

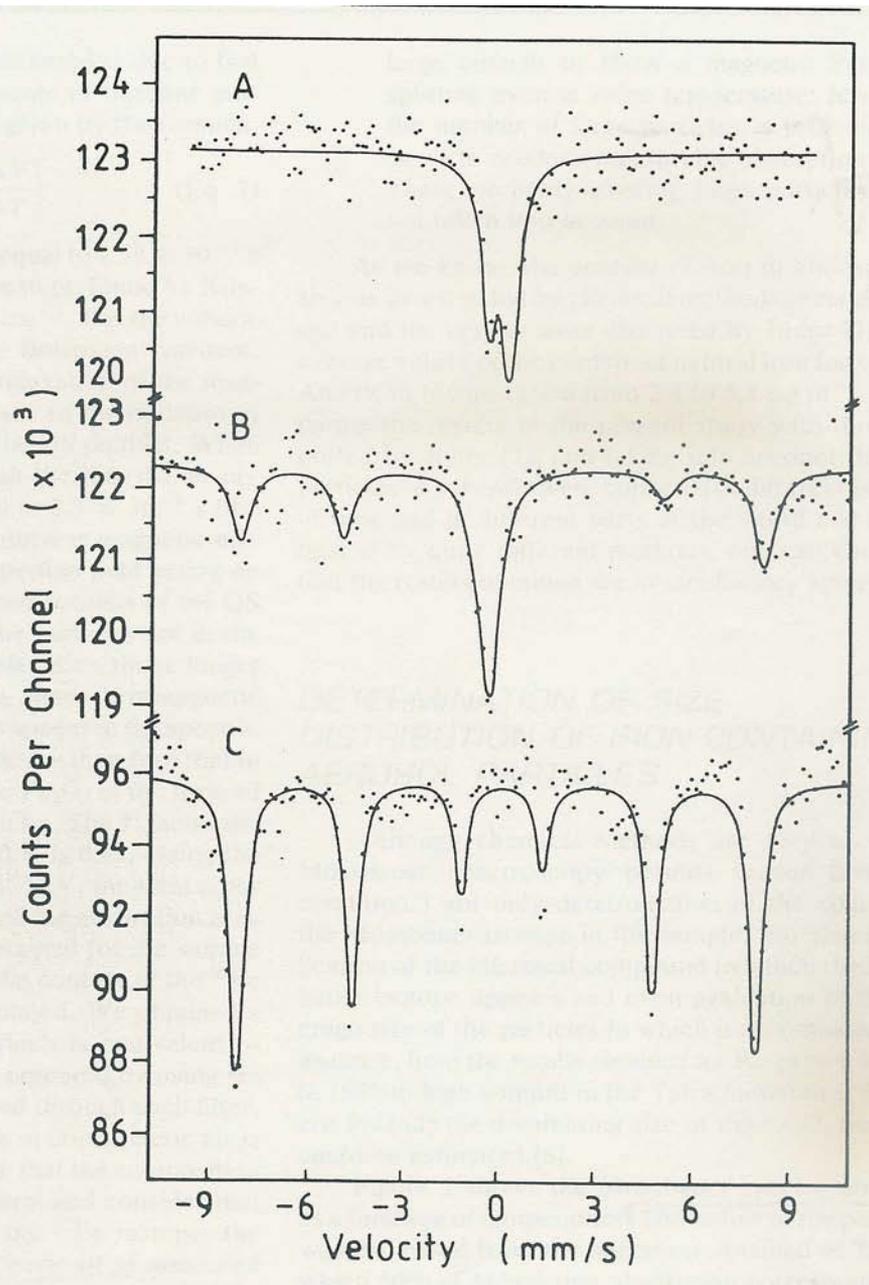
# Ecological Aspects of Mossbauer Study of Iron-Containing Atmospheric Aerosol

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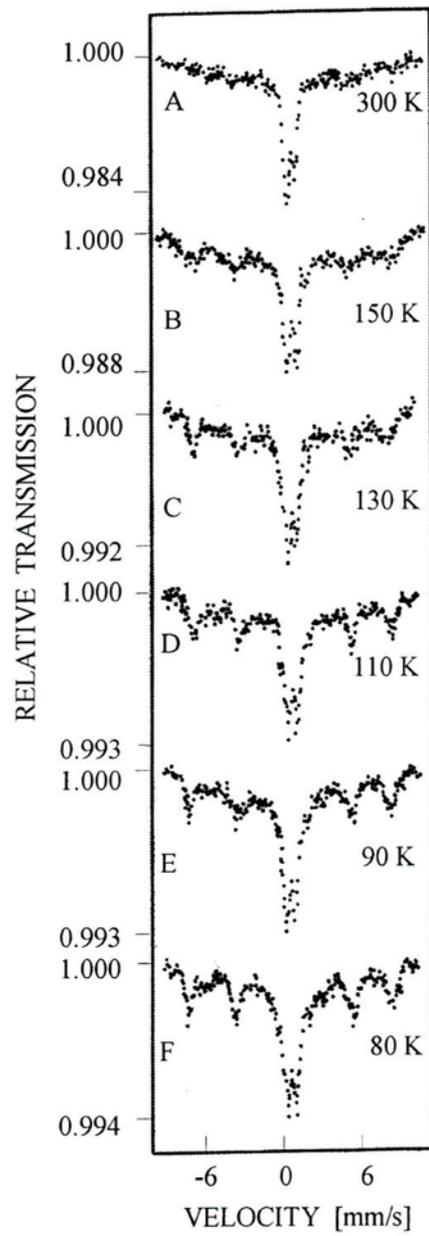
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- For the first time the Mössbauer effect was successfully used to study the properties and concentration of iron in the air in early seventies.
- The first paper :
- M. Kopcewicz and B. Dzienis,
- **Tellus 23, (1971), 176.**



- For the first time the Mössbauer spectroscopy was applied to estimate the size of the  $\alpha$  - Fe<sub>2</sub>O<sub>3</sub> particles in the atmospheric aerosol collected at Kasprowy Wierch and presented in the paper :
- B. Kopcewicz and M. Kopcewicz, **Tellus 30, (1978), 662.**
- Figure shows the Mössbauer spectra recorded as a function of temperature.



- The relaxation time is given by the formula:
- $\tau_R = \tau_0 \exp(KV/kT)$
- The radius of the particles was estimated from the spectrum obtained at 75K, in which 50% of the Mössbauer absorption corresponds to the magnetically split spectral component and 50% to the QS doublet.
- In this case, it can be assumed that the relaxation time is comparable to the observation time, so the volume of the particle can be evaluated from Equation.

- The radius of the dominating particles of  $\alpha$ -**Fe<sub>2</sub>O<sub>3</sub>** estimated in this way was about **5.5 nm**.
- In addition to the dominating size, cut-off of the size distribution can be estimated: maximum radius of iron-containing particles was **larger than 5.5 nm but smaller than 8.5 nm**.
- The particle size distribution differs for different sampling sites and reveals characteristic seasonal variations.
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## Introduction- why atmospheric aerosol?

- Aerosols are the minor, compared to gases, components of the atmosphere, but their role is enhanced by their omnipresence, interactions with atmospheric radiation, and participation in chemical reactions and cloud formation processes.
- It was not until 1950s that the regulation of particulate substances in the ambient air has been recognized as an important issue in pollution control. Since that time, the particle size, beside the total concentration of suspended particles, started to be an important subject of environmental studies.

## Why iron?

- Iron is the most abundant transition metal in the atmosphere.
- The main sources of iron-containing particulate matter are related
  - to human activity and include soil dust, emission from industrial operations, oil- and coal-fired power plants, exhaust from car engines, and
  - to natural sources, such as volcanic fumes, extraterrestrial particles and meteor showers.

- The influence of iron in the atmosphere is a complex matter and is
  - a function of its concentration,
  - chemical environment,
  - speciation and
  - solubility.
- **The iron can participate in a variety of homogeneous and heterogeneous electron-transfer reaction.**

- In complex catalytic chain reactions iron may increase the oxidation rate of S(IV) to S(VI).
- In recent years iron started to be the subject of many investigations because of its significant role in the catalytic oxidation of SO<sub>2</sub> in the atmosphere in relation to acid rain.

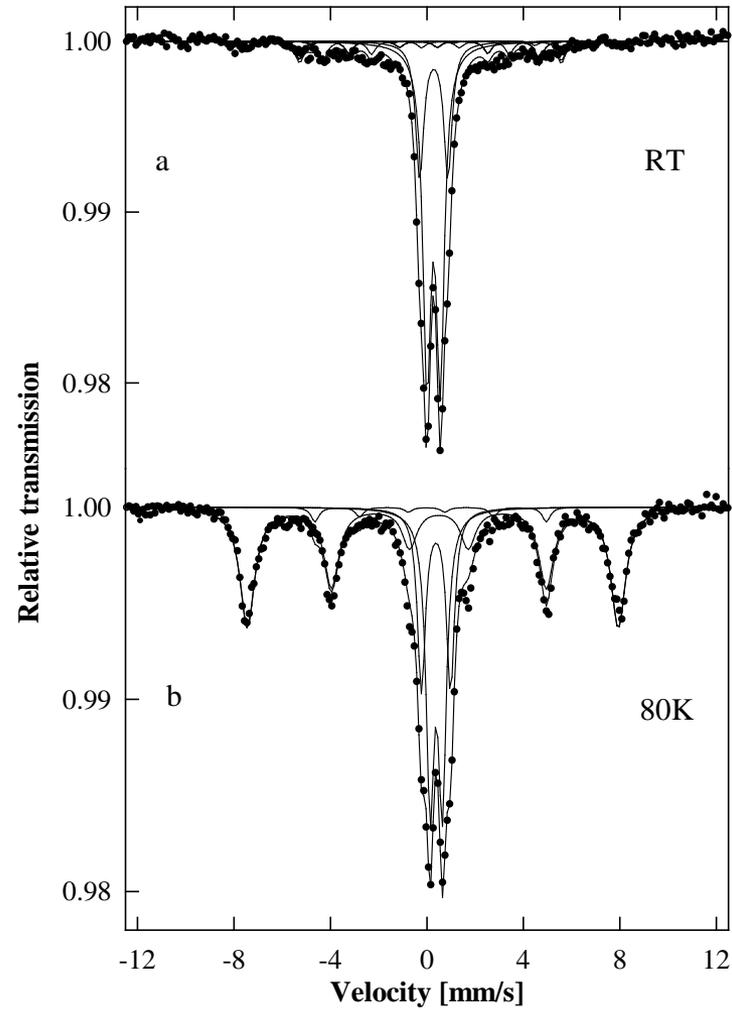
- **In photochemical reactions iron complexes are the sources of OH radicals and H<sub>2</sub>O<sub>2</sub> compound.**
- The mineral form of the particulate iron-containing matter is important for both the dissolution rate and the photo reactivity of the particles.
- Iron in the Fe<sup>2+</sup> and Fe<sup>3+</sup> state is a dominant central atom in complexes with water, ammonia, sulfate, organic compounds (e.g., formate, acetate), and with chelating groups influencing the dissolution behavior.

# Experimental details

## The samples preparation

- The samples used in the study were prepared by using membrane filters (Synpor II) usually used in the measurements of air radioactivity. Atmospheric air was pumped through each filter and volume of air passed was measured. Filters were collected in period from early seventies to 1997.
- The samples for the Mössbauer measurements were prepared by dissolving the filters in acetone, evaporating, and pressing the residue between two thin, iron free, aluminum foils.
- Each sample consisted of 15 filters obtained from the same site during 15 successive days. The volume of air pumped through the 15 filters varied from approximately 600 to 1200 m<sup>3</sup>

# Identification of iron-containing phases



- The paramagnetic doublets with a distribution of quadrupole splitting values of  $\Delta$  in the range of 0.55 – 1.1 mm/s may originate from the following sources:
- **(i)**  $\text{Fe}^{3+}$  cations in the oxyhydroxides such as ferrihydrite,  $\beta\text{-FeOOH}$  and  $\gamma\text{-FeOOH}$ ,
- **(ii)**  $\text{Fe}^{3+}$  - bearing minerals and
- **(iii)** the iron-containing compounds ( $\alpha\text{-Fe}_2\text{O}_3$  and/or  $\alpha\text{-FeOOH}$ ) in the form of ultra fine particles in superparamagnetic state.

In more detailed analysis

(fitting procedure based on distribution of quadrupole parameters)

the broad quadrupole doublet may be described by two doublets:

$$\delta_1 = 0.37 \text{ mm/s}, \Delta_1 = 0.6 \text{ mm/s}$$

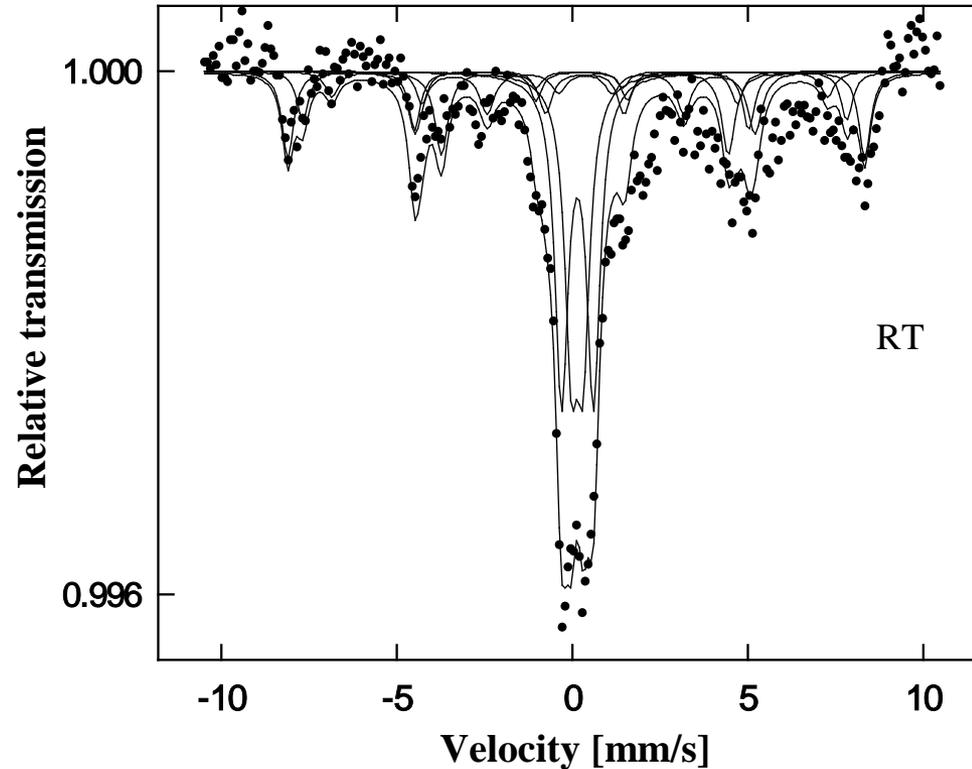
$$\text{and } \delta_2 = 0.38 \text{ mm/s}, \Delta_2 = 0.9 \text{ mm/s}.$$

- In the Mössbauer measurements performed at room temperature the poor crystallinity of ferrihydrite causes broad distributions of hyperfine parameters which results in a broad doublet, with the average quadrupole splitting in the range of 0.7 – 0.9 mm/s:
- the poorer the crystallinity the larger the quadrupole splitting.

- The Mössbauer parameters obtained in the fitting procedure to the experimental data presented above suggest the presence of the **ferrihydrates,  $\gamma$ -FeOOH (lepidocrocite) and superparamagnetic  $\alpha$ -FeOOH (goethite)** particles in the aerosol sample.
- It is in agreement with the results obtained using “wet chemistry”. Pehkonen et al. suggested that a significant fraction of the relative atmospheric iron in the urban aerosol could be presented as
- **amorphous iron hydroxide [am-Fe(OH)<sub>3</sub>]** which can slowly transform to goethite and lepidocrocite.

- Results of experiments performed by Pehkonen et al. on the photoreactivity of the different synthetic iron phases ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\alpha$ -FeOOH,  $\gamma$ -FeOOH and ferromaghemite) and ambient aerosol in the presence of important atmospheric organics (formate, acetate, formaldehyde and oxalate) have been shown that the fastest rates of photoreduction of Fe(III) to Fe(II) were observed for ferromaghemite as the electron acceptor and formate as the electron donor.
- **Natural iron-containing aerosol particles** revealed photochemical behavior **similar to ferromaghemite and  $\gamma$ -FeOOH** which suggested that a significant fraction of the atmospheric iron could be present as a ferromaghemite and lepidocrocite.
- What was only postulated by Pehkonen et al. it was measured in the Mössbauer experiments presented above.

The more complicated Mössbauer spectra were obtained in Zakopane in winter months.



## The main differences:

- **In Zakopane:** more than 50% of the iron-containing aerosol particles appear in the form of magnetically ordered compounds already at room temperature Mössbauer spectra, which suggests that atmospheric aerosol particles in Zakopane are much bigger than at Kasprowy Wierch.
- The 16% of the collected iron-containing aerosol appears in the form of a coarse fraction of hematite, about 16% in the form of magnetite, about 6% as goethite and 12% as iron sulfides ( $\text{Fe}_{1-x}\text{S}$ ).

- Size distribution of particles and the chemical composition of aerosol collected at Kasprowy Wierch (e.g. magnetic lines related to bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) become similar to that observed in Zakopane in summer months.
- This similarity can be interpreted in terms of **the turbulent and convective vertical transport of pollutants from local sources**. The vertical transport is much more effective in summer than in winter.
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# Conclusions

- In order to control air pollution effectively, it is necessary to understand in detail the physical and chemical processes that govern its formation and transport.
- It have been shown that the Mössbauer spectroscopy is a very useful technique for identification of iron-containing phases but.....time consuming!



- The physical properties combined with the chemical composition of the aerosol allow identification of the **source of the particles**.
- Seasonal changes and shape of terrain help for this identification (changes in turbulence!)
- iron sulfides - coal combustion related to house heating (fortunately decreasing)
- iron oxides and oxyhydroxides regardless of the season suggests that the car traffic in town strongly contributes to air pollution and that the influence of the automobile emission continuously increases – strong influence on photoreduction of Fe(III) to Fe(II).