THE PIEZOELECTRICITY OF THE CALCITE

GABRIEL DIACONU, CORINA HĂDĂREANU and IRINA RUSU

The paper contains experimental data concerning the test of the phenomenon of piezoelectricity in calcite, marble and micritic limestone. The results are argued theoretically.

There is no doubt that calcite is one of the most frequent minerals in the petrographical system of the earth's crust. According to the observations made by sedimentologists, it seems that 25 percent of the volume of sedimentary rocks on the earth consist of carbonate rocks, among which the limestones ... "the monomineral rock consisting exclusively or at least prevailingly of calcite" ...(Rădulescu, 1965), are the most prominent. At the same time, calcite is one of the main objects of investigation of the speleologists, interested in the study of speleothems, as either monocrystals or crystalline aggregates (Hill, Forti, 1986).

The following lines are intended to present the results of a research focussing on an as yet unstudied physical property of calcite : piezoelectricity.

Our laboratory experiment was aimed to establish the causes of several natural processes outlined by the study of the red clays occurring on the limestones from Cloşani area. The presence of red clays on the karstified surface of the limestones had been ascribed to a natural piezoelectric field (Diaconu, 1984).

In developing the experiment, the use of a static method was preferred, since the microwave methods, although highly accurate, are inoperative in the case of calcite, a mineral of reduced mechanical resistance at high frequency vibrations. A mechanical stress of a liniar type was applied, followed by a sudden distension. The maximum loading was kept within pre-established limits (10—50 kgf/cm^2), that ensured the integrity of the sample.

The experimental device (Fig. 1) consisted of a hydraulic press, provided with a pressure gauge and an electronic voltmeter of 100 μV accuracy (Digital Multimeter E 0302).

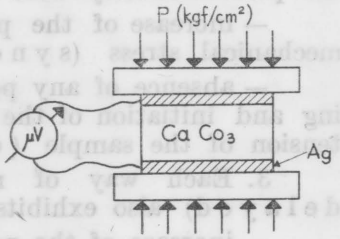

Fig. 1. — The experimental device.

In order to eliminate the impurities, each sample was treated, prior to testing, in a microwave bath. Subsequently, two of the parallel faces of the sample were metalized with silver in vacuum, in order to provide the electrical contact.

The elimination of any water traces, (which could have determined the depolarization of the crystal) was achieved by keeping the samples for ,30 minutes at a temperature of 400° C. The whole experiment was developed under rigorous hygrometric and thermal control, at humidity and temperature values that allowed no condensation of the atmospheric water on the faces of the sample.

The first stage of the experiment took under study pure calcite monocrystals, extracted from the caves Cloșani (Mehedinți Mountains) and Tecuri (Sebeș Mountains).

Perfectly plane and parallel faces were obtained by cleavage through thermal shock, introducing the samples in liquid nitrogen.

The next stage of the experiment was performed on samples of two carbonate rock types (marble and micritic limestone), purposely chosen at the opposite extreme limits of the crystallinity degree. The rocks were deliberately tested in only one particular way, the justification of which is given below.

Observations performed on calcite speleothems from caves led to the conclusion that almost all the microcrystals, either isolated or associated in aggregates, have the A^3 axis of their network structure orientated parallel to the gravitational axis. Since all carbonate rocks undergo fracturing or cleavage along the rhombohedral faces, we supposed that the constitutive grains of the carbonate lithic aggregates (predominantly calcitic) obey the same laws concerning the orientation of the A^3 axis and thus the carbonate rock could have physical properties identical or very close to those of the constitutive mineral, the calcite. Therefore, from several samples of marble and micritic limestone we cut pieces (about 3—4 mm thick) according to the natural cleavage faces of the rock. In all, 20 samples of monocrystallinic calcite, 10 samples of marble and 10 samples of micritic limestone were studied.

CONCLUSION OF THE EXPERIMENT

1. All samples exhibited indisputable manifestations of the piezoelectricity.

2. According to the experiment, two ways of manifestation of the piezoelectricity were identified:

— increase of the polarization voltage proportional to the applied mechanical stress (s y n c h r o n o u s b e h a v i o u r), and

— absence of any polarization voltage during the mechanical loading and initiation of the voltage after loading removal, during the distension of the sample (d e l a y e d b e h a v i o u r).

3. Each way of manifestation (either s y n c h r o n o u s or d e l a y e d) also exhibits two types of piezoelectrical answers:

— increase of the polarization voltage proportional to the applied mechanical stress, followed by an exponential discharge, analogous to that occurring in a capacitor (t h e n o r m a l b e h a v i o u r), and

— increase of the polarization voltage, followed by a polarity inversion and ending in the exponential discharge, analogous to that occurring in a capacitor (t h e b e h a v i o u r w i t h i n v e r s i o n).

4. Summing up the two previous paragraphs, four types of behaviour were outlined: s y n c h r o n o u s n o r m a l, s y n c h r o n o u s w i t h i n v e r s i o n, d e l a y e d n o r m a l and d e l a y e d w i t h i n v e r s i o n.

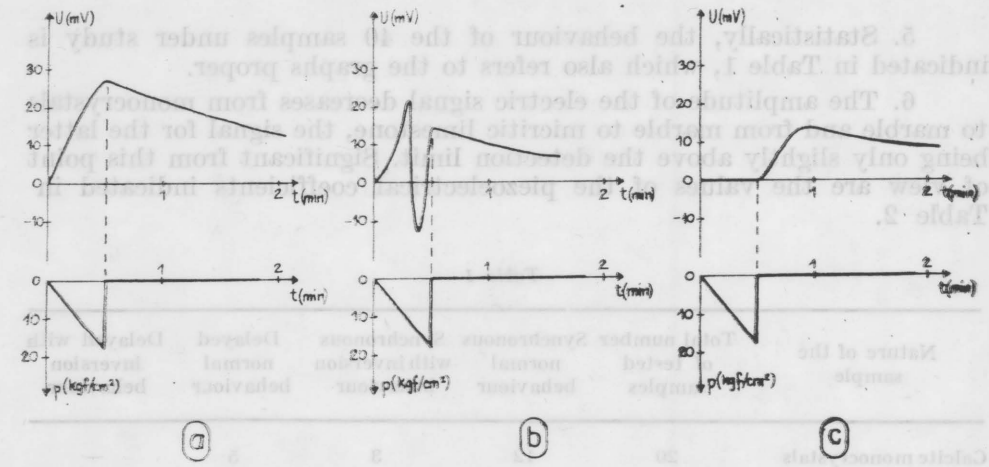

Fig. 2. — The piezoelectrical behaviour of calcite monocrystals. a) Synchronous normal behaviour ; b) Synchronous with inversion behaviour ; c) Delayed normal behaviour.

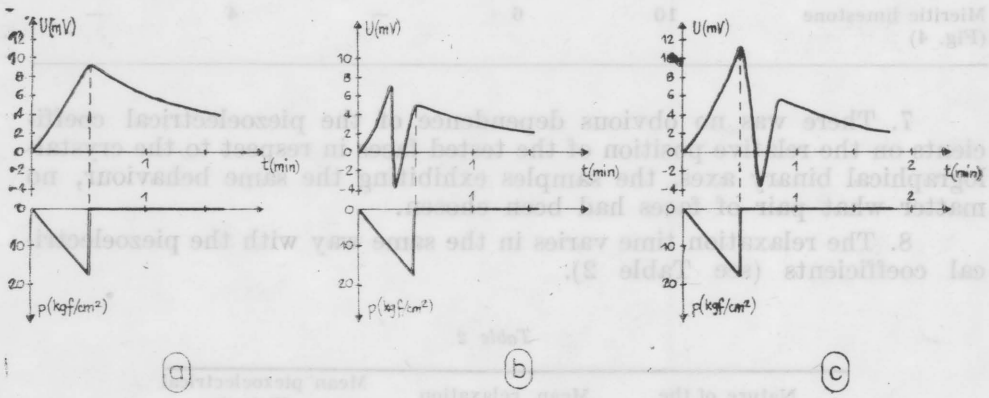

Fig. 3. — The piezoelectrical behaviour of marble. a) Synchronous normal behaviour ; b) Synchronous with inversion behaviour ; c) Delayed with inversion behaviour.

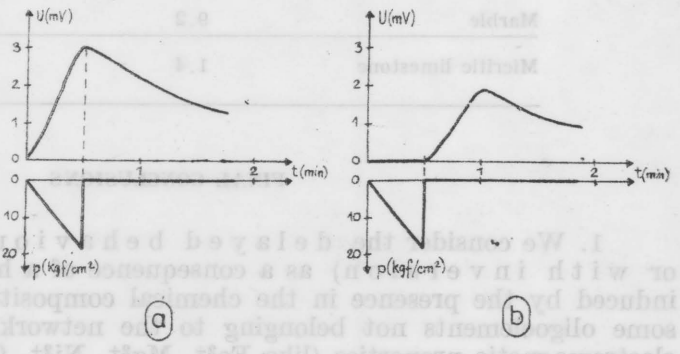

Fig. 4. — The piezoelectrical behaviour of micritic limestone. a) Synchronous normal behaviour ; b) Delayed normal behaviour.

5. Statistically, the behaviour of the 40 samples under study is indicated in Table 1, which also refers to the graphs proper.

6. The amplitude of the electric signal decreases from monocrystals to marble and from marble to micritic limestone, the signal for the latter being only slightly above the detection limit. Significant from this point of view are the values of the piezoelectrical coefficients indicated in Table 2.

Table 1

Nature of the sample	Total number of tested samples	Synchronous normal behaviour	Synchronous with inversion behaviour	Delayed normal behaviour	Delayed with inversion behaviour
Calcite monocrystals (Fig. 2)	20	12	3	5	—
Marble (Fig. 3)	10	3	2	—	5
Micritic limestone (Fig. 4)	10	6	—	4	—

7. There was no obvious dependence of the piezoelectrical coefficients on the relative position of the tested faces in respect to the crystallographical binary axes, the samples exhibiting the same behaviour, no matter what pair of faces had been chosen.

8. The relaxation time varies in the same way with the piezoelectrical coefficients (see Table 2).

Table 2

Nature of the sample	Mean relaxation time (min)	Mean piezoelectrical coefficients (mV. cm^2/kgf)
Calcite monocrystals	18.7	0.735
Marble	9.2	0.435
Micritic limestone	1.4	0.098

FINAL CONCLUSIONS

1. We consider the d e l a y e d b e h a v i o u r (either n o r m a l or w i t h i n v e r s i o n) as a consequence of a hysteresis phenomenon induced by the presence in the chemical composition of the samples of some oligoelements not belonging to the network and having specific electromagnetic properties (like Fe^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+}, etc.).

2. The polarity inversion (either synchronous with inversion or delayed with inversion behaviour) could be determined by the "run" of the electrical charges, imposed by either the instantaneous appearance or pre-existence of a mechanical macle during the experiment, or the appearance of a local electric field, caused by a network imperfection. We consider the first supposition as being more plausible, the inversion behaviour being exhibited also by marbles (Table 1), which frequently include crystalline grains associated in polysynthetic macles.

3. The variation of the relaxation time in concordance with the piezoelectrical coefficients (Table 2) is conditioned by the internal structure of the tested samples : in the case of the finely grained ones (micritic limestone) the equilibrium will be re-established faster than in the case of the coarser grained ones (marble) or than in the case of monocrystals, the internal friction forces decreasing in this order.

4. It is not difficult to explain why this property has been ignored so many years : a well-known postulate asserts that piezoelectricity is particular only to those crystals whose classes of symmetries are devoid of a symmetry center (Jeludev, 1973). The calcite, which belongs to the rhombohedral system, the ditrigonal scalenoedric class, has the symmetry formula $A^3 3A^2 3PC$, representing a third order axis, three second order axes, three planes of symmetry and a center of symmetry (Bolgiu, 1974). From this point of view it seems that calcite, having a center of symmetry, could not be supposed to exhibit piezoelectricity.

A more in-depth approach to the network structure of crystallization of this mineral species allows a slightly different interpretation of the above symmetry formula.

If calcite had been a chemical compound consisting of only two elements (like hematite Fe_2O_3 for instance, which crystallizes in the same symmetry order and class) the spatial geometrical relationships (as indicated by the symmetry formula) would have been perfect. Calcite being the result of several coordinate bonds between the Ca^{2+} cations, located in the knots of the elementary cell, and the CO_3^{2-} anions, coaxially and symmetrically placed along the A^3 axis of the same cell (Diaconu, 1986), the existence of a center of symmetry is only partially real. More specifically, only in respect to the spatial position of the Ca^{2+} cations the center of symmetry exists. The CO_3^{2-} anions have opposite direction orientations (Fig. 5), which fact "annuls" the center of symmetry materialized by the Ca^{2+} cations. In what way is this annullment achieved?

Theoretically, the CO_3^{2-} anions are planar and symmetrical complex ions (Nenițescu, 1972) (Fig. 6a), a central atom of carbon being covalently bound to three oxygen atoms located on the same plane, at angles of 120°. Yet, very detailed XR studies have shown that, practically, in the carbonate ions, the planar disposition of the oxygen atoms, bound to the central carbon atom, was real, but the symmetry was disturbed by the polarization action of the C^{4+} ion on the O^{2-} surrounding ions (Lippmann, 1973) (Fig. 6b). This fact complicates the symmetry relationships in the intimacy of the network structure, where the hexagyroidal connec-

tions of the oxygen atoms from a CO_3^{2-} to the ones corresponding to the adjoining CO_3^{2-} no longer satisfy the conditions required by a center of symmetry, becoming trigyroidal relationships, and thus degenerating into a simple A^3+P combination, devoid of a center of symmetry (Fig. 7).

Finally, considering that the obtained results are conclusive enough, we intend to try in the future to investigate this phenomenon, piezoelectricity, not only on the cave speleothems, but also on the carbonate rock bodies, through systematic measurements performed both in the underground and on outcrops.

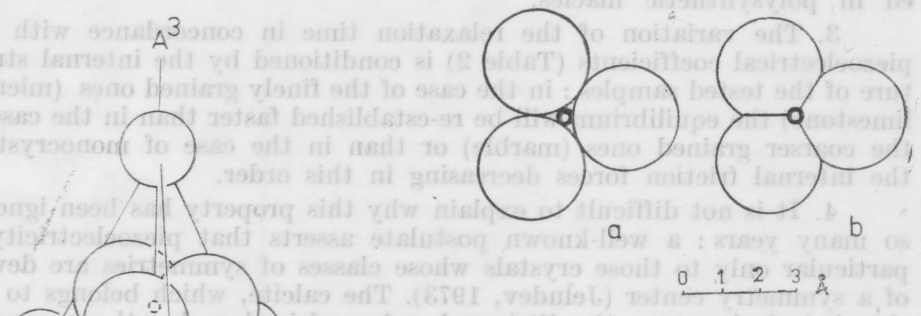

Fig. 6. — The complex ion CO_3^{2-} : a) Theoretical form ; b) Polarized form.

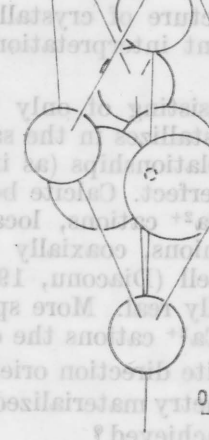

Fig. 5. — The rhombohedral elementary cell of calcite ($2CaCO_3$).

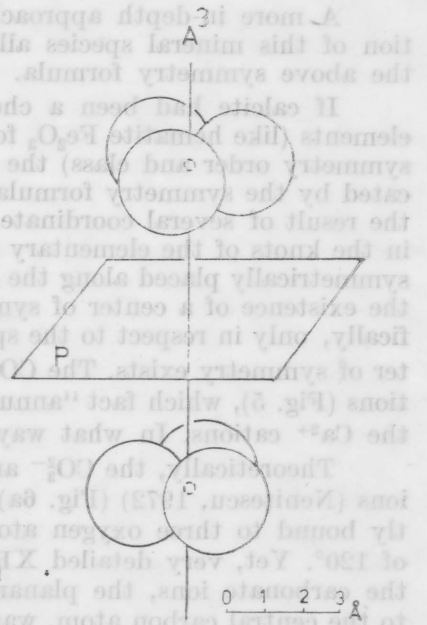

Fig. 7. — The trigyroidal relationship at the CO_3^{2-} ions.

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"Emile Racovitza" Speleological Institute
Bucharest

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