

VARIATION OF CRYSTALLINITY IN A TERTIARY IRONCRUST OF BELGIAN LORRAINE

BY

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SUMMARY. — An ironcrust of South-East Belgium has been studied by several techniques. The results show a great difference in crystallinity, explained as due to manganese substitution of iron in goethites.

RÉSUMÉ. — *Variation de cristallinité dans une induration ferrugineuse tertiaire de Lorraine belge.* — Une induration ferrugineuse du SE de la Belgique a été étudiée à l'aide de différentes techniques. Les résultats montrent de grandes différences dans la cristallinité, différences qui sont attribuées aux degrés de substitution du fer par le manganèse au sein de la goéthite.

SAMENVATTING. — *Variatie van kristalliniteit in de tertiaire ijzerhoudende verharding van Belgisch Lotharingen.* — Een ijzerhoudende verharding van Zuid-Oost België werd bestudeerd met behulp van verschillende technieken. De resultaten tonen grote verschillen aan in de kristalliniteit die toegeschreven worden aan de substitutiegraden van het ijzer door het mangaan in de goethiet.

1. Introduction

Preliminary results of a palaeomagnetic dating of a Tertiary ironcrust in South-East Belgium showed important differences in magnetic behaviour, which needed further investigation.

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The regional distribution and different outcrops of the ironcrust were studied by HUFTY (1959) and SOUCHEZ-LEMMENS (1968, 1971). Their conclusions were :

- The ironcrust is not a pedological horizon, but an absolute iron accumulation on a freatic watertable ;
- The climate during the genesis should be subtropical ;
- The accumulation occurred during the second half of the tertiary and the beginning of the quaternary ;
- The source of the iron is supposed to be regional (the overlaying clay formation) ;
- The ironcrusts are not related to geological surfaces, but to old erosion surfaces ;
- The main precipitate is iron oxyhydroxide (goethite).

In the region studied, Souchez-Lemmens discovered two main surfaces. The upper surface (the eldest, Tertiary) is 60 to 35 m above the lower one, the latter being locally rich in manganese. Due to granulometric effects of the parent material in which the iron precipitated, the crust has a different outlook showing scaley lamellous in fine grain sediments (e. g. Ethe clay, Caraxian), and very compact and hard iron sandstone in the sandy sediments (e. g. Stockem sands, Lotharingian). Those sands are nearly pure quartz.

2. Methods, Results and Discussion

2.1. *Field observations.*

The samples studied are from the outcrop in an old quarry NW of the small village of Châtillon (fig. 1). In the plateau of Châtillon, both levels of iron accumulation are observed. We studied only the sandy faces of the upper level.

In the profile, the ironcrust has very sharp boundaries. Horizontally, there is an important difference within the crust itself (fig. 2). Normally, the crust is a very hard iron sandstone, 7.5 YR 2/3 to 5 RP 2/5 (brownish black to purplish black). Here we took sample VA. In this compact sandstone, we find some nodule-shaped forms with ocher-sands, 3.75 YR 4/8 to 7.5 YR 6/8 (reddish brown to orange). These sands are still cemented, but can be easily broken down by hand. Out of these sands we took VB. In some parts of the outcrop, the iron crust becomes blackish sandy, softly cemented over the total thickness of the crust (up to 40 cm). The colour varied between 10 RP 2/2 and 5 YR 2/2 (very dark reddish brown to brownish black). This part is represented by sample VC.

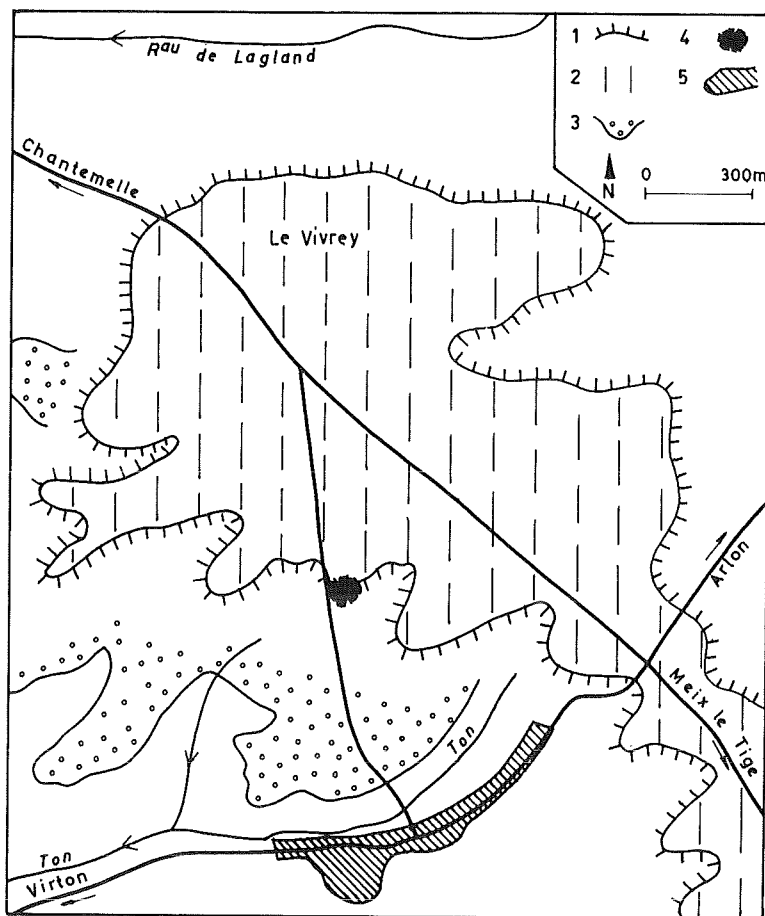


Fig. 1. — Localisation.

1. Border of the "plateau de Châtillon".
2. Ironcrust, upper level.
3. Ironcrust, lower level.
4. Quarry studied.
5. Châtillon-village.

2.2. X-Ray Diffraction.

The three samples were examined in a vacuum Guinier camera with $\text{CrK}\alpha$ rays for 30 min at 30 mA and 30 kV. All showed very clearly the quartz reflections. Samples VB and VC did not show any other clear

reflections above the background. Sample VA showed distinct goethite lines, which fitted the ASTM standard very well. Other experiments revealed goethite in the other samples.

Châtillon (CHA1)

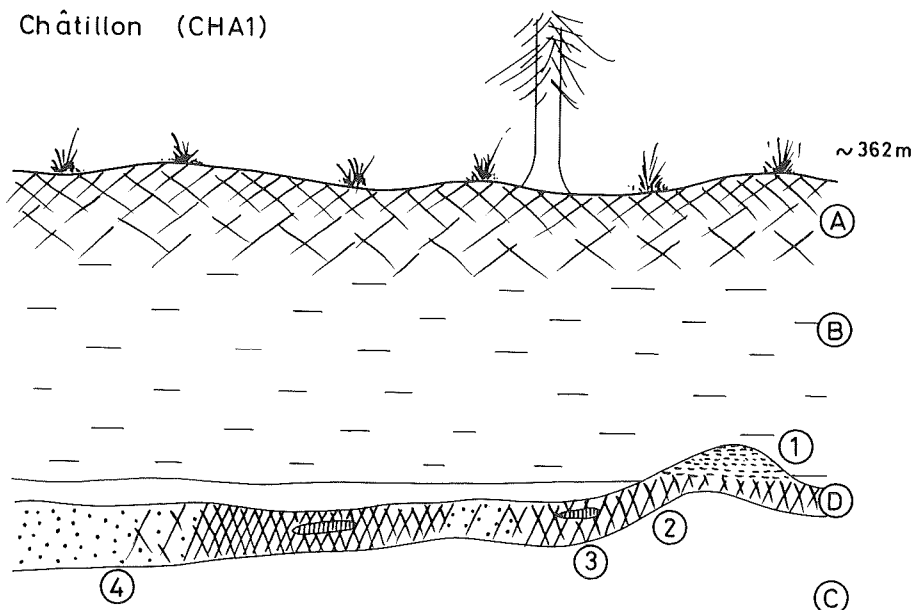


Fig. 2. — Profile.

- | | |
|-------------------------|--|
| A. Soil | 1. Scaley laminated. |
| B. Ethe clay (2 m) | 2. VA very hard compact ironsandstone. |
| C. Stockem sands (16 m) | 3. VB ocher (5 × 20 cm nodules). |
| D. Ironcrust (7-40 cm) | 4. VC black sands. |

2.3. Optical and Thermal analysis (DTA).

The powdered samples were studied optically by immersion in methylene iodide, which allows to estimate high refraction indices. DTA was performed with a BDL-apparatus, porcelain cups were used. The analysed sample was covered by Al_2O_3 to the same weight as the inert Al_2O_3 filled cup to minimize drift. Heating rate was $10^\circ/\text{min}$.

Sample A powder consists more than half of rather round grains up to 40 micrometer diameter with a reddish brown colour, very high relief non pleochroic and very high birefringence with typical undulatory extinction. These characteristics are for fibrous goethite. To the crushed quartz particles adheres some yellowish brown material, with lower refraction and isotropics.

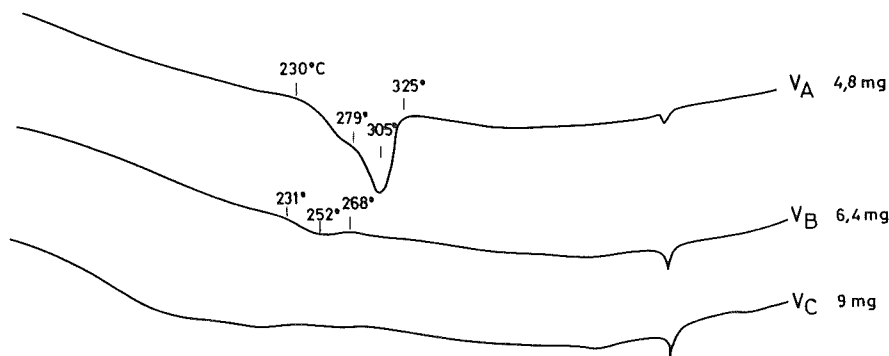


Fig. 3. — D.T.A. curves.

Heating rate 10° C/min.

The DTA shows, apart from a small quartz peak, only a complex endotherm between 230° and 325°. The peak value of the strong symmetric endotherm lies at 305°, while the form of the previous shoulder indicates a mixing with another fase peaking around 255°. In the absence of any γ - α Fe_2O_3 exotherm we must conclude the lack of lepidocrocite. The main endotherm corresponds then to well crystallized goethite. As for symmetrical peaks the peak temperature is not considerably diminished by our micro-apparatus, its low position must be ascribed to the small particle size of the fibrous crystallites. The shoulder phase represents most probably the less well or even not yet crystallized isotropic monohydrate.

Sample B powder shows besides the much more abundant, around 70%, crushed quartz grains two different iron phases. Most frequent are irregular agglomerates, brownish-yellow with a refraction around 1.9-2, non pleochroïc and isotropic. Petrografically we will follow the usage of DEER *et al.* to call them limonite. Around 5% of flaky grains, yellowish brown have a low refraction around 1.6 show first order birefringency oriented clay material.

The DTA curve shows more quartz and a weak endotherm between 231° and 268° culminating at 252°. It is clear that this is identical with the shoulderphase of sample A and is due to the amorphous "limonite".

The very weak and broad endotherm around 500° is due to dehydroxilation of the clay material which at this temperature should be illitic.

Sample C powder shows the quartz grains with thick firmly adhering black opaque coatings of a manganese mineral. To some grains adheres a brown film, sometimes detached in clear flakes brownish-yellow when very thin, reddish brown when thicker and which are strictly non pleochroïc.

Relief is moderate in methylene-iodide (1.9-2) and they are perfectly isotropic. Clear "limonite". The DTA curve shows not much apart the quartz peak. There is a faint indication of some clayey material which was not observed as such optically and may be present in the black manganese precipitate which is otherwise thermally inert. An extremely weak endothermal indication around 196° must represent the rare clear limonite films which certainly is a different phase from the 250°-limonite of the other samples.

2.4. *Electron microscopy.*

The electron microscope yields distinct images for the three samples (fig. 3 – the upper line at the base is about 10 µm). VA Shows a quartz grain with small platy particles and needles on it, up to 10 µm diameter. VB shows sub-rounded particles, diameter up to 1.5 µm. The well-rounded particles of VC have the same range of diameters.

2.5. *Chemical Analysis.*

Three partial dissolution techniques were used :

- Oxalate extraction (SCHWERTMANN 1964), pH = 3, 4 hours digestion time, UV-free ;
- Dithionite extraction (HOLMGREN 1967), ambient temperature, 16 hours ;
- HCl 8 N, 15 min boiling.

The aliquots were analysed colorimetrically.

Fe : O-phenanthroline

Mn : Potassiumpermanganate

Al : Eriochrome Cyanine R

Ti : Peroxide (no Ti was detected in the samples).

The results are presented in table 1.

The oxalate extraction is a very weak one for amorphous iron oxides (SCHWERTMANN 1964). Samples VA and VB have a small amount of extractable Fe. VC has a very high Fe-oxalate content. The Mn-content is very similar, so the Fe/Mn ratio is about 1 for the three samples.

Dithionite-extractable iron is believed to be the free iron. These aliquots show the highest Fe-content in VA, a little bit less in VB and even more less in VC. The Mn-content is analogous regarding the oxalate extraction (as expected). This brings the Fe/Mn ration to about 1.30 and 380 for VC, VB and VA. The oxalate/dithionite ratio for Fe is a good measurement for the amorphous fraction, and shows the higher content of amorphous Fe in VC.

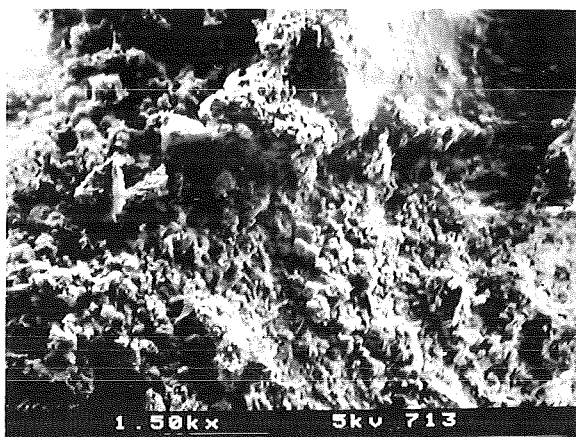
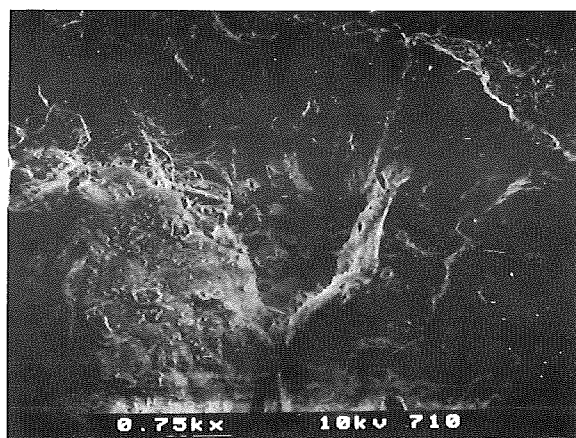


Fig. 4. — Electron microscope photographs of VA
VB
VC

Table 1
Chemical analyses

mg/g	oxalate		dithionite		HCl 8 N		
	Fe	Mn	Fe	Mn	Fe	Mn	Al
VA	1.12	.85	266.75	.71	266.88	.80	2.04
VB	1.84	1.29	41.10	1.48	44.0	1.35	4.20
VC	33.53	34.20	37.45	32.64	41.0	34.40	4.20
	Fe/Mn		Fe/Mn		Fe/Mn	Fe/Al	Mn/Al
VA	1.32		375.70		333.60	130.82	0.39
VB	1.43		27.77		32.59	10.48	0.32
VC	0.98		1.15		1.19	9.76	8.19
	oxal/dith (%)			dith/HCl (%)			
	Fe		Mn		Fe		Mn
VA	0.4		119.7		100.0		88.7
VB	4.5		87.2		93.4		109.6
VC	89.5		104.3		91.4		94.9

The third extraction (HCl 8 N) shows the total iron, which is nearly the same as the dithionite extracted Fe ; so the samples mainly have free iron oxides. Also the Mn-content is in the same range as for the other extractions. Here we also did an Al-determination. The slight difference in Al-content is remarkable. Samples with the same Al-content can be different for oxalate and dithionite extraction crystallinity. The Mn/Al ratio is the indicator for a good explanation. NORRISH & TAYLOR (1961) reported in their investigation on the substitution by Al in goethites a decrease of the particle size, which leads to a higher oxalate/dithionite ratio. Here we have an analogy, not due to Al, but caused by Mn.

2.6. Rock Magnetic Analysis.

Rock magnetic measurements, especially the Néel temperature found during stepwise thermal demagnetization experiments, confirmed the results of Mössbauer spectroscopy and D.T.A. as α -FeOOH being the dominant magnetic mineral present in the examined ironcrust. The observed remanent magnetization is, according to the origin of the goethite, a chemical remanent magnetization.

Goethite is antiferromagnetic (FORSYTH *et al.* 1968) with a c-axis spin orientation, and a Néel temperature ranging from 67° to 130°C but generally

at around 110°C as found by Mössbauer measurements. It commonly possesses an additional weak but variable ferromagnetism (STRANGWAY *et al.* 1968, HEDLEY 1971), which is highly anisotropic along the c-axis and which has a highly variable saturation value ranging from 10^{-3} to $1 \text{ G. cm}^3.\text{g}^{-1}$ (HEDLEY 1971).

Although the ferromagnetism may be due to the presence of impurities such as protohematite inclusions within the crystal lattice or in small grains because of unpaired spins, it is commonly regarded as due to spin unbalances in the two antiferromagnetic sublattices. This spin unbalance may be the result of lattice distortions caused by preferential location of imperfections such as vacancies or iron substitution like Si^{4+} or Al^{3+} (HEDLEY 1971).

The rock magnetic properties were measured not on the powder samples as in the other experiments but oriented cylindrical cores with a diameter of 2.5 cm and a length of about 2.2 cm. Three samples, VA = CHA1EO4, VB = CHA1EO2SO1 and VC = CHA1EO3SO2 were chosen on basis of their colour and cementation characteristics so that they were likely analogous with the powdered ones. The second sample is a little more black compared to the VB sample chosen for the other experiments. A great difference in structure sensitive magnetic properties such as the remanence, coercive force and weak magnetic field susceptibility was found between VA, VB and VC. The natural remanent magnetisation (N.R.M.), which was measured with a high sensitivity spinner magnetometer JR-4, is higher in VA than in VB and VC, and is also highly variable. The latter indicates that the N.R.M. is not a bulk property of goethite but must be attributed to spin unbalance or other magnetic phases present. The other analysis favours the first explanation.

Also great differences were found in low field bulk susceptibility (table 2), which was measured with a KL-1 bridge. The low field susceptibility of VA is about 4.5 times higher than those for VB and VC. This is probably an indication of a better crystallinity in VA (STRANGWAY *et al.* 1968).

Table 2
Magnetic parameters

Sample	N.R.M. (A.m^{-1})	k (S.I.)
VA = CHA1EO4	$21,4 \cdot 10^{-6}$	$548 \cdot 10^{-6}$
VB = CHA1EO2SO1	$4,29 \cdot 10^{-6}$	$124 \cdot 10^{-6}$
VC = CHA1EO3SO2	$8,67 \cdot 10^{-6}$	$118 \cdot 10^{-6}$

The coercive force spectrum and relaxation times were obtained by stepwise demagnetisation in increasing alternating fields (A.F.). The range of the relaxation times is fundamental to all palaeomagnetic investigations as only part of that primary remanence will be preserved when the rock contained initially at least some particles with relaxation times greater than the age of the rock.

The relaxation time τ in A.F. fields for single domain grains is given by the following expression (NEEL 1949), which is dominated by the exponential factor :

$$\tau^{-1}_{\substack{(0,\pi) \\ (\pi,0)}} = C \cdot \left(1 \pm \frac{h}{H_c}\right) \cdot \left(1 - \frac{h^2}{H_c^2}\right)^{1/2} \cdot \exp\left(-\frac{v \cdot J_s (H_c \pm h)^2}{2 \cdot H_c \cdot k \cdot T}\right)$$

C = ca. 10^{10} s^{-1}

k = Boltzmann's constant

h = applied field

J_s = spontaneous magnetization

H_c = coercive force

v = volume

T = temperature

Application of an A.F. lowers τ and will cause the magnetization of some grains to follow the A.F. A smooth decrease of the A.F. towards zero will leave the magnetization of those grains in the direction of the easy axes which we can assume to be in random positions. Stepwise increase of the A.F. allows us to determine the coercitivity spectrum up to the maximum field of 0.1 Tesla applied.

The N.R.M. of sample VA decreased very slowly and still 85% of the initial N.R.M. was left at 0.1 Tesla (fig. 5), which indicates that the remanence is carried mainly by grains with very high coercivities. At least two magnetization components are present in VB and VC. The increase in low A.F. noticed in sample VB is the result of nearly opposing components with different stabilities.

The directional behaviour during stepwise A.F. demagnetization can be followed in the Zijderveld diagrams (fig. 5) where the dots represent the projections of the north-seeking end of the remanence vector on the horizontal plane and the open circles the projections on the vertical plane containing the true N-S direction. In all three samples the magnetization vector points towards south, below the horizontal plane in VA and above it in VB and VC. In contrast to VA, where hardly any change in direction is noticed during A.F. demagnetization, great changes occur in low and medium A.F. in VB and VC before the magnetization decreases toward the origin, indicating the presence of at least two magnetization components.

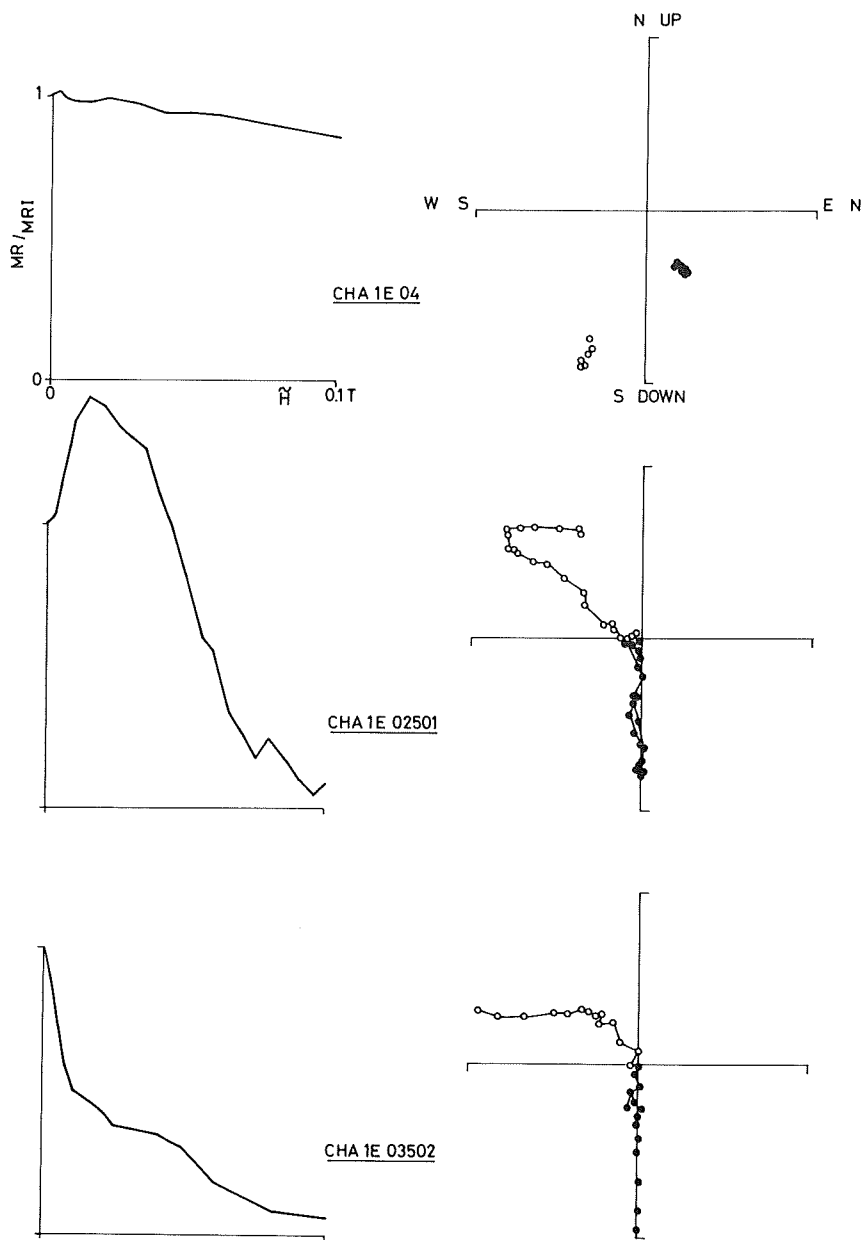


Fig. 5. — A.F. Demagnetization.

A very high resistance to A.F. demagnetization, such as VA was also found by SYMONS (1966) in a late Precambrian iron ore in Canada. These high stabilities can be explained by an exchange anisotropy between the weak ferromagnetism and the antiferromagnetic lattice (MEIKLEJOHN & BEAN 1957).

2.7. Mössbauer analysis.

Mössbauer spectra were collected using a conventional constant acceleration spectrometer. A ^{57}Co source in Rh matrix with an activity of about 15 mCi was used. Velocity calibration was obtained with an iron foil reference absorber.

Goethite has been intensively studied by M.S. (Mössbauer Spectroscopy), and especially the isomorphous substitution of Fe^{3+} by Al^{3+} has been well investigated. Briefly summarized, it can be stated that the isomorphous substitution has great influence on the magnetic hyperfine field.

A linear relation between the internal magnetic field (at 77° K) and the Al substitution is given by GOLDEN *et al.* (1979): $H \text{ (T)} = 50,0 - 0,177 (\% \text{ Al})$. Those authors found a better relation if they took into account the surface area (S.A.), which increases because of the decreasing particle size due to the substitution: $H \text{ (T)} = 49,8 - 0,136 (\% \text{ Al}) - 0,011 (\text{S.A.}) (\text{m}^2\text{g}^{-1})$. MURAD & SCHWERTMANN (1983) found similar results. Another way to detect the substitution is proposed by FLEISCH *et al.* (1980). By thermoscanning they detect T_{\min} , the temperature at which the least counts in the used channel occur: $T_{(\min)} = 381^\circ \text{ K} - 722 (x)$. So they found a linear relation between this T_{\min} and x (= Al-substitution).

In our experiments, we took spectra of the three samples at different temperatures and also of a magnetically enriched sample CHA1 (E13), analogue to VA. Fig. 6 shows the spectra analysis for internal magnetical field (H) distribution of the sextet and the quadrupole splitting (Q) distribution of the doublet. At 80 K, the spectrum shows a typical sextet with lines broadening to the centrum. This effect can be explained by the magnetic interaction among the crystallites, as recently stated by MØRUP *et al.* (1983) or as due to isomorphous substitution (FLEISCH *et al.* 1980). The observed value for H is around the expected value of 50,4 T (GOODMAN 1979), but has a distribution to lower values. At higher temperature, the internal magnetic field decreases and obtains a more important spreading of the values. This explains the greater asymmetry of the six peaks. At room temperature, the magnetic field is about 34,0 T; lower as the expected value for pure goethite.

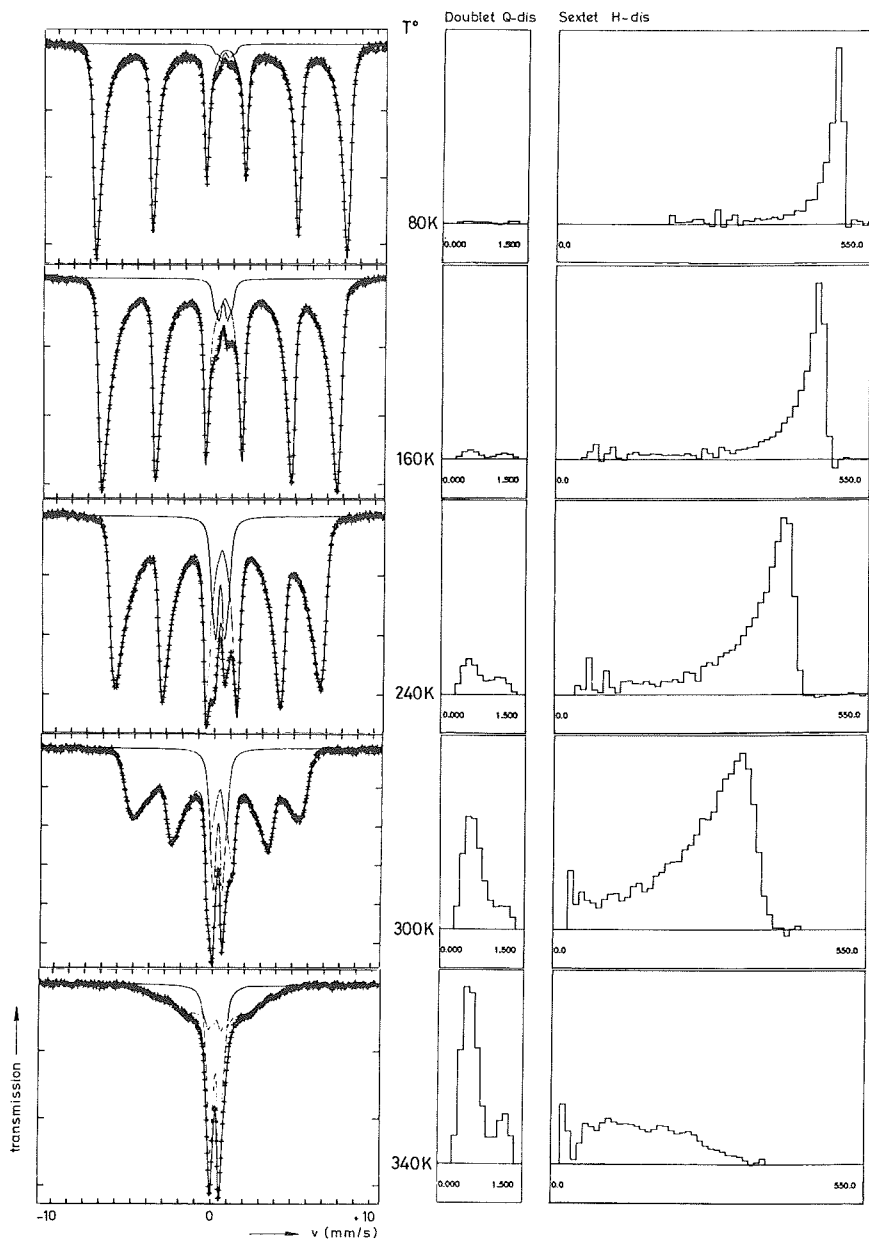


Fig. 6. — Mössbauer spectra of CHA1.

More important is the doublet, which is already detectable at 80 K. This doublet increases gradually with rising temperature. One should expect the grain size distribution of a very old iron precipitation to be quite homogeneous, because of the analogy in precipitation environment and the long ageing period. The (super) paramagnetic effect ($\tau = c^{-1} \cdot \exp(Kv/kT)$; K = effective anisotropy constant) is usually correlated with V_{cr} or d_{cr} ($= V_{cr}^{1/3}$). V_{cr} is the volume at which the relaxation time becomes too small to be detected by M.S., so that the magnetic hyperfine field sextet disappears. Values of SYZDALEV (1970) and GREAVES & JONES (1978) give a range of ca. 110 Å to about 180 Å for the temperature range of 80 K to room temperature which was used. The gradually increasing doublet means that there is a continuous distribution of the particle size between those values. However an other possibility remains. One should take into account the possible differentiation of the K -values. Isomorphous substitutions might give some distribution in anisotropy constants.

A second remark on the Q -distribution of the doublet is the double population in this distribution. One population is about 0.5 - 0.6 mm/s (the expected value for goethites) and a second, less important population is near to 1.1 - 1.2 mm/s. A solution can be proposed, analogous to the fit of GOODMAN & LEWIS (1981), who fitted an aluminous goethite having two doublets, with a quadrupole splitting of 0.49 and 0.77 mm/s. Isomorphous substitution can give a second doublet with different Q , but Al^{3+} does not seem to be the right substitution to explain the high Q -value of sample CHA1. BANCROFT *et al.* (1967) stated that Mn-neighbours have great influence on the Q of iron. In iron containing manganites also the high Q (1.3 - 1.4 mm/s) is explained as a Jahn-Teller distortion effect by Mn^{3+} in the second co-ordination sphere (KRISHNAMURTHY *et al.* 1981).

The three reference samples show quite remarkable differences (fig. 7). VA is a perfect sextet at 80 K and becomes more assymetric at room temperature. Perhaps only a very small doublet contributes to the spectrum. At low temperature VB shows a broadened sextet, which becomes a doublet at room temperature. Sample VC is even at 80 K, a broad doublet with a small magnetic contribution from the goethite lines. At room temperature it becomes a doublet, a little widened at the top to the Q -distribution.

3. Conclusions

All these experiments show a great difference in crystallinity of the three samples, selected from the Tertiary ironcrust of South-East Belgium. Despite the old age and the perfect possibility of ageing, there is an important difference, even in a small range of distance.

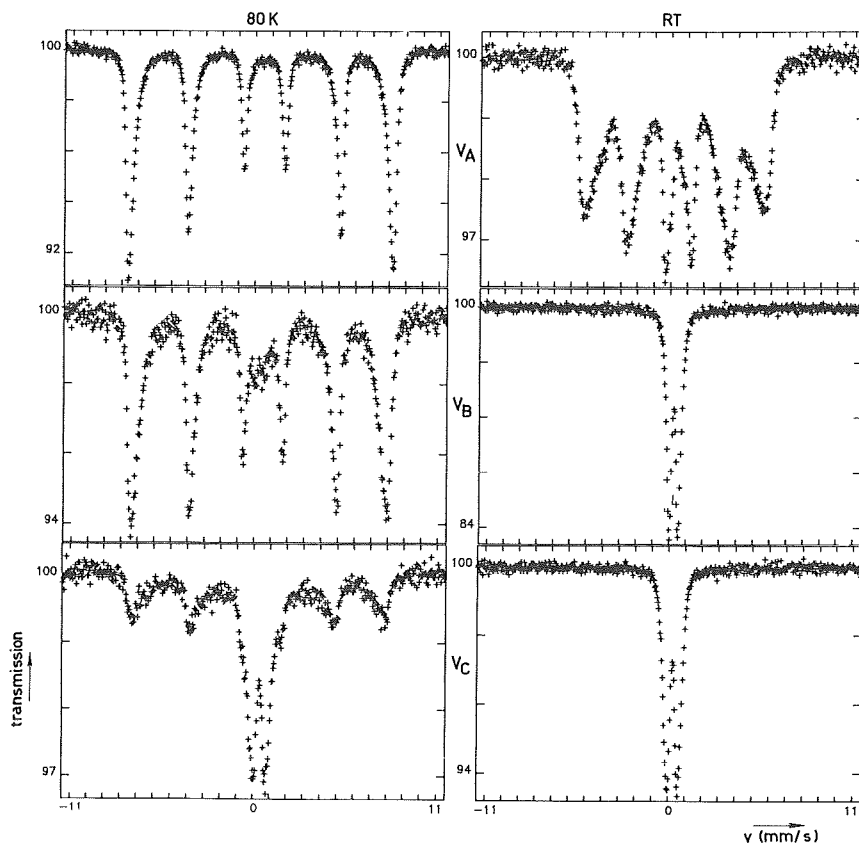


Fig. 7. — Mössbauer spectra at 80 K and room temperature of VA, VB and VC.

According to the experimental results, we may assume that the differences in crystallinity is a crystal size effect, due to the isomorphous substitution of Fe^{3+} by Mn^{3+} . It is already stated in literature (SMITH & EGGLETON 1983) that goethite can contain many impurities (Al, Si, Mn) and is isostructural with groutite ($\alpha\text{-MnOOH}$). Also the analogy of the iron radii and the ion-oxygen bondlength are remarkable analogue for Mn^{3+} and Fe^{3+} (TROMMEL 1983) (Table 3).

Table 3

ionic radii (Å)		oxygen-bond length (Å)			
		co-ord. n°	Mn^{III}	Fe^{III}	Ti^{III}
Ti^{3+}	.76	4	1.85	1.87	(1.91)
Mn^{3+}	.66	6	2.01	2.01	2.06
Fe^{3+}	.64	8	(2.15)	2.11	(2.17)
Al^{3+}	.51				

Elements in favour of the Mn-substitution and the effect for the crystallinity are : the small variation in Al-content compared to the Mn-content variation, the high quadrupole splitting for the M.S. and the great differences of magnetic behaviour during the demagnetization experiments and M.S. These results show : (a) that an incorporation of Mn in the lattice of goethite is possible, (b) this substitution has great influence on the crystallinity of the goethite, (c) the difficulty of using goethite-ironcrusts for absolute dating.

The crystallinity of goethite precipitates on freatic watertable depends not only on age, climate and eco-system conditions, but is also very variable because of coprecipitates as Al and Mn, which can result in isomorphous substitution and particle size decrease.

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