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High-Sensitivity Apparatus for Measuring Linear Thermal Expansion: Preliminary Results on the Response of Marbles to Thermal Cycles.

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Summary. - The aim of this paper is to present a high-sensitivity apparatus for measuring the thermal expansion of rocks, minerals and solids in general. The measurement of the magnitude of the linear expansion of a sample at any temperature of its heating-cooling cycle can be obtained with resolution equal to or better than 10 nm. Preliminary results on marble samples having different petrographic features are reported.

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1. - Introduction.

The measurement of thermal expansion in rocks is a subject of considerable interest to several sciences, such as mineralogy, geophysics, structural engineering, etc. Therefore, it has been extensively studied by means of several techniques.

In this paper a new apparatus for thermal-expansion measurement is presented. Its most attractive feature is that it allows the recording of a sample's thermal expansion due to heating-cooling cycles from ambient temperature up to some hundred degrees Celsius with the same resolution at every single temperature of the cycle. Our method permits the detection of the thermal expansion by a static and a dynamic procedure contemporaneously, retaining the features of both.

In a static procedure the temperature of the material under investigation is maintained constant for a certain interval of time, and the variation of length that takes place during the passage from one temperature to the other is subsequently measured. The measurement is thus carried out between two different states of thermal equilibrium, and this leads to accurate knowledge of the change in length with temperature.

In a dynamic procedure the temperature is varied continuously, and the variation of length simultaneously recorded. This procedure is less accurate than the static method for measurement of sample lengthening because the temperature in the sample interior may not be uniform, but it is useful to study the temporal evolution of the thermal expansion with respect to that of the temperature.

At present our procedure is the following: the sample is heated at a low rate up to the temperature of interest, then it is kept at that temperature until it reaches thermal equilibrium; dilation *versus* time is continuously recorded. The condition of thermal equilibrium is fulfilled when the slope of the dilation curve is zero with respect to the time axis for a long enough interval of time. This operation is repeated for all the required temperatures (fig. 1 shows an example of a recorded cycle). Thus, we can say that our apparatus performs the measurement with a combination of static and dynamic procedures.

The equipment was employed to study the behaviour of marble samples subjected to small temperature variations in heating-cooling cycles and, mainly, to determine the minimum values of temperature at which marbles undergo permanent length changes.

Marble is widely used in monuments, and, outdoors, undergoes alterations due to daily and seasonal temperature changes, resulting in a progressive loss of cohesion which depends on the strong anisotropy of the calcite thermal-expansion coefficients.

The same alteration takes place in almost all the holocrystalline, polymineral rocks having sufficiently coarse grain. This alteration is often the most important cause of the decay of marble monuments.

Rosenholtz and Smith [1, 2] demonstrated that marble heated up to 700 °C shows, after cooling down to ambient temperature, a permanent residual strain. Franzini *et al.* [3] showed, by means of water absorption measurements, that the same phenomenon is already present for heating up to 110 °C.

The experimental results reported here show that these effects can be observed at still lower temperatures, thus confirming the daily and seasonal temperature changes as the chief cause of the alteration of outdoor marbles.

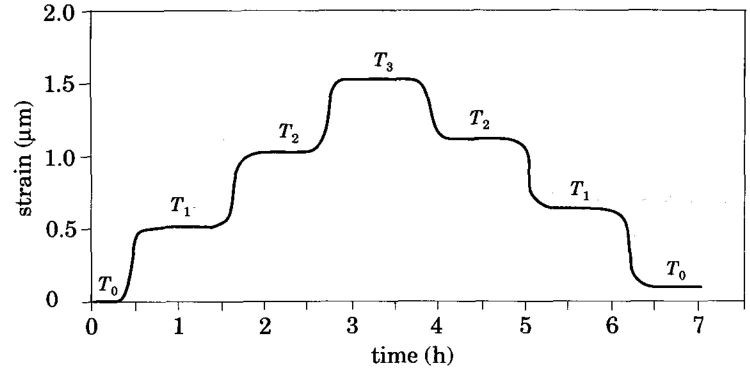

Fig. 1. – Heating-cooling cycle of marble A recorded *versus* time. T_0 (= 18 °C) is the ambient temperature, T_3 (= 48 °C) the maximum temperature of the cycle and, in this case, the cracking temperature. The intermediate temperatures T_1 and T_2 are 28 °C and 38 °C, respectively.

In this phase of the research, temperature variations above the mean ambient temperature have been studied, but similar effects are believed to exist at lower temperatures.

2. – Experimental equipment and sample preparation.

The dilatometer is based on an apparatus designed for the measurement of refraction, dispersion and absorption of gases at relatively high pressure [4], and has been subsequently employed for other measurements as well [5, 6].

This apparatus, whose block diagram is shown in fig. 2, allows measurement of the change in resonance frequency of a microwave resonator (as well as the change in its quality factor, which is of little interest here, however) compared to that of a reference resonator. The two resonators are identical, so a differential measurement between their resonance frequencies is made by means of a pulse technique transforming the frequency differences between the resonators into time intervals whose width is proportional to the amplitude of the frequency change. Then, these intervals are converted into potential differences, ΔV, and recorded.

When both resonators are tuned to the same frequency $(\Delta V = 0)$, ΔV becomes negative or positive when the resonance frequency of one resonator is higher or lower than that of the other.

In our case tha variation in the frequency is induced by the variation in the height of the resonator caused by the sample's thermal expansion. The change in length of the sample and the variation in height of the resonator are of exactly the same magnitude and opposite in sign.

The sensitivity of our apparatus is equal to about $(\Delta\nu/\nu) = 10^{-8}$, therefore we could measure an elongation of less than about 1 nm. In fact, the resonator frequency of our

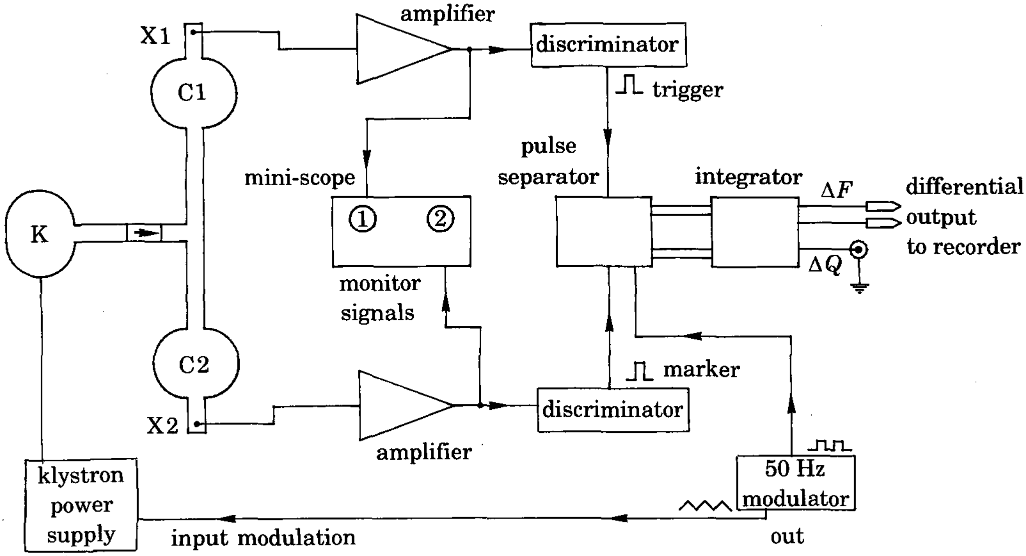

Fig. 2. – Block diagram of the spectrometer on which the dilatometer is based. K: klystron, C1 and C2: resonators, X1 e X2: crystal diodes.

microwave cavity, resonating in the TE_{011} mode, is about 9.6 GHz for height $h = 4.1$ cm and radius $R = 2.05$ cm; thus, from the relation

$$\Delta\nu/\nu = (\Delta h/h)/[(3.832 * 2/\pi)^2 + 1],$$

the theoretical minimum detectable elongation is derived.

The dilatometer was calibrated using a piezoelectric translator (P-249.20 of Physik Instrumente) whose maximum dilation is 10 μm with an applied voltage of 1000 V and whose linearity is certified to be in the range of 0 to 200 V. The response of our apparatus to rectangular pulses, between the voltages $+V_0$ and $-V_0$, was recorded, and it reproduced the wave form with a good signal-to-noise ratio, up to $V_0 = 50$ mV; this voltage, peak to peak, corresponds to a translation of 1 nm, with an accuracy of several per cent.

The samples are cylinders of about 8 mm in diameter and length ranging from 9 to 12 mm; their bases are flat and parallel to each other. The samples are inserted between two fused silica rods (as shown in fig. 3) whose ends have about the same dimensions and the same conformation (flat and parallel ends) as that of the sample.

One of these rods rests on a fixed mounting, the other acts on the mobile terminal wall of the resonator according to the sample thermal expansion. During heating, the sample lengthens and, pushing the rod, shortens the resonator height, thus increasing the resonator frequency; during cooling the opposite occurs. After the sample is placed, the resonators are tuned to the same resonance frequency, making their heights equal by means of micrometer screws moving the terminal wall of the resonators. The thermal expansion of the sample is produced by the Joule heating of a coil of isolated copper wire for transformer or of constantan wire wound around the sample and supplied with a variable direct current.

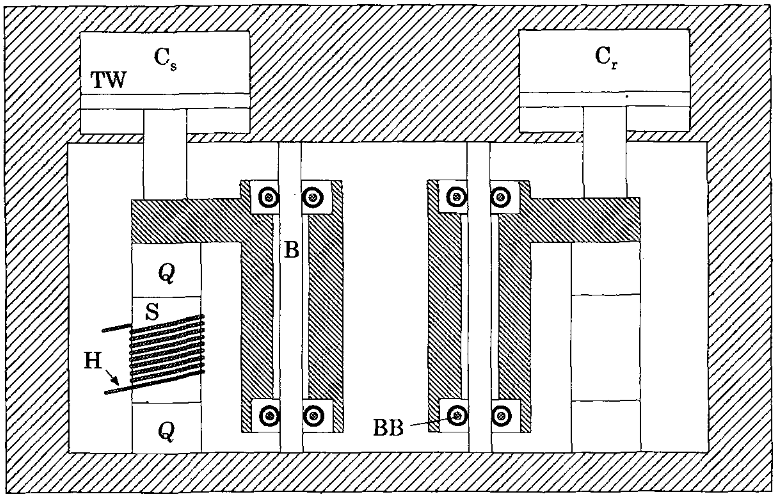

Fig. 3. – Simplified drawing of the apparatus components which transduce the sample length changes into equal-height variations of the microwave resonator. C_S is the resonator on which the sample S acts, pushing the terminal wall TW during the heating expansion. C_r is the reference resonator, Q fused silica rods, H heater, B inox steel bar and BB ball bearings ensuring the minimum friction to the slide moving the terminal wall. The sample and fused silica rods are represented in enlarged scale for the sake of clarity.

The sample temperature is measured by a thin thermocouple placed in a hole drilled in the middle of the cylinder. The resolution Δt of the thermometer is about 0.1 °C: therefore a change in the length of the sample, ΔL, is meaningless if it is less than $\lambda \cdot L \cdot 0.1$ cm, where λ is the sample coefficient of the linear thermal expansion and L its length. For a marble sample 1 cm long, $\Delta L \leqslant 10^{-6}$ cm for $\lambda \leqslant 10^{-5}\,{}^{\circ}\mathrm{C}^{-1}$.

The microwave apparatus is kept at constant temperature with a resolution of $\leqslant 0.1$ °C, to avoid errors from changes in the ambient temperature. Although any temperature change would not result in the measurement of a frequency variation because the temperature change affects both the resonators (dug in the same block of aluminium), thus changing the resonance frequencies of both resonators at the same time and by the same amount, the temperature control is necessary in order to keep both at the same temperature.

The sample, which is also in the temperature-controlled box, is kept at constant temperature with the same resolution, therefore it is affected by random variations in temperature of ± 0.1 °C. In order to solve the problem, we placed at the reference resonator another sample, identical to that under investigation and located in the same manner but without heating it. In this way the temperature changes, affecting both samples, do not affect the measurement of the thermal expansion induced by the heating of only one of them.

In conclusion, the sensitivity of our system is fundamentally limited by the poor resolution of the temperature measurement, so that for marble the minimum meaningful measurable strain is $\leqslant 10$ nm, assuming λ of the marble $\leqslant 10^{-5}\,{}^{\circ}\mathrm{C}^{-1}$. In order to improve the apparatus sensitivity by one order of magnitude, we intend to replace the thermometer with another with a resolution of 0.01 °C, so that the maximum sensitivity of the dilatometer can be attained.

All the examined samples were prepared with all possible caution to avoid structural damage. Several cylinders of marble were cut from large blocks with water-cooled diamond core drills: they were 8 mm in diameter and ranged in length from 9 to 12 mm. Their bases were made flat and parallel to each other.

In addition, samples of granite and basalt were selected in order to compare their behaviour with that of the marbles.

3. – Results and discussion.

The experimental data for three different types of marble a granite one and a basalt one are reported (for petrographic features, see table I). All the examined samples were «virgin», that is, they had not been subjected to any stress before the sampling process.

In accordance with the literature, the rate of sample heating or cooling was set at 1 °C/min, in order to avoid a spatial temperature gradient which might produce microcracks in the sample.

In light of the apparatus sensitivity, we defined the «cracking temperature», T_c, as the maximum temperature of the first heating-cooling cycle, at the end of which the sample undergoes a permanent change in length equal to or greater than 30 nm, that is three times the minimum meaningful variation in length.

In fig. 4, 5 and 6 the thermal-expansion behaviour of the three types of marble (named A, B and C) for several temperature cycles at successively higher temperatures is reported.

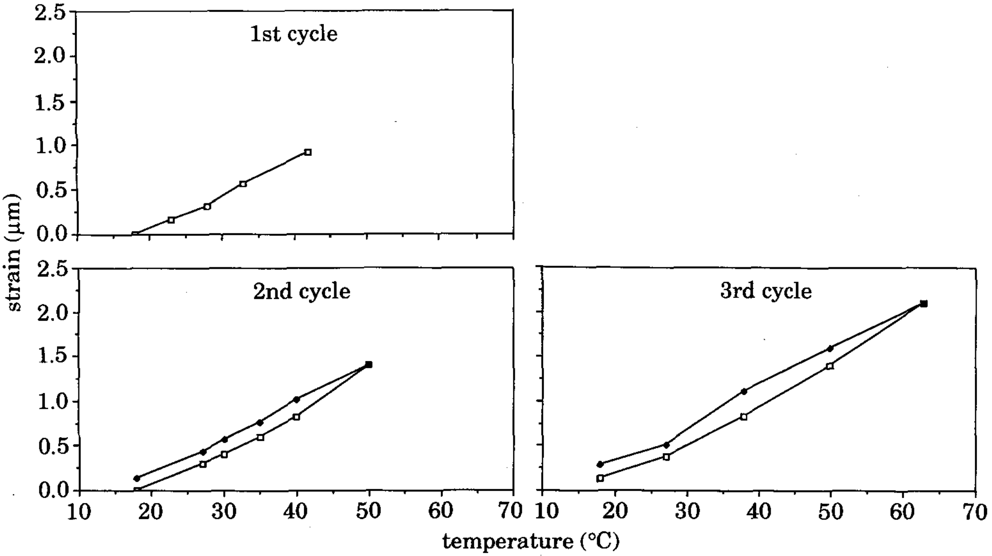

Fig. 4. – The thermal-expansion behaviour of marble A.

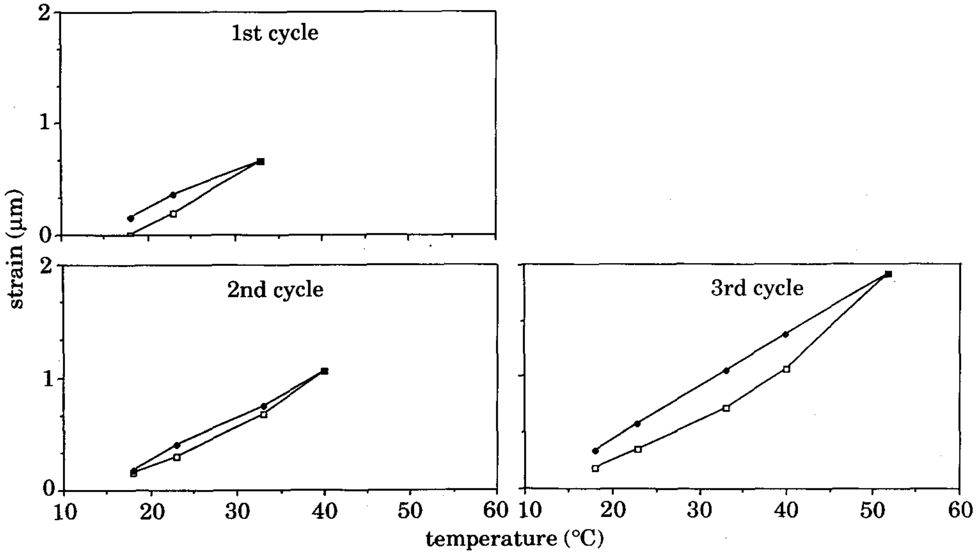

Fig. 5. – The thermal-expansion behaviour of marble B.

The representative points were obtained with the procedure described in the introduction. The time required to reach thermal equilibrium varies from sample to sample, but is always greater than one hour. In order to check the apparatus, this time was extended up to one day with no detectable variation of the dilation formerly recorded at equilibrium.

The main features that can be drawn from the experimental data are summarized in the following:

1) The «cracking» temperatures are much lower than those reported in previous

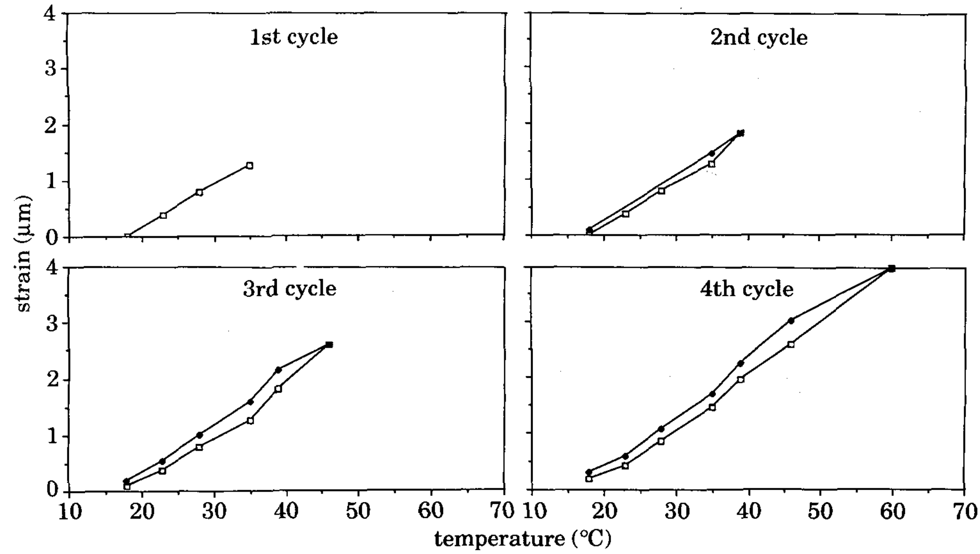

Fig. 6. – The thermal-expansion behaviour of marble C.

Table I.

	Texture	Grain size range (mm) (mean value)	Notes
marble A	partially polygonal	0.01 ÷ 0.3 (0.13)	No accessory minerals
marble B	polygonal	0.06 ÷ 0.4 (0.25)	No accessory minerals. Very frequent mechanical twins, rare growth twins.
marble C	partially polygonal iso-oriented	0.03 ÷ 0.2 (0.1)	No accessory minerals. Very frequent mechanical twins.
granite	hypidiomorphic	(2.8)	Microperthitic orthoclase, quartz, plagioclase, biotite, zircon, apatite. Altered.
basalt	doleritic	(0.7)	Plagioclase, chlorite, olivine, magnetite. Altered.

papers [3]; for marbles A and C they are about 50 and 42 °C, respectively. Marble B exhibits an anomalous behaviour, presenting permanent strain at temperatures just above room temperature, that is 18 °C. The appearance of permanent strain in these graphs occurs at a temperature only a few Celsius degrees from the maximum temperature of the preceding cycle, and its magnitude is much greater than the criteria for considering it permanent.

2) A hysteresis loop appears in all heating-cooling cycles. In the graphs where the maximum cycle temperature is low and the sample presents no residual permanent

strain, that is, where the hysteresis loop is closed, the points representing the cooling cycle are not reported, because the difference between them and the representative heating points is too small for the scale taken.

3) The points of the heating curve beyond the first detected permanent strain lie in a path that is a little higher than the heating path of the previous cycle, but lower than that of cooling.

4) The value of ε_0, the permanent change in length at room temperature, increases when the maximum temperature of the successive cycles increases. This value does not vary (within the limits of our apparatus sensitivity) if the maximum temperature of the following cycle is kept the same as the foregoing one, at least for three repeated cycles.

5) The ratio $\varepsilon_0 / \Delta L(T_c)$, where $\Delta L(T_c)$ is the observed thermal expansion at the cracking temperature in the heating part of the cycle, ranges from 0.1 to 0.05 for samples of marble A and C and has values higher than 0.18 for the samples of marble B.

6) There is a noticeable difference between the dilations of marbles A and B and that of marble C, for which the thermal-expansion coefficient is about 1.8 time greater than those of the others.

The thermal-expansion data of the granite sample (fig. 7) show a similar behaviour. In fact, the cycle having a maximum temperature of 45 °C produces a residual strain that is about 7% of the maximum expansion.

The basalt, on the contrary, shows no permanent variation in length for temperatures up to 330 °C (fig. 8). This result is in good agreement with the data reported by Richter *et al* [7].

Experiments performed on quartz monocrystals and fused silica rods have shown no permanent length changes at the end of the heating-cooling cycles whose maximum temperature was as high as that of the basalt cycle.

4. - Conclusions.

The experimental results demonstrate the high sensitivity and reliability of the presented apparatus, coupled with the advantages of easy employment and set-up. Furthermore, the sensitivity can be improved even by one order of magnitude simply by re-

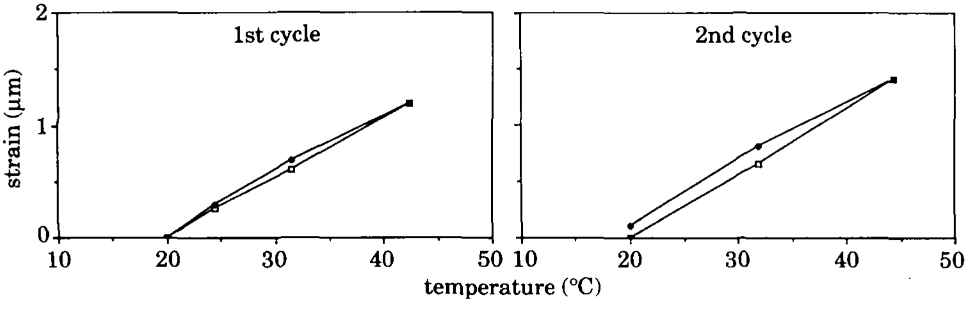

Fig. 7. – The thermal-expansion behaviour of granite.

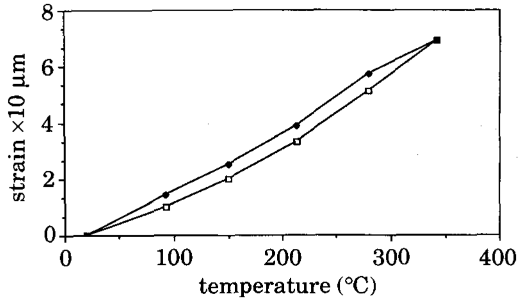

Fig. 8. – The thermal-expansion behaviour of basalt.

placing the thermometer used with another having an accuracy greater by a factor ten.

The results on the marbles demonstrate that permanent strain occurs at temperatures only slightly higher than the mean ambient temperature, so that alterations of this material seem to be inevitable outdoors, if the behaviour of these three types can be generalized.

The next step in our research will be the study of the behaviour of these materials at temperatures below the mean ambient temperature, in order to see if the cooling-heating cycle (for instance from mean ambient temperature to several degrees below 0 °C) presents the same features (cracking temperatures and hysteresis loops) as heating-cooling cycles. The knowledge, for a given marble quality, of its heating and cooling cracking temperatures (granted exists) would be very useful for the understanding of its behaviour in open-air exposition.

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REFERENCES

[1] J. L. Rosenholtz and D. T. Smith: *Am. Mineral.*, **34**, 846 (1949).
[2] J. L. Rosenholtz and D. T. Smith: *Am. Mineral.*, **35** 1049 (1950).
[3] M. Franzini, C. Gratziu and M. Spampinato: *Rend. Soc. It. Mineral. Petrol.*, **39**, 47 (1983).
[4] A. Gozzini *et al*: *C. R. Acad. Sci.*, *(Paris)*, (1953) 237.
[5] N. Benevento: Thesis, Università degli Studi di Pisa (1971/1972).
[6] A. Ascenzi *et al.*: *C. R. 12eme Colloque OHD (Rennes)*, (1989) 377.
[7] D. Richter and G. Simmons: *Rock Mech. Min. Sci. Geomech.*, **11**, 403 (1974).