

Werk

Jahr: 1974

Kollektion: fid.geo

Signatur: 8 Z NAT 2148:40

Digitalisiert: Niedersächsische Staats- und Universitätsbibliothek Göttingen

Werk Id: PPN1015067948_0040

PURL: http://resolver.sub.uni-goettingen.de/purl?PPN1015067948_0040

LOG Id: LOG_0054

LOG Titel: Kinetics of oxidation processes in titanomagnetites

LOG Typ: article

Übergeordnetes Werk

Werk Id: PPN1015067948

PURL: <http://resolver.sub.uni-goettingen.de/purl?PPN1015067948>

OPAC: <http://opac.sub.uni-goettingen.de/DB=1/PPN?PPN=1015067948>

Terms and Conditions

The Goettingen State and University Library provides access to digitized documents strictly for noncommercial educational, research and private purposes and makes no warranty with regard to their use for other purposes. Some of our collections are protected by copyright. Publication and/or broadcast in any form (including electronic) requires prior written permission from the Goettingen State- and University Library.

Each copy of any part of this document must contain these Terms and Conditions. With the usage of the library's online system to access or download a digitized document you accept the Terms and Conditions.

Reproductions of material on the web site may not be made for or donated to other repositories, nor may be further reproduced without written permission from the Goettingen State- and University Library.

For reproduction requests and permissions, please contact us. If citing materials, please give proper attribution of the source.

Contact

Niedersächsische Staats- und Universitätsbibliothek Göttingen
Georg-August-Universität Göttingen
Platz der Göttinger Sieben 1
37073 Göttingen
Germany
Email: gdz@sub.uni-goettingen.de

Kinetics of Oxidation Processes in Titanomagnetites

V. Kropáček

Geophysical Institute, Praha

Received January 2, 1974

Abstract. On four samples of titanomagnetites, representing four different stages of oxidation of titanomagnetites in basalts of the Bohemian Massif, the kinetics of the process of oxidation have been studied in detail. The effect of the heating and cooling rates in determining the thermomagnetic curves was determined, using the heating rates of 1, 4, 10 and 40 °C/min. The effect of heating is analysed on the oxidation of the primary titanomagnetite if the temperature is gradually increased. In a similar way the kinetics of the increment of the saturation magnetization have been studied as a function of the time of retention at the temperatures of $T = 350, 400, 450$ and 500 °C. In one particular case of retention for 3000 min at $T = 400$ °C the state of total oxidation of the original phase was achieved in primarily partially oxidized titanomagnetites. Estimates of the activation energy of the individual sample give values between 0.4 and 0.2 eV mol⁻¹.

Key words: Magnetic Properties — Titanomagnetites — Thermal Treatment.

1. Introduction

During a detailed study of the magnetic properties of basalts from the area of the Bohemian Massif (Kropáček and Pokorná, 1974) it was found that the thermomagnetic curves of most samples displayed strong irreversible changes of the saturation magnetization σ_s and of the Curie temperature θ when heated. Analogous patterns were observed recently by a number of authors (Wasilewski, 1969; Creer *et al.*, 1970; Sanver and O'Reilly, 1970; Ozima and Ozima, 1972), who explained them by the oxidation taking place in the titanomagnetites. In the samples studied the irreversible changes differed in intensity with the degree of the primary oxidation of the titanomagnetite. For this reason the effect bearing on the oxidation (the heating rate, maximum heating temperature, the time the sample is kept at an increased temperature) are analysed in this paper with 4 samples, representing the different stages of the initial oxidation.

2. Experimental Methods

The thermomagnetic measurements of the temperature dependence of the saturation magnetization, $\sigma_s/\sigma_{s0} = f(T)$, were carried out with an MW-1 thermomagnetic balance (Suess, 1962). σ_{s0} is the value the saturation

magnetization at $T = 20^\circ\text{C}$ and σ_s is the value the saturation magnetization at temperature T . The samples were heated under free access of air. The magnetic field applied amounted to 10 kOe. The temperature of the sample, located in a silver capsule, was measured by means of a silver-constantan thermo-couple, the head of which is formed by the capsule itself. The accuracy of the temperature measurements was about 2°C . The instrument was calibrated experimentally from the known value of the saturation magnetization of pure nickel (Kropáček, 1967). The remanent magnetization of saturation σ_{RSO} and its temperature dependence were measured by a LAM-2 astatic magnetometer (Pešina, 1967), supplemented with a small non-magnetic oven. The sample temperature was determined on contact with a PT—PtRh thermo-couple with an accuracy of 3°C . The rock samples for measuring σ_s were of isometric shape, weighing 100–150 mg, and cubes, 8 cm^3 in volume, were used for measuring σ_{RS} . The titanomagnetite samples, used for measuring, were in powder form (size of grain 0.04–0.02 mm) with a weight of 10 to 15 mg. The titanomagnetites were separated from the rocks magnetically, the resultant purity of the fraction being about 90%. RTG-diagrams have been determined by means of the RTG-goniometer HZG-3 using the radiation due to $\text{Co}\alpha$ (filter Fe). The lattice constants were derived from tables (Dettmar and Kircher, 1956). The titanomagnetite samples, used for measuring the RTG-diagrams, were in powder form, weighing 30–40 mg.

3. Sample Characteristics

With a view to the type of thermomagnetic curve the investigated set of 100 rocks (Kropáček and Pokorná, 1974) could be divided into four groups, differing in degree of oxidation of the titanomagnetites they contained. One characteristic sample was then selected from each group, the properties of which were studied further. The thermomagnetic curves of these four selected rock samples are shown in Fig. 1. For the sake of comparison, curves of the temperature dependence of the saturation magnetization in a 10 kOe field and curves of the temperature dependence of the remanent magnetization of saturation, measured in the absence of the field after the sample had been magnetized by a 10 kOe field, are also shown. The differences between both types of curves with a given sample indicate that the titanomagnetites, present in the rock, become oxidized during heating.

The overall chemical composition of the separated titanomagnetites is represented in the field of the ternary system $\text{FeO—TiO}_2\text{—Fe}_2\text{O}_3$ in Fig. 2. Titanomagnetite No. 202 is formed by a solid solution of $0.3\text{ Fe}_3\text{O}_4 \cdot 0.7\text{ Fe}_2\text{TiO}_4$ and represents an unoxidized titanomagnetite. Sample No. 201 is a weakly oxidized titanomagnetite which has been displaced from the

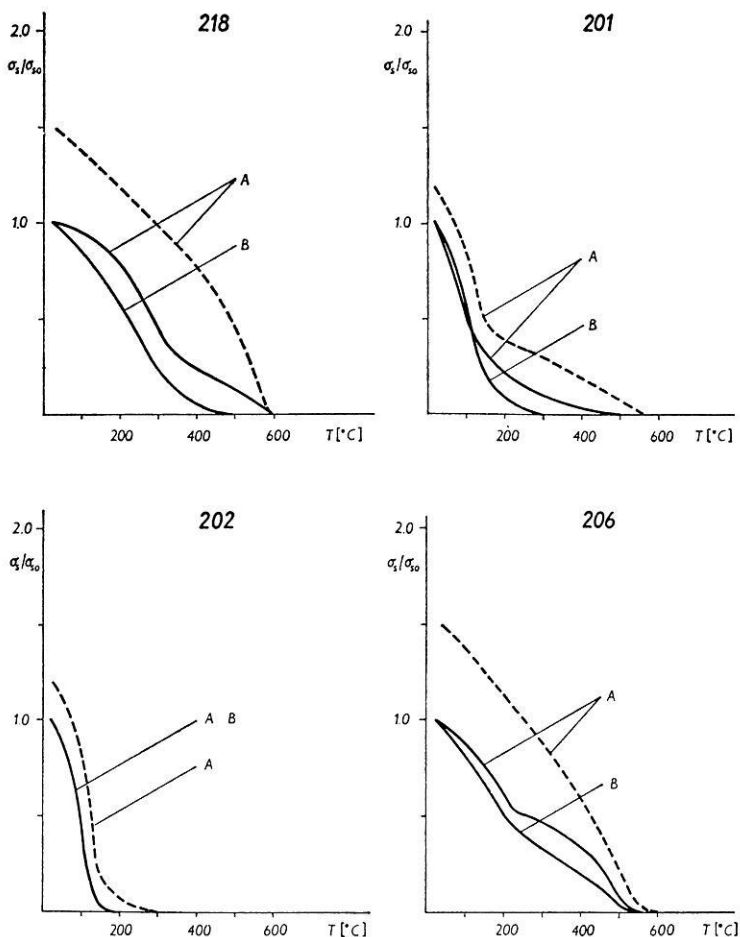


Fig. 1. Temperature dependence of the saturation magnetization of the original rocks: curve A — full line, during heating, dashed line, during cooling; curve B — temperature dependence of the remanent magnetization of saturation. Heating and cooling rate $10^{\circ}/\text{min}$

basic series of solid solutions magnetite — ulvöspinel along the line of oxidation into the field of the so-called “general titanomagnetite” (Akimoto *et al.*, 1957). Intermediately oxidized titanomagnetites are represented by sample No. 218 and strongly oxidized titanomagnetites by sample No. 206, which lie completely in the field of the general titanomagnetite. The differences between the samples can also be clearly distinguished on the RTG-diagrams (Fig. 3). Sample No. 202 has marked narrow diffraction lines, typical of a homogeneous solid solution with a lattice parameter of $a =$

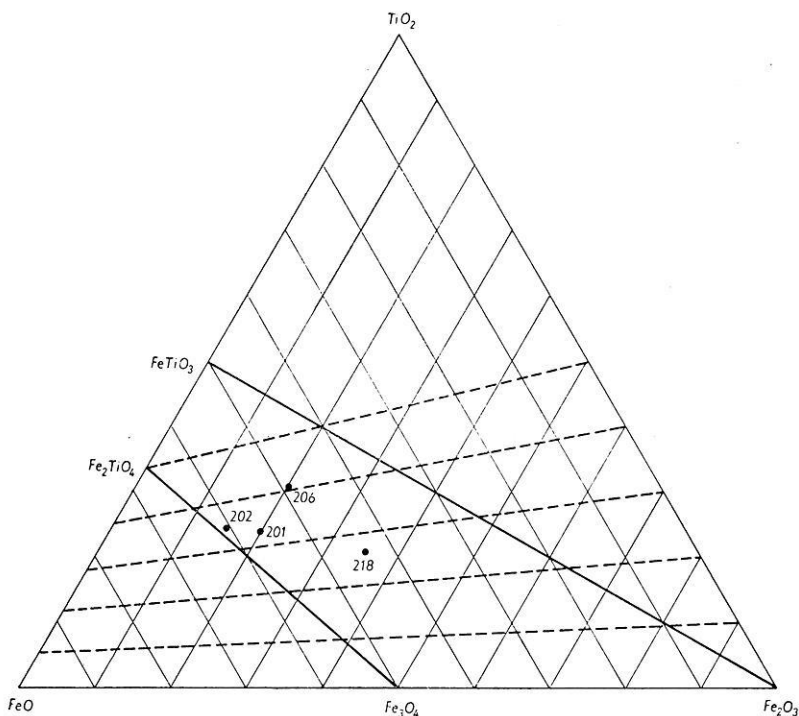


Fig. 2. Chemical composition of the investigated titanomagnetites in the ternary system of $\text{FeO}-\text{TiO}_2-\text{Fe}_2\text{O}_3$

8.48_2 \AA . The weakly oxidized titanomagnetite No. 201 displays observable weak expansions of the diffraction lines due to the presence of submicroscopic “daughter phase” particles of a different lattice constant. For the initial phase $a = 8.46_5 \text{ \AA}$. A diffraction line doublet, indicating the presence of two different phases, can be seen in the intermediately oxidized titanomagnetite sample No. 218 ($a_1 = 8.45_8 \text{ \AA}$ and $a_2 = 8.42_7 \text{ \AA}$). The strongly oxidized titanomagnetite No. 206 also displays a doublet of diffraction lines, however, in addition to these there are also lines due to the presence of ilmenite.

4. The Kinetics of Oxidation Processes

4.1 The Effect of the Heating Rate

Fig. 1 indicates that the measured temperature dependence of the saturation magnetization in the rocks becomes distorted as a result of the oxidation of the titanomagnetites. This effect is enhanced when the titanomagnetites are measured on their own. However, this also means that the

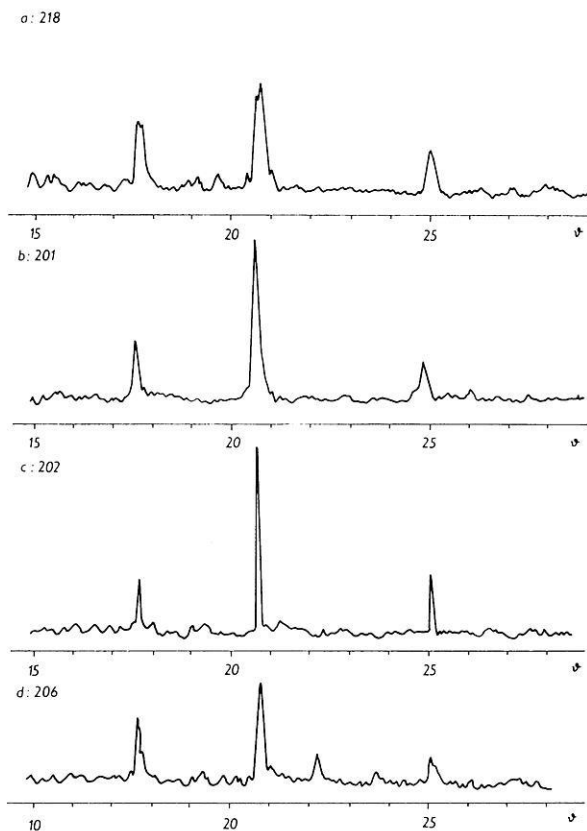


Fig. 3. Part of a simplified RTG-diagram for the titanomagnetite samples investigated. Radiation Co_{α} , filter Fe

shapes of the titanomagnetite curves must also reflect the applied heating rates. If the heating is slow, the oxidation effects will be strong and, if the heating is fast, the oxidation effects will be weak. For this reason the temperature dependence of the saturation magnetization, $\sigma_s/\sigma_{s0} = f(T)$, was measured at different rates of the heating (1, 4, 10 and 40 °C/min). The results obtained are represented in Fig. 4. The curves clearly show that the effect of heating rate is most markedly reflected in the heating rate curves for sample Nos. 206 and 218, when the values of the saturation magnetization increase in the temperature range of 350–450 °C at low heating rates in these samples. This increase is caused by a combination of two effects, acting oppositely. First of all, there is the decrease of the value of the saturation magnetization with temperature and, secondly, the increase of the value of the saturation magnetization of the daughter phase with a higher Curie

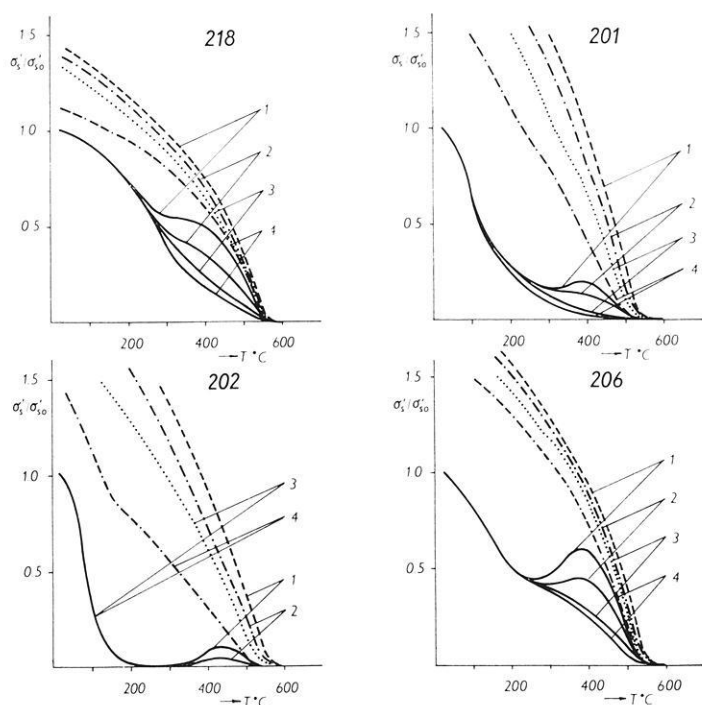


Fig. 4. Temperature dependence of the saturation magnetization at different heating rates. Curve 1 — 1°C/min, curve 2 — 4°C/min, curve 3 — 10°C/min, curve 4 — 40°C/min. Full line — during heating

temperature, generated by the oxidation of the primary phase. The shape of the resultant curve of saturation magnetization is then determined by the superposition of both effects. At high heating rates of about 40°C/min the decrease of the value of σ_s with the temperature constitutes the predominant effect, and the oxidation is not manifested. The fact that the oxidation nevertheless occurs, is proved by the curves, obtained during cooling, which display a considerable increment of the daughter phase. At low rate of heating, within the limits of 1–4°C/min., the effect of the oxidation is prevailing, what results into formation of new mineral phase. The newly formed phase is characterized by increased value of saturation magnetization σ_s .

In samples Nos. 202 and 210 the effect of the oxidation during heating is relatively weak; in sample No. 202, however, spontaneous magnetization (caused by the daughter phase) reoccurs at temperatures of 350–520°C although the sample had already been in a paramagnetic state (the Curie temperature of the primary phase $\theta \sim 150^\circ\text{C}$). However, the values of the

saturation magnetization after heating and cooling indicate that the proportion of the daughter phase increases markedly in the sample with the decrease of the heating and cooling rate. By comparing the values of the saturation magnetization after the imposed temperature cycle one finds that the largest proportion of the daughter phase is formed with weakly oxidized titanomagnetites. In strongly oxidized samples this proportion is substantially lower.

4.2 The Effect of Temperature on the Oxidation

In order to determine the temperature at which manifestations of oxidation occur, i.e. at which the saturation magnetization changes, step-test measurements were made. From the collection of samples one is heated to temperature T and cooled, another sample of the same collection is heated to increased temperature $T = +25^\circ\text{C}$ and cooled, etc. In order to suppress the manifestations of oxidation at temperatures lower than the maximum temperature of the step, the heating rate adopted was $40^\circ\text{C}/\text{min}$. The data obtained are shown in Fig. 5. This indicates that observable changes occur at temperatures of 350°C and more. It was also found that the primary phase is partly preserved, even after heating to a temperature of 600°C , only in sample No. 202. The curves of sample No. 202 after heating to temperatures of $475\text{--}500^\circ\text{C}$ and the initial curve of sample No. 210 (which are practically identical) indicate that the initial state of sample No. 201 is the same as the state of sample No. 202 after partial oxidation, achieved by heating to temperatures of $475\text{--}500^\circ\text{C}$. In samples Nos. 218 and 206 the value decreases at first after heating to temperatures of upto 450°C , and only after heating to temperatures of over 450°C does the value of σ_{80} increase to a value in excess of the initial value.

4.3 The Effect of the Heating Period on the Oxidation

The results obtained clearly show that the oxidation of the titanomagnetites will depend strongly on the time for which the sample is heated to a certain constant temperature. Fig. 6 shows the change of the saturation magnetization due to heating for a period of 1 hour to temperatures of $350, 400, 450,$ and 500°C in the four samples investigated. The saturation magnetizations during cooling, having retained the temperature T for a certain interval, are also shown, as well as curves of further heating to 600°C . Clearly, for identical intervals of temperature retention the proportion of the newly formed oxidation phase increases with the temperature being retained roughly exponentially. One can also see that the proportion of the daughter phase decreases with the degree of oxidation of the primary phase. By comparing the curves in Figs. 5 and 6 it is possible to

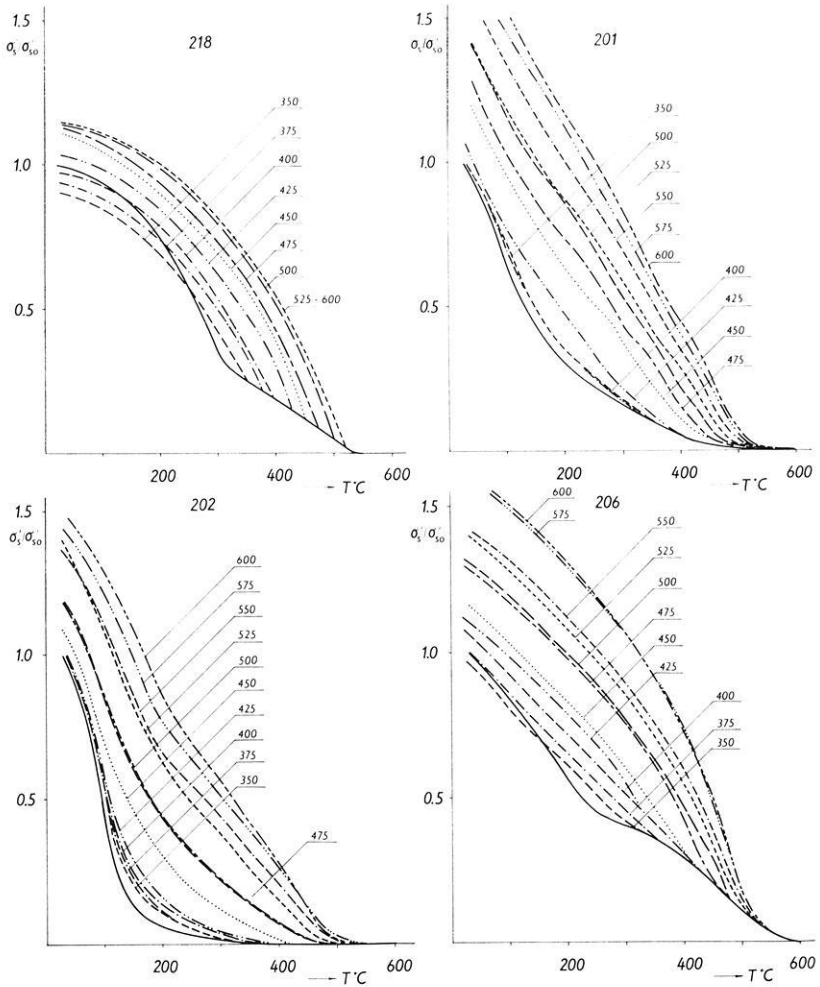


Fig. 5. Step-test. Thermomagnetic curves for gradually increasing maximum temperatures of heating in steps of 25°C . Full line — during heating. Heating rate $40^{\circ}\text{C}/\text{min}$, cooling rate $40^{\circ}\text{C}/\text{min}$

reduce the period of temperature retention at one temperature to the retention period at another, or to the heating temperature. For example, sample No. 202 will yield identical curves of the temperature dependence of the saturation magnetization by heating to 450°C and retaining this temperature for 50 mins, or by rapid heating at a rate of $40^{\circ}\text{C}/\text{min}$ to 525°C and immediate cooling. After evaluating this identity qualitatively it was found that a certain degree of oxidation of the titanomagnetite is

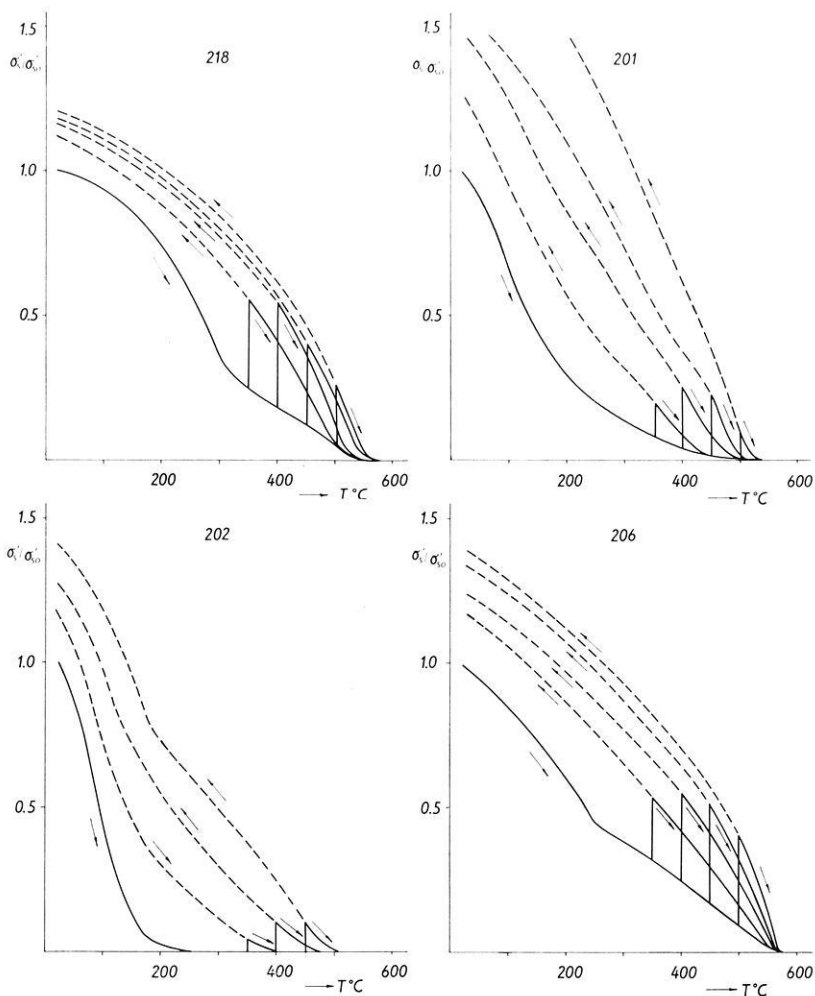


Fig. 6. Variation of the values of the saturation magnetization for a retention period of $t = 60$ mins at temperatures of 350, 400, 450 and 500 C. Full line — during heating and for $T = \text{const.}$, dashed line during cooling after retention 60 mins at $T = \text{const.}$ has been terminated

achieved when the retention period increases roughly exponentially with decreasing retention temperature, provided states close to total oxidation are not considered.

Fig. 6 also shows that not even after heating to a temperature of 500 °C for a period of 60 mins is the state of complete oxidation of the primary titanomagnetite achieved due to steady increase of the value of σ_{s0} . There-

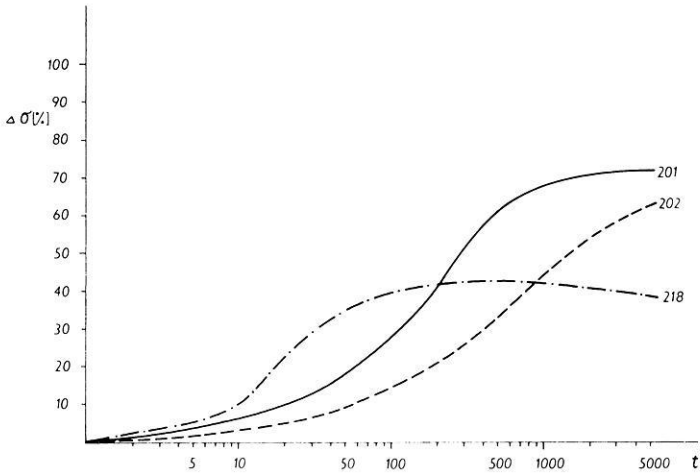


Fig. 7. Time dependence of the increment of the saturation magnetization when the temperature is retained for the time t at $T = 400^\circ\text{C}$

fore, σ_s was measured at a temperature of 400°C for considerably longer retention periods. Thus the increment $|\sigma_s = \sigma_s(400^\circ\text{C}, t) - \sigma_s(400^\circ\text{C}, t=0)|$ was investigated, where $\sigma_s(400^\circ\text{C}, t=0)$ is the value of the saturation magnetization when a temperature of $T = 400^\circ\text{C}$ has been achieved, and $\sigma_s(400^\circ\text{C}, t)$ is the value of the saturation magnetization at temperature $T = 400^\circ\text{C}$ after the interval of t (min) has elapsed. The results of these measurements for samples Nos. 201, 202 and 218 are given in Fig. 7. It was found that the increase in magnetization was at first roughly exponential, however, the rate of increase then diminished as a result of the decrease of the amount of the hitherto unoxidized phase, and reached a steady state which represents the state of complete oxidation of the initial titanomagnetite. This state is reached in sample No. 218 after $t \sim 100$ mins, in sample No. 201 after $t \sim 900$ mins, and in sample No. 202 this state had not been reached even after $t > 3000$ mins. It is evident that the first derivative of these curves yields the instantaneous rate of oxidation and formation of the new phase, because the measurement is proportional to the magnetic moment which is a linear function of the contents of the given phase. Maximum instantaneous rate is achieved in sample No. 218 at $t \sim 25$ mins, in sample No. 201 at $t \sim 230$ mins, and in sample No. 202 at $t \sim 700$ mins.

5. Discussion

It follows from the results presented that the oxidation of natural titanomagnetites depends on the temperature at which the process occurs, on the time of oxidation at an increased temperature, and on the initial

degree of oxidation of the titanomagnetite. Moreover, there exists a qualitative identity different times of retention at different elevated temperatures. For example, in sample No. 202 an identical state is achieved by heating to a temperature of 560 °C with immediate cooling, heating to 500 °C, at which temperature the sample is retained for 14 mins, and by heating to 400 °C, this temperature being retained for 130 mins. This dependence is approximately exponential. By extrapolating to 20 °C one finds that the period required for complete oxidation of the titanomagnetite is roughly 10^7 years. This is of considerable importance for palaeomagnetic research into rocks containing titanomagnetites, because the rocks should not contain primary magnetization, syngenetic with the rock, after this period.

The oxidation of the titanomagnetites in the investigated samples apparently takes place, according to the pattern presented by O'Reilly and Banerjee (1967), which may be described as the "second stage of oxidation". The increment of the saturation magnetization at $T = 400$ °C as a function of the time of heating is at first exponential, which corresponds to the results of measurements, carried out by Creer *et al.* (1970); after that, as a result of the decrease in the volume of the primary phase, hitherto unoxidized, deceleration occurs, the process of oxidation of the titanomagnetite only terminating after a certain period, and the process of oxidation of the (daughter) magnetite on haematite begins. By computing the value of the activation energy of the process, according to Creer *et al.* (1970), from the equation

$$\ln \tau = -\ln A + E/RT,$$

where τ is the time constant, A is a constant, E is the activation energy, R the gas constant, and T the absolute temperature, one obtains the following values for the individual samples: No. 202 $E \sim 0.4$ eVmol⁻¹, No. 201 $E \sim 0.3$ eVmol⁻¹, and No. 218 $E \sim 0.2$ eVmol⁻¹. These values are lower than the value in the paper of Creer *et al.* (1970). However, they do correspond to the values of the activation energy, determined by Bleil (1971).

References

- Akimoto, S., Katsura, T., Yoshida, M.: Magnetic properties of the Fe₂TiO₄-Fe₃O₄ system and their change with oxidation. *J. Geomagn. Geoelectr.* 9, 165-178, 1957
- Bleil, U.: Cation distribution in titanomagnetites. *Z. Geophys.* 37, 305-319, 1971
- Creer, K. M., Ibbetson, J., Drew, W.: Activation energy of cation migration in titanomagnetites. *Geophys. J.* 19, 93-101, 1970
- Dettmar, H. K., Kircher, H.: Tabellen zur Auswertung der Röntgendiagramme von Pulvern. Weinheim: Verlag Chemie 1956

- Kropáček, V.: Thermal changes in the magnetic properties of an anomalously magnetic mineral, *J. Geomagn. Geoelectr.* 19, 323–334, 1967
- Kropáček, V., Pokorná, Z.: Magnetische Eigenschaften basischen neovulkanischen Gesteine der Böhmisches Masse und ihre Zusammenhänge mit petrologischen Charakteristiken. *Travaux Inst. Géophys. Acad. Tchécosl. Sci. Geofyzikální sborník 1973*. Praha: Academia 1974 (in press)
- O'Reilly, W., Banerjee, S.K.: The mechanism of oxidation in titanomagnetites: a magnetic study. *Min. Mag.* 36, 29–37, 1967
- Ozima, M., Ozima, M.: Activation energy of unmixing of titanomaghemite. *Phys. Earth Planet. Interiors* 5, 87–89, 1972
- Pešina, B.: A multi-purpose astatic magnetometer. *Travaux Inst. Géophys. Acad. Tchécosl. Sci.*, No. 278, *Geofyzikální sborník 1967*. Praha: Academia 1968
- Sanver, M., O'Reilly, W.: Identification of naturally occurring non-stoichiometric titanomagnetites. *Phys. Earth Planet. Interiors* 2, 166–174, 1970
- Suess, R.: Eine magnetische Waage zur Bestimmung der Sättigungsmagnetisierung von Gesteinsproben. *Z. Mess. Regeln* 5, 33–38, 1962
- Wasilewski, P.: Thermomagnetic analysis: Experimental factors. *J. Geomagn. Geoelectr.* 21, 655–667, 1969

Dr. V. Kropáček
Geophysical Institute
141 31 Praha 4, CSSR
Spořilov