

ON THE TEMPERATURE AND PRESSURE DEPENDENCES OF THE EFFECTIVE THERMAL CONDUCTIVITY OF GRANITES

by

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The results of experimental measurements of the temperature dependence of the effective thermal conductivity of various granite samples obtained by the absolute stationary method in the temperature and pressure ranges of 273-523 K and 0.1-400 MPa, respectively, are analyzed. The power-law character of the temperature dependence of the effective thermal conductivity for all measured granite samples at atmospheric pressure is established. We have shown that pressure significantly affects the power law of the temperature dependence of the effective thermal conductivity of granite samples. A low-parameter description of the temperature-pressure behavior of thermal conductivity is proposed. A correlation is established between its components.

Key words: *thermal conductivity, high pressure, temperature, granites*

Introduction

The most common in the continental crust rocks are granites, which are natural composite materials with a fairly structural structure, which contain quartz, potassium feldspar, acid plagioclase, mica, and other minor inclusions. The study of their thermophysical properties under conditions of natural occurrence is an urgent task, both from a fundamental and from an applied point of view. Indeed, patterns of the effective thermal conductivity of granites in a natural occurrence provide fairly accurate information about the processes of propagation and scattering of thermal waves in the earth's crust.

Heat transfer processes in solids with an ordered crystalline structure have a wave nature. These processes are described by the Eucken [1] and Debye [2] models, which have a temperature dependence $\lambda \sim T^{-1}$. At the same time, heat transfer processes in solids with an amorphous structure are of an activation nature (*i.e.*, heat transfer from atom to atom), which have a temperature dependence $\lambda \sim T^{0.5}$. In disordered crystalline solids, atoms occupy the correct position in the nodes of the crystal lattice, but the order of the atoms is not observed, the masses of atoms and their force constants randomly change from node to node. Block boundaries and lattice defects also have a significant effect. All this leads to the complex na-

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ture of the heat transfer process in multicomponent structures with complex and variable ordering [3-5]. Internal stresses during hydrostatic compression cause a change in the volume and elastic parameters of the lattice and the development of longitudinal and transverse deformations.

In the general case, as shown in a number of our recent works, for example, [6, 7], and also references in these publications, the temperature dependence of most natural and artificial composite materials at a fixed pressure is rather well described by a power law:

$$\lambda(T) \propto (T)^n \quad (1)$$

Most of the works, including recent ones [8-11], are aimed at studying only the effect of temperature on the effective thermal conductivity of rocks. As a result, thermal properties of rocks at various depths of the earth's crust are estimated without taking into account rock pressure. However, under the influence of pressure in dielectrics and rocks, changes in physical and thermodynamic parameters occur. Under pressure in solids and, especially, in rocks, internal stresses of a complex nature arise, which lead to a decrease in the inter-atomic distance and the amplitude of atomic vibrations, significantly increase their maximum frequency, which is associated with the Debye temperature. The dependence of the maximum atomic vibration frequency on the wave vector is often depicted as a dispersion curve. Based on the Leibfried-Sheiman equation [12], pressure should lead to a linear increase in the lattice thermal conductivity of dielectrics and semiconductors due to an increase in the maximum atomic frequency and associated with the Debye temperature. On the other hand, under pressure, especially in its initial stage, energy conditions are created to increase the maximum frequency of defect vibrations, which reach the block boundaries, bring these boundaries into an excited non-equilibrium state and change the kinetics of grain-boundary processes.

When constructing baric dependences of rocks, for example, [13, 14], a linear approximation is usually used after some pressure (~100 MPa) and in isolation from the temperature dependence. Despite satisfactory agreement at sufficiently high pressures, this may not be entirely adequate when considering thermal processes occurring over a wide range of pressures, including the initial (near atmospheric pressure) region.

Experiment

For an experimental study of the temperature-pressure dependence of effective thermal conductivity at high pressures, we took natural samples of four granites: the Dagestan deposit, the depth ~3000 m, density 3.2 g/cm³, porosity 1% (sample 1); Kola Peninsula deposit, surface deposits, density 2.54-2.57 g/cm³, porosity 1-2% (samples 2-4).

The thermal conductivity was measured using the absolute stationary method. The set-up made it possible to measure at hydrostatic pressure up to 400 MPa in the temperature range 273-523 K. The argon gas ($\lambda = 0.019$ W/mK) served as the pressure transmitting medium. A detailed description of the installation is given in [15, 16].

Results and discussion

Figure 1 shows the experimental pressure dependences of the thermal conductivity of granites (Samples 1-4), made for six fixed temperatures.

Applying the power law, eq. (1), to both the variable, T , and the fixed, T_0 , temperatures, in the description of the temperature-pressure dependence of thermal conductivity, we can go to dimensionless quantities:

$$\lambda(T, P) = \lambda(T_0, P) \left(\frac{T}{T_0} \right)^{n(P)} \quad (2)$$

or

$$\lambda(T, P) = \lambda(T_0, 0) f_{T_0}(P) \left(\frac{T}{T_0} \right)^{n(P)} \quad (3)$$

where $\lambda(T_0, P)$ is the baric dependence of thermal conductivity for the fixed temperature T_0 and $n(P)$ – the baric dependence of the exponent, $f_{T_0}(P) = \lambda(T_0, P) / \lambda(T_0, 0)$. If the pressure functions appearing in eq. (3) are represented as $f_{T_0}(P) = 1 + \delta_{T_0}(P)$, $n(P) = n_0[1 - \nu(P)]$, then the equation itself can be rewritten in the form:

$$\lambda(T, P) = \lambda(T_0, 0) [1 + \delta_{T_0}(P)] \left(\frac{T}{T_0} \right)^{n_0[1 - \nu(P)]} \quad (4)$$

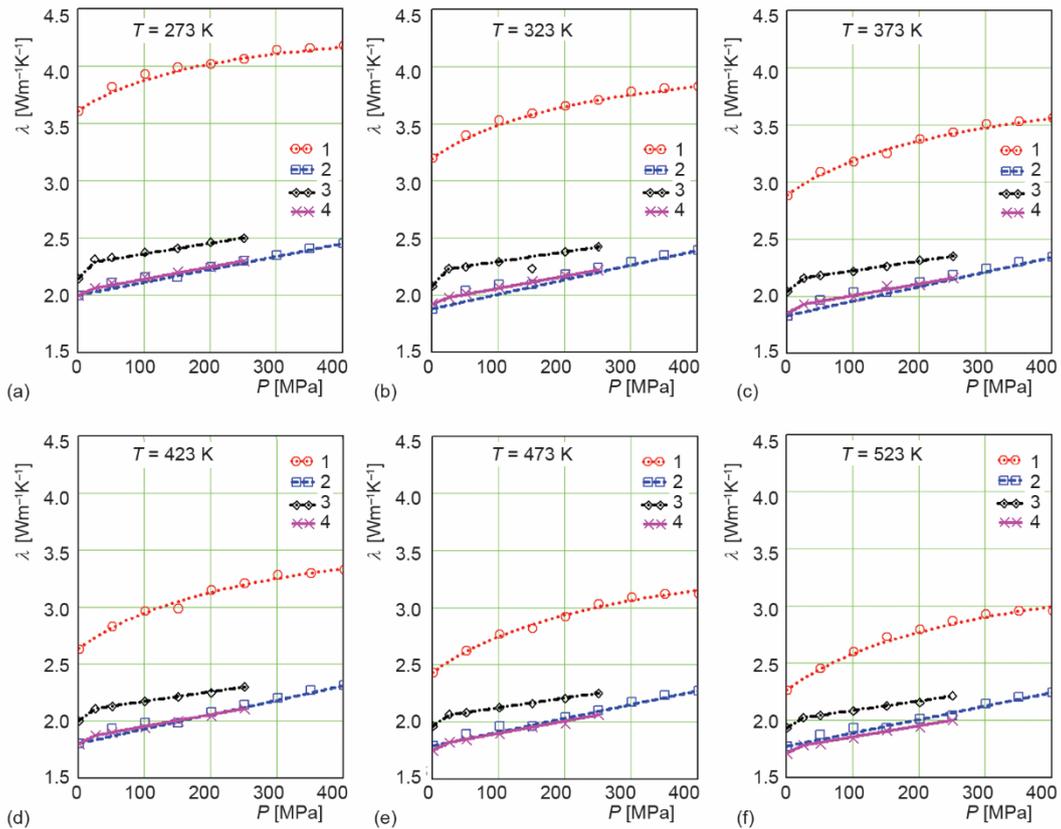


Figure 1. Experimental (Samples 1-4) thermal conductivity pressure dependences of granites for the fixed temperatures

Equation (4) is more convenient for a comparative analysis of various materials, the absolute values of the thermal conductivity of which can vary greatly. This representation al-

lows us to distinguish only two reference quantities $n_0 = n(0)$ and $\lambda(T_0, P)$ and 2-D pressure functions, $\nu(P)$ and $\delta_{T_0}(P)$. The dependence $\nu(P)$ (as well as the value of n_0) is an objective parameter that depends on pressure and does not depend on the choice of temperature T_0 , while $\delta_{T_0}(P)$ depends parametrically on this parameter.

For the Sample 1, having a greater crystalline order than the Samples 2-4, the experimental dependence $\delta_{T_0}(P)$ for any fixed T_0 can be represented with good accuracy in the form:

$$\delta_{T_0}(P) = \frac{1 + \alpha \frac{P}{P_0^*}}{1 + \frac{P}{P_0^*}} - 1 \quad (5)$$

where the quantity α has a physical meaning: the ratio of the highest thermal conductivity to the thermal conductivity at zero pressure, and P_0^* is a constant having a pressure dimension and determining the steepness.

Let us discuss the physical meaning of the quantities included in empirical eq. (4). The absolute value and the sign determine the degree of ordering of the composite compound at zero pressure. The value -1 corresponds to a fully ordered crystalline structure, the value $+0.5$ corresponds to an amorphous media. Intermediate values provide an effective measure of the ordering of the compound as a whole. The parameter $\nu(P) = [1 - n(P)/n_0]$ determines the change in the temperature dependence of the compound as a function of pressure. Since (as it is discussed in our introduction) the absolute value of the exponent indicates the degree of crystalline ordering, the dependence $\nu(P)$ may also indicate a change in crystalline ordering with applied pressure. As a rule, the absolute value of the coefficient n decreases, and thus $\nu(P)$ has a positive sign and does not exceed unity (for most of the compounds considered $\ll 1$) over the entire range (in our case, the set-up allowed us the studies up to 400 MPa).

The dependence $\delta_{T_0}(P)$, together with the value of thermal conductivity at zero pressure [$\lambda(T_0, P)$], completely determines the pressure dependence of the thermal conductivity at the fixed temperature T_0 . We should note that atmospheric pressure (0.1 MPa) for our pressure ranges (up to 400 MPa) can be considered very close to zero.

The dependences $n(P)$ (obtained from the temperature dependences for each pressure) are presented in fig. 2(a) – Samples 1-4. In turn, fig. 2(b) presents the experimental values $\nu(P)$ for Samples 1 and 2. A very large scatter the second sample is due to small absolute values of the coefficient n , which increases the error in the calculation of this value. For the same reason we do not provide data for the Samples 3 and 4. Figure 2(b) contains also approximating curves, to which we will return later. The dependences $\delta_{T_0}(P)$ for some T_0 are presented in fig. 3. As can be seen from figs. 2(b) and 3, the dependences $\nu(P)$ and $\delta_{T_0}(P)$ are quite strongly correlated with each other. This is especially evident for Sample 1. Moreover, for the temperature $T_0 = 473$ K both dependences can be described with fairly good accuracy by a single low-parameter empirical expression. In this case, eq. (4) becomes:

$$\lambda(T, P) = \lambda_0 [1 + \nu(P)] \left(\frac{T}{T_0} \right)^{n_0 [1 - \nu(P)]} \quad (6)$$

Equation (6) allows to completely describe the dependence $\lambda(T_0, P)$ according to an experimentally determined coefficient $\lambda_0 = (\lambda(473 \text{ K}, 0))$ (thermal conductivity at the fixed tem-

perature $T_0 = 473$ K and zero pressure) and the empirical dependence $\nu(P) = \delta_{473\text{ K}}(P)$. Turning back to figs. 2(b) and 3(e), the dependences $\delta_{473\text{ K}}(P) = \nu(P)$ for Samples 1 and 2 there are shown by solid and dashed lines correspondently. For Samples 2-4, the temperature dependence of the thermal conductivity of which indicates less crystalline ordering, the dependence $\nu(P) = \delta_{473\text{ K}}(P)$ in the studied range can be approximated linearly. Thus, for Granite 1, the dependence $\nu(P) = \delta_{473\text{ K}}(P)$ shown in figs. 2(b) and 3(e) was calculated according to eq. (5) with $\alpha = 1.52$, $P_0^* = 300$ MPa, and for Granites 2-4 as $\nu(P) = \delta_{473\text{ K}}(P) = 6.55 \cdot 10^{-4} P$ [MPa].

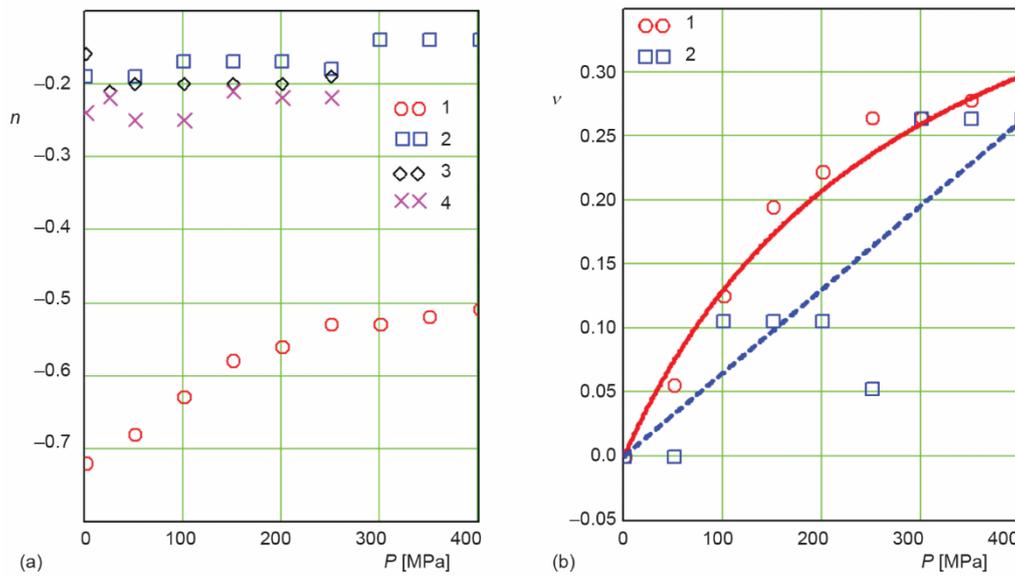


Figure 2. The dependences $n(P)$ (a) Samples 1-4 and $\nu(P)$ (b) Samples 1 and 2

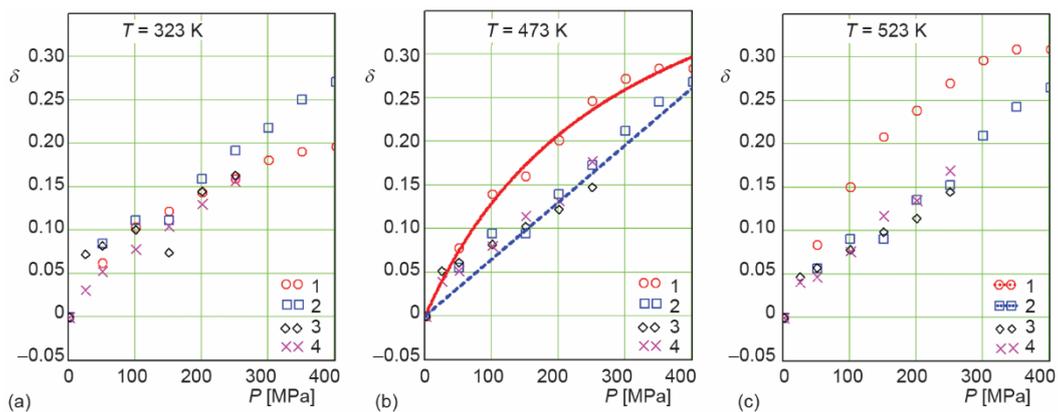


Figure 3. The dependences $\delta_{T_0}(P)$ for the set of fixed temperatures T_0

Figure 4 shows the result of calculating the temperature dependences $\lambda(T_0, P)$ for three fixed pressures by eq. (6) in comparison with the experimental results. It should be es-

pecially noted that the solid curves were obtained using eq. (6) without additional fitting coefficients, which indicates a very good agreement between the obtained equation and the experimental description.

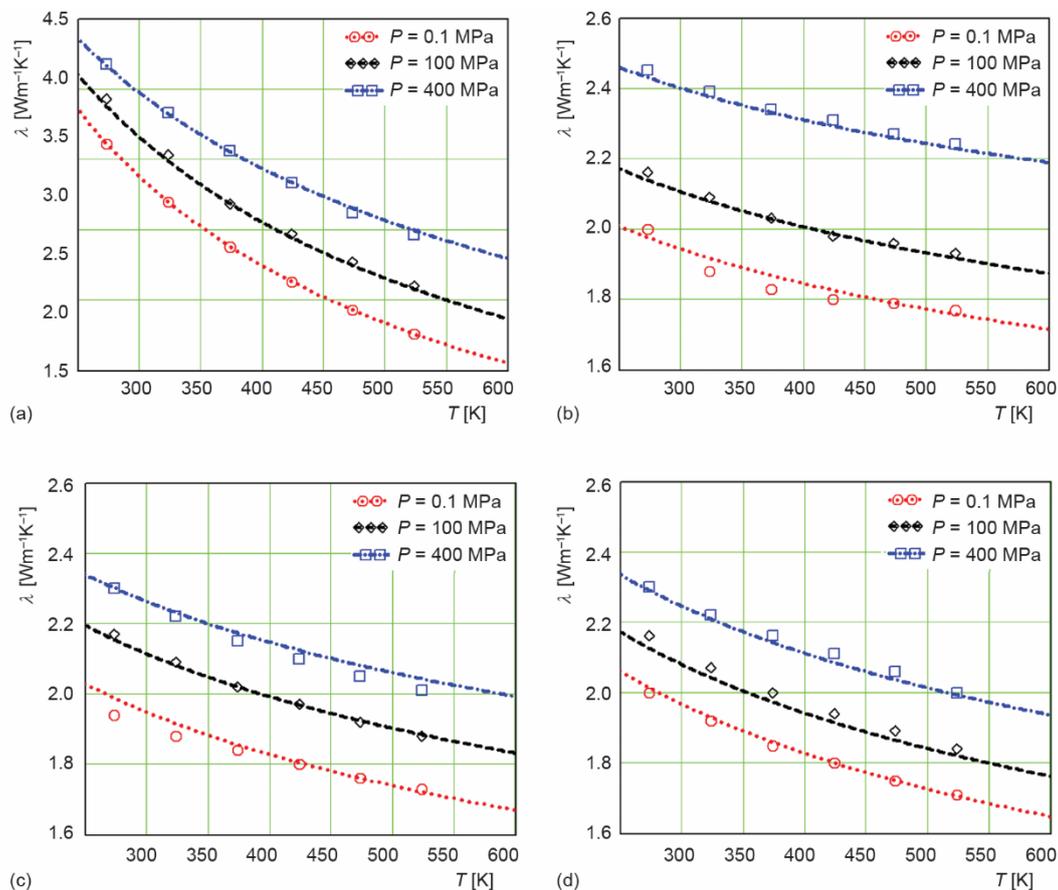


Figure 4. Experimental thermal conductivity temperature dependences of granites; (a)-(d) for Samples 1-4, respectively, for the fixed pressures

In a very recent work [11] devoted to the study of the temperature properties of granites, the obtained temperature dependence is quite different from the power law, eq. (1). Nevertheless, the decreasing nature of the dependence, taking into account a rather large error, the data presented can be approximated by the eq. (1) with the factor $n \approx 0.2$. So, for we can conclude, that for their granite at atmospheric pressure both absolute value of thermal conductivity (2.2 W/mK at $T = 273$ K) and coefficient n approximately correspond to our samples 2-4. Authors of another very recent work [17] presents the results of studying the temperature-pressure dependence of thermal properties (including thermal conductivity) for granitoids from room temperature to 950 K and pressures from 500-1500 MPa. However, unfortunately, this work does not present the results of measurements at atmospheric (near-zero) pressure, which complicates the comparison with our conclusions.

Recently [18] we have presented the results of measurement of heat capacity at constant pressure, C_p , and thermal diffusivity, K , by the non-stationary method using NETZSCH

equipment (LFA 457 MicroFlash and DSC204F1) [19]. Heat conductivity in this case is calculated as $\lambda = KC_p\rho$, where ρ is the sample density. In these studies we used a sample identical to our Sample 1. The data on thermal conductivity with a quite high accuracy coincided with the data obtained by the stationary method in the same temperature region and just prolong the obtained dependence up to 700 K. The experimental dependence of the specific heat is shown in fig. 5.

To approximate the experimental data [17], we used the Maier-Kelley empirical equation [20]:

$$C_p(T) = c_0 \left[a + b \frac{T}{T_0} - d \left(\frac{T}{T_0} \right)^{-2} \right] \quad (7)$$

where c_0 , a , b , and d are the equation parameters, which depend of the fixed temperature T_0 . For $T_0 = 473$ K we have obtained the following parameter values:

$$c_0 = 682 \text{ Jkg}^{-1}\text{K}^{-1}, \quad a = 1, \quad b = d = 0.065 \quad (8)$$

So this fixed temperature $T_0 = 473$ K seems to be also close to optimal one allowing us to equate the two parameters, b and d , turning the third one, a , into unity, which is impossible in the general case for an arbitrary fixed temperature.

The solid line in the fig. 5 shows the temperature dependence of the specific heat of Granite 1 according to eq. (7) for parameter values (8), and the circles, according to experimental data. The dashed curve shows the dependence calculated according to the Debye theory (the Debye temperature corresponding to the experimental data is close to 670 K). As we can see both curves are very close to experimental data and unlike [11] we have not seen any features.

Our results can be extrapolated -to higher temperatures, at least to the vicinity of the first expected phase transition: the α - β transition of quartz, where its usual form with trigonal symmetry reversibly transforms into a form with hexagonal symmetry. The temperature of this transition is 845 K at atmospheric pressure and increases to 945 K at 375 MPa. [21] As revealed in [11], cracks probably associated with this transformation begin to appear after ~500 K and begin to be significant after 750 K. Between 900 K and 1150 K cracks do not change much, but the number of cracks gradually increases. Meanwhile, the connectivity of cracks is slowly increasing. At higher temperatures the partial melting leads to the thermal damage. [11] On the other hand, it must be taken into account that the melting temperature (including partial) of a complex composite compound can decrease with increasing pressure, especially with significant fluid and moisture saturation. In the outlined pressure range (up to 400 MPa), the experimental temperature dependence taken at atmospheric pressure and sufficiently well obeying the power law up to ~800-900 K, for example, [22] can give the possibility for the sufficiently reliably estimation of the effective thermal conductivity in a wide PT -range using the pressure dependences $n(P)$ and $\lambda(T_0, P)$ obtained at relatively lower tempera-

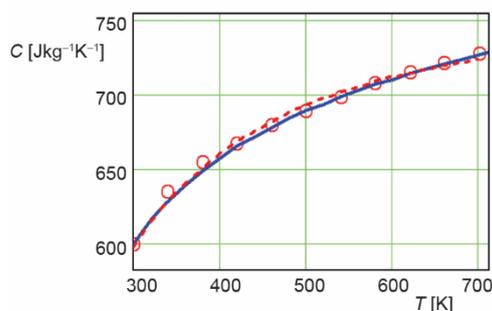


Figure 5. The specific heat vs. temperature for the Sample 1, $P = 0.1$ MPa

tures. The extrapolation of the power law of the temperature dependence for pressures above several hundred MPa should be carried out with more caution, as evidenced by the experimental data given in [17]. In addition, the application of such pressures can lead to a change in the structure of the sample and its properties after depressurization.

Conclusions

The paper presented the analysis of the experimental temperature-pressure dependences of the effective thermal conductivity obtained by the absolute stationary method for granites, based on which we have proposed a low-parametric descriptions, have established some correlations between their baric components, and have discussed their physical meaning.

Manifestly, the generalization of obtained results to a wide class of granites requires additional experimental studies. At the same time, our results provide the basis for optimistic forecasts for our approach.

Further work seems to be interesting in the directions as follows.

- Refining the optimal characteristic temperature, T_0 , at which the best correlation between $\nu(P)$ and $\delta_{T_0}(P)$ in eq. (4) is observed.
- Verifying of the universality of this temperature for granites and its variation for other rocks.
- Revealing its physical meaning.
- Search of correlations between the absolute value $\lambda(T_0, P)$, and the character of the functions $\nu(P)$ and $\delta_{T_0}(P)$.

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Nomenclature

a, b, d	– dimensionless parameters in Maier-Kelley empirical equation, [–]	P_0^*	– parameter with dimension of pressure (we also used [MPa] with the indication), [Pa]
c_0	– parameter with dimension of specific heat, [$\text{Jkg}^{-1}\text{K}^{-1}$]	T	– temperature, [K]
C_P	– specific heat at constant pressure, [$\text{Jkg}^{-1}\text{K}^{-1}$]	T_0	– fixed (or characteristic) temperature, [K]
K	– thermal diffusivity, [m^2s^{-1}]	<i>Greek symbols</i>	
$n, n_0, \nu, \delta, \alpha$	– dimensionless parameters in empirical equations for PT -dependences of thermal conductivity, [–]	λ	– thermal conductivity, [$\text{Wm}^{-1}\text{K}^{-1}$]
P	– pressure (we also used [MPa] with the indication), [Pa]	λ_0	– parameter with dimension of thermal conductivity, [$\text{Wm}^{-1}\text{K}^{-1}$]
		ρ	– density (we also used [gcm^{-3}] with the indication), [kgm^{-3}]

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