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Thermally stimulated currents in rocks

E. Dologlou-Revelioti¹ and P. Varotsos²

¹ University of Athens, Department of Geology, Geophysics-Geothermy Division, Athens, Greece

² University of Athens, Department of Physics, Athens, Greece

Abstract. Thermally stimulated currents (T.S.C) have been observed in seven rock samples, selected intentionally to represent the mean crustal structure in Greece. All these rock samples exhibit a transient thermally stimulated current. These currents are observed when the rock samples are heated at a certain rate, *with* and *without* the application of any external electric field. The main properties of these thermally stimulated currents are:

1. All the rock samples showed the maximum value of the T.S.C within a narrow temperature range, i.e. between 6° C and 23° C.

2. The T.S.C spectrum is complex, presumably due to different kinds of impurities in the rocks and different dipole mechanisms.

3. The relaxation times of the dipoles, as obtained from the T.S.C, are of the order of 1 min at temperatures ~20° C.

4. The values of the migration enthalpy are of the order of some eV.

Key words: Rocks – Stimulated currents – Relaxation parameters

Introduction

Since 1981 the electric field of the earth has been continuously monitored at various sites in Greece. Before each sizeable earthquake a transient variation of the electrotelluric field was observed with a time-lag between 6 h and 1 week. An extensive description of the physical properties of this precursor was published by Varotsos and Alexopoulos (1984a, b, 1986).

The above field observations were motivated from the following tentative physical model: rocks usually contain piezoelectric material (e.g. quartz) in a non-perfect directional distribution. Before an earthquake, and in the region close to the focus, the stress gradually increases so that an electric field is generated. Furthermore, this stress-variation may decrease the relaxation time of the dipoles existing in the rocks (whenever the migration volume is negative, see below). It can then be shown (Varotsos et al. 1982) that when the stress reaches a certain value, i.e. the so-called critical stress σ_{cr} , a transient current is emitted (we assume,

of course, that $\sigma_{cr} < \sigma_{fr}$, where σ_{fr} denotes the stress at which the rocks fracture). Details of this model have been published by Varotsos and Alexopoulos (1986).

If the basic assumptions of the above scheme are correct (i.e. existence of dipoles due to the aliovalent impurities and creation of the electric field due to the piezoelectric inclusions) then the rocks should also emit transient currents upon a gradual increase of temperature, which results in a decrease of the relaxation time of dipoles. It is the object of this paper to report on the existence of such thermally stimulated currents in natural rocks.

Theory

Relaxation of dipoles

When an aliovalent impurity ion, e.g. M^{+2} , is introduced into an ionic crystal of the form $A^+ B^-$, a number of cation vacancies are formed for reasons of charge compensation (Varotsos and Miliotis, 1974). A portion of these vacancies is attracted by aliovalent impurities and forms “complex dipoles” which can change their orientation when subjected to an external electric field. The relaxation time τ , needed for them to change orientation, depends on temperature T and pressure P according to the formula (Varotsos and Alexopoulos, 1981; Varotsos et al., 1980)

$$\tau(T, P) = \tau_0 \exp(h_m/kT) \quad (1)$$

where τ_0 is the pre-exponential factor, h_m is the enthalpy of the orientation process and k Boltzmann's constant. The relaxation time τ always decreases, because τ_0 and h_m are positive, with increasing temperature as obvious from Eq. (1). On the other hand, its variation with increasing pressure depends on the algebraic sign of the quantity

$$U_m = \frac{\partial g_m}{\partial P} \Big|_T \quad (2)$$

(index “ m ” = “migration”) where g_m is the Gibbs energy of the re-orientation process and U_m the so-called migration volume (Varotsos and Alexopoulos, 1980). Whenever U_m is positive, Eqs. (1) and (2) indicate that the relaxation time τ increases when hydrostatic pressure P also increases; on the other hand, if $U_m < 0$ the relaxation time τ decreases with increasing pressure (Varotsos et al., 1982).

Thermally stimulated currents

Depending on the procedure followed for the application of the external electric field, thermally stimulated currents

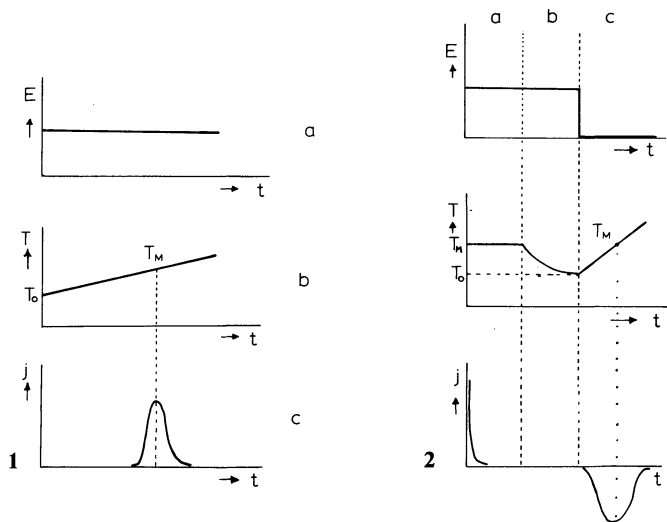


Fig. 1 a-c. Schematic representation of the thermally stimulated polarization current techniques

Fig. 2 a-c. Schematic representation of the thermally stimulated depolarization current techniques

can be detected due to either “polarization” or “depolarization” of dipoles.

The experimental procedure for a thermally stimulated polarization current (McKeever and Hughes, 1975) consists of the following steps (Fig. 1).

Assume an unpolarized solid at a relatively low temperature T_0 , so that the relaxation time $\tau(T_0)$ is appreciably high (e.g. several hours). At this temperature an external electric d.c. field E (Fig. 1 a) is applied for a time $t \ll \tau(T_0)$. The dipoles – due to their large relaxation time – remain randomly orientated. The temperature T is now increased (Fig. 1 b) at a constant rate and, hence, the relaxation time decreases. As the temperature reaches the “stimulation temperature” T_M (McKeever and Hughes 1975), the relaxation time of dipoles becomes sufficiently short; then, under the influence of the applied external electric field, the dipoles

tend to align with the field direction and, hence, produce a polarization π . This polarization is equivalent to the emission of charges from the outer surface, with a current density $j = \frac{d\pi}{dt}$ (Fig. 1 c). This current is termed the “thermally

stimulated polarization current” (T.S.P.C) and is a transient phenomenon because it almost vanishes when all dipoles have been aligned with the external electric field as far as the thermal motion allows it.

A thermally stimulated depolarization current (T.S.D.C) can be detected according to the following procedure, consisting of three steps (Bucci et al., 1966):

A) In the first step (Fig. 2, stage a), a constant electric field E is applied at a high temperature T and for a time t appreciably larger than the relaxation time $\tau(T)$ of the dipoles. All dipoles can then freely rotate and align with the external field E . A current appears due to this alignment of the dipoles.

B) Now the solid is cooled to an appreciably low temperature T_0 , so that the relaxation time $\tau(T_0)$ reaches values of the order of several hours. Although switching off the external electric field E , the dipoles remain aligned with this field (Fig. 2, stage b).

C) Now we increase the temperature T at a constant rate (Fig. 2, stage c). The relaxation time $\tau(T)$ decreases gradually and thus the dipoles become free to rotate into random directions, so that a thermally stimulated depolarization current is emitted. It has a maximum (Bucci et al., 1966) at a certain temperature T_M .

In summarizing, we can say that solids containing dipoles will emit transient polarization or depolarization currents when they are heated. This, however, assumes that an external electric field has been used for the (re)orientation of these dipoles. So far, such currents *have not been detected in the absence of any external field*. In the case of rocks, however, piezoelectric or pyroelectric inclusions (Parkhomenko, 1971) give rise to an internal electric field which may substitute the above-mentioned external electric field. In order to examine this possibility, experiments without any application of an external electric field have been carried out on a large variety of rocks.

Table 1. Chemical analysis of rock samples (%)

Chemical compounds	Rock type						
	Sample 1 Granite	Sample 2 Mica-schist	Sample 3 Sipoline	Sample 4 Crystalline limestone	Sample 5 Marble	Sample 6 Gneiss	Sample 7 Limestone
SiO ₂	71.80	65.0	17.30	2.70	0.60	72.00	1.30
CaO	1.64	2.0	40.50	49.00	54.50	0.35	54.00
Al ₂ O ₃	15.50	16.00	3.60	0.85	0.11	13.50	0.32
Fe ₂ O ₃	0.14	1.50	2.15	1.16	0.26	2.50	0.21
FeO	0.50	7.00	–	–	–	0.15	–
MnO	0.03	0.07	0.13	0.01	0.006	0.03	0.01
MgO	0.17	3.00	1.38	3.31	0.83	1.05	0.56
Na ₂ O	4.56	0.50	0.27	0.02	0.02	2.70	0.09
K ₂ O	4.12	2.00	1.20	0.02	0.02	5.70	0.10
Cr ₂ O ₃	–	–	–	–	–	–	–
TiO ₂	0.12	1.00	–	–	–	0.20	–
H ₂ O	0.60	4.00	–	–	–	–	–
Heat loss	–	–	3.2	42.7	43.4	1.5	43.0

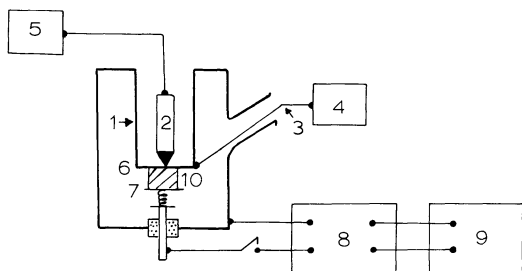


Fig. 3. Experimental set up. 1 Cryostate; 2 heating element; 3 Fe-Const thermocouple; 4 digital millivoltmeter; 5 A.C. power supply (0–250 V); 6–7 Pt electrodes; 8 vibrating reed electrometer Cary 401; 9 pen chart-recorder; 10 sample

The experiment

Due to the fact that all rocks contain aliovalent impurities it is natural to expect that they contain complex dipoles of the form “aliovalent impurity + vacancy” or “aliovalent impurity + interstitial”. Thus, by applying the thermally stimulated current technique to them, one should expect, in principle, the detection of a thermally stimulated current.

Seven samples of various rock types representing the mean crustal structure of Greece (Papanikolaou 1980, 1984) have been studied in this way. Their chemical composition is given in Table 1. A brief description of the instrumentation used for the experiments is given below (see also Triantis, 1983).

The apparatus (Fig. 3) consists of two chambers made of stainless steel. The inner chamber (cryostate in Fig. 3) is filled with air. A heating element and nitrogen liquid were used to heat and cool the samples, respectively. The samples had typical dimensions of $1\text{ cm} \times 1\text{ cm} \times 0.5\text{ cm}$ and were placed between two Pt electrodes. The temperature was measured by a Fe-Const thermocouple and the measuring junction was positioned as close to the sample as practicable. When using a heating rate $b = 4\text{ K/min}$, the temperature difference between the upper and lower part of the

sample does not exceed 1–2 K (this fact has been verified by experiments with two thermocouples positioned at the upper and lower part of the sample, respectively). In any case, this temperature gradient can not be the origin of the observed T.S.C current for reasons discussed below.

Therefore, when using heating rate $b = 4\text{ K/min}$, the systematic uncertainties in temperature must be 2 K at most. Electrical connection with the electrodes was provided through Teflon insulated connectors in the outer chamber. Thermally stimulated currents were measured with a Cary 401 electrometer and displayed on a YEW-3057 pen chart-recorder.

It should be emphasized that test noise measurements were carried out by heating at a constant rate, from -80°C to $+100^\circ\text{C}$, without putting any sample between the electrodes. In these cases, no current was observed with an intensity three orders of magnitude smaller than the maximum current described below. Therefore, the noise level can be considered as 10^{-14} A at most.

The Teflon insulation, is continuously kept at room temperature in order to avoid thermocurrents from Teflon (Kostopoulos et al., 1980, 1981). It should also be mentioned that T.S.C currents for Teflon measured by ourselves, and by Bucci (Bucci et al., 1966), are three orders of magnitude smaller than the observed T.S.C for our rock samples.

The following type of experiments were carried out on each rock sample. *Without* the application of any external electric field, the rock sample was cooled down from room temperature to $T = -80^\circ\text{C}$ and then heated at a constant temperature rate of 4 K/min up to $T = 100^\circ\text{C}$.

Results

The measured thermally stimulated current spectrum for each rock sample is depicted in Figs. 4–10. The spectra are complicated, probably due to the various migration mechanisms and/or types of complex dipoles contained in the rocks. For a single mechanism, however, and at any temperature, the value of the relaxation time τ can be calculated

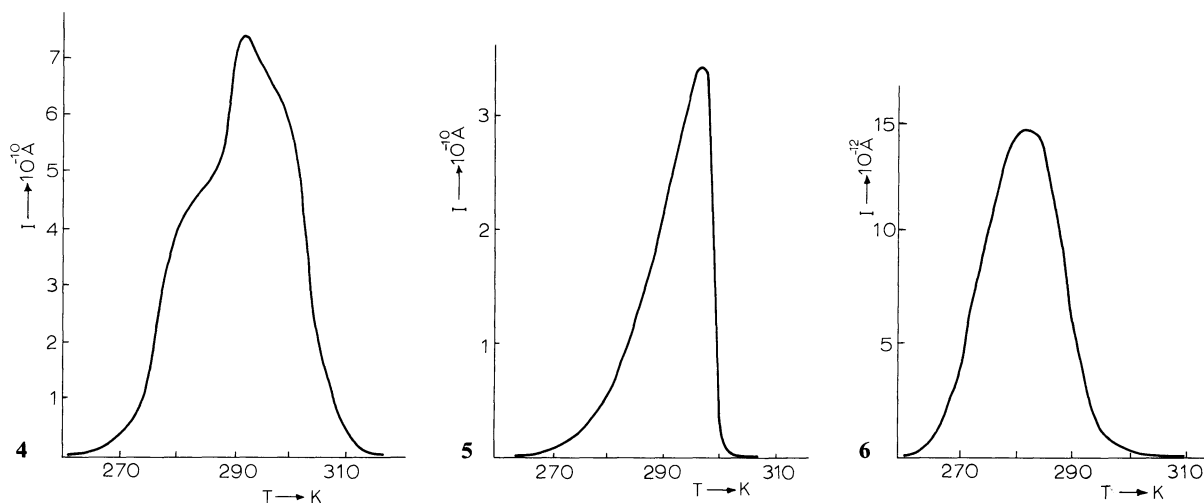


Fig. 4. Spectrum of the current emitted from granite for gradual temperature increase ($b = 4\text{ K/min}$)

Fig. 5. Spectrum of the current emitted from mica-schist for gradual temperature increase ($b = 4\text{ K/min}$)

Fig. 6. Spectrum of the current emitted from sipoline for gradual temperature increase ($b = 4\text{ K/min}$)

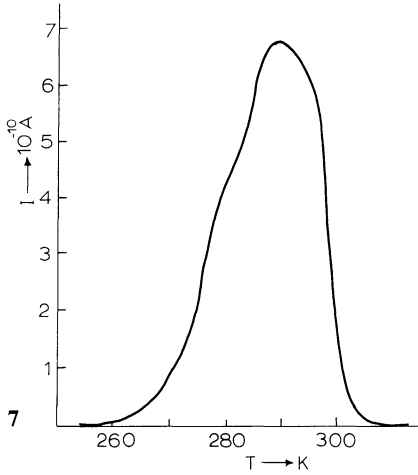


Fig. 7. Spectrum of the current emitted from crystalline limestone for gradual temperature increase ($b=4$ K/min)

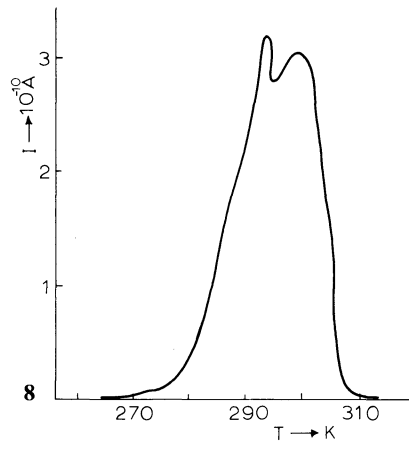


Fig. 8. Spectrum of the current emitted from marble for gradual temperature increase ($b=4$ K/min)

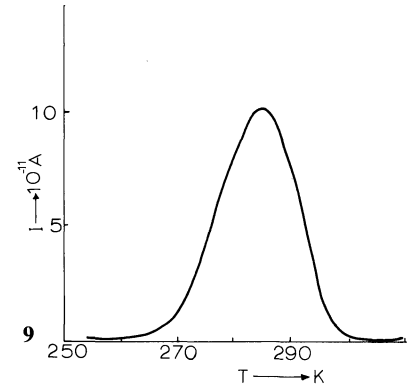


Fig. 9. Spectrum of the current emitted from gneiss for gradual temperature increase ($b=4$ K/min)

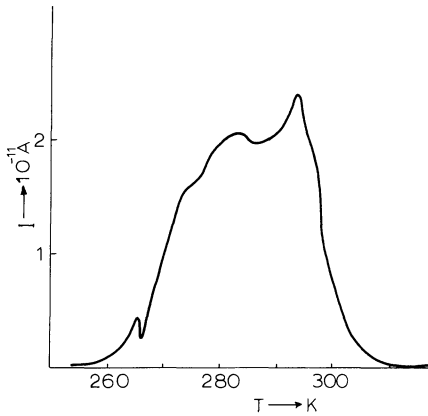


Fig. 10. Spectrum of the current emitted from limestone for gradual temperature increase ($b=4$ K/min)

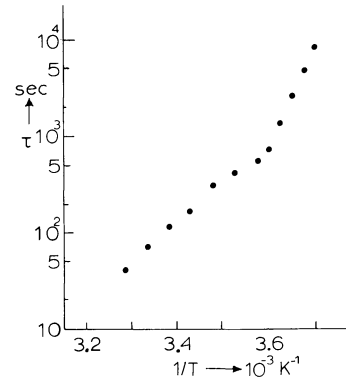


Fig. 11. Variation of the relaxation time τ versus $1/T$ for granite

from the formula (Bucci et al., 1966):

$$\ln \tau = \ln \tau_0 + \frac{h_m}{kT} = \ln \frac{\int_0^{\infty} I(T) dT}{b I(T)} \quad (3)$$

where $b = \frac{dT}{dt}$. The integral of the right-hand side can be

obtained graphically. Due to the lack of knowledge of the various mechanisms involved, we apply Eq. (3) for the lower-temperature tail of our experimental curve. It should be clarified that, although T_M and the shape of the I spectrum depend on b , the relaxation times calculated from Eq. (3) do not depend on the heating rate. The resulting τ values for the case of granite, are depicted in Fig. 11 in the form of a $\ln \tau$ vs $1/T$ plot. An inspection of this plot shows that the low-temperature part can be described approximately by a straight line which – according to Eq. (3) – indicates the existence of a single overwhelming mechanism (or type) of dipole for the low part. A least-squares fit to the straight line leads to the values of τ_0 and h_m corresponding to that mechanism.

Table 2. Relaxation parameters of the various rock samples

Rock sample	T_M (K)	τ_0 (s)	h_m (eV)	$\tau(T_M)$ (s)
Granite	292 ± 2	$(1^{+3}_{-0.5}) \times 10^{-33}$	2.0 ± 0.2	165 ± 50
Mica-schist	296 ± 1	$(1^{+3}_{-0.5}) \times 10^{-21}$	1.3 ± 0.1	40 ± 10
Sipoline	281 ± 2	$(2^{+4}_{-0.6}) \times 10^{-34}$	2.0 ± 0.1	90 ± 20
Crystalline limestone	289 ± 2	$(0.2^{+1.2}_{-0.8}) \times 10^{-23}$	1.4 ± 0.1	140 ± 30
Marble	293 ± 1	$(1.7^{+4}_{-0.3}) \times 10^{-30}$	1.8 ± 0.1	165 ± 30
Gneiss	285 ± 1	$(4^{+4}_{-0.3}) \times 10^{-28}$	1.6 ± 0.1	108 ± 10
Limestone	294 ± 2	$(8^{+8}_{-1.2}) \times 10^{-27}$	1.5 ± 0.2	76 ± 10

This procedure was applied to all samples and resulting values of τ_0 and h_m are given in Table 2. In the same Table we have inserted the corresponding T_M values along with the “apparent” relaxation time $\tau(T_M)$ resulting from Eq. (3) by applying it at $T=T_M$. Due to the complexity of the spectrum, it is obvious that the latter values of $\tau(T_M)$ do not have a direct physical meaning but only give the order

of magnitude of the relaxation time belonging to the predominant mechanism at $T = T_M$.

A striking result obtained from Table 2 is that, in a large variety of rocks, the T_M values vary only within a narrow range, i.e. from 6° C to 23° C. A large number of T.S.C spectra were obtained after testing samples of the same material or repeating the experiment with the same sample under the same conditions. In both cases, no significant differences were observed in the T.S.C spectra, concerning T_M and the relaxation parameters τ_0 and h_m .

In addition, experiments with a different orientation of the mica-schist sample were carried out, but the influence of the structural anisotropy of the mica-schist on the T.S.C spectrum was dubious.

Discussion

The following, very tentative, physical model is proposed in order to explain the above transient electrical current in the absence of any external electric field.

From the chemical analysis (Table 1) and from the mineral composition of the samples, it is easily observed that all rock samples contain a number of ionic crystals (e.g. Na_2O) which are carriers of "complex dipoles". Also, all samples contain either a piezoelectrical material (e.g. quartz SiO_2) or a pyroelectric one. As rock has a complex structure consisting of various minerals with different thermal expansion coefficients, internal stresses will arise when cooling or heating the sample. They stimulate the piezoelectric inclusions to produce a piezoelectric field E . Furthermore, a change in the temperature creates a pyroelectric field (Zheludev, 1971). We must point out that although one could expect – due to the random distribution of quartz grains in the rock – the sample as a whole not to show any piezoelectric effect, Parkhomenko (1971) established the existence of piezoelectric effects in a number of rock types (e.g. gneiss, granite, etc.) and also measured the piezoelectric moduli of these rocks.

Thus, a piezoelectric or pyroelectric field is generated due to piezoelectric and/or pyroelectric effects by simply cooling and heating the sample. During the whole experiment, this field acts as an external electric polarizing field applied to the dipoles within the rock sample. Briefly, we have the following situation. When gradually heating from low temperature, an internal electric field is generated (due to piezoelectric-pyroelectric effects). When increasing the temperature T , the dipoles – already existing in the sample – will become more and more mobile and will be able to align with this internal field, giving rise to a thermally stimulated polarization current.

The above model is further strengthened by the following experimental fact. Measurements have been carried out *with* application of an external d.c. electric field (a few kV/cm), as illustrated in Fig. 2a. This external field was applied at room temperature T_p , for a time t_p (~ 10 min) long enough compared to the relaxation time $\tau(T_p)$ of the dipoles at room temperature. Following the procedure depicted in Fig. 2a, a T.S.C current was observed with maxima at temperatures T_M which *are the same* as in the case of the experiments without the external field. A series of such current spectra (i.e. *with* an external electric field) has been described by Dologlou (1984).

In order to preclude any possibility that the observed current is an artifact or a result of the asymmetrical heating

of the sample, the study of various samples of the same block or repeated measurements by turning a given sample upside down led to the following results:

A) Samples from the same block do not show the same current polarity and the same current intensity. This proves that the current is not due to a temperature gradient.

B) Repeated measurements on the same sample, in the same orientation, give the same current polarity.

C) Reversing the sample, the current polarity changes; thus indicating that the polarity is a property of the sample and simultaneously excluding an artifact due to the experimental set up.

Repeating the experiment with different heating rates from 1 K/min to 6 K/min, the temperature T_M of the maximum current was shifted as expected.

Conclusions

Summarizing the present experimental results, we point out the following. During gradual variation of temperature and in the absence of any external electric field, all rock samples give rise to a transient electric current (10^{-9} to 10^{-11} A) which is a maximum at roughly one and the same temperature T_M (\sim room temperature). The relaxation time at $T = T_M$ is of the order of 1 min. A very tentative physical model is suggested which explains the observed results qualitatively.

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