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Levynes and Erionites from Sardinia, Italy

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Abstract. Three samples of levyne and two of erionite from three different localities of Sardinia are described. In two samples, levyne and erionite are intergrown by epitaxy. The levynes exhibit close chemical compositions with Ca>Na>K; as for their lattice constants, *a* is very similar in all three samples, while *c* of one sample is rather smaller than that of the other two. Unit cell dimensions of both erionites and chemical composition of one are also given. In addition, the following data are reported for the levynes: refractive indices for all three samples, density for two and DTA for one. The existence of levyne-erionite intergrowth is emphasized, and support is given to the idea that this intergrowth is much more common than the literature would suggest.

Introduction

Levyne and erionite are two rare zeolites not yet found in Italy. The oldest findings of levynes have been reported from Iceland, Ireland, Colorado and Faröe (see references in Doelter, 1921) and in Czechoslovakia (Hibsch, 1927). Quite recently, Walker (1960) stated that levyne is one of the most widespread zeolites in the basalts of Antrim (Northern Ireland). Chatterjee (1971) found it at Bhopal (India); Shimazu and Mizota (1972) described a fine intergrowth levyne-erionite from Chojabaru, Iki Island, Japan.

Erionite in crystals has also been found in a limited number of places, namely Oregon (Eakle, 1898; Staples and Gard, 1959), Washington (Kamb and Oke, 1960), Faröe (Hey, 1959), Carinthia (Zirkl, 1963) and in four localities in Japan (Shimazu and Kawakami, 1967; Harada *et al.*, 1967; Kawahara *et al.*, 1967; Shimazu and Yoshida, 1969; Shimazu and Mizota, 1972; Muchi *et al.*, 1972). More frequent were the findings of microcrystalline erionite of sedimentary genesis in cenozoic tuffs of Wyoming, Nevada, South Dakota, Oregon, California (Deffeyes, 1959; Sheppard and Gude, 1969) and also of Tanzania (Hay, 1964).

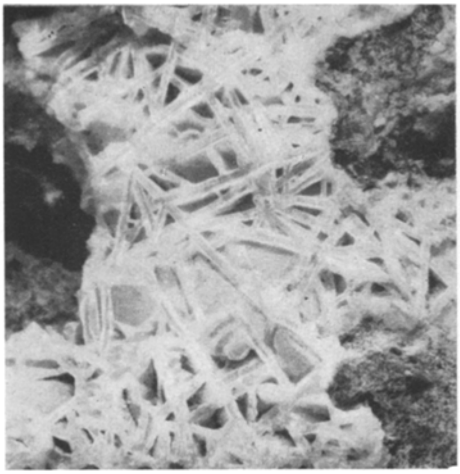
Three findings of levyne and two of erionite from three different localities of Sardinia, Italy, are the subject of this report.

R.R. was responsible for the electron microprobe analyses; the other experimental and field work was carried out by E.P. and E.G.

Localities and Mode of Occurrence

The three occurrences are:

Sample 1. On the road from Padria to Montresta, 50 m before the T-junction for Villanova Monteleone (Nuoro).



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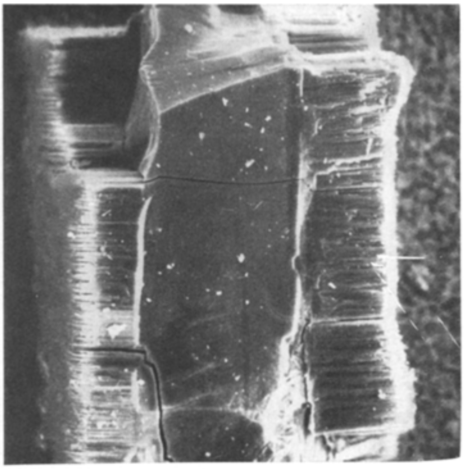

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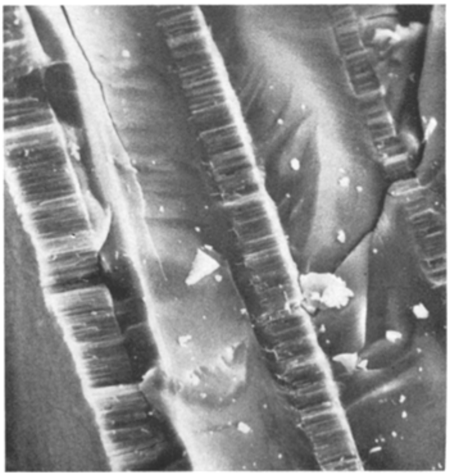

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Fig. 1. Optical photograph of the sample 2. The lamellae are formed by a central part of levyne and by two very thin external layers of erionite. The levyne-erionite intergrowth is emphasized in the micrograph of Fig. 2. Magnification: × 7

Fig. 2. Scanning electron micrograph of a lamella of the sample 2. The levyne (vitreous luster mass) is sandwiched between two layers of fibrous erionite. Magnification: × 220

Fig. 3. Scanning electron micrograph showing the intergrowth of levyne (vitreous luster layers) and erionite (fibrous layers) in the sample 3. Magnification: × 550

Sample 2. Just outside the village of Montresta (Nuoro) on the road to Padria, there is a country road to the right. The minerals occur at an excavation about 100 m down this road on the right-hand side.

Sample 3. On the road from Nurri to Orroli (Nuoro), there is a mule-track leading off to the right from near a horse-pond. The minerals occur in rocks and boulders strewn along the track, about 100 m from the road.

In Sample 1, levyne is present as dull, white crystals of irregular shape, associated with water-clear crystals of chabazite in fractures of a reddish andesitic rock.

In Sample 2, levyne and erionite are associated in lamellae forming a characteristic sandwich-like intergrowth (see Fig. 1) and interlacing; the lamellae, about 0.1 mm thin and up to 5 mm in diameter, coincide with the (0001) plane of both minerals and consist of a central vitreous part of levyne which is coated on both sides by compact fibrous erionite, the fibres being *c*-elongated and normal to the plane of the lamellae. This epitaxy of erionite on levyne is clearly visible in the picture in Fig. 2, taken with a scanning electron microscope. This sample was found in a fracture of a weathered andesite.

In Sample 3, levyne and erionite exhibit the same epitaxial growth as in Sample 2, but in this case the fibrous layers of erionite are very thin, and can only be observed under the scanning electron microscope (see Fig. 3). The lamellae occur in small cavities of a compact andesite.

Owing to the intimate association of levyne and chabazite (Sample 1) and levyne and erionite (Samples 2 and 3), the following observations have to be made regarding some of the experimental data. The quantity of levyne separated by hand-picking from chabazite in Sample 1 was sufficient for the measurement of specific gravity, refractive indices, TG and DT analyses. Only one little crystal of levyne was separated from erionite in Sample 2. The refractive indices were measured on this fragment. In Sample 3, the presence of erionite in very thin layers alternating with thicker layers of levyne was detectable only under the scanning electron microscope. The fragments of levyne on which the refractive indices, density and water content were determined were checked for homogeneity under an optical microscope. It is thus possible that, owing to contamination by erionite, the above mentioned data obtained for this sample are not accurate. The erionite analysis of this sample is not reported here; it is considered as being unreliable, for the spot size of the microanalyzer (see next chapter) is as large as the erionite sheets ($\sim 10\ \mu$), and hence the results are influenced by the intergrown levyne.

X-Ray Study

The cell dimensions of levyne and erionite are given in Table 1. The cell dimensions of levyne were derived by a L.SQ. refinement program using the reflections measured on a Philips powder diffractometer with Ni-filtered Cu-Kα radiation. Cubic $Pb(NO_3)_2$ was used as an internal standard; the reflections were indexed according the accurate indexing of Kerr (17–535 ASTM card). The cell dimensions of erionite were measured on single-crystal rotation photographs.

All three samples of levyne have an almost identical *a* dimension, whereas *c* is very close in Samples 2 and 3 but considerably less in Sample 1.

Both samples of erionite have very close cell dimensions.

Chemical Composition

Electron microprobe analyses of Si, Al, Ca, Na, K were carried out using an ARL instrument with a take-off angle of 55 1/2°. The instrument was operated at

Table 1. Unit cell dimensions (Å) of levynes and erionites. Error in brackets

	Levynes			Erionites	
	No. 1	No. 2	No. 3	No. 2	No. 3
a	13.376 (4)	13.337 (7)	13.338 (4)	13.34 (2)	13.32 (2)
c	22.728 (5)	22.953 (8)	23.014 (9)	15.16 (1)	15.15 (2)

Table 2. Chemical analyses, atomic ratios and densities of levynes and erionite

	Levynes			Erionite
	No. 1	No. 2	No. 3	No. 2
SiO_2	47.80	49.76	47.33	54.21
Al_2O_3	20.75	19.09	21.66	15.68
CaO	9.33	8.88	10.30	5.45
Na_2O	1.74	1.71	1.36	0.86
K_2O	0.19	1.05	0.65	4.27
H_2O	20.37	19.51	20.22	19.53
Sum	100.18	100.00	101.52	100.00
Si	11.94	12.35	11.69	8.94
Al	6.11	5.58	6.31	3.05
Ca	2.50	2.36	2.73	0.96
Na	0.84	0.82	0.65	0.28
K	0.06	0.33	0.20	0.90
O	36.00	36.00	36.00	24.00
H_2O	16.98	16.14	16.66	10.74
$D_{meas.}$	2.11 ± 0.01		2.13 ± 0.02	

10 kV, 0.1 μA beam current and approximately 10 μ spot size in order to avoid damage to or disintegration of the sample. These conditions were selected after testing various settings of the instrument for loss of Na using one zeolite grain mounted for this purpose. Ten readings for each sample were taken for a counting time of 10 secs each. An_{50} synthetic plagioclase glass was used as a standard for Si, Al, Ca, Na; Kokomo sanidine for K. Corrections were applied following the "Bence-Albee" method (Bence and Albee, 1968; Albee and Ray, 1970), by the computer program EMPADR VII written by Rucklidge and Gasparrini (1969) and subsequently modified by Steele (1973). Water loss was determined on levyne Samples 1 and 3 by means of TG analyses using a thermal analyser manufactured by B.D.L. (Bureau de Laison, Paris).

The results of the chemical analyses and the atomic proportions are reported in Table 2. In the same Table are reported the density values for levyne Samples 1 and 3 measured with a torsion microbalance by immersion in toluene according to Berman (1939).

Optical Properties

As already mentioned in the introduction, the only optical study carried out was the determination of refractive indices of levyne. The results obtained by the double variation method are reported in Table 3. For Sample 1, a mean index was the only measurement possible, owing to the very low birefringence of the mineral. The values obtained for Sample 3 are not very reliable since the crystals were contaminated by erionite.

Table 3. Refractive indices of levynes. Error in brackets

	No. 1	No. 2	No. 3
ω	$N_{\text{medium}} = 1.4981$ (5)	1.4889 (5)	1.5102 (5)
ε	Very low birefringence	1.4870 (5)	1.5018 (5)

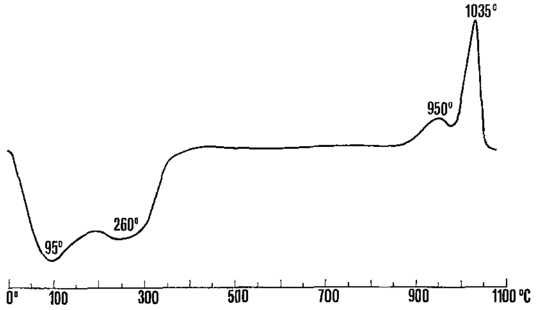

Fig. 4. DTA curve of levyne (sample No. 1). Rate of heating: 5° C/min

DTA

Since no DT curve has ever been reported for levyne we thought it worth performing this analysis on levyne Sample 1. The DT curve is reported in Fig. 4. The curve is characterized by an initial very broad endothermic band with two maxima at 95° C and 260° C. The exothermic reactions occur at 950° C and 1 035° C, the first being asymmetric and not very sharp, while the second is symmetrical and sharp. The shape of this curve indicates that water loss occurs over a wide range of temperature; this was confirmed by TG study.

Conclusions

The data on levynes reported here enrich our knowledge of this zeolite. As a matter of fact, only in a few cases is a complete set of data (chemical analysis, unit cell dimension, density, refractive indices) available for the levynes listed in the introduction. The samples from Sardinia are similar both in cation content ($Ca > Na > K$) and in $Si/(Si + Al)$ ratio to all other levynes, except for that from Chojabaru, Japan (Shimazu and Mizota, 1972), which has $Na > K > Ca$. As for the lattice parameters, *a* is fairly constant, while *c* is rather variable, although no correlation between *c* and any chemical variable has yet been detected.

The chemical composition and lattice constants of the erionites here described are fairly close to the values listed for this zeolite by Sheppard and Gude (1969).

We think it is proper, at this point, to emphasize the existence of the levyne-erionite intergrowth, for, although it seems to be very common, it has previously been described only once (Shimazu and Mizota, 1972).

Walker (1951 and 1959) describes levynes from Antrim as nearly always having thin lamellae (0001); half of the observed crystals exhibit an "alteration to a fibrous mineral with satiny lustre, the fibres lying normal to (0001) of the levyne".

Cross and Hillebrand (1885) recorded a fibrous mineral from Golden, Colorado, closely associated with levyne. Their analysis of the fibrous mineral proved to be almost identical with that of levyne from the same locality. They concluded: "it cannot be referred to any definite species from present data".

Chatterjee (1971) describes levyne from Bhopal, Deccan, as tabular crystals, often in sheaf-like aggregates; he states: "like the latter" (Iceland's levyne) "the mineral is often accompanied by an altered fibrous material".

We are convinced that in all three preceding cases the material described was actually an levyne-erionite intergrowth due to epitaxy. We think that in such intergrowths both zeolites have a similar genesis, and that the erionite is not an alteration product of the levyne.

It should be noted that the intergrowth levyne-erionite always occurs as lamellae, and this is also true of the Sardinian samples; our sample of levyne without erionite does not exhibit lamellae. In our opinion this is a general truth, i.e. lamellar levyne is always intergrown with erionite. Therefore, we invite every mineralogist faced with a levyne sample to pay attention to the possible existence of an intergrowth with erionite, especially if the crystals are lamellar.

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