

RIETVELD STUDIES OF THE ALUMINIUM-IRON SUBSTITUTION IN SYNTHETIC GOETHITE

J.-L. Hazemann (a), J.-F. Bézar (b) and A. Manceau (a)

(a) Lab. Mineral. Cristal. (UA 09 CNRS), Université Paris 6-7, F-75252 Paris, France

(b) CPS (UA 453 CNRS), Ecole Centrale, F-92295 Chatenay, France and
LURE, Université Paris Sud, F-91400 Orsay, France

ABSTRACT

The substitution of iron by aluminium plays an important role in geological processes. A solid solution domain exists between the two isomorphous crystals goethite, FeOOH , and diasporé, AlOOH : 33% of iron can be substituted by aluminium in goethite.

A set of synthetic minerals have been prepared with Al/Fe ratio up to 33%. They have been characterized by x-ray powder diffraction and compared to other samples, either synthetic or natural.

Studied samples are monophasic. The variation of lattice parameters or atomic coordinates proves that the substitution mechanism does not obey a Vegard law. Moreover these results are strongly dependent on the synthesis condition.

INTRODUCTION.

Iron and Aluminium oxihydroxides are very common on earth surface. Ionic radii of Fe^{3+} and Al^{3+} are similar, the α , β , γ phases of FeOOH and AlOOH have isomorphous structure, this allows substitution in these minerals. Such mixed phase occurs in aluminium substituted goethite $\alpha\text{-Fe}_x\text{Al}_{1-x}\text{OOH}$ which are commonly encountered in bauxitic ores and soils.

The study of the structure of synthetic samples is necessary to understand the natural ones and the process of their genesis. A short range order analysis using polarized EXAFS has recently been achieved, hematite-like clusters can be observed in diasporé [1]. A similar demixion might occur in goethite, a study of Al substituted goethite has been started by EXAFS and X-ray powder diffraction. The aim of this paper is to report first structural results obtained on both synthetic and natural samples by Rietveld analysis.

EXPERIMENTAL.

Three series of synthetic samples have been investigated. The first set has been synthesized from FeSO_4 solution at 40°C [2], 8 samples, G_xAl , covering the whole solid solution domain have been prepared, their Al/Fe ratio x are in the range 0 to 33%.

Two other sets of synthetic samples have been studied, they were prepared in a ferric solution by Schwertmann [3]. Their Al/Fe ratio is in the range 0 to 17% for the set ($\text{G}_{50}/0$ - $\text{G}_{50}/6$) prepared at 25°C and 0 to 8% for the set ($\text{G}_{40}/0$ - $\text{G}_{40}/6$) prepared at 70°C.

Three natural monophasic samples have also been investigated.

The diffraction pattern have been recorded with Cu K α radiation (Phillips PW 1729 generator and PW1120/90 goniometer, 2 sets of 1° Sollers slits, 0.2mm receiving slit and graphite analyser). The data have been collected up to 140°2 θ , the step value was chosen at 0.04°2 θ , corresponding to 6 points above the half height of well separated line. 3216 points have been recorded with a time of 15 seconds to get valuable data at high angles. We have used the XND Rieveld program which was first designed for analysing real-time experiments [4]. This program uses Voigt line profile in order to allow convolution of various broadening factors. Preferred orientation functions use spherical harmonics. The sample dependent function in the line profile can also be expanded on spherical harmonics to take into account the various crystalline shapes. This was necessary with our samples in which some crystallites are platelets or needles. ESD given here are the classical Rietveld ESDs's, to take into account local correlation a magnification factor of 2 has to be use [5]. Indicated values of R_{Bragg} are background corrected, they correspond to 270 non-zero I_{hkl} .

RESULTS.

All the pattern have been refined, the results well agree with model consisting of only one crystallized phase which is a goethite-like crystal in which aluminium ion is included.

For all the sample, preferred orientation functions has to be taken into account., it agrees with goethite needles along c laying in the plane of the sample, this orientation effect decreases with the substitution. The refinements quality are similar for all synthetic samples (R_{wp} =7-14%, R_{p} =6-10%, GoF =1.3-2.5, R_{Bragg} =8-14%) and higher with natural samples (R_{wp} =13-16%, R_{p} =9-11%, GoF =3.0-3.5, R_{Bragg} =12-15%). To improved them, as significative data can be seen at high angles, an attempt to refine anisotropic thermal factors has been made : the refinement index have been improved, the parameters were not really modified but the anisotropic values obtained were without physical meaning. So the results are given with isotropic thermal factors.

A typical plot is given in fig[1]. The agreement between observed and calculated curve is good, the complex drawing observed at high angles is well taken into account in the model which have been used.

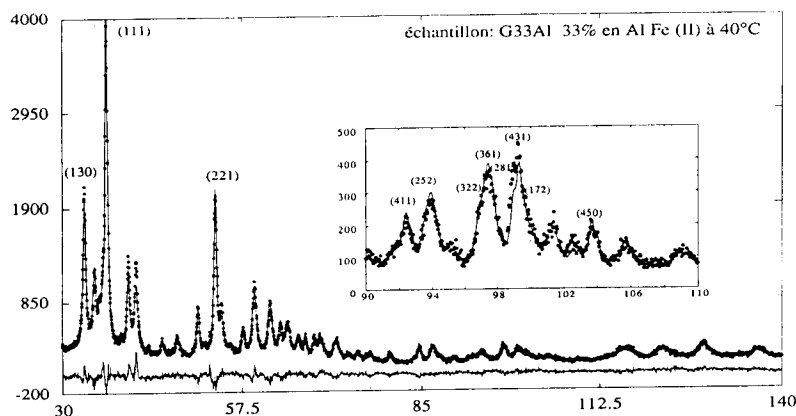


Fig. 1 : Observed and calculated plot of the sample G33AL.

NON SUBSTITUED GOETHITE AND DIASPORE.

Both crystallized in $Pbnm$ space group, with atoms Me (Al, Fe), O_1 and O_2 in the mirror. The cell contains 4 groups $MeO_1(O_2H)$. This structure can be described as a hexagonal compact lattice made by the oxygen atoms O_1 and O_2 , this lattice being slightly distorted along (0,0,1). Half of the octahedral sites are filled with metal ions, the others appear as vacancies (fig. 2).

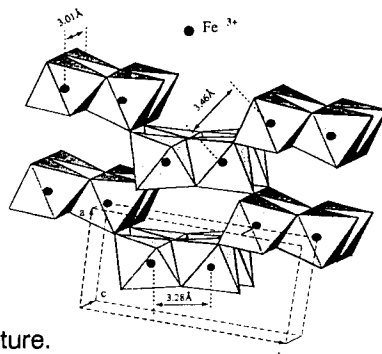


Fig. 2 : The goethite structure.

Structural results concerning non-substituted sample are compared in table 1. No difference can be noticed between our refinement of natural diaspoire and those previously reported on ALOOD [6], 4 kinds of distances between aluminium and oxygen are observed ($Al-O_1$: 1.86, 1.92Å, $Al-O_2$: 2.00, 2.089Å). On the contrary small differences can be noticed between our synthetic samples and with FeOOD [7, 8], but in all cases they are characterized by only two kinds of distances between iron and oxygen ($Fe-O_1$: 1.94Å, $Fe-O_2$: 2.09Å). This coordination difference between diaspoire and goethite plays an important rule in the substitution mechanism.

Sample	a(Å)	b(Å)	c(Å)	x(Me)	y(Me)	x(O_1)	y(O_1)	x(O_2)	y(O_2)
G50/0	4.6188	9.9528	3.0236	0.0466	-0.1448	0.714	0.2006	0.192	0.0517
G40/0	4.6158	9.9545	3.0233	0.0479	-0.1458	0.708	0.1988	0.197	0.0527
G00Al	4.6048	9.9595	3.0230	0.0477	-0.1461	0.708	0.1996	0.204	0.0531
AlOOH	4.4031	9.4252	2.8452	0.0450	-0.1451	0.713	0.1990	0.200	0.0537

Table 1 : Cell parameters and atomic positions of pure sample, (ESD are on last digit).

LATTICE PARAMETERS OF SUBSTITUED SAMPLES.

Lattice parameters obtained in the Rietveld refinement of the various sample are drawn on fig. 3 in comparison with a line representing the Vegard law. Samples prepared using ferrous iron are characterized by a constant a parameter, b and c are decreasing but with a slower rate than in the Vegard law. On the contrary for ferric samples, b and c variation agrees with the Vegard law, the a variation seems also in agreement for the high temperature prepared sample and has a intermediate behaviour for the samples prepared at lower temperature.

Lattice parameters appears to depend not only on the substitution ratio but also on the history of the sample. This explains the results reported in earlier paper [9-12] which were not in agreement, it is not possible to calculate the substitution ratio as proposed by Thiel [9], but the knowledge of this ratio and the lattice parameters gives us some information on the sample synthesis. By example, the accidental pH variation which occurred in preparing ferrous sample G20Al has an obvious effect.

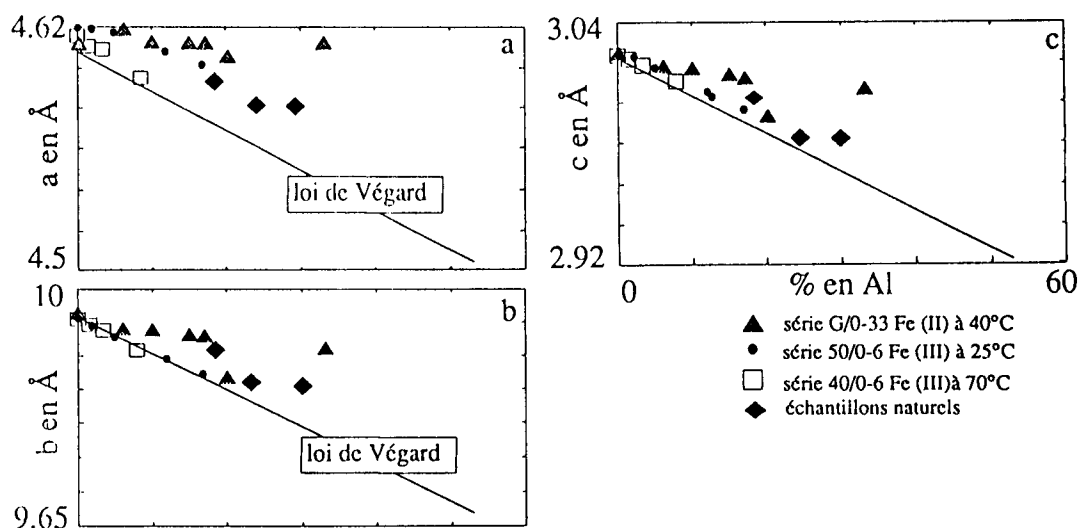


Fig. 3 : Lattice parameters versus Al/Fe ratio.

STRUCTURAL PARAMETERS.

The (x, y) atomic parameters of the 3 atoms have been refined. They do not obey to a linear law between the goethite and the diaspoire structure, the deviation is small but have a systematic character in each set of sample. This has to be related to the small (0-33%) solid solution domain observed in these compounds.

In order to understand the structural change with substitution ratio, we have calculated the most important atomic distances Me-O₁, Me-O₂, O₁-O₁ and O₂-O₂.

For sample prepared using ferrous salts, the metal-oxygen distances are splitted in four, that is as if the presence of few aluminium ions was breaking the regular octaedral symmetry, giving it a new bonding, which also differs from diaspoire, the shorter length being not the same. A similar behaviour can be observed in the ferric, low temperature samples. The behaviour of ferric, high temperature samples is not so obvious, but in this set the substitution ratio are smaller and a Vegard law is observed on lattice parameters.

A similar behaviour of the series is also observed on the distances between oxygen. The O₂-O₂ distance across vacancy is smaller than those deduced from a Vegard law. On the contrary, the other distances O₁-O₁ between chains or O₂-O₂ between octaedra (fig. 4) are bigger than the Vegard law ones. This behaviour is characteristic for the ferrous and the low temperature ferric series, and appears in the most substituted samples of the last set.

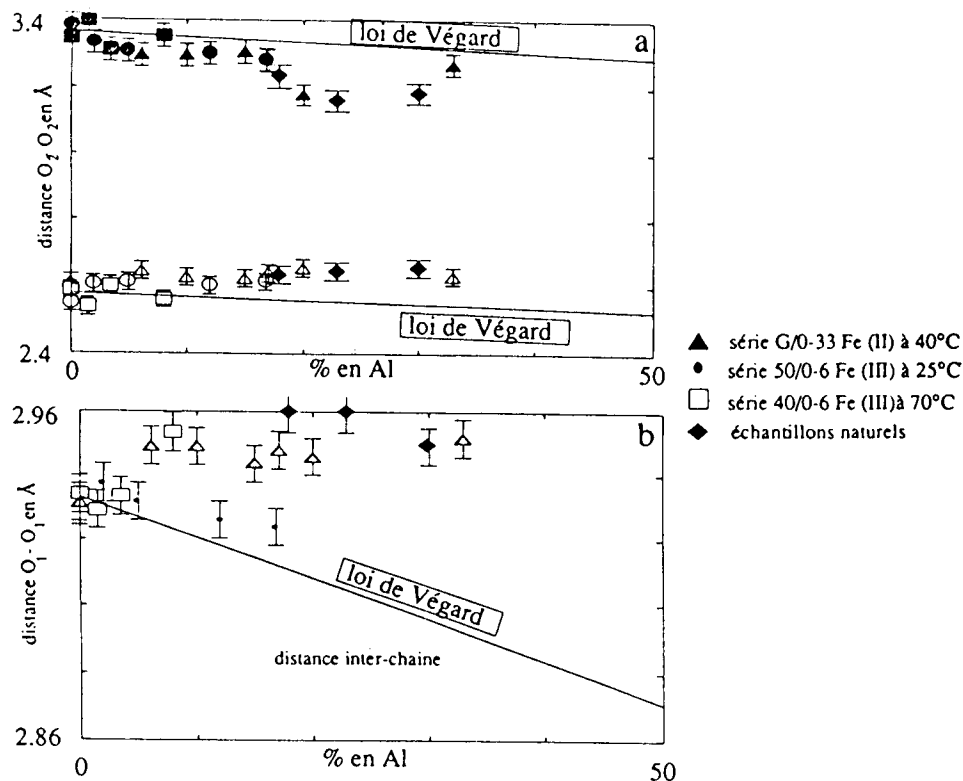


Fig.4 : Variation of oxygen-oxygen distances.

PROFILE ANALYSIS.

In all the pattern, we have recorded, the line profile depends on the sample quality, the instrumental broadening being weak. A strain/size analysis reveal that for the pure ferrous goethite both causes are equivalent. Increasing the substitution ratio, the size effect rise up in natural or ferrous goethite in which strains decrease (fig.5). On the contrary, the size effect decrease in ferric goethite. The G20Al samples, for which a pH accident occurred, exhibits here also an irregular behaviour revealing an high level of internal strains.

CONCLUSION.

For similar substitution ratio, the structure of substituted goethite strongly depends on the synthesis conditions. This is obvious in the a parameter, which can be constant for a large range of substitution in case of ferrous synthetis. With such a behaviour, far from a Vegard law, solid solution can only exists in restricted domains.

From a structural point of view, a solid solution is not observed, it looks like if a new structure with a more regular oxygen packing was existing, substituted ions needing more room. This lack of solid solution at lattice scale and the appearance of a new structure suggest that Al might not be randomly substituted for Fe in the goethite framework. First EXAFS results confirm this hypothesis and indicate that Al atoms tend to cluster along the single octahedral chains.

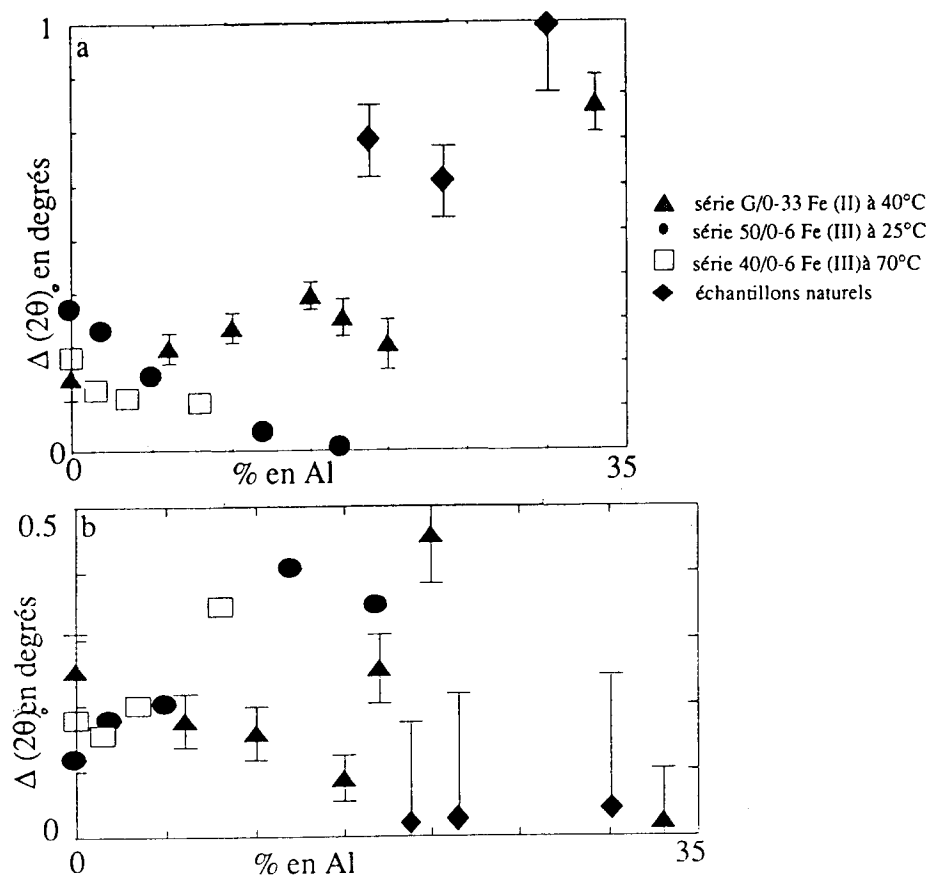


Fig. 5 : Angular widths due to size effect (a) and strains (b).

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