with energy steps of 1 eV and 2 eV respectively. Spectra were calibrated with respect to metallic Ga.

The Ga K-edge XANES spectra (Fig. 1) of the products have been compared to 4 and 6 coordination number spectra and indicate the presence of ^{67}Ga in GaGoe4 suggesting that the individual Ga-O distances are similar.

The radial distribution functions (Fig. 2) show constant distances for the first and two neighboring contributions. The first peak of the Fourier transforms of the Ga-series corresponds to 6 oxygen atoms at 2.00 Å. This distance of the first Ga-neighbors is similar for all the Ga-products. The fit of the second peak, relative to the Fe-Ga and Fe-Fe pairs, is consistent

with the chemical Fe/Ga ratio. The fitting procedures show no evidence of preferential 2E (edge sharing), or/and 2E' (edge sharing) + 4 DC (double corner sharing) site substitutions.

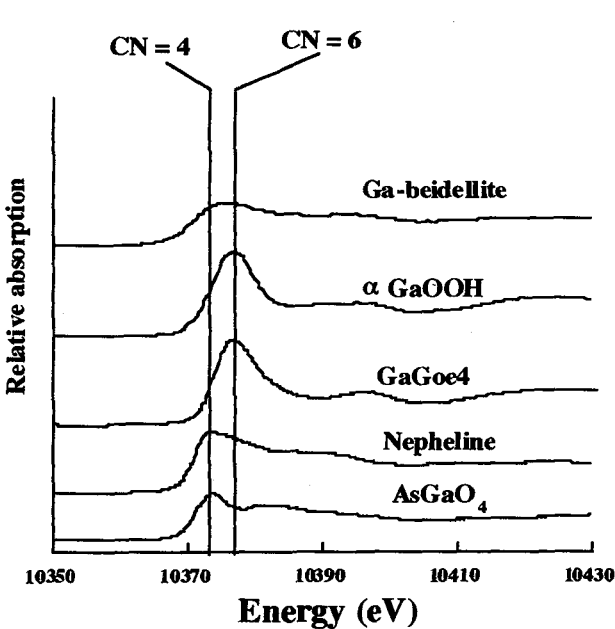


Fig. 1 : XANES spectra at the Ga K-edge

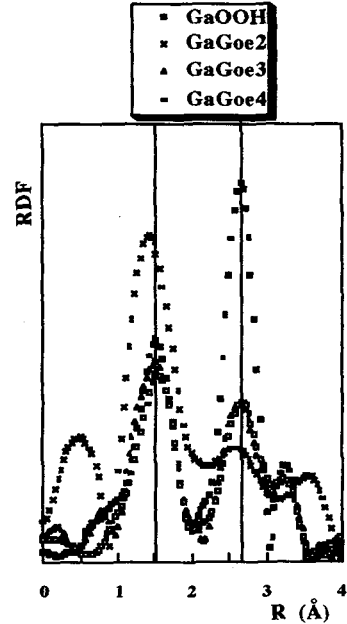


Fig. 2 : Peaks of the first and second atomic pairs.

3. CONCLUSION

Firstly we observed a similarity between the Al/Fe [5,6,7] and Ga/Fe mechanisms of substitutions, according to our XRD, XANES and EXAFS data analyses. Secondly in regard to XAFS results no Ga segregation clearly appeared. This indicates a weak Ga-Fe affinity in lateritic weathering profiles and could permit a potential revalorisation of Al ore deposits due to the economical interest of Ga in high technology.

4. REFERENCES

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