

COMPOSITION AND GENESIS OF THE FERRUGINOUS SANDSTONES OF THE DIEST AND THE POEDERLEE FORMATIONS (BELGIUM)

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ABSTRACT. - A study of mineralogical and especially chemical characteristics of different sedimentary units composed of ferruginous sandstones alternating with very glauconiferous sandy materials of the Diest and the Poederlee formations has shown that the genesis of the sandstones cannot be explained by a weathering in situ of Fe-bearing minerals, viz. glauconite, or by other pedogenetic processes. The strong relative increase of Fe against Al in the ferruginous sandstones, compared to the values determined in glauconite, suggest that a high amount of iron, present in the sandstones, is supplied directly during the sedimentation.

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INTRODUCTION.

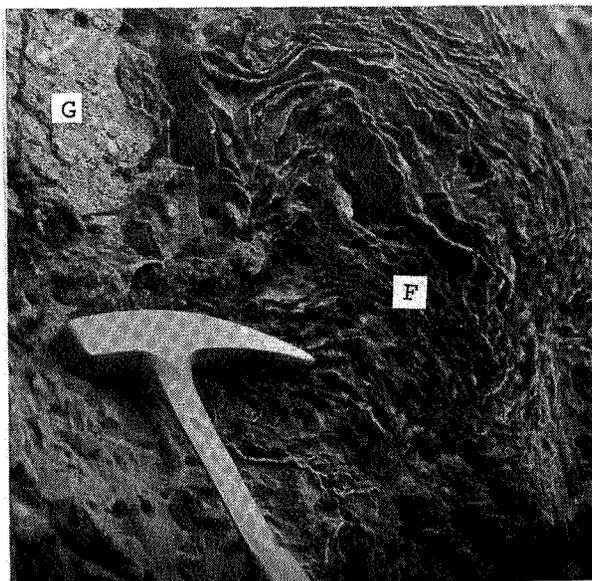
The Diest and the Poederlee formations form many outcrops in Belgium. The Diest formation can be considered as the most important Tertiary substratum in the "Hageland", an area east of Louvain. Both formations mainly consist of a complex of alternating sandlayers rich in glauconite and ferruginous sandstones. Glauconite is a sand-size mineral with a dioctahedral mica structure rich in Fe in octahedral position.

Different theories have been presented on the formation of these iron-rich sandstones based on geomorphological and stratigraphical observations. The formation of these iron-sandstones has been explained by pedogenetic processes under a warmer, more tropical climate at the end of the Tertiary (SCHEYS, 1955). The continuous stratigraphic layering of the sandstone banks has also been connected with phreatic watertables (TAVERNIER, 1954). D'HOORE (1953) believes that the formation of these iron-sandstones is the result of an absolute accumulation, because the parent material is very rich in weatherable minerals, viz. glauconite, which can give up rather high amounts of Fe and those free iron compounds will accumulate downwards (HOEBEKE and DEKEYSER, 1955).

All proposed hypotheses are unable to explain (1) the local wavy or even broken layering of sandy material and ferruginous sandstones (2) the presence of unweathered glauconitic material between two or inside the sandstone layers (Photo 1). Even in recent scientific contributions each sandstone layer and the underlying glauconitic sands are still considered as one sedimentary unit, of which the upper part is strongly weathered (DE MEUTER and LAGA, 1976). This implies that up to now, it is still accepted that the high amount of iron present in these sandstones, has originated from in situ wea-

thered glauconite.

This paper discusses the mineralogical and the chemical composition of different ferruginous sandstone samples in order to check the proposed hypotheses on their genesis.



MATERIALS AND METHODS.

At different localities in the region of Diest and Poederlee two kind of samples were collected : ferruginous sandstones and glauconiferous sandy material. Crushed sandstone samples and glauconite, separated with

a magnetic separator, are used for mineralogical and chemical analysis.

Iron and aluminum extractable in dithionite-citrate. (Fe_2O_3 dith., Al_2O_3 dith.) (DE CONINCK and HERBILLON, 1969).

Treatment with Na dithionite, added in powder to a Na citrate-Na hydrogen carbonate solution of pH 7.3, at a temperature of 75°C ; colorimetric determination of the reduced Fe with orthophenantroline (Fe_2O_3 dith.); and of Al extracted (Al_2O_3 dith.) by atomic absorption.

Total chemical analysis (INGAMELLS, 1966; OMANG, 1969)

Fusion of 100 mg of sample with Li_2CO_3 and H_3BO_3 at 1000°C . The melt is dissolved in conc. HCl. Al and Si are determined by atomic absorption in a N_2O -acetylene flame. Ti is determined colorimetrically with chromotropic acid.

Treatment of 100 mg of sample with HF + HNO_3 + HClO_4 until the solution is clear; the evaporation residue is dissolved in conc. HCl. Na, K, Ca, Mg and Mn are determined by atomic absorption in an air-acetylene flame. Fe is determined colorimetrically with sulfosalicylic acid and P is determined also spectrophotometrically with ammonium vanadate and ammonium molybdate.

HCl treatment (DE CONINCK et al., 1975)

500 mg of material are treated overnight at 80°C in 1N HCl. The solid is separated from the extracting solution by centrifugation, washed with acetone and alcohol until free of Cl^- and used for X-ray diffraction. In the solution Al, Fe, Mg and K are determined in a way similar to the total chemical analysis.

X-Ray diffraction.

Oriented dithionite-treated and also HCl-treated samples are X-ray diffracted using a Philips X-ray apparatus (PW 1050/25) with $\text{CoK}\alpha$ radiation. The dithionite-treated samples are also run after heating at 550°C for 2 hours.

RESULTS AND DISCUSSION.

MINERALOGY OF THE FERRUGINOUS SANDSTONES (Fig. 1).

The dithionite-treated X-ray diffractograms of some ferruginous sandstones of the Diest formation show the following composition: mica (spacings at 10, 5 and 3.33 \AA), quartz (spacings at 4.26 and 3.33 \AA) feldspars (reflection at 3.23 \AA) and probably kaolinite (spacings at 7.2 and 3.55 \AA). The mica is probably a glauconite as indicated by the rational series of 10 \AA with broad reflection at 10 \AA and 3.33 \AA and the weak 5 \AA spacing (DE CONINCK et al., 1972; DE CONINCK, 1978). The broad peaks are due to the fact that hydrated cations are present between a certain number of layers (VAN RANST and DE CONINCK, 1982). Experiments on pure glauconite samples have shown that this mineral is dissolved in HCl, whereas the other mica minerals withstand this treatment (Fig. 2) (DE CONINCK, 1978). The presence of a large amount of K^+ in the extract of this treatment thus confirms that glauconite is present in the sample. The spacings at 7.2 and 3.55 \AA normally indicate the presence of kaolinite. But these spacings are destroyed

by the HCl treatment, whereas kaolinite is normally resistant to this treatment. This inconsistency may be due to the fact that kaolinite in the samples is not well crystallized.

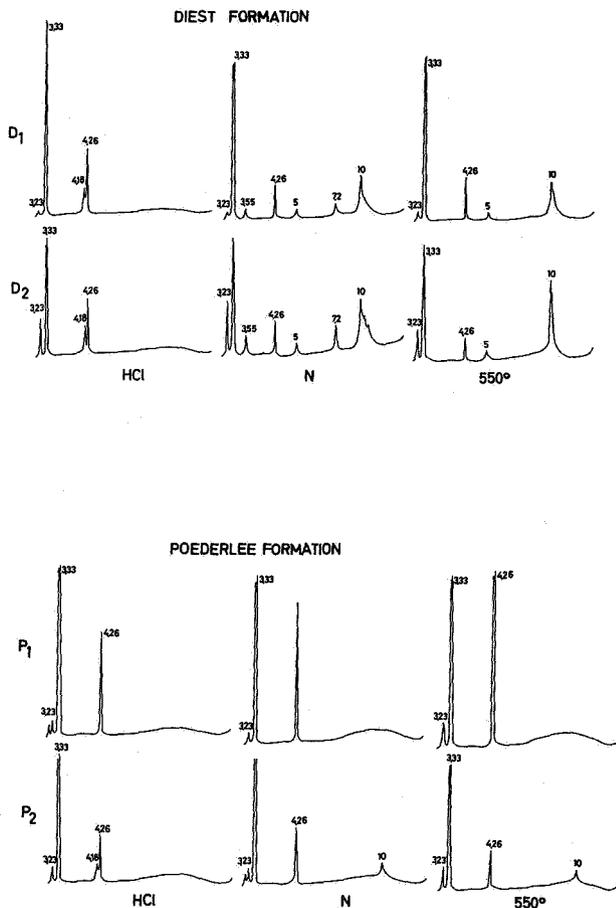


Fig. 1 - X-ray diffraction patterns of some ferruginous sandstones of the Diest and the Poederlee formations after dithionite (N) and after HCl treatment; the dithionite treated samples are heated at 550°C .

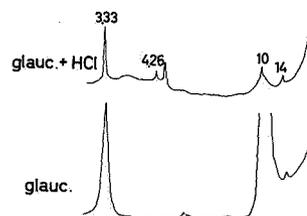


Fig. 2 - X-ray diffraction patterns of glauconite before and after HCl treatment. The reflections present after HCl indicate another mica mineral and quartz.

Before the HCl treatment the presence of crystalline Fe minerals cannot be detected but after the treatment a ray at 4.18 Å appears, characteristic for goethite. This suggests that HCl has preferentially dissolved the amorphous Fe components leaving goethite at least partly undissolved and causing a relative accumulation of it.

The dithionite-treated X-ray diffractograms of the sandstones of the Poederlee formation show a dominance of quartz and much lower amounts of feldspars. The sample P2 has also glauconite (dissolved in HCl). Goethite is observed after the HCl treatment.

CHEMICAL COMPOSITION OF SOME SEPARATED GLAUCONITE SAMPLES (Table 1)

TABLE 1 - Chemical composition of three separated glauconite samples in %.

	G1	G2	G3
SiO ₂	47.17	46.10	47.36
Al ₂ O ₃	7.76	6.84	7.97
Fe ₂ O ₃	24.39	25.77	24.26
MgO	2.94	2.86	3.04
K ₂ O	7.77	7.69	7.73
Na ₂ O	0.02	0.01	0.02
CaO	0.08	0.20	0.16
TiO ₂	0.10	0.14	0.08
MnO	0.01	0.01	0.01
P ₂ O ₅	0.15	0.16	0.17
H ₂ O	9.81	10.46	9.26
Tot.	100.20	100.24	100.06

The total chemical composition of the separated glauconite samples shows lower K and higher H₂O contents than the values given in literature for glauconites (GRIM, 1968; CLOOS et al., 1961). This indicates that a greater part of the charge is not neutralized by unexchangeable K⁺, but by hydrated exchangeable cations. It is however important to mention that the three analyzed glauconite samples contain 7 to 8% Al₂O₃ besides about 25% Fe₂O₃.

CHEMICAL COMPOSITION OF THE FERRUGINOUS SANDSTONES (Table 2)

All the analyzed sandstone samples, except P1, contain more than 50% Fe₂O₃, of which a very high amount is extracted with dithionite-citrate. These sandstones have very low Al₂O₃ contents (ranging from 0.09 to 2.5 %) compared to those in glauconites.

HCL TREATMENT OF THE FERRUGINOUS SANDSTONES (Table 3)

This treatment extracts almost all Fe and Mg, except in the sample P2. The high amounts of Fe extracted, indicate that goethite not dissolved by HCl and observed in the diffractograms represents only 2% of the total content of Fe present. The high amounts of K, extracted in the samples D1 and D2, proves the presence of glauconite as well as of another mica, which is probably muscovite.

COMPARISON OF SOME MOLAR RATIOS IN THE GLAUCONITES AND IN THE FERRUGINOUS SANDSTONES (Table 4)

Comparison of the molar ratios of Fe on the other important elements in the glauconites at one side and in the ferruginous sandstones of the Diest and the Poederlee formations at the other side, shows that the ferruginous sandstones are characterized by a strong relative increase of Fe against the other considered elements, if the sandstone layers in the upper part of the sedimentary units are considered as being the weathering products of the underlying glauconitic sands. The relative increase of Fe against Mg and K can be explained by a weathering in situ in well-drained conditions, because due to the rather high pKa values of Mg and K these elements will be leached out after they are released from the mineral structures. But the increase of Fe against Al cannot be explained by weathering in situ. Both elements are indeed immobile in well-drained conditions and they can be translocated only as organo-metallic complexes. But the large amounts of Fe and Al released on weathering of glauconite would immobilize the organo-metallic complexes (DE CONINCK, 1980).

TABLE 2 - Chemical composition and dithionite-extracted Fe₂O₃ (Fe₂O₃ dith.) and Al₂O₃ (Al₂O₃ dith.) of the ferruginous sandstones of the Diest (D) and the Poederlee (P) formations.

	D1	D2	P1	P2
SiO ₂	33.45	30.95	68.15	30.33
Al ₂ O ₃	2.09	2.50	0.09	1.09
Fe ₂ O ₃	53.61	53.33	26.12	56.51
MgO	0.51	0.50	0.01	0.73
K ₂ O	1.23	0.97	0.11	0.30
Na ₂ O	0.02	0.02	0.03	0.01
CaO	0.09	0.09	0.03	0.04
TiO ₂	0.12	0.10	0.03	0.21
MnO	0.05	0.04	0.02	0.06
P ₂ O ₅	0.25	0.31	0.22	0.34
H ₂ O	9.68	10.40	6.01	10.66
Tot.	101.10	99.21	100.82	100.28
Fe ₂ O ₃ dith.	49.77	46.21	25.93	44.67
Al ₂ O ₃ dith.	1.13	1.13	0.01	1.09

TABLE 3 - HCl 1N treatment of the ferruginous sandstones of the Diest (D) and the Poederlee (P) formations;
 I : extracted amounts in % of the total sample;
 II : extracted amounts in % of the total content of the considered element.

	I				II			
	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O
D1	1.42	52.71	0.50	0.60	68	98	98	49
D2	1.54	52.26	0.42	0.45	62	98	84	46

P1	0.09	26.12	0.01	0.01	100	100	100	9
P2	0.57	55.63	0.08	0.08	52	98	11	27

TABLE 4 - Some molar ratios of the glauconites (G) and of the ferruginous sandstones of the Diest (D) and the Poederlee (P) formations.

	G1	G2	G3	D1	D2	P1	P2
Fe ₂ O ₃ /Al ₂ O ₃	2.14	2.40	1.94	16.37	13.62	181.67	33.06
Fe ₂ O ₃ /MgO	2.09	2.28	2.01	26.63	26.92	-	19.54
Fe ₂ O ₃ /K ₂ O	1.85	1.97	1.85	25.62	32.41	136.25	110.53

CONCLUSIONS.

The mineralogical and chemical study of the ferruginous sandstones of the Diest and the Poederlee formations shows a dominance of quartz and smaller amounts of feldspars, glauconite and probably kaolinite, embedded in an iron-rich matrix. Most of the iron-rich matrix is amorphous with some goethite. The high amounts of Fe, generally exceeding 50% and the high Fe₂O₃/Al₂O₃ ratio in these sandstones cannot be explained by a weathering in situ or by other pedogenetic processes.

These findings imply that glauconite cannot be considered as the only source of the iron present in the ferruginous sandstones and suggest that the high amount of Fe₂O₃ dith. present in these sandstones has been supplied directly during the sedimentation. The presence of ferruginous sandstone layers in the upper part of the sedimentary units may indicate unfavourable conditions for the synthesis of glauconite at the time of sedimentation.

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