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MÖSSBAUER SPECTROSCOPY OF THERMAL AND RADIATION EFFECTS IN IRON MINERALS AND ITS APPLICATIONS TO GEOCHRONOLOGY+

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This review concerns some works on thermal and radiation effects in iron minerals which are potentially usefull for geological dating.

There are only a few of such works among the limited number of Mössbauer spectroscopy studies of irradiated iron minerals. Moreover until now only at most correlations between Mössbauer spectra and geological dating have been suggested.

For these reasons, our purpose is to emphasize the possible applications to geochronology of Mössbauer studies of thermal and radiation effects in minerals, a field which has been practically unexplored.

From radiation damage studies in solids we know that in general two kinds of effects can be observed:

a) physical effects: such as atomic displacements, formation of vacancies and other lattice defects;
b) chemical effects: radiolysis, with the formation of free radicals and appearance of new chemical species.

Both effects arise from direct energy transfer by collisions and by ionization and excitation of atoms and molecules when the irradiating particle passes through the solid.

It is also well known that thermal effects can either compete with radiation effects (annealing) or, in many cases, si-

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mulate the radiation effects. Thus, vacancies can be created in many solids either by radiation or by heating. Thermal decomposition of complex molecules frequently leads to the same chemical species obtained by radiolysis.

The possibility of application of Mössbauer spectroscopy for dating procedures arises from the same principles on which are based a number of geochronological methods. In such methods, as for instance in thermoluminescence, one measures the radiation effects which accumulates in the solid by the intensity of the light emitted when the sample is heated at high temperatures. The electrons which are responsible for the emission of light are located in sites which remain stable at temperatures far above the ambient temperature. Otherwise the memory of the radiation effect would be bleached by the temperature fluctuations of the environment.

The radiation effects which manifest themselves in the Mössbauer spectra, must be accumulative and also not sensible to temperature variations as discussed above. In order to be usefull for geochronology, other processes in the mineral should not compete with the radiation effects. For example, with some type of micas the same effects are observed by irradiation or in the weathering process of the mineral. Since it is not possible to distinguish between both contributions to the changes occuring in the mineral, no dating method can rely on such effects.

One of the first studies which attempt to correlate geological time with Mössbauer hyperfine parameters is reported in the work of T.V. Malysheva and collaborators with glauconites[1][2][3].

These studies are based on the fundamental observation that order-disorder phenomena which occurs in minerals should be age dependent. The measurement of the age dependence is within the possibilities of Mössbauer spectroscopic measurements.

Real crystals and in particular minerals, present defects in the solid lattice. The degree of ordering in the vicinity of iron atoms in grains of these solids is dependent on the concentration of defects, which is a function of the temperature.

In an isothermal process one expects a spontaneous decrease in the number of defects around the iron atoms with time, since the free energy of the crystal decreases with decreasing number of defects. The decrease in the number of defects arises from their migration in the lattice towards the surface of the crystal. For this reason the number of defects at the vicinity of an iron atom decreases according to the diffusion rate of the defects in the mineral at room temperature, since we are considering non heated minerals. The rate of diffusion is so slow that the ordering process around the Fe ions proceeds on the geological time scale[2].

The value of the electric field gradient acting at the iron nucleus is a function of the number of defects which are present at a given moment in the first, second, etc. coordination spheres[2]. As a consequence one expects a decrease of the quadrupole splitting and the linewidth as a function of time, at a rate depending on the spontaneous ordering around the iron ions by the diffusion mechanism described above.

The work of Malysheva et al was done with thermally undisturbed glauconites of general formula $(K,Na,Ca)(Fe^{3+},Al^{3+},Fe^{2+},Mg^{2+})(Si,Al,Ti)(O_{2-x}OH_x).nH_2O$.

The age of these minerals can be determined by the argon-potassium method, which also gives information on the degree of geological disturbance of the minerals, since the Ar/K ratio is temperature dependent.

The Mössbauer spectrum of glauconites shows a marked dependence on the history of the mineral. The undisturbed minerals, which did not warm up above 100°C, exhibit a partially resolved intense doublet due to Fe^{3+} with a small contribution of the Fe^{2+} ions (Fig. 1).

The results obtained by Malysheva in minerals with ages varying from 10^5 to 10^9 years shows that the quadrupole splitting and the linewidth of the Fe^{3+} ion exhibit a tendency to decrease with time. About 26 of such samples were measured and a linear decrease of few percent on the value of hyperfine interactions at the Fe^{3+} ion is observed (Fig. 2 and 3). This is in the order of

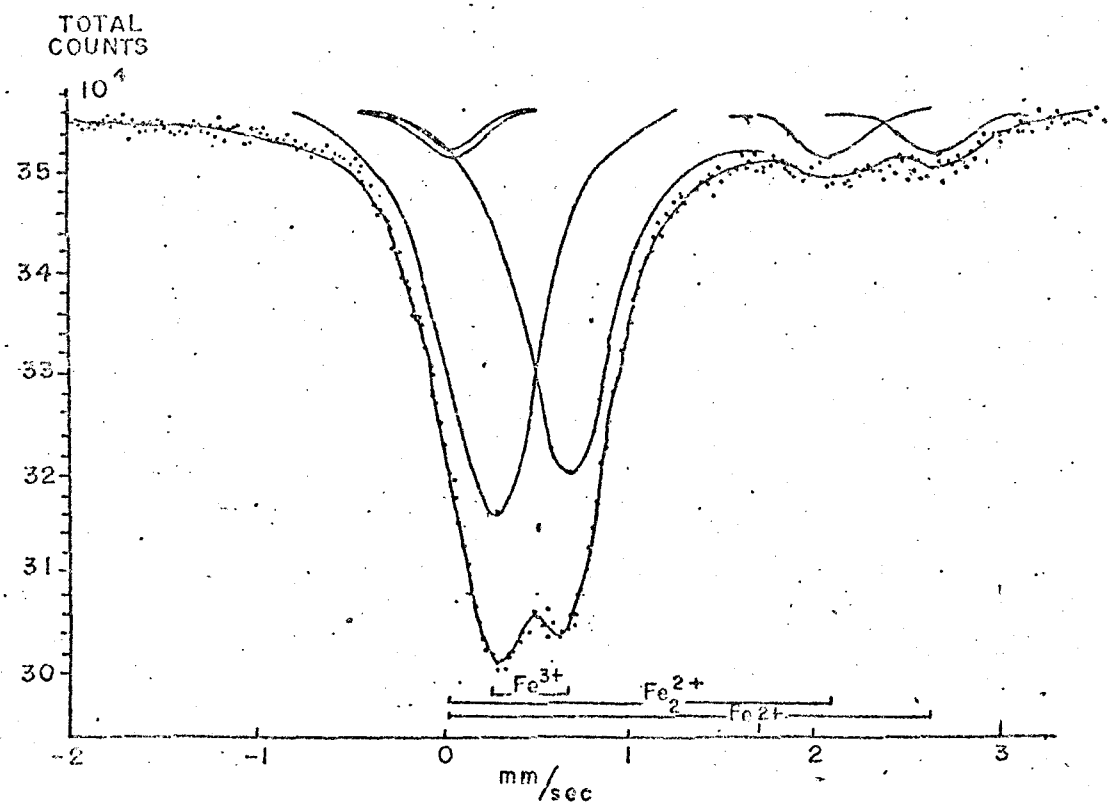

Fig. 1

Mössbauer spectrum of thermally undisturbed glauconites

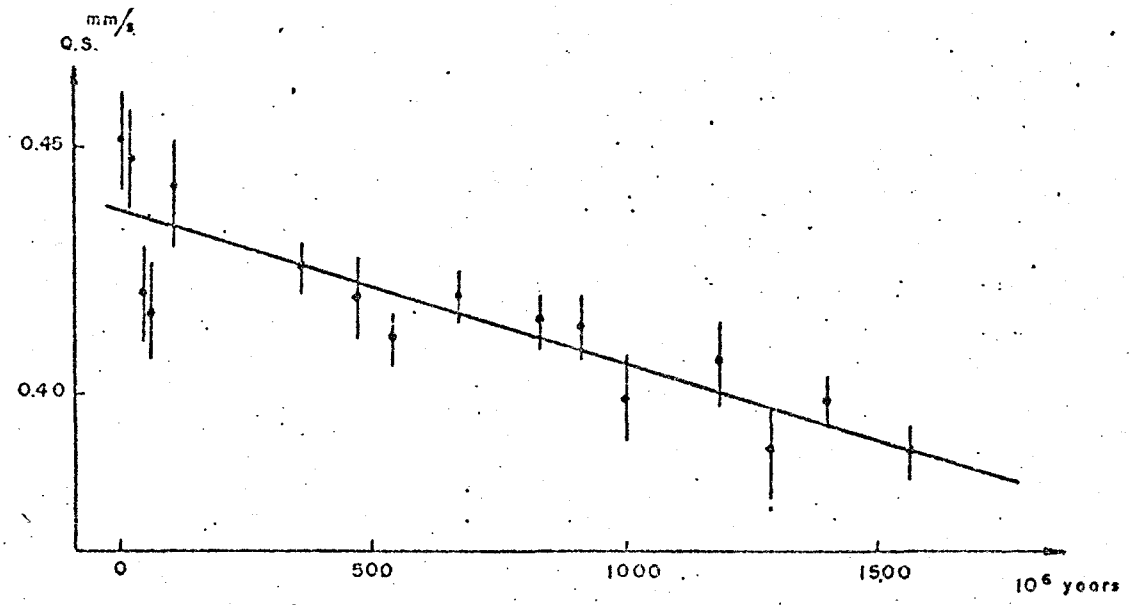

Fig. 2

Dependence of the quadrupole splitting ΔE of the Fe^{3+} ion in glauconites of several geological ages

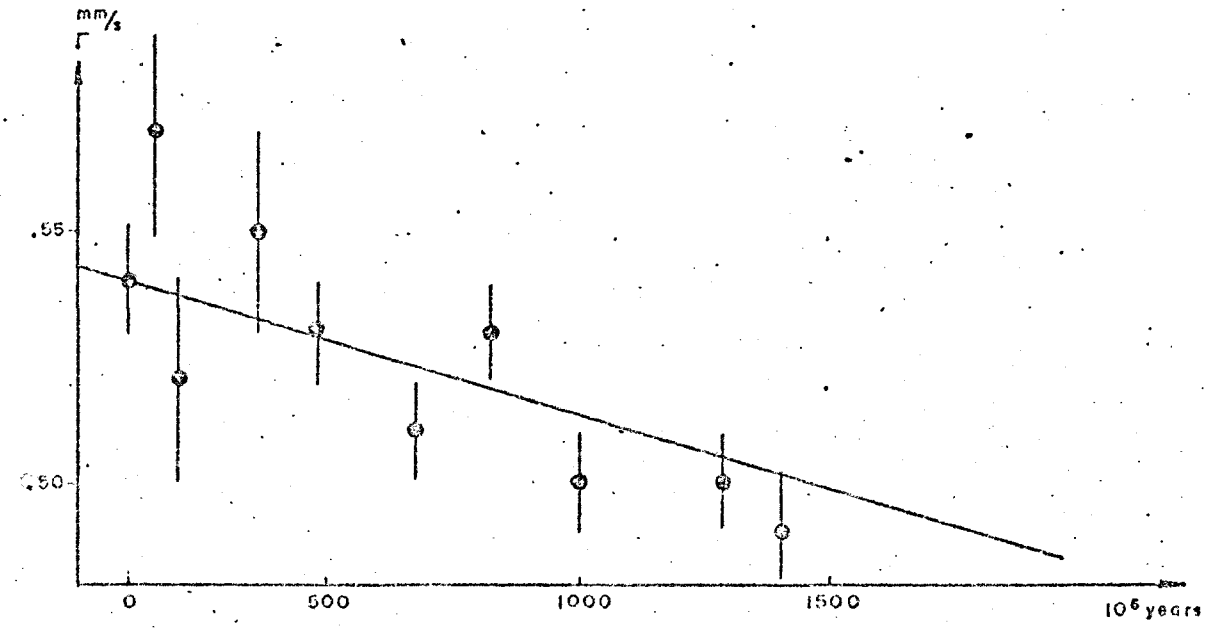

Fig. 3

Dependence of the linewidth of the Fe^{3+} ion in glauconites of several geological ages

magnitude of the expected effect due to diffusional migration in the crystals.

We have investigated the possible influence of radiation effects in the order-disorder processes in iron minerals.

It is clear that the possibility of using Malysheva results for dating measurements requires that other factors do not interfere with the slow diffusion process of the defects in the crystals.

Radiation effects, either by direct influence on the atoms or by creating new lattice defects, can in principle interfere with the kinetics of the diffusion process.

In order to see if this is a real cause of interference we choose the orthopyroxene silicate minerals as an ideal system for the study of radiation effects in the ordering process of the Fe atoms[4].

The order-disorder relation in the distribution of iron and magnesium atoms over two or more sites in orthopyroxenes is a frequent subject of investigation and detailed knowledge of such systems is available[5]. The conditions of ideality (in thermodynamical sense) of this system allows one to use the Fe-Mg distribution as a basis for geothermometry measurements[6].

We have studied the effects of electron irradiation (2 MeV electron beam) on orthopyroxenes which have been previously investigated by X-Ray diffraction and Mössbauer spectroscopy[6].

The samples were irradiated at low temperatures with the minerals immersed in liquid nitrogen, and with electron dosis up to 5000 Megarads. The Mössbauer spectrum was measured in order to detect any alteration on the distribution of Fe^{2+} ions at the two sites M_1 and M_2 of the orthopyroxenes.

A small effect was observed, which decayed in time even at the low temperatures in which the samples were irradiated and kept for a few days. This effect is not due to a modification of the Fe^{2+} distribution in the mineral. It has been attributed to the formation of a transient state at the M_2 site and is probably due to an excited charge state of the Fe^{2+} ion which decays to its original configuration[4].

It appears from this result that, as has been previously observed with many solids, atomic displacements less frequently occur by the electron irradiation. Punctual defects such as vacancies or excited electronic states are usually created in the radiation process and their annealing behaviour varyes from one system to other.

Thus, in many studies with iron compounds one frequently observes that oxidation and reduction processes occur in the solid as radiolytic effects[7]. Depending on the composition of the solid, one can observe either an oxidation or a reduction of the iron species, or even competition of both processes.

In order to establish a dating procedure on such radiolytic effects it is first necessary to determine if these oxidoreductions do not anneal at room temperatures and if similar electron transfers do not occur by geochemical processes other than radiation. If so, one can attempt to base a dating procedure on the ratio of oxidized to reduced iron states in the mineral, by comparison with some standard unirradiated sample.

This is the work of V.P. Ivanitskiy, I.V. Matyash and F. I. Ravich, with samples of biotites[8].

The effects of irradiation with Co-60 gamma-rays in these type of micas were investigated in order to compare with samples which occur in contact with uranium minerals. It is assumed that the artificial irradiation simulates the damage that arises in the micas associated with the uranium ores.

The overall effect of irradiation of biotites is an oxidation of Fe^{2+} to Fe^{3+}. The mechanism for such oxidation is assumed to be a defect formation of O^- ions from the radiolysis of the OH of the mica.

However, what is relevant for our purpose is that the Fe^{3+} affected by radiation shows Mössbauer lines at different positions, as compared with the unirradiated samples.

A detailed analysis of the Mössbauer spectra of the unirradiated and irradiated biotites indicates that the radiation induces a Fe^{3+}_{II} quadrupole doublet which corresponds to the preferential oxidation of Fe^{2+} in the trans-octahedral site as compared to the Fe^{2+} occuring in the cis-octahedral site in the mi -

cas (Fig. 4).

The iron in biotite in contact with uranium minerals differs from that in ordinary biotite by presenting a relatively large amount of Fe^{3+}_{II}. By assuming that the Fe^{3+} which is located in this site arises exclusively from radiation effects the authors calculated the age of the biotite sample. Thus an artificial dose of 2.5×10^{10} rad (equivalent to the dose delivered in an uranium ore for 2.5×10^{8} years) is sufficient to convert 8% of the Fe^{2+} to the Fe^{3+}_{II} trivalent state. Since the amount in the Fe^{3+}_{II} site from the biotite around a typical ore was found to be larger by a factor of 7 it indicates an age of $7 \times 2.5 \times 10^{8} = 1.75 \times 10^{9}$ years.

The oxidation of biotite by radiation has been confirmed by the work of V. Drago, E. Baggio Saitovitch and J. Danon[9]. Biotites with different Fe^{2+}/Fe^{+3} ratio of composition were irradiated with 2 MeV electrons at low temperatures and at room temperature. In all cases it is always an oxidation of Fe^{2+} to Fe^{3+} which occurs. The Mössbauer spectra of these micas (Fig. 5) do not exhibit annealing at room temperature. The hydrogenation of the samples regenerate the original amount of Fe^{2+} ions in the micas.

The use of protons as an irradiation agent also leads to an oxidation of the iron in biotites, as has been recently demonstrated by Mössbauer spectroscopy[10].

In the work of Drago et al a carefull comparison with thermal effects has been made. The conclusions are that heating the micas leads to the same oxidation effect observed with irradiation. It is thus important for dating purposes to ensure that the oxidation process observed in biotite does not arise from the fact that the samples were subjected to high temperatures during their geological history. Other geochemical process with biotites also leads to the oxidation of Fe^{2+} ions, which again introduces difficulties for establishing dating procedures on the oxidation ratio.

In last work which we will discuss is based on the results of R. Scorzelli, E. Baggio Saitovitch and J. Danon on elec

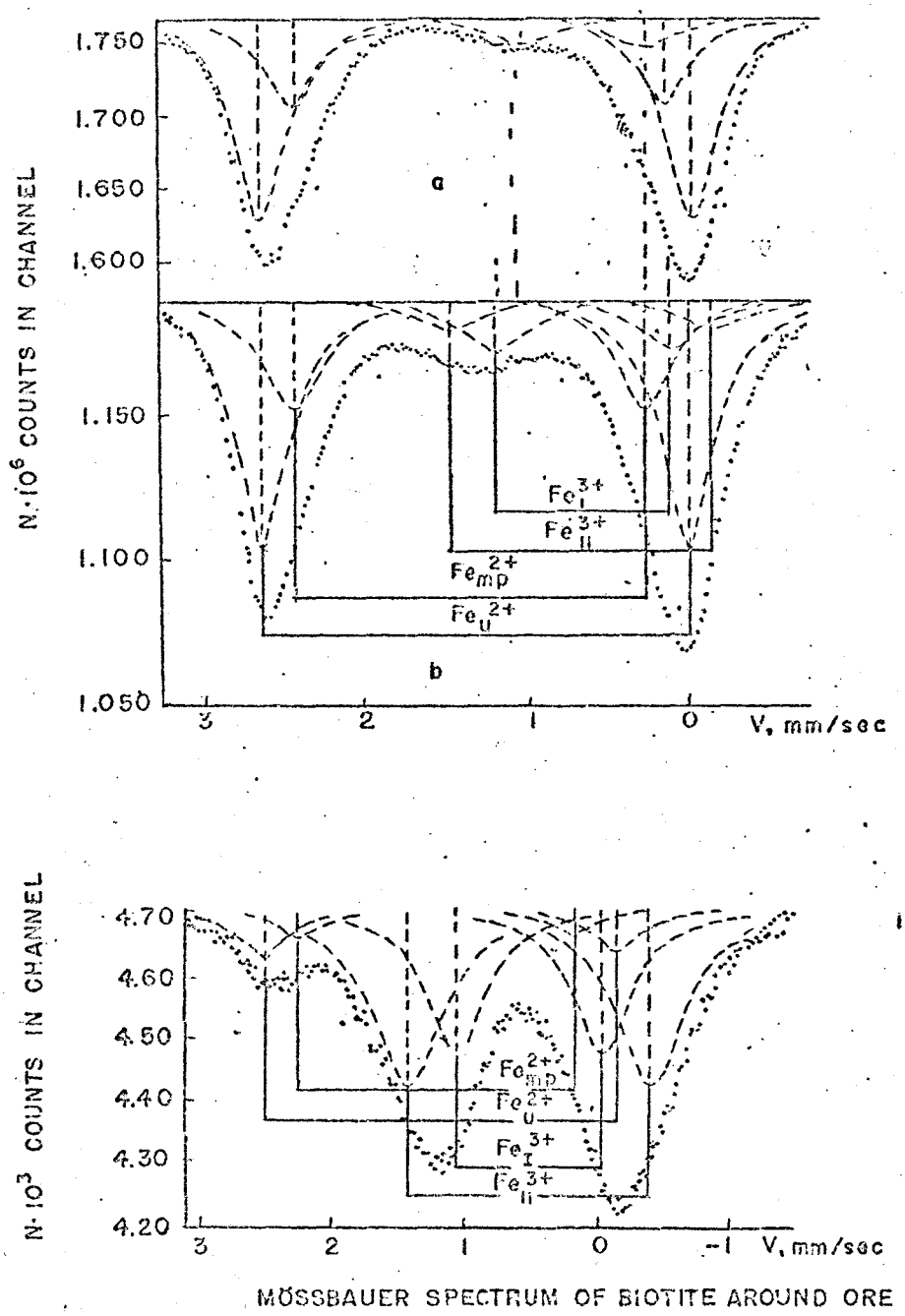

Fig. 4
Biotite Mössbauer spectra: a) unirradiated; b) irradiated with Co^{60} gamma radiation (2.5×10^{10} rads); c) around an uranium ore.

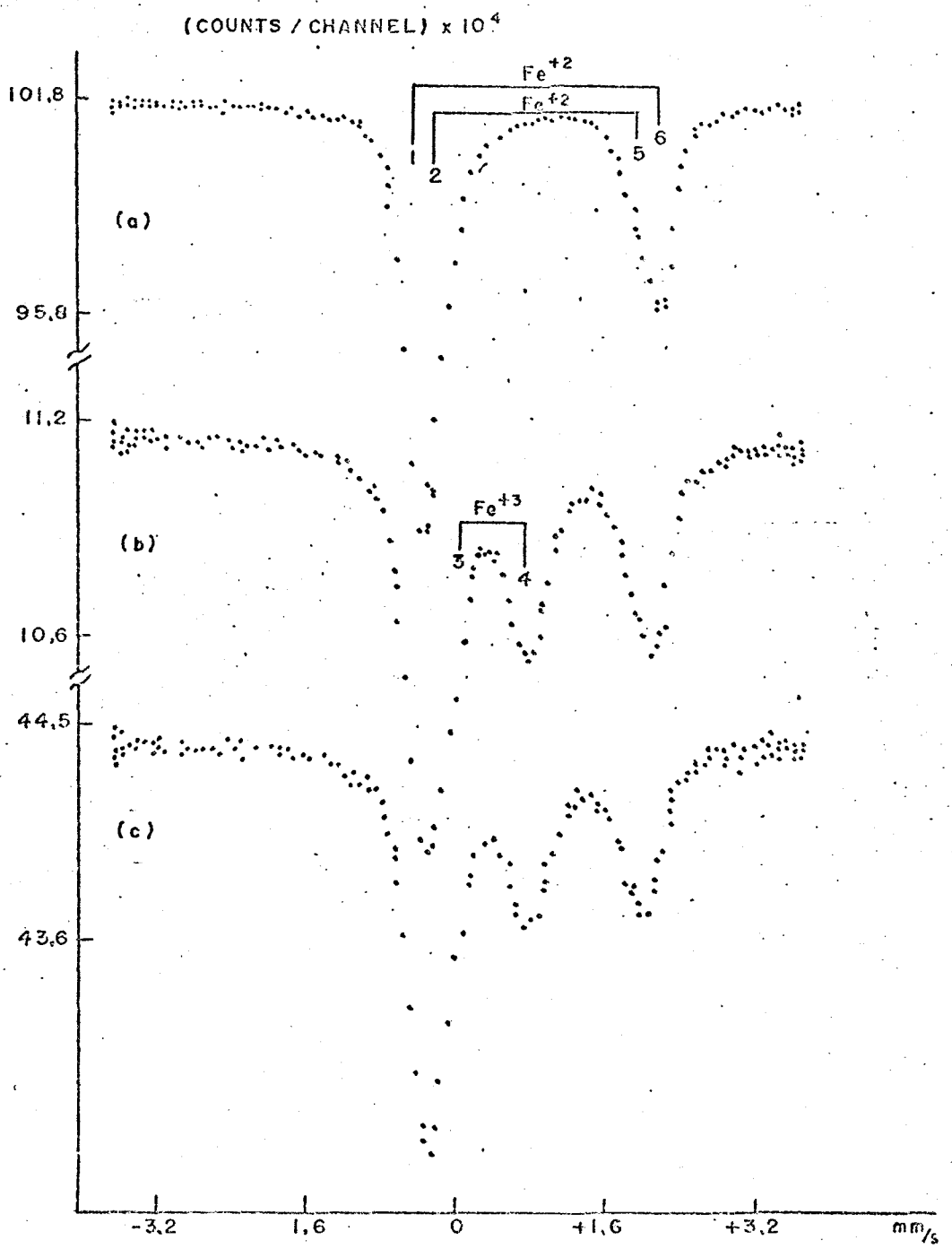

Fig. 5

Biotite Mössbauer spectra: a) unirradiated; b) irradiated with 2 MeV electrons (for 3 hours and 30 μA); c) heated in inert atmosphere during 7 hours at 600°C.

tron irradiation of tourmalines.

The tourmaline mineral is a boron-aluminum silicate in which iron is a substitutional impurity.

The thermal and radiation behaviour of black tourmalines of the Schorl type which contains a relatively high amount of iron (few percent), was investigated by Mössbauer spectroscopy and the results reported in a recent publication[11].

The Mössbauer spectra of all samples exhibited two quadrupole splittings, with isomer shifts corresponding to an Fe^{2+}_{I} doublet with much larger intensity and a broadened inner Fe^{2+}_{II} doublet (Fig. 6). The amount of Fe^{3+} was found to be less than 1%.

The area ratio of the two doublets was found to vary in large proportions among samples of different origins.

The Mössbauer spectra obtained with a black tourmaline submitted to an increasing dosis of radiation with 2 MeV electrons are illustrated in Fig. 6. It can be seen that the major effect of the irradiation is to increase the area of the inner doublet. These effects do not anneal at room temperature.

The origin of the inner doublet in these tourmalines was attributed to radiation effects in the mineral[12]. The wide variation of the area ratio of the two doublets in tourmalines from various origins would be due to different dosis of radiation absorbed by the minerals during their geological history.

On this basis one could expect to find a correlation between the area ratio and the age of the tourmalines.

Preliminary results obtained with 4 samples are listed in Table I. The age measurements correspond to argon-potassium determinations on the feldspath roch in which tourmalines are found.

The small number of cases investigated until now does not allow a definite conclusion about the validity of the correlation between the area ratio of the iron doublets and the age of the tourmalines*.

*We are assuming that the samples have been submitted to comparable average annual radiation dosis. The determination of the U, Th and K content of one of our samples by gamma-gamma coincidence spectroscopy led to a total internal dosis of about 0.6 rads/year.

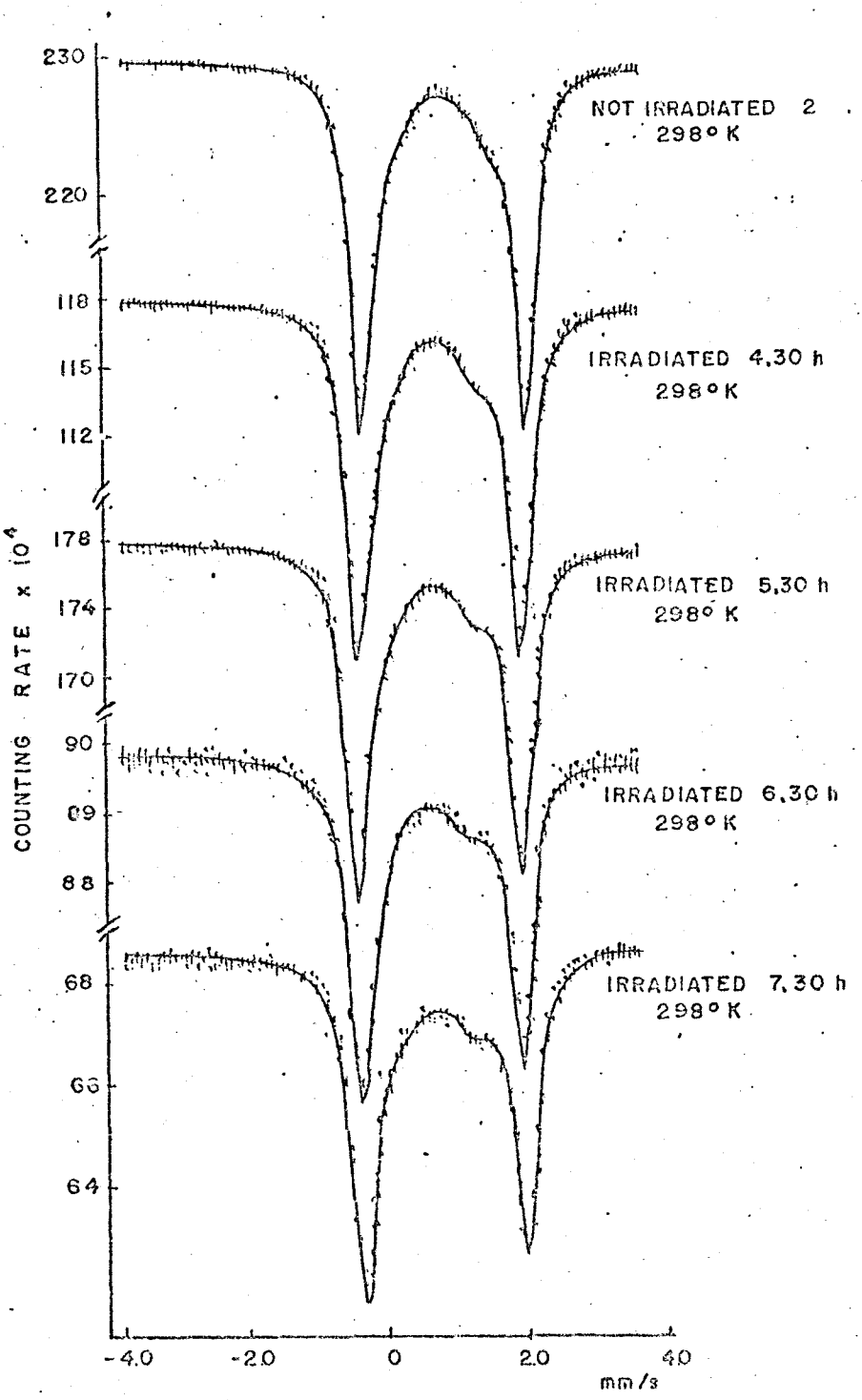

Fig.6

Mössbauer spectra of black-tourmaline irradiated with different dosis by 2 MeV electrons in an electron linear accelerator

Conclusions

The analysis of the few studies on the possibilities of using the Mössbauer effect in geochronology reveal that the subject is still in development and no reliable method has yet been proposed for such purpose.

The correlations between hyperfine interactions of the Mössbauer spectroscopy and geological time observed in some iron minerals may eventually be a basis for geochronological procedures. However, in order to achieve such aim it is necessary to make a clear distinction between radiation effects and other factors such as thermal annealing, weathering process etc.

A better comprehension of the electronic process and crystal effects envolving the iron Mössbauer probe in minerals when subjected to thermal and radiation effects is required in order to establish a sound basis for such methods.

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TABLE I

A_1 % Outer Doublet	A_2 % Inner Doublet	Age (Years) K/Ar
66.57	33.43	470×10^6
83.68	16.32	447×10^6
89.93	10.07	405×10^6
$\sim$ 95.00	< 2.00	255×10^6

Area of Mössbauer outer doublet A_1 and inner doublet A_2 in percentage for tourmaline samples of ages measured by the K/Ar method