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INVESTIGATION OF IRON CONTAINING ATMOSPHERIC AEROSOLS

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Résumé. — En appliquant la technique de l'effet Mössbauer on a étudié les variations saisonnières des concentrations du fer dans l'air atmosphérique. Les mesures sont faites dans le domaine de températures allant de 300 K à 75 K pour les échantillons préparés des filtres. La concentration du fer dans l'air a été calculée à partir des spectres Mössbauer par la *méthode du champ*. L'analyse des spectres Mössbauer montre que le fer est lié en Fe_2O_3 sous forme de particules ultrafines en état superparamagnétique. Les mesures ont permis d'évaluer les dimensions des particules d'aérosol contenant le fer. On a discuté la relation des variations saisonnières des concentrations du fer avec l'activité des météors. On a essayé de trouver la relation entre la pollution de l'air et la concentration du fer atmosphérique.

Abstract. — The seasonal variations of iron concentration in atmospheric air were studied using the Mössbauer technique. Mössbauer measurements were performed in the temperature range from 300 K to 75 K for samples prepared using filters through which a given volume of air was pumped. The concentration of iron in air was calculated by the *area method* from the experimental spectra obtained. From the shapes of the Mössbauer spectra it was inferred that iron appears as Fe_2O_3 in the form of ultrafine particles in the superparamagnetic state. The temperature measurements made it possible to estimate the size of iron containing aerosol particles. Correlation of the seasonal variations of iron concentration with meteorite activity was discussed. Attempts were made to find a relation between the air pollution and the concentration of iron in atmospheric air.

1. Introduction. — During the last few years Mössbauer investigations of the properties of iron containing atmospheric aerosols were conducted in our laboratory [1], [2], [3]. It was found that the concentration of iron varies considerably with time, site and meteorological conditions. Studies of these variations and of the size of iron containing particles of the aerosol may throw some light on the sources of iron in the atmosphere.

In the present work Mössbauer investigations of the seasonal variations of iron concentration in atmospheric air were continued and extended to samples collected from various sites in Poland. The concentration of iron in the air was calculated by the *area method* in the same way as in [1], [2], [3]. From the Mössbauer measurements at various temperatures it was possible to estimate the size of iron containing particles, which, together with the seasonal variations of iron concentration, suggests the extraterrestrial origin of iron in the air. It was also inferred that industrial air pollution contribute considerably to the concentration of iron in air.

2. Experimental. — The samples used in the present study were prepared, using membrane filters usually

used in the measurements of air radioactivity. Atmospheric air was pumped through each filter and the volume of the air passed was measured. The air pollution with dust, in mg/m^3 , was given for each filter. The filters were supplied from two sites in Poland: Wrocław (South-West Poland) and Kasprowy Wierch (a 1985 m high summit in the Tatra mountains, Southern Poland), in the period from June 1972 to May 1974.

The samples for the Mössbauer measurements were prepared by dissolving the filters in acetone, evaporation, and pressing the residue between two thin aluminium foils. Each sample consisted of 15 filters obtained from the same site during 15 successive days. The volume of air pumped through 15 filters was approximately $1\,700\text{ m}^3$ and $1\,000\text{ m}^3$ for Kasprowy Wierch and Wrocław, respectively. Thus, two samples per month were prepared for each site. Such samples were used in the Mössbauer measurements as absorbers. The Mössbauer measurements were performed in a transmission geometry, using a constant acceleration Nokia Electronics Co. spectrometer with a 800 channel analyser. The ^{57}Co in a palladium matrix of 50 mCi activity was used. The measurements were carried out in the temperature range from 300 K to 75 K, using the

Oxford Instruments Co. continuous flow CF-104 cryostat. The temperature of the sample was measured using a cryogenic linear temperature sensor, and the temperature stability, controlled by means of the Oxford Instruments Co. precision temperature controller, was better than ± 0.2 K for all temperatures at which the measurements were performed.

The parameters of the Mössbauer spectra were computed by fitting the Lorentzian line shapes to the experimental data, using the least-squares method.

3. Results and discussion. — The typical Mössbauer spectra obtained at room temperature both for Kasprowy Wierch and Wrocław consist of a quadrupole doublet (*QS*) with $\Delta E_Q = 0.65$ mm/s (Fig. 1A). However, in several spectra obtained for the samples from Wrocław magnetic hfs lines appear (see discussion below).

To calculate the concentration of iron in the sample it is necessary to establish in what chemical compound is iron contained. Such an information can be obtained from the Mössbauer measurements at different temperatures which were performed in the temperature range from 300 K to 75 K for a typical sample from Kasprowy Wierch. The results are shown in figure 1. As can be seen, the decrease of the intensity of the *QS* doublet with decreasing temperature is accompanied by a simultaneous increase of the intensity of the magnetic hfs lines which appear in the spectra obtained at temperatures below 150 K. The magnetic hyperfine field $H = 520$ kOe and the isomer shift $\delta = 0.38$ mm/s calculated for the magnetic fraction of the spectra correspond exactly to magnetic hf field and isomer shift of α -Fe₂O₃ [4]. Such a temperature behaviour of the spectra is typical of small superparamagnetic particles of α -Fe₂O₃ [1], [4]. The disappearance of the hfs lines when the temperature is increased is due to fast relaxation of the magnetic moment of ultrafine particle, and the relaxation time is given by the formula :

$$\tau = \tau_0 \exp\left(\frac{KV}{kT}\right) \quad (1)$$

where τ_0 is the frequency factor equal to 1.58×10^{-9} s for Fe₂O₃, K is the anisotropy constant found in [4] to be 4.1×10^4 erg/cm³, V is the volume of the ultrafine particle, k is Boltzmann constant, and T is the temperature. Fast relaxation of the magnetic moment of the particle leads to the collapse of the magnetic hfs spectrum to the *QS* doublet. When the relaxation time is shorter than the Mössbauer observation time, in our case equal to 2.5×10^{-8} s, than the spectrum consists of the *QS* doublet only. This shows that the particles are in the superparamagnetic state. For relaxation times longer than 2.5×10^{-8} s the particles show ferromagnetic behaviour and magnetic hfs lines appear in the spectra. The temperature measurements show therefore that in our samples iron is contained in

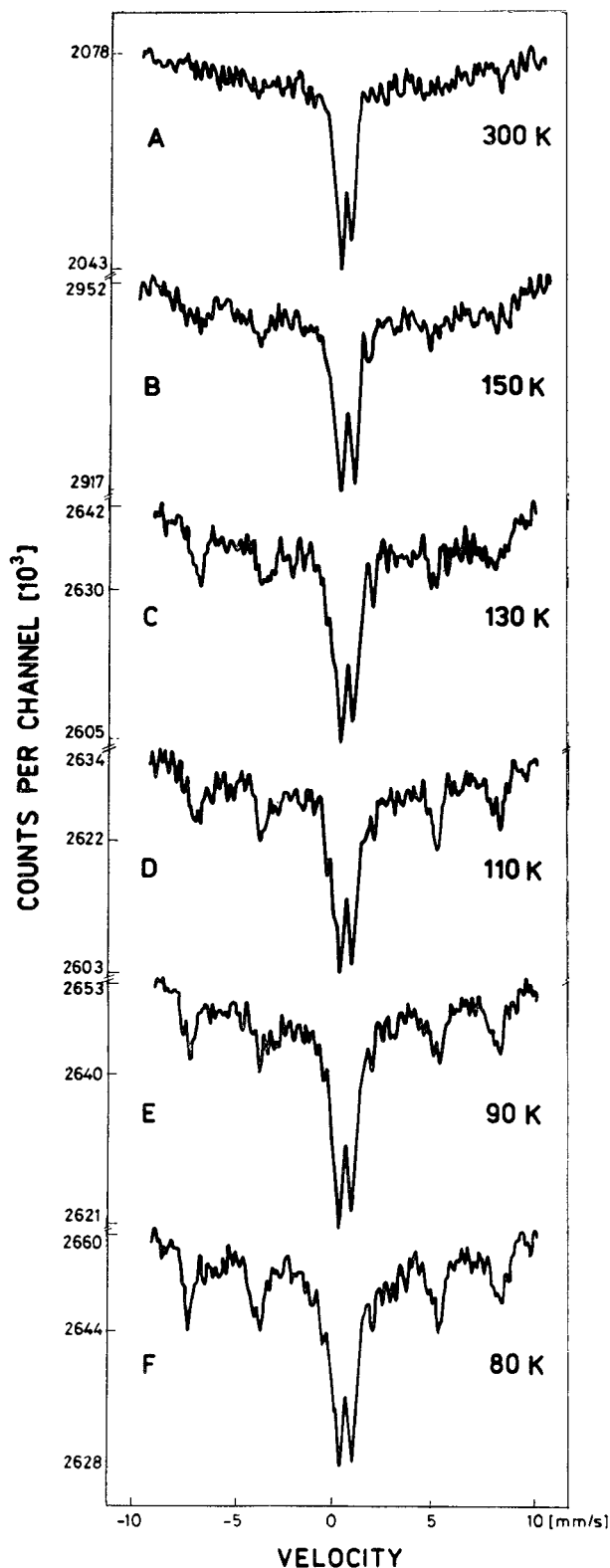


FIG. 1. — Mössbauer spectra obtained as a function of temperature for the sample from Kasprowy Wierch.

α -Fe₂O₃ in the form of ultrafine superparamagnetic particles.

From the results obtained the dominating size of the

Fe_2O_3 particles can be estimated. The radius of the particles was estimated from the spectrum obtained at 75 K in which 50 % of Mössbauer absorption corresponded to the nonmagnetic part (QS doublet) of the spectrum, and 50 % to the magnetic hfs part. In this case it can be assumed that the relaxation time is comparable to the observation time, and the volume of the particles can be evaluated from Eq. (1). The radius of the dominating particles of Fe_2O_3 estimated in this way was about 55 Å.

As can be seen from Eq. (1) the relaxation time is comparable at 300 K to the observation time for the particle radius of 85 Å. So, for particles smaller than 85 Å superparamagnetic behaviour dominates at 300 K. Since in the spectra obtained for our samples no magnetic hfs lines were observed at 300 K, one can infer that the maximum radius of Fe_2O_3 particles is larger than 55 Å but smaller than 85 Å.

The Mössbauer measurements were performed for 45 samples from Kasprowy Wierch and 38 samples from Wrocław. For all samples the concentration of ^{57}Fe in the sample was calculated from the experimental spectra, using the *area method* [5]. We made use of the method given by Hafemeister and Brooks Shera [5] which is normally used for the calculation of the f -factor from the measured area under the Mössbauer lines. Since the density of the Mössbauer isotope in the sample is used when calculating the f -factor, the content of the resonant isotope in the absorber can be inferred from the knowledge of the f -factor for the absorbing material. Comparing the theoretical absorption area with the experimentally measured absorption area and reversing the method given in [5] one can evaluate the content of the Mössbauer isotope in the sample in the same way as in our recent papers [1], [2], [3]. Since all samples were prepared using 15 filters through which a given volume of air was pumped, it was possible to estimate the concentration of ^{57}Fe per cubic meter of air.

In figure 2 the seasonal variations of ^{57}Fe concentration in air obtained from Wrocław (A) and Kasprowy Wierch (B) are presented. As can be seen in figure 2, the

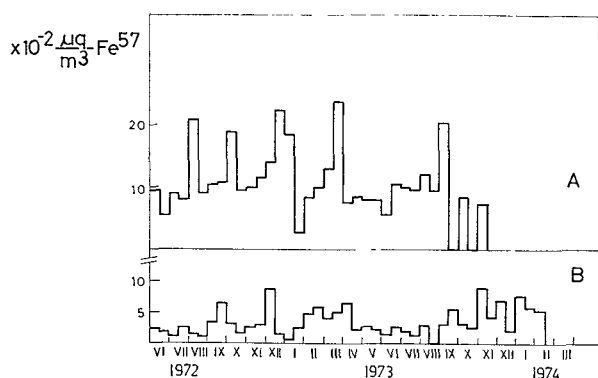


FIG. 2. — Seasonal variations of iron concentration in air obtained for Wrocław (A) and Kasprowy Wierch (B).

shape of both diagrams is very similar. The peaks of high concentration of ^{57}Fe occur in similar periods in both sites. The maximum iron concentration was observed at the turn of September and October, and November and December. A somewhat smaller concentration of iron was observed in February and March. The lowest concentration of ^{57}Fe was observed in summer. Such a low iron concentration in June and July has been reproduced in the subsequent year. The regular seasonal variations of the iron concentration for a given site are helpful in the discussion of the sources of iron in air, because they allow to eliminate the disturbances due to industrial air pollution.

Comparison of iron concentration for Kasprowy Wierch and Wrocław suggests that industrial air pollution has a noticeable influence on the content of iron in air. Industrial air pollution measured as dust concentration in the air is by an order of magnitude larger for Wrocław than for Kasprowy Wierch. The increase of air pollution is accompanied by an increase of iron concentration. However, this relation is not linear. The relative content of iron, given as a ratio of iron to dust concentration, is much larger for the samples from Kasprowy Wierch than for the samples from Wrocław. This suggests that a considerable part of iron containing particles comes to the troposphere from the upper layers of the atmosphere. Moreover, the increase of iron concentration in Wrocław was accompanied by a considerable change of the shape of the Mössbauer spectra obtained for the several samples from Wrocław. In these spectra the magnetic hfs lines appeared beside the QS doublet at 300 K whose line positions correspond to Fe_2O_3 . Such a complex spectrum can be due to the coexistence of particles of two dominating sizes: small ones — corresponding to the QS doublet, and large ones — contributing to the magnetic hfs lines. It seems that the large iron containing particles are of industrial origin and the small particles are of extraterrestrial origin. The seasonal variations of iron concentration and the nonlinear character of the relation between iron and dust concentration in air suggest that possible sources of iron in air can be both sporadic meteors and meteor showers. As it is well known iron is the most abundant element in meteor material.

The presented attempt of the interpretation of seasonal variations of iron concentration in atmospheric air is well supported by our results concerning the size of iron containing particles. As it was said above, the radius of the dominating particles containing Fe_2O_3 was determined at about 55 Å. Rosinski [6] calculated that particles of 5 to 100 Å in diameter can be produced in the process of condensation of meteoritic vapour. Meteors penetrate the atmosphere from the space and their interaction with the atmosphere produce deceleration and heating which lead to the evaporation of the meteor material. Subsequently these vapours can condense. The size distribution of the condensed vapour particles depends on the competing rates of

agglomeration and diffusion processes. These rates differ according to the initial particle concentration in the meteorite train, which varies with the meteor size. The calculations [6] performed for pressures corresponding to a height of 80-110 km above the Earth's surface indicate that particles with average diameter of 10 to 60 Å can be formed in the first ten seconds following the ablation of the meteorite. Then the agglomeration process which follows the condensation of the meteor vapours, occurring under different conditions, leads to the formation of much larger particles with the diameter of the order of 10^{-4} cm, which approach the Earth's surface. However, in our experiments very small, 55 Å particles were observed. This suggests that large particles formed in the agglomeration process may be composed of ultrafine particles. In our case the size of ultrafine superparamagnetic particles should be understood as the radius of a magnetically ordered region which as a whole has a large magnetic moment. Such particles do not interact with neighbouring regions by magnetic coupling; thus in the Mössbauer spectra no magnetic hfs lines are observed. However, such noninteracting superparamagnetic particles may be connected mechanically and in the process of

transport of particles through the atmosphere can be considered as one large particle. Since agglomeration process occurs under considerably different conditions than condensation of particles just after the ablation, the resulting large particles can be non-homogeneous. Such a form of particles approaching the Earth's surface is strongly supported by our Mössbauer measurements.

It seems that the Mössbauer investigations can be rewarding in the search for the sources of iron in air and may be useful in the studies of the properties of iron containing particles of aerosols. However, a detailed consideration of the effect of meteor activity on the concentration of iron in air would require an analysis of numerous samples taken from different sites for a long period of time.

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