



# Measurements of the dielectric properties of limestone under pressure and their importance for seismic electric signals



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## ABSTRACT

The pressure and temperature evolution of an intense dielectric relaxation mechanism in as-received and wetted limestone (from Ioannina region (Greece)) are studied experimentally through complex impedance spectroscopy. The relaxation time decreases on compression, yielding a negative value for the corresponding activation volume. Furthermore, the role of water incorporated in the mineral was examined, revealing the remarkable fact that water not only enhances the absolute value of negative derivative of Gibbs energy with respect to pressure but also lowers significantly the energy barrier of the corresponding physical processes. Both findings are crucial for the explanation of the sensitivity of an electrotelluric station at Ioannina region in detecting Seismic Electric Signals emitted prior to earthquakes.

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## 1. Introduction

Negative activation volume is – by definition – related with a process, the characteristic activation energy of which is reduced as pressure is increased, or in other words by increasing pressure the corresponding process (that may comprise various relaxation mechanisms) becomes energetically more favorable to occur and the corresponding relaxation time is reduced. In general, there is no restriction as far as the sign of activation volume is concerned. The experiments show that negative activation volumes are not commonly found (Fontanella et al., 1982, 1996; Papathanassiou et al., 2010, 2011, 2012; Sakellis et al., 2012). However, the negative activation volumes are of key importance for the validity of the mechanisms proposed for the generation mechanism of seismic electric signals (SES). These are low frequency electric signals that are observed (Varotsos and Alexopoulos, 1984a, 1984b; Varotsos et al., 2002, 2003a, 2003b, 2005, 2006a, 2006b) before earthquakes. Varotsos et al. (1982), (see also Varotsos and Alexopoulos, 1986) treated the earth's crust as a solid rich in 'dipoles' in a polarizing field (i.e., the mechanical stress field), and assumed that negative activation volumes

exist in rocks. They asserted that the gradually increasing stress in the focal area before an earthquake reduces the relaxation time of these 'dipoles'. Thus, at a certain critical stress (pressure), smaller than that at which rupture occurs, the relaxation time of 'dipoles' becomes short and the 'dipoles' undergo a transition from random-orientation state to an oriented one. This yields the emission of a transient polarization current before the rupture, which constitutes, an SES. SES are observed at stations situated on certain localities in the Earth's crust termed sensitive. In these localities, the electric field variations are considered to be significantly enhanced due to both large-scale and small-scale heterogeneous properties of the earth's crust (Varotsos and Lazaridou, 1991).

It is the basic scope of the present paper to investigate the existence of negative activation volume in limestone samples which were collected from Ioannina region (in Northwestern Greece) where a sensitive SES recording station is located. In addition, the critical role of water incorporated within these samples was also studied in detail for the following reasons: The time evolution of the stress field prior to an earthquake, results in the dynamic compression of water-filled rocks (Morgan and Nur, 1986; Morgan et al., 1989). Specifically in rocks, strong structural and compositional heterogeneity as well as porosity give rise to several polarization mechanisms such as, interfacial polarization, double layer polarization, space charge polarization, and defect dipole polarization (Correia, 1997; Varotsos, 2005). Furthermore, when pores are filled – partially or fully – with water, dielectric properties are enhanced on the one hand and on the other hand water induces dilatancy when rock is pressurized. The latter occurs in the hypocenter area of an earthquake which is surrounded by water saturated porous

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rock with fluid-filled pore channels and the pre-earthquake stage is assumed to be accompanied by the appearance of fresh cracks in the fracture zone (Surkov et al., 2002).

## 2. The methodology for the analysis of the laboratory measurements-Background

We first present some theoretical concepts which shall be used to evaluate the data and calculate the activation volume. In solids, the pressure  $P$  variation of the defects Gibbs energy  $g$ , according to the process that is related to, formation (f), migration (m) or both (act), defines a volume  $v^i \equiv (\partial g^i / \partial P)_T$ , where  $T$  is the temperature and the superscript  $i$  stands for f, m or act according to the corresponding process. Gibbs activation energy is defined as  $g^{\text{act}} = h^{\text{act}} - Ts^{\text{act}}$  where  $h^{\text{act}}$  and  $s^{\text{act}}$  are the activation enthalpy and entropy, respectively.

According to the rate theory, the relaxation time is given by

$$\tau(P, T) = (\lambda\nu)^{-1} \exp\left(g^{\text{act}}/k_B T\right) \quad (1)$$

where  $\nu$  is the vibration frequency of the relaxing charge carrier,  $\lambda$  is a geometrical constant,  $g^{\text{act}}$  is the Gibbs activation energy for relaxation,  $T$  denotes the absolute temperature and  $k_B$  is the Boltzmann's constant. Differentiating Eq. (1) with respect to  $(k_B T)^{-1}$ , at constant pressure, we get

$$\left(\partial \ln \tau / \partial (1/k_B T)\right)_P = h^{\text{act}}. \quad (2)$$

To obtain the last equation,  $\ln(\lambda\nu) + (s^{\text{act}}/k_B)$  is assumed as being constant indicating that Arrhenius behavior describes the temperature dependence of the relaxation time. Differentiating with respect to pressure at constant temperature, we have

$$\left(\partial \ln \tau / \partial P\right)_T = -\frac{\gamma}{B} + \frac{v^{\text{act}}}{k_B T} \quad (3)$$

where  $\gamma \equiv -(\partial \ln \nu / \partial \ln V)_T$  is the Grüneisen constant ( $V$  denotes the volume) and  $B \equiv -(\partial P / \partial \ln V)_T$  is the isothermal bulk modulus. For a Debye relaxation, the tangent loss angle function  $\tan \delta \equiv \text{Im}(\varepsilon) / \text{Re}(\varepsilon)$  (where  $\text{Im}(\varepsilon)$  and  $\text{Re}(\varepsilon)$  are the imaginary and the real part of the (relative) complex permittivity  $\varepsilon$  (reduced to its value of free space)), exhibits a maximum at frequency  $f_{\text{max, tan}\delta} = \sqrt{\varepsilon_s / \varepsilon_\infty} / (2\pi\tau)$ , where  $\varepsilon_s$  and  $\varepsilon_\infty$  denote the static and high-frequency (relative) permittivity, respectively. The partial derivatives of the natural logarithm of the last relation with respect to reciprocal temperature and pressure, respectively, give

$$\left(\partial \ln \tau / \partial (1/k_B T)\right)_P = \frac{1}{2} \left(\partial \ln(\varepsilon_\infty / \varepsilon_s) / \partial (1/k_B T)\right)_P - \left(\partial \ln f_{\text{max, tan}\delta} / \partial (1/k_B T)\right)_P \quad (4a)$$

$$\left(\partial \ln \tau / \partial P\right)_T = \frac{1}{2} \left(\partial \ln(\varepsilon_\infty / \varepsilon_s) / \partial P\right)_T - \left(\partial \ln f_{\text{max, tan}\delta} / \partial P\right)_T. \quad (4b)$$

Combining Eq. (2) and Eq. (4a), as well as Eq. (3) and Eq. (4b) leads to

$$h^{\text{act}} = \frac{1}{2} \left(\partial \ln(\varepsilon_\infty / \varepsilon_s) / \partial (1/k_B T)\right)_P - \left(\partial \ln f_{\text{max, tan}\delta} / \partial (1/k_B T)\right)_P \quad (5a)$$

$$v^{\text{act}} = k_B T \left\{ \frac{\gamma}{B} + \frac{1}{2} \left(\partial \ln(\varepsilon_\infty / \varepsilon_s) / \partial P\right)_T - \left(\partial \ln f_{\text{max, tan}\delta} / \partial P\right)_T \right\}. \quad (5b)$$

We stress that the relations (4b) and (5b) presume an Arrhenius temperature dependence of  $\tau$  (Varotsos and Alexopoulos, 1979;

Varotsos et al., 1993). Furthermore, we note that to a first approximation, when analyzing the experimental results, the term  $(\partial \ln(\varepsilon_\infty / \varepsilon_s) / \partial P)_T$  in the right hand side of these two relations is neglected since it is small and comparable to the experimental error, as will be further explained in Section 4.

## 3. Experimental setup and the samples measured

We first describe the samples measured and then summarize the experimental setup.

### 3.1. Samples

Samples of polycrystalline calcite ( $\text{CaCO}_3$ ), of approximately 2 mm thickness and parallel surfaces with an area of about 2 cm<sup>2</sup> were immersed (and keeping) in distilled water at 363 K for one week. Continuous weighting during the water-saturation process shows that saturation was achieved in two days. Water-saturation at elevated temperature has the advantage that the expansion of the specimen and the subsequent dilation of the pore cavities assist diffusion of water molecules. Weighting the sample before and after the wetting process determines the accommodated water within the hydrated rock at about 0.5 wt.% (Papathanassiou et al., 2011, 2012).

### 3.2. Experimental setup

The samples are placed inside the pressure vessel, which uses silicone oil as the pressure transmitting fluid, of a Novocontrol GmbH (Germany) high pressure apparatus operating from ambient pressure to 0.33 GPa and thermostated at the desired temperature, from room temperature to 373 K. Silver paste (Granville) was placed on the parallel opposite surfaces of the specimen to achieve good contact between the metallic electrodes and the sample. A very thin insulating layer of epoxy covered the specimen to prevent contamination from the pressure transmitting fluid. Jacketing with araldite has been suggested by the manufacturer of the pressure apparatus (Novocontrol, Germany; see Reisinger et al., 1997). The manufacturer of the pressure vessel suggested independently the use of epoxy layer in order to jacket the sample. The pressure system was connected with a Solartron impedance analyzer operating from 10<sup>-2</sup> to 10<sup>6</sup> Hz while measurements in the frequency domain were monitored by a computer.

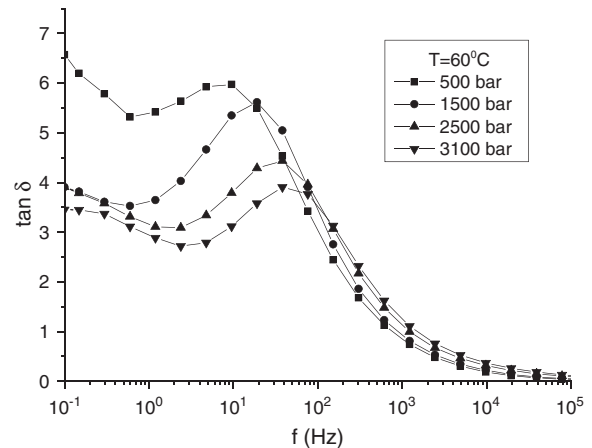


Fig. 1. Isotherms (333 K) of  $\tan \delta$  vs frequency of as-received limestone at various pressures.

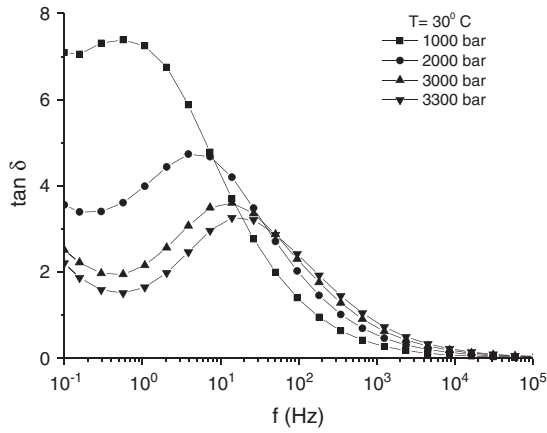


Fig. 2. Isotherms (303 K) of  $\tan \delta$  vs frequency of wetted limestone at various pressures.

4. Experimental results

Complex impedance measurements at various temperatures and pressures were performed for the as-received and the wetted limestone (polycrystalline calcite,  $\text{CaCO}_3$ ). Isothermal and isobaric measurements were performed from 313 K (40 °C) to 363 K (90 °C) and from ambient pressure to 3200 bar.

At Figs. 1 and 2 isothermal  $\tan \delta$  as a function of frequency  $f$  at various pressures is depicted for the as-received and wetted specimens respectively, while at Figs. 3 and 4, the variation of  $\ln f_{\max, \tan \delta}$  upon  $1/k_B T$  is shown. It is obvious that increasing pressure results in a subsequent displacement of the peak at larger values of frequency, thus, to a decrease of the relaxation time of the corresponding dielectric mechanism. This, in turn, indicates the existence of a negative activation volume which characterizes the dielectric mechanism. Increasing pressure lowers the energy barrier, making easier the response of the particular mechanism to an external stimulation (e.g. in the presence of a field). Next, the activation energy and absolute value of the activation volume are estimated employing the information extracted from Figs. 3 and 4 (slope of the fitting line) and using Eq. (5b) respectively. To a first approximation, as already mentioned in Section 2, the term  $(\partial \ln(\epsilon_\infty/\epsilon_s)/\partial P)_T$  was neglected as it is small (of the order of  $10^{-5}$ ) and comparable to the experimental error.

The results are presented in Table 1 and shall be discussed in more detail in the next section. Outlining these results, the activation volume of the wetted sample ( $39 \text{ cm}^3/\text{mol}$ ) is found roughly twice as that of the

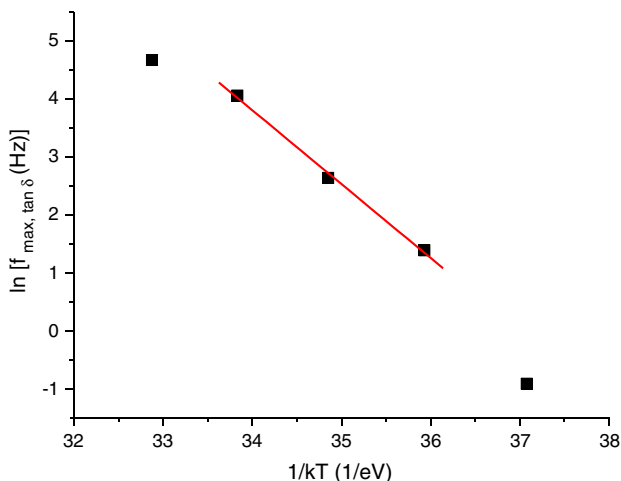


Fig. 3.  $\ln f_{\max, \tan \delta}$  is plotted against  $1/k_B T$  for the as-received limestone at  $P = 2000$  bar.

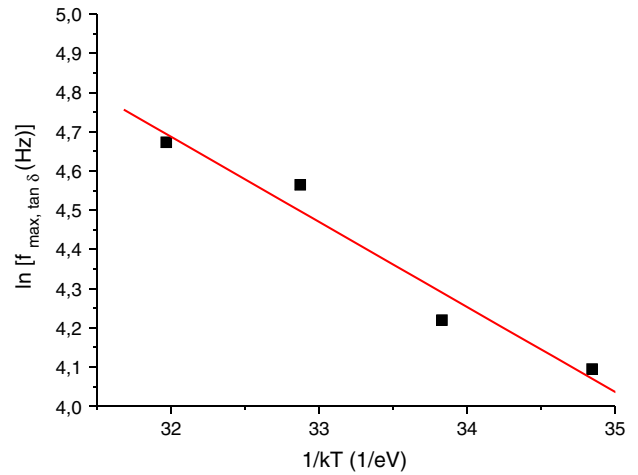


Fig. 4.  $\ln f_{\max, \tan \delta}$  is plotted against  $1/k_B T$  for wetted limestone at  $P = 2000$  bar.

as-received ( $18 \text{ cm}^3/\text{mol}$ ), while the activation energy is astonishingly lower for the latter (about six times), designating the critical role of water to the enhancement of the mechanism.

5. Discussion

Inspecting the experimental results in detail, two main novel features outstand. The first is that water is correlated with processes that are related to the negative activation volume, inducing a larger perturbation (larger activation volume), while at the same time a novel feature is recorded experimentally: water lowers the energetic threshold for the mechanism to be activated by more than 80%. The structural and compositional heterogeneity of limestones seems to be the underlying cause for the appearance of negative activation volumes, while the presence of water has a dual role. On the one hand enhances the phenomenon by filling the pores, while on the other gives rise to new mechanisms. Negative activation volume is known to be very rare. Specifically, the activation volume of general rocks is not known, thus, it is not either known how rare negative activation volume is. Solving this problem is difficult and hundreds of samples may have to be tested. Though it is difficult to correspond to the negative activation volume the manifestation of specific microscopic mechanisms, it is most likely that the interaction of water with the solid surface of the grains induces new polarization mechanisms stemming from the electrochemical interaction of the water with  $\text{CaCO}_3$ . Indicative is the case of leukolite (Papathanassiou et al., 2010). In Fig. 6,  $\tan \delta$  versus frequency for leukolite is shown, at 349 K for two different pressures for a wetted sample and at the same temperature for an as-received sample. It is clear that water in this case practically induces a new mechanism with negative activation volume. Furthermore, water enhances grain-boundary diffusion process operation on the surface of the grains i.e., dynamics of bulk entities relax in a manner that yields negative activation volume, compared with their dynamics within the interior of the grain. Different specimens though, have different topologies and

Table 1

The activation energy and the activation volume for the as-received and the wetted limestone (polycrystalline calcite,  $\text{CaCO}_3$ ).

	$(\partial \ln f_{\max, \tan \delta} / \partial P)_T$ (* $10^{-4} \text{ GPa}^{-1}$ )	$v^{\text{act}}$ ( $\text{cm}^3/\text{mol}$ )	$h^{\text{act}}$ (eV)
As-received limestone	$2.9 \pm 0.3$	-18	$1.27 \pm 0.06$
Wetted limestone	$6.7 \pm 0.7$	-39	$0.22 \pm 0.03$

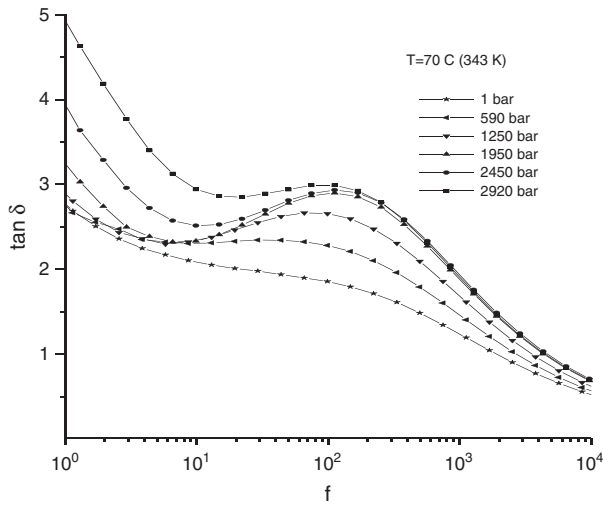


Fig. 5. Isotherms of  $\tan\delta$  versus frequency for granodiorite at various pressures.

network of channels accessible to water, resulting in different values of the activation enthalpy  $h^{act}$  and activation volume  $v^{act}$ .

Given the existence of quasi-dipoles characterized by negative activation volume, and pressure increase towards a critical value, the relaxation time of the quasi-dipoles becomes so short – or from another point of view the energy barrier lowers so much – for them to undergo a transition from a random-orientation state to an oriented one, thus emitting a transient polarization current. This seems to be consistent with the basic concepts of the SES generation model mentioned in Section 1. Recall that the limestone samples measured here come from the Ioannina region where a SES (sensitive) station (VAN) is located (Varotsos et al., 2011). The present findings of negative activation volume follow previous results from another SES sensitive station in Keratea (central Greece) from where granodiorite (Papathanassiou et al., 2011, 2012) rock samples (which is the underlying rock) were

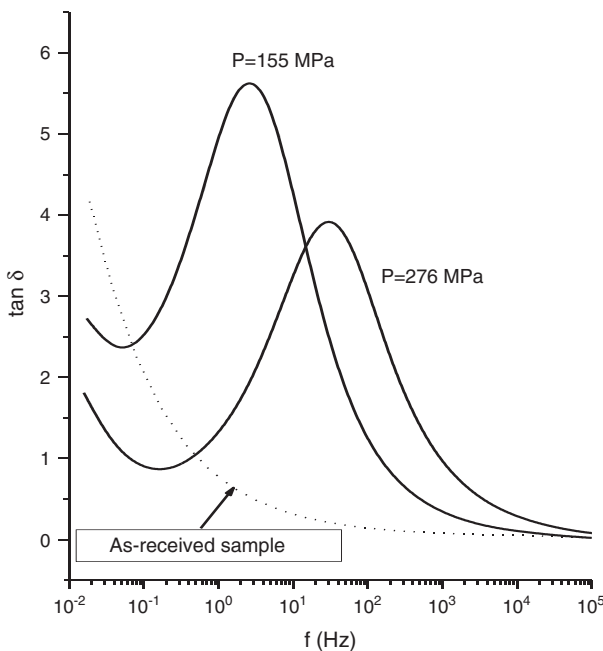


Fig. 6.  $\tan\delta$  versus frequency for leukolite at 349 K for two different pressures. The dashed line is a measurement for the non-hydrated leukolite.

studied and a negative activation volume ( $v^{act} = -9 \text{ cm}^3/\text{mol}$ ) was also found (Fig. 5).

## 6. Conclusions

Complex impedance spectroscopy measurements revealed negative activation volume for the limestone from Ioannina region. This finding, apart from its physical importance in itself, is linked to the SES sensitivity of Ioannina station and thereby, supports the theoretical model which was suggested as a physical explanation for the SES generation before an earthquake. Additionally, the role of water incorporated in the samples measured was examined. It was found that water not only enhances the value of negative activation volume but also lowers up to six times the energy barrier of the corresponding physical processes.

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