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A CLASSIFICATION OF GOETHITE MINERALS BASED ON THE MÖSSBAUER BEHAVIOUR

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Résumé. — Les effets de la réduction de la taille des grains dans des échantillons naturels de goéthite sont décrits, comme ils se manifestent en spectroscopie Mössbauer, en diffraction de rayons X et en thermogravimétrie. Nous avons trouvé une corrélation entre la dimension moyenne des grains et le type de formation des minerais. Nous proposons une classification dans laquelle les minerais, selon la forme générale de leur spectre Mössbauer, se présentent en trois classes qui correspondent aux différents types de formation.

Abstract. — In this paper grain size effects in mineralogical goethite samples are described, as they appear in Mössbauer spectroscopy, X-ray diffraction, and thermogravimetric analysis. A correlation is laid between the grain size and the type of formation. According to the general shape of their Mössbauer spectra, the naturally occurring goethite samples can be classified in three groups, corresponding to different types of formation.

1. Introduction. — Mössbauer spectroscopy has been found to be a useful technique for obtaining information on the previous history of certain minerals, mainly based on the ferrous-ferric ratio, or on the cation distribution among different available lattice sites [1]. In this paper we will describe how the general shape of the Mössbauer spectrum of goethite can be used to get some powerful indications about the genesis of the sample under study.

For several years, the Mössbauer spectrum of goethite has been a controversial subject [2-6]. Its physical properties seem to vary from one sample to another, but at the moment there is good agreement in that this behaviour must be explained as a grain size effect [7]. In this way it is well known that the Mössbauer spectrum of goethite can vary from a well determined six-lines spectrum to a doublet, due to the grain size.

Goethite minerals are mostly formed in the sedimentary cycle, in the first place by weathering of iron containing oxides, sulfides, carbonates, silicates, or by chemical or organic precipitation from an iron containing solution. A few cases are known where goethite is formed from a hypogenic solution. Because of these different types of formation, it can easily be understood that there is a large variety in the mean grain size of the different samples, and this fact should have a strong influence on the Mössbauer spectrum.

2. Experimental results. — We have investigated twelve mineralogical goethite samples from different, but known origin. In figure 1 their Mössbauer spectra at room temperature are shown. The shape of the spectra varies from a perfectly determined six-lines

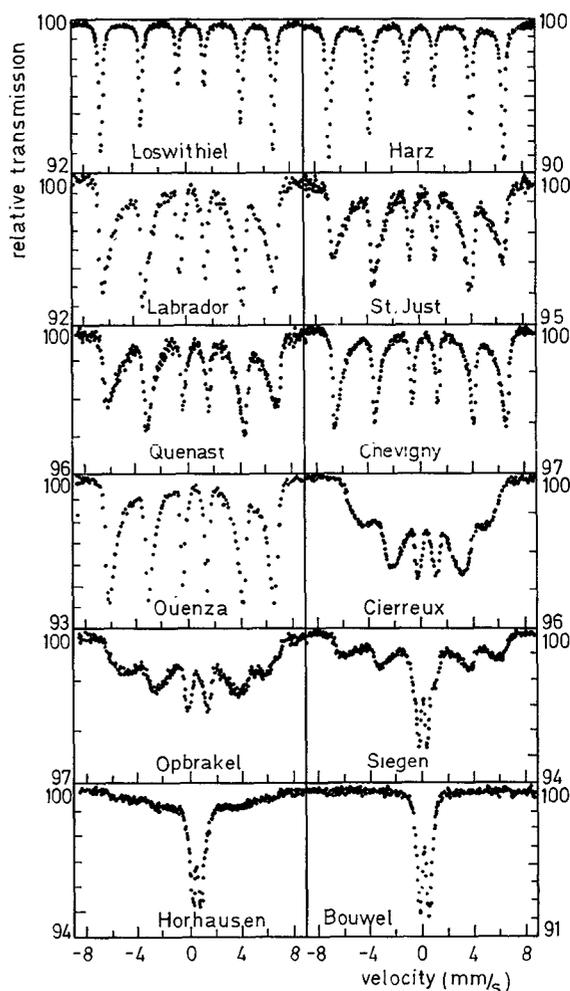


FIG. 1. — Mössbauer spectra at room temperature of twelve naturally occurring goethite samples.

spectrum, over an asymmetrically broadened one, to a paramagnetic doublet, indicating a decrease of grain size in going from the Loswithiel sample to the sample from Bouwel. Evidence of the grain size effects is also found in the X-ray diffraction patterns of the samples and in thermogravimetry. X-ray diffraction pointed out that the only iron bearing fraction in all samples is indeed goethite. In some of the samples, we found also some reflections due to SiO_2 , but this compound has no influence on the Mössbauer spectrum. In figure 2 the X-ray diffraction patterns of some of the

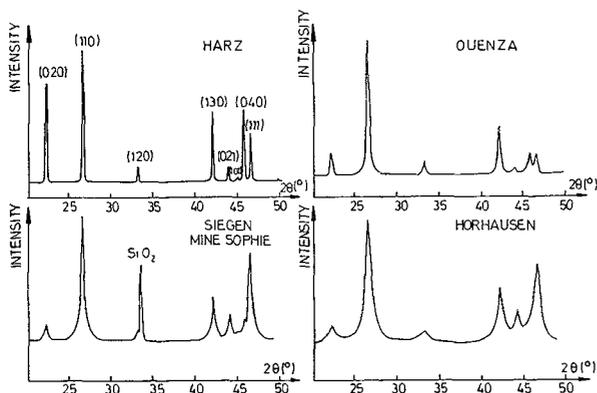


FIG. 2. — X-ray diffraction patterns of four goethite minerals.

samples are shown. There is clearly a significant line broadening in most samples. This line broadening is due to the small grain size and shows the same tendency as the Mössbauer spectra.

The X-ray diffraction pattern as well as the Mössbauer spectrum, obtained on the Siegen sample, shows a remarkable feature. The Mössbauer spectrum contains a paramagnetic doublet component, superimposed on a component, still having a rather large hyperfine field. Correspondingly, in the X-ray diffraction pattern we see that the reflections consist of a more or less narrow peak superimposed on a broad base. The

presence of two fractions with different grain size provides an explanation for this phenomenon. In our opinion the fraction with the larger grain size is formed by recrystallisation of the smaller grains. Figure 3 shows the results of a thermogravimetric

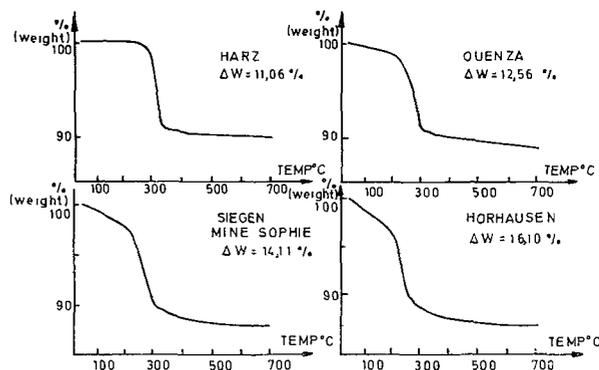
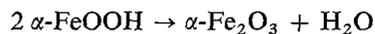


FIG. 3. — Thermogravimetric analysis of four naturally occurring goethites. ΔW is relative to the weight of the resulting hematite.

study on some of the samples. Only for the Harz sample the loss of weight in the reaction



corresponds well to the theoretically calculated loss, which is 11.17 % of the final weight of the hematite. In going to samples with smaller grain size the loss of weight increases, and reaches 16.10 % in the sample from Horhausen. The decomposition temperature decreases and there is also a significant loss of weight at low temperatures.

So, although the grain size effects are visible by many experimental techniques, their most striking effect is observed in the Mössbauer spectrum.

3. **Discussion.** — From the shape of the Mössbauer spectra we propose to classify the goethite samples in

TABLE I

Finding-Place	Geological origin	Classification
Loswithiel (Cornwall, G. B.)	Unknown	I
Harz mountains (Germany)	Hydrothermal	I
Labrador (Canada)	Hydroxilation of sedimentary heamatite	II
St Just (Cornwall, G. B.)	Weathering of sulfides and oxides	II
Quenast (Belgium)	Weathering of sulfides and silicates	II
Chevigny (France)	Weathering products of limestones redeposited in vugs	II
Ouenza (Algeria)	Oxidation of sedimentary carbonates followed by a recrystallisation	II
Cierreux (Belgium)	Weathering products of sandstones and shales redeposited in porous sandstone	II
Opbrakel (Belgium)	Weathering of glauconites bearing sands	II
Siegen (Germany)	Weathering of hydrothermal siderite + recrystallisation (partial)	II/III
Horhausen (Germany)	Weathering of hydrothermal siderite	III
Bouwel (Belgium)	Biogenic	III

three groups, corresponding to the different types of formation. This classification is given in table I together with the origin of the different samples.

In class I the samples with a well defined six-line spectrum, showing narrow lines, are collected. They are both of hydrothermal-like origin. For the Harz sample an ore microscopic investigation points strongly to this kind of formation. The origin of the Loswithiel sample is unknown to us, but, according to its large grain size, it has to be formed under extreme conditions, probably resembling those of hydrothermal deposits at relatively low temperatures.

The samples, belonging to this class, show also very narrow X-ray diffraction peaks and they do not contain any excess of water.

Class II groups the samples with an asymmetrically broadened six-lines Mössbauer spectrum. They are all found to be formed by weathering of oxides, sulfides and silicates or by redeposition of resolved primary hydroxides and oxides. It is clear that such processes give rise to particles with intermediate grain size. A physical explanation for the shape of the asymmetrically broadened lines in the Mössbauer spectrum is given in another contribution to this conference [9].

The X-ray diffraction patterns of these samples consist of somewhat broadened lines and all samples

contain some excess of water, the loss of weight being about 13 %. The decomposition step is still reasonably sharp, but there is already some loss of water at low temperatures.

The samples, that are grouped in class III, mainly show a paramagnetic doublet in their Mössbauer spectrum. They are formed either by direct weathering of siderite (FeCO_3) formations or in a biogenic way. The loss of large molecules (e. g. CO_2) during the formation implies that only small particles are formed. The X-ray diffraction peaks are strongly broadened and there is a great excess of water in these materials. The decomposition to $\alpha\text{-Fe}_2\text{O}_3$ is smeared out over a large temperature range.

Although this classification can certainly not be seen as an absolute one, the authors believe to have pointed out that the Mössbauer spectrum gives a reliable and a fast indication on the possible genesis of goethite minerals.

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