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MÖSSBAUER SPECTROSCOPY OF AIRBORNE PARTICULATE MATTER

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Résumé. — La spectroscopie Mössbauer a été utilisée pour l'analyse de poussières atmosphériques collectées par filtration. Nous avons identifié divers composés du fer en nombre et en proportions variables suivant le degré de pollution de la zone de prélèvement. En particulier les aérosols provenant de l'érosion naturelle ont pu être discriminés de ceux issus de sources anthropogéniques.

Abstract. — Mössbauer spectroscopy has been used to determine the valence and chemical composition of iron mobilized in air. The method allows source identification of iron aerosols; particularly soil derived iron aerosols are characterized against iron originated through anthropogenic processes.

1. Introduction. — Iron is the major constituent of the whole earth (35.0 %) and the fourth major constituent of the earth's crust (4.5 %). The atmosphere contains less than 0.000 1 % by mass of iron, however, airborne particulate matter is composed of 1.0 to 5.0 % by mass of iron. Since large amounts of iron are mobilized in the earth's crust, atmospheric Fe is generally assumed to be soil derived. It is clear that anthropogenic emissions may also account for iron emissions into the atmosphere, however, models of identification of air pollution sources are lacking of consistency to explain the origin and occurrence of iron aerosols. In the present contribution, nuclear gamma resonance (NGR) spectroscopy is used to investigate the problem of iron in the atmosphere.

2. Experimental. — **2.1 SAMPLE COLLECTION.** — Atmospheric particulate matter was collected (a) by filtration through air conditioning filters and (b) by means of an electrostatic precipitator. Sampling was carried out in specific areas, carefully selected because of the particularity of their environment (Table I).

TABLE I

Location of the sampling areas

(a) Remote areas	College Station (Texas, USA) Louvain-la-Neuve (Belgium)
Marine areas	Ostend (Belgium) Saint-Malo (Brittany, France)
(b) Urban areas	Brussels (Belgium) Antwerp (Belgium) Barcelona (Spain) Copenhagen (Denmark)
(c) Industrial areas	La Louvière (Belgium) Charleroi (Belgium) Wasmuel (Belgium) Montignies (Belgium)

Except for Montignies-le-Tilleul, all samples were collected on air conditioning filters, with sampling periods lasting from one to a few weeks according to location and renewal cycles. At Montignies, airborne particulates were collected downwind of steel industries for five hours (700 m³) with an electrostatic precipitator.

2.2 SAMPLE ANALYSIS. — Mössbauer analysis are performed with a five millicuries ⁵⁷Co(Pd) source and a conventional thin NaI scintillator coupled to a 512 channels analyzer. Sample thicknesses for atmospheric particulate matter of 100 mg/cm² allow significant absorption in 5 to 50 hours counting times. The spectra are taken with the absorber at room or at liquid nitrogen temperature.

The Mössbauer spectra are fitted by computer to be resolved in their fundamental chemical components. Three kinds of components characterized by three typical spectra were systematically considered :

(a) A doublet with a quadrupole splitting of about 2.5 mm/s and an isomer shift of about 1.0 mm/s corresponding to high spin iron II compounds.

(b) A doublet with a quadrupole splitting of about 0.5 mm/s and an isomer shift of about 0.1 mm/s corresponding to paramagnetic or superparamagnetic iron III species.

(c) A sextet with splitting values of about 16.5, 9.5 and 2.5 mm/s corresponding to ferromagnetic iron III species.

In some cases, another sextet is revealed in the residue of the fitting.

Figures 1 to 3 present the data and the fit of three typical spectra.

3. Results. — The results of the computer fitting are summarized in table II. There is a marked diffe-

TABLE II

Theoretical and calculated hyperfine parameters for dusts originated from different regions

Source $^{57}\text{Co}/\text{Pd}$; Absorber at R. T.			Calculated values			
Compound	Parameter	Theoretical values	Texas	Ostend	Saint-Malo	Louvain-L-N.
Fe II high spin	QS (mm/s)	$1.5 < QS < 3.0$			2.38 ± 0.02	2.27 ± 0.09
	IS (mm/s)	$1.0 < IS < 1.5$			1.09 ± 0.01	1.16 ± 0.05
Fe III paramag.	QS (mm/s)	$0 < QS < 1.0$	0.70 ± 0.02	0.73 ± 0.01	0.87 ± 0.01	0.69 ± 0.03
	IS (mm/s)	$-0.1 < IS < 0.4$	0.20 ± 0.01	0.20 ± 0.01	0.12 ± 0.01	0.14 ± 0.12
Fe II high spin	QS (mm/s)	$1.5 < QS < 3.0$	Brussels 2.80 ± 0.07	Antwerp 2.09 ± 0.05	Barcelona 2.34 ± 0.02	Copenhagen 2.25 ± 0.11
	IS (mm/s)	$1.0 < IS < 1.5$	0.85 ± 0.03	1.12 ± 0.03	1.10 ± 0.09	1.00 ± 0.05
Fe III paramag.	QS (mm/s)	$0 < QS < 1.0$	0.73 ± 0.01	0.63 ± 0.01	0.86 ± 0.01	0.73 ± 0.01
	IS (mm/s)	$-0.1 < IS < 0.4$	0.20 ± 0.07	0.18 ± 0.01	0.12 ± 0.01	0.17 ± 0.01
Fe III ferromag.	H_{eff} (kOe)	517 $\left\{ \begin{array}{l} \alpha\text{-Fe}_2\text{O}_3 \\ \gamma\text{-Fe}_2\text{O}_3 \end{array} \right.$ 488 499	508 ± 4	502 ± 4	497 ± 4	501 ± 2
	IS (mm/s)	0.22 $\left\{ \begin{array}{l} 0.11 \\ 0.25 \end{array} \right.$	0.12 ± 0.06	0.12 ± 0.06	0.00 ± 0.07	0.10 ± 0.03
Fe II high spin	QS (mm/s)	$1.5 < QS < 3.0$	La Louvière ~ 2.35	Charleroi ~ 1.0	Wasmuel 2.83 ± 0.08	Montignies 0.92 ± 0.04
	IS (mm/s)	$1.0 < IS < 1.5$				
Fe III paramag.	QS (mm/s)	$0 < QS < 1.0$	0.73 ± 0.02	0.69 ± 0.02	0.75 ± 0.02	0.60 ± 1.28
	IS (mm/s)	$-0.1 < IS < 0.4$	0.19 ± 0.01	0.21 ± 0.01	0.21 ± 0.01	0.17 ± 0.34
Fe III ferromag.	H_{eff} (kOe)	517 $\left\{ \begin{array}{l} \alpha\text{-Fe}_2\text{O}_3 \\ \gamma\text{-Fe}_2\text{O}_3 \end{array} \right.$ 488 499	512 ± 2	505 ± 2	535 ± 3	
	IS (mm/s)	0.22 $\left\{ \begin{array}{l} 0.11 \\ 0.25 \end{array} \right.$	0.18 ± 0.05	0.15 ± 0.04	0.20 ± 0.05	
Fe metal	H_{eff} (kOe)	330	331 ± 2			
	IS (mm/s)	-0.16	-0.15 ± 0.05			
Fe ₃ O ₄	H_{eff} (kOe)	491 453				496 451
	IS (mm/s)	0.20 0.45				0.18 0.32
		At R. T. ratio 2/1				

(1) The theoretical values were taken in the books *Chemical applications of Mössbauer spectroscopy* by GOLDANSKII V. I. and HERBER R. H., p. 209; and *Mössbauer spectroscopy* by GREENWOOD, N. N. and GIBB, T. C. p. 241.

(2) The quadrupole splitting occurring in some ferromagnetic compounds has not been taken under consideration since it was not reasonably estimable from the data.

TABLE III

Relative abundance of the compounds
calculated by the ratio of the peaks areas

	Fe II	Fe III paramag.	Fe III ferromag.	Fe métal	Fe ₃ O ₄
Texas		100 %			
Ostend		100 %			
Saint-Malo	33 %	67 %			
Louvain-L-N.	23 %	77 %			
Brussels	20 %	51 %	29 %		
Antwerp	16 %	71 %	13 %		
Barcelona	21 %	68 %	11 %		
Copenhagen	10 %	61 %	29 %		
La Louvière	6 %	36 %	45 %	13 %	
Charleroi	< 1 %	31 %	69 %		
Wasmuel	11 %	47 %	42 %		
Montignies	< 1 %	22 %			78 %

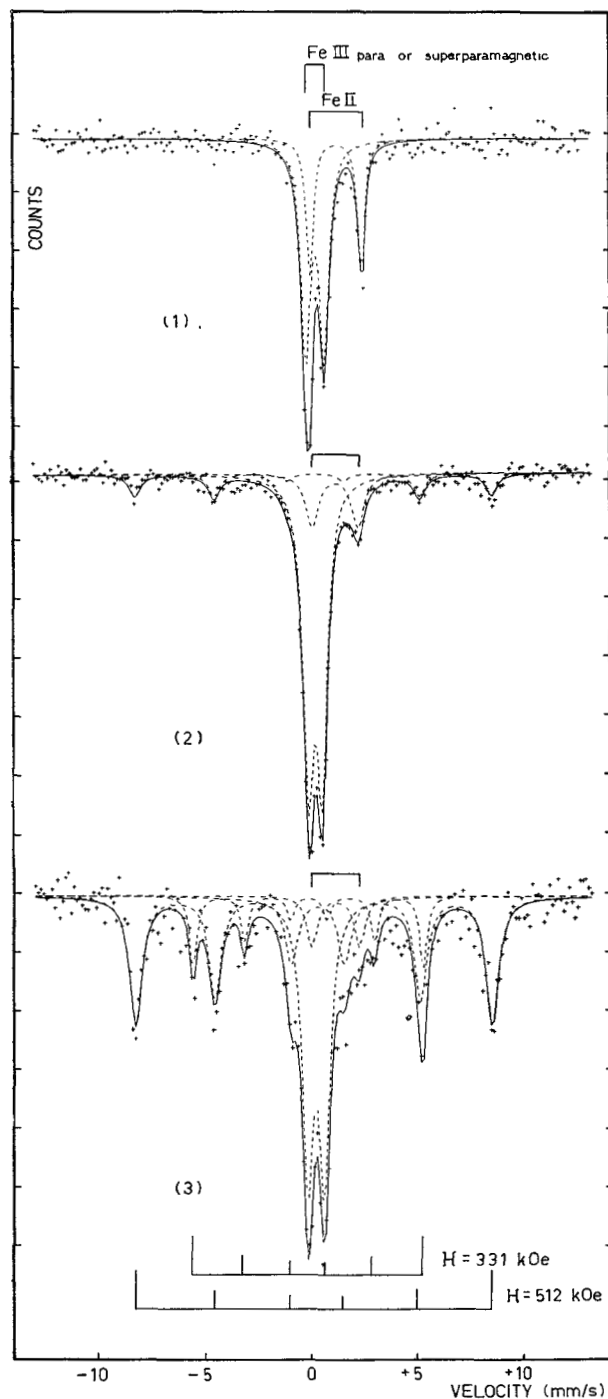


FIG. 1 to 3. — Mössbauer spectra of atmospheric particulate matter. (1) origin : Saint-Malo. (2) origin : Antwerp. (3) origin : La Louvière.

rence in the compounds detected and their ratio, according to the origin of the dust. However, no drastic change appears in the spectra when the absorber is cooled to liquid nitrogen temperature 100 K.

In remote areas the spectra are resolved into two well distinct doublets. One is assigned to a divalent iron of high spin ; the other to a paramagnetic trivalent iron compound.

In urban areas, the sextet of a ferromagnetic iron

compound is clearly visible in addition to the two former doublets.

In industrial zones, the spectra are much more complex and difficult to resolve. Nevertheless quite satisfactory fits may be obtained by careful computer fitting.

3.1 IDENTIFICATION OF THE PRODUCTS. — Although a simple comparison of the hyperfine parameters with the parameters of known iron compounds is insufficient to lead to an univocal identification of the products, some credible indications may be inferred from our spectra.

(a) *Ferrous compounds* : The ability for oxidation of iron II is well known. However when incorporated in particularly stable crystal configurations such as silicates the ferrous compounds may be very stable e. g. they are natural constituents of rocks and minerals. As it seems unlikely that human activities would lead to emissions of stable Fe II, the observation of a high percentage of Fe II in airborne particulate matter may lead to the conclusion that soil is the major source of the collected dust. This is the situation that occurs in unpolluted areas.

(b) *Paramagnetic ferric compounds* : several ferric compounds have parameters corresponding to those observed in our spectra, but one of the most probable, which is also found in soil and rust in all moderate climate regions, is the hydrated iron oxide FeOOH . Chemical analysis would be necessary to detect all the anions accompanying the iron ; a work in this way is in progress on the sulfate anion.

(c) *Ferromagnetic ferric compounds* : it seems quite reasonable to suppose that the ferromagnetic fraction consists of iron oxides, but it is not possible to distinguish which modification occurs. The line width varies from 0.6 to 1.0 mm/s revealing a mixture of various components. The observed magnetic splitting represents only a mean value, close to the parameter of Fe_2O_3 or sometimes to those of Fe_3O_4 .

The principal sources of Fe_2O_3 and Fe_3O_4 are associated to combustion and ferrous industries.

(d) *Superparamagnetism* : Small ferromagnetic particles do conserve an important magnetic moment ; however flipping time decreases with the number of aligned spins i. e. with particles dimensions.

At room temperature, for particles sizes less than 100 Å, the lifetime of the Mössbauer level exceeds the relaxation time and the spectra shows only a paramagnetic structure.

As very small particles are collected and analyzed, most of the paramagnetic fraction previously designated as Fe^{3+} *para* might be superparamagnetic Fe^{+3} *ferro*.

In order to get further information about this problem, we intend to perform two typical experiments :

— heating the dust, to dehydrate the hydroxides, if any, and

— lowering the temperature of the absorber to liquid helium since liquid nitrogen temperature is insufficient to reveal important changes in the spectra.

4. Discussion. — The relative abundances of the compounds, as calculated from peaks areas, are summarized in table III. The attribution of some sextets to Fe_2O_3 , Fe metal or Fe_3O_4 is based only on a similitude of hyperfine parameters and must be taken with caution.

In spite of these restrictions, the differences in valence and chemical composition between iron aerosols from different areas are striking when comparing the NGR spectra of remote areas and urban or industrial regions. The assumption that, in remote areas, most of the atmospheric iron is soil derived is confirmed by the fact that the Mössbauer spectra of atmospheric dusts are quite similar to those of clay minerals from moderate climate regions.

In cities, the contribution of anthropogenic emission of iron increases relatively to the natural sources. Combustion of oil and coal and rust mobilized by weathering processes may be an important source of iron in airborne particulate matter. Mössbauer spectra of rust and soot are very similar to those of the matter collected in the towns.

The third group of sampling zones is constituted by steel industrial regions. The iron originated through natural processes is almost completely masked by the emissions of factories.

If the presence of Fe_3O_4 is not surprising, quite remarkable is the observation in La Louvière of a compound possessing the parameters of metallic iron. This could be due to the vicinity of the sampling zone to the factories. Although metallic iron is quickly oxidised by air, an external crust of oxide may protect a core of metal for a time long enough for sampling and analysis.

5. Conclusions. — Whenever airborne material is quantitatively analyzed, one is usually restricted to the

detection and the determination of the elements. Even though Mössbauer spectroscopy is not an exceptionally efficient technique in the field of quantitative evaluation, it offers the unique advantage of yielding precise information concerning the oxidation state and the chemical bonds of the atom under consideration.

One might regret that only iron has the right Mössbauer characteristics and is present in airborne particulates at concentrations high enough. Nevertheless its wide abundance allows it to be a quite efficient probe of the amount and the nature of atmospheric pollution.

We have been able to observe that, in regions with a moderate climate, a six-line ferromagnetic spectrum is representative of human activities, while such spectra are not found for samples collected in rural areas. So far ferromagnetic oxides may be considered as tracers for the dispersion of the pollution associated to industrial and urban districts. Divalent iron, on the contrary, has an exclusive natural origin and its concentration yields some information on the erosion and dust suspension processes. Species as metallic iron are specific to typical industrial emissions; their study is representative of dispersion area of the airborne particulates.

Mössbauer spectroscopy gives also informations concerning the chemical changes which polluting elements undergo during their transit in the atmosphere. The particular chemistry of some species in close contact with air might also tell us some useful information on the self-purification capacity of the biosphere.

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Note. — See also the papers of M. KOPCEWICZ and B. DZIENIS in *Tellus* XXIII (1971), 2 and *Tellus* XXV (1973), 2.