Experimental study of kinetics of isothermal dehydroxylation of natural goethite

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Changes of saturation magnetization on time during the process of isothermal dehydroxylation of natural goethite are studied. The activation energy of the phase transition goethite \rightarrow hematite was determined and the estimation of structural stability of investigated goethite faction in the earth's surface was also carried out.

Key words: goethite, hematite, isothermal kinetics, saturation magnetization

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The reaction of goethite dehydroxylation α -FeOOH·nH₂O $\rightarrow \alpha$ -Fe₂O₃+nH₂O is the most common process of hematite (α -Fe₂O₃) formation in sedimentary rocks. However, kinetic studies of this phase transition are still not enough to answer the questions of how long this process is extended in time under natural conditions and how great mineralogical stability of goethite is. Meanwhile, it is very important to know in order to assess the possibility of formation and preservation of both primary and secondary chemical magnetization (*CRM*), especially in red sedimentary formations during diagenesis.

In this work a kinetic study was carried out on natural goethite fraction, which was a dense powder aggregates consisting of needle-shaped particles (with an average size of 400x50 nm), elongated along the crystallographic *c*-axis of goethite. According to the results of X-ray powder diffraction (XRPD) analysis, the original fraction was described by the orthorhombic (space group *Pbnm*, Z = 4) unit cell with a = 4.6095 Å, b = 9.9699 Å, c = 3.0250 Å and volume V = 139.02 Å³, in close agreement with standard values (ICDD PDF-2 Release 2008 database, card 00-029-0713). Average crystallite sizes *L* (or more exactly the regions of coherent X-ray scattering along the normal to reflecting (*hkl*) planes calculated from the broadening of the diffraction peaks) for primary goethite were ~ 34.8 nm, ~ 50.6 nm and > 70 nm along the [100], [010] and [001] directions, respectively, which is consistent with a needle-like morphology.

The study of transformation of the primary goethite fraction by dynamic thermogravimetry (TG) (a constant heating rate of $v = 10^{\circ}$ C/min from room temperature till 1000 °C in air) showed ~ 0.49 % of weight loss of starting material by heating to 150 °C (corresponding to the loss of the chemisorbed surface water) and decrease ~ 9.62 % of weight between 240 and 370 $^{\circ}$ C (due to the removal of structural hydroxyls (OH) and corresponding to the endothermic transformation from the goethite elementary lattice to the hematite one). Further heating up to 1000 $^{\circ}$ C yielded an additional ~ 0.96 % of weight loss. Thus, non-isothermal TG analysis showed a total amount of weight loss after the phase transformation in air was a bit larger than the theoretical expectation (10.1 %) for stoichiometric goethite. Based on these results, the formula of the starting goethite can be written in the form of FeOOH \cdot 0.0538H₂O. According to thermomagnetic (by saturation magnetization J_S) analysis (v = 4⁰C/sec) of initial samples, the Neel temperature (T_N) of goethite fraction was ~ 120 ⁰C, the temperature range of the phase transition goethite \rightarrow hematite was (250 - 380) ⁰C, the Curie temperature (T_C) of formed hematite was ~ $673 \, {}^{\circ}$ C. According to XRPD data final hematite phase was characterized by the following parameters (after goethite decomposition at 250 °C for 312 hours): a = 5.036 Å, c = 13.753Å. V = 302.1 Å³ in the hexagonal setting R3C at L > 60 nm in crystallographic direction [110], which coincided with the texture axis of α -Fe₂O₃ particles.

In the present study the kinetics of dehydroxylation of α -FeOOH into α -Fe₂O₃ was investigated in air under isothermal conditions using a magnetometer method by *in situ* measuring the change in saturation magnetization (J_s) for 312 hours in a constant magnetic field of 0.65 Tesla during heating at

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one of 11 temperatures between 183 ^oC and 273 ^oC. The first relatively low temperature corresponding to the beginning of the process of dehydroxylation was chosen in order to bring your laboratory experiments to real environmental conditions, but still be able to conduct them on selected laboratory time scale; the highest temperature of isothermal heating, according to the results of TG analysis of fresh samples, corresponded to the interval of maximum reaction rate.

The isothermal dependences of the change of saturation magnetization on the time of induced dehydroxylation of original goethite fraction are depicted in Fig. 1. In the kinetic curves $J_S(t)$ behavior can be traced the following regularities: marked decrease of J_S at an initial period of time (A segment), than follows a period of change in the falling slope; herewith, in the temperature range (198 - 273) ^oC, one or two (B and C respectively) segments of exponential decrease of saturation magnetization, the locations of which vary with temperature, are shown on the $J_S(t)$ curve. Moreover, the slope of C segment of the $J_S(t)$ curve is always the steepest than in the previous segments. It is also significant that the kinetic curves of the $J_S(t)$, recorded during the decomposition of goethite fraction during 312 hours at T ≥ 204 ^oC, show a little different and stable (within the measurement accuracy) values of J_S at the final stages of the $J_S(t)$ measurements (D segment), covering the most significant period of time at this reaction stage (Fig. 1). It is also important to note that as a result of the isothermal dehydroxylation of goethite the maximum drop in saturation magnetization was ~ 2 times.



Fig. 1. Changes in saturation magnetization as a function of time (logarithmic scale) and the temperature of dehydroxylation of the initial goethite fraction. The numbers *1-11* marked curves corresponding to different reaction temperatures: *1 - 183* °C, *2 - 187* °C, *3 - 191* °C, *4 - 198* °C, *5 - 204* °C, *6 - 210* °C, *7 - 216* °C, *8 - 223* °C, *9 - 235* °C, *10 - 248* °C, *11 - 273* °C. *A*, *B*, *C* and *D* are characteristic segments of the curves discussed in the text.

According to thermomagnetic analysis of annealed samples (Fig. 2) it was found that the dehydroxylation of goethite during 312 hours at T = 183-198 ^oC leads to the coexistence of goethite and hematite phases. Moreover, it was found that in the course of the reaction (with a temperature increase) T_n of the residual goethite steadily increases from 120 to 191 ^oC, the maximum phase transition temperature decreases from 380° C to 367° C, whereas T_C of the hematite components is ~ 668-671 ^oC. Herewith, the observed increase of the $J_s(T)$ of hematite component, probably dues to the Hopkinson effect – increasing of the weak ferromagnetic moment of the hard magnetic material in an external magnetic field which is small compared with the saturation fields. The samples, which were dehydroxylated during the same time period at $T \ge 204$ ^oC, are always of single phase with $T_C \sim 673$ ^oC (Fig. 2).

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On the basis of X-ray diffraction studies of the samples subjected to prolonged isothermal dehydroxylation [*Gribov and Dolotov*, 2011] and analysis of published data we can make the following preliminary conclusions. The initial (*A*) section of the kinetic $J_S(t, T)$ curve (Fig. 1) is obviously the result of the manifestation of weak ferromagnetism of starting goethite with $T > T_n$. Recession $J_S(t)$ for arbitrarily selected *A* and *B* sections corresponds to dehydroxylation, which leads to the hematite formation on the surface of goethite grains and within them, respectively. Completion of the recession $J_S(t)$ (*D* section of this curve) corresponds to a complete phase transformation at the reaction temperature indicated on the graph.

For selected (*B* and *C*) sections of predominantly exponential reduction in the magnetization of the kinetic $J_S(t)$ curves, the values of the effective activation energy (*E*) of hematite formation from goethite, calculated from the linear dependence of experimentally obtained Ln(dJ_S/dt) vs. 1/T within the temperature range of 204–273 ⁰C, were equal and made up ~ 201.48 kJ/mol. This fact indicates that the rate-limiting step of the process of goethite dehydroxylation is the diffusion of Fe³⁺ cations. It should be also noted that this *E* value is in a good agreement with that obtained from the thermogravimetric method in a similar decomposition temperature range of original samples [*Gribov and Dolotov*, unpublished manuscript, 2012]. For comparison, the values of the activation energies of goethite dehydroxylation according to literature data are in the range of 88 – 247 kJ/mol, and are largely dependent on the size of the goethite particles [*Cornell and Schwertmann*, 2003].



Fig. 2. Thermal demagnetization curves of saturation magnetization for samples dehydrated during 312 hours at different temperatures: $I - 183 \ {}^{0}\text{C}$, $2 - 191 \ {}^{0}\text{C}$, $3 - 198 \ {}^{0}\text{C}$, $4 - 210 \ {}^{0}\text{C}$, $5 - 223 \ {}^{0}\text{C}$, $6 - 273 \ {}^{0}\text{C}$.

The temporal extrapolation of the magnetometric kinetic curves to the J_S values, corresponding to the total transformation of goethite into hematite, allowed to estimate the time t^* , required to complete the phase transition in the investigated temperature range (204 to 273 °C). The linearity of the obtained dependence $\ln t^*$ vs. 1/T (Fig. 3) gives the possibility of its extrapolation to lower temperatures, i.e. allows us to enter the times that are not available for laboratory researches. As occurred, in natural conditions the total spontaneous transformation of investigated goethite fractions can be implemented for the period of ~ 1 or ~10 million years only in the case of a regional heating of the rock to temperatures of ~ 85 and ~ 73 °C, respectively. These estimates give a reason to believe that in the earth's surface in goethite-bearing sedimentary rocks the formation of hematite with attendant *CRM* components does not occur during or immediately after deposition but rather it is occurred over a long period of time enough to span one or more geomagnetic polarity reversal. In such cases, the spontaneous dehydroxylation of goethite to hematite may play a definite role in the chemical remagnetization of red sedimentary formations in the hypergenesis zone.



Fig. 3. The dependence of the calculated time (logarithmic scale) of complete hematization of the original goethite fraction against inverse Kelvin temperature (1/T). The solid line drawn on the graph is the best linear fit to the data points.

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