

# Cesanite, $\text{Ca}_2\text{Na}_3[(\text{OH})(\text{SO}_4)_3]$ , a sulphate isotypic to apatite, from the Cesano geothermal field (Latium, Italy)

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**ABSTRACT.** Cesanite occurs both as a solid vein (1 cm thick) and as a cavity-filling of an explosive breccia in core samples of the Cesano 1 geothermal well (Cesano area, Latium, Italy).

Cesanite is colourless, medium to coarse grained, soft ( $H = 2$  to  $3$ ) and light ( $\rho_{\text{meas}} 2.786 \pm 0.002 \text{ g cm}^{-3}$ ). It is uniaxial negative,  $\epsilon = 1.564$ ,  $\omega = 1.570$ , with space group  $P6_3/m$  and cell parameters  $a = 9.442$  (4),  $c = 6.903$  (3) Å, for  $c/a = 0.730$ . Identifying spacings are 8.161, 2.822, 2.727, 1.844 Å, in X-ray powder patterns strikingly similar to those of apatite. The chemical formula (microprobe analyses on two grains) is  $\text{Ca}_{1.53}\text{Sr}_{0.03}\text{Na}_{3.42}\text{K}_{0.02}[(\text{Cl}_{0.06}\text{F}_{0.06}\text{OH}_{0.44})(\text{S}_{2.99}\text{O}_{12})] \cdot 0.44\text{H}_2\text{O}$ , while the theoretical formula, derived from considerations on structural identity with apatite, is  $\text{Ca}_2\text{Na}_3[(\text{OH})(\text{SO}_4)_3]$ . Cesanite is the end member of the apatite-wilkeite-ellestadite series where  $[\text{PO}_4]^{3-}$  is entirely substituted by  $[\text{SO}_4]^{2-}$ , the charge balance being made up by  $\text{Na}^+$  substituting for  $\text{Ca}^{2+}$ .

THE Cesano geothermal field is located east of Lake Bracciano, north of Rome (Latium, Italy), where volcanic and pyroclastic rocks related to the Pleistocene activity of the Sabatini volcanic system occur. The field is currently being drilled by ENEL, the Italian National Electricity Board, because of its rather high heat-flow anomaly combined with a structural high of the carbonatic basement under a cover of mainly pyroclastic material (Baldi *et al.*, 1976a,b; Funicello *et al.*, 1976, 1979). So far, exploitation has proved to be difficult because of the technical problems related to the highly concentrated brines (Calamai *et al.*, 1975).

Common occurrences are gypsum and anhydrite, although unusual minerals like glaserite  $\text{K}_3\text{Na}[\text{SO}_4]_2$ , görgeyite  $\text{K}_2\text{Ca}_5[\text{SO}_4]_6 \cdot \text{H}_2\text{O}$  (Funicello *et al.*, 1979), kalistrontite  $\text{K}_2\text{Sr}[\text{SO}_4]_2$  (Maras, 1979), and glauberite  $\text{Na}_2\text{Ca}[\text{SO}_4]_2$ , have also been detected in core samples.

Another unusual mineral, initially misidentified as a phosphate on the basis of X-ray powder diffraction analyses, has been repeatedly detected in several cores. Eventually, a solid vein (1 cm thick) in a core sample at 1252.10-1254.10 m below surface in the Cesano 1 well was found. Although the X-ray powder pattern was very similar to that of apatite, the mineral was eventually recognized to be a sulphate on the basis of a SEM-EDS analysis. Detailed studies showed it to be a new species, with a crystal structure isotypic with that of apatite (V. Tazzoli, private communication).

Apatite-like sulphates are not new in the mineralogical record. Caracolite  $\text{Na}_3\text{Pb}_2[\text{Cl}(\text{SO}_4)_3]$ , described by Websky in 1886, was recognized to be isotypic with apatite by Fletcher as early as 1889 (see Schneider, 1967, 1969). Apatite itself shows wide substitutions of the  $[\text{PO}_4]^{3-}$  group by equal amounts of  $[\text{SiO}_4]^{4-}$  and  $[\text{SO}_4]^{2-}$  leading to ellestadite  $\text{Ca}_5[(\text{F},\text{Cl},\text{OH})(\text{SiO}_4,\text{SO}_4)_3]$  (McConnell, 1937), and hydroxylellestadite (Harada *et al.*, 1971), through to the intermediate variety wilkeite  $\text{Ca}_5[(\text{F},\text{O},\text{Cl},\text{OH})(\text{SO}_4,\text{SiO}_4,\text{PO}_4)_3]$  (Eakle and Rogers, 1914).

However, this is the first report of a Ca-Na-sulphate, the fluorine-bearing synthetic equivalent of which has been known for a long time (Klement, 1939; Dihn and Klement, 1942). A reported natural occurrence of similar material, named sulphate-apatite (Vasilieva *et al.*, 1958) lacks comprehensive analytical data.

The new mineral has been named cesanite after the locality of occurrence. The description of the species and proposed name have been approved by the Commission on New Minerals and Mineral Names of the IMA. Type material is deposited in the Museum of Mineralogy of the University of Rome (specimen no. 24316/1). Material from the same vein has been also presented to the Naturhistorisches Museum Wien (Austria) and to the City Museum of Natural History, Milan (Italy).

*Occurrence.* Cesano 1 geothermal well is located 2.3 km north of the village of Cesano, right on the edge of the Baccano caldera. We here defer from a detailed discussion of the structural geology, volcanology, stratigraphy, as well as the mineralogy of the Cesano wells since they have been reported elsewhere (Baldi *et al.*, 1976a, b; Funicello *et al.*, 1976, 1979). It is just stressed that the Cesano 1 well was drilled to a depth of 1430 m. A volcanic sequence (mainly phreatomagmatic pyroclastics with few interbedded lava flows) extends to 1070 m, and is followed by a flyschoid allochthonous complex (shales, marls, sandstones, and limestones: Middle-Cretaceous to Miocene) down to 1390 m. Marls and marly limestones with cherts and flints, supposed to be the upper part of the Tuscan Nappe, the so-called 'Carbonatic Basement' conclude the drilled sequence.

Hydrothermal minerals have been found in all the horizons: the most frequent are sulphates and calcite; occasionally ankerite, dolomite, K-feldspar, magnesian calcite, sulphides, and zeolites could be detected.

The vein, which yielded cesanite, görgeyite, and pyrite, occurs within the marls of the allochthonous complex and it is clearly related to the self-sealing process of the fractures. Such a vein is at about 45° from the vertical defined by the walls of the core; the stabilized temperature value at this depth is 190°C.

The vein is white, with sugary texture and grain size ranging from 0.2 to 1.5 mm. Individual crystals, mostly subhedral and loosely packed, can be easily removed. In general they do not show preferred orientation but, rather, a kind of decussate texture with rational grain boundaries. Occasionally small vugs can be seen, where individual crystals show development of the upper terminal faces. Some vugs are coated by a thin crust of brownish-grey fine-grained gypsum. Close to the walls of the vein,

cesanite crystals are smaller, and are intergrown with görgeyite.

*Physical properties.* Cesanite is white massive but colourless in individual grains. Crystals are transparent to translucent, mostly subhedral, short prismatic, hexagonal shaped, usually with no terminal faces and an elongation to diameter ratio between 2:1 and 4:1. They show a pronounced cleavage normal to the elongation and striations on the prism faces. Single crystals show greasy lustre, while agglomerates occasionally appear quite silky. Careful and gentle pressure to separate individual grains enabled a few euhedral crystals to be isolated. The prisms  $\{10\bar{1}0\}$  display a slight flattening according to two parallel faces, and, correspondingly, an upper pyramid  $\{10\bar{1}1\}$  with two faces better developed than the others. They are truncated by a pinacoid  $\{0001\}$  or by another unevenly developed pyramid  $\{10\bar{1}1\}$ , simulating a sphenoidal end. Occasionally twins according to  $\{10\bar{1}0\}$  were also detected.

Hardness was measured by scratching the crystals (Mohs' scale: 2-3). Density, measured by floating two small crystals in a mixture of acetone and methylene iodide, is  $2.786 \pm 0.002 \text{ g cm}^{-3}$ . A similar measurement, carried out using diluted Clerici solution, gave densities ranging between 2.96 and  $3.02 \text{ g cm}^{-3}$ , thus suggesting that some reaction could occur (i.e. adsorption of TI).

The solubility of cesanite in water is low, although etch-pits develop after prolonged contact with distilled water. With HCl and H<sub>2</sub>SO<sub>4</sub>, both cold and hot, the grains show rounded edges; however, on the whole, they remain clear. On the contrary, reactions with hot HNO<sub>3</sub> not only produce corroded edges, but also a superficial film of white powdery material. Cesanite crystals are entirely dissolved in aqua regia after a short time.

In thin section cesanite is colourless, non-pleochroic, moderately birefringent, uniaxial with negative elongation and optic sign. Refractive indices, measured in white light using the method of the colour fringes of the Becke line on crystals oriented on the universal stage, are  $\omega = 1.570(2)$  and  $\varepsilon = 1.564(2)$ .

*X-ray data.* Powder diffraction data of cesanite are listed in Table I. They have been obtained by low speed diffractometry (1/4°/min) both on pure and Si-added smear mounts. The intensities reported in Table I were directly measured on diffractometer traces and may reflect orientation effects due to the well-developed cleavage.

The X-ray pattern is very similar to those of apatite and wilkeite; consequently it was indexed by comparison with the indices reported in ASTM cards (nos. 9-432, 6-454) for these two minerals. Initial unit-cell parameters were then calculated

TABLE I. X-ray powder diffraction data of cesanite

hkli	$d_{\text{obs}}, \text{\AA}$	$I_e/I_0$	hkli	$d_{\text{obs}}, \text{\AA}$	$I_e/I_0$
10 $\bar{1}$ 0*	8.161	8	31 $\bar{4}$ 2*	1.895	14
10 $\bar{1}$ 1*	5.263	5	32 $\bar{5}$ 0*	1.877	4
11 $\bar{2}$ 0*	4.720	46	21 $\bar{3}$ 3*	1.844	71
11 $\bar{2}$ 1*	3.896	66	32 $\bar{5}$ 1*	1.811	21
0002*	3.448	87	41 $\bar{5}$ 0*	1.785	13
10 $\bar{1}$ 2*	3.167	13	40 $\bar{4}$ 2	1.759	12
21 $\bar{3}$ 0*	3.092	20	30 $\bar{3}$ 3		
21 $\bar{3}$ 1*	2.822	60	0004	1.724	20
11 $\bar{2}$ 2*	2.784	25	41 $\bar{5}$ 1		
30 $\bar{3}$ 0*	2.727	100	32 $\bar{5}$ 2	1.648	12
20 $\bar{2}$ 2*	2.636	49	22 $\bar{4}$ 3		
30 $\bar{3}$ 1*	2.535	14	31 $\bar{4}$ 3*	1.615	9
21 $\bar{3}$ 2*	2.302	10	42 $\bar{6}$ 0*	1.547	11
31 $\bar{4}$ 0*	2.269	47	21 $\bar{3}$ 4*	1.509	7
22 $\bar{4}$ 1*	2.234	4	42 $\bar{6}$ 1*	1.506	7
31 $\bar{4}$ 1*	2.155	12b	50 $\bar{5}$ 2*	1.478	11
30 $\bar{3}$ 2*	2.134	5b	51 $\bar{6}$ 0	1.457	14
11 $\bar{2}$ 3	2.069	6	51 $\bar{6}$ 1	1.454	18
20 $\bar{2}$ 3*	2.004	10	41 $\bar{5}$ 3	1.437	11
22 $\bar{4}$ 2*	1.948	32			

Experimental conditions: Cu/Ni, 50 kV, 30 mA, Si internal standard  $1/4$   $2\theta$   $\text{min}^{-1}$ . Indexing on the basis of the hexagonal cell  $a = 9.442(4)$ ,  $c = 6.903(3)$ . The reflections marked with asterisk are those used for refinement.

using twelve accurately identified reflections. These preliminary cell data were then used as starting parameters for the computation of the final cell (Table I) as well as of the indices of all the observed reflections with the self-indexing least-squares program of Appleman and Evans (1972). The extinction conditions of the  $P6_3/m$  space group, typical of apatite, were used during this calculation.

The final cell parameters computed from the powder pattern compare well with those directly measured on single-crystals (personal communication of V. Tazzoli).

**Crystal chemistry.** Electron microprobe analyses were performed with a Cambridge Geoscan instrument. Running conditions were: 15 kV gun potential,  $1 \times 10^{-8}$  A specimen current,  $\sim 80 \mu\text{m}$  probe diameter, 20 sec counting time. The reference standards were synthetic anorthite (for Ca) and natural analysed orthoclase (for K), jadeite (for Na), and celestine (for Sr and S). This sulphate was chosen as standard because the S-K $\alpha$  peak shifts considerably as a function of the sulphur coordination state (Chapell and White, 1968; Lovering and Widdowson, 1968). No evidence of other elements (Si, P, Mg, Fe, and As) was found within the sensitivity of WD microprobe. Raw data were corrected for dead time, background, linear instrumental drift, and ZAF effects using the un-

published program ELEXA, coded by one of the authors (G.C.) for the UNIVAC 1100/20 computer.

Under the electron beam, even when this is strongly defocused as in the present case, cesanite readily decomposes making repeated spot analyses very difficult. Although a slight zonation (core to rim: CaO + 0.55%, Na<sub>2</sub>O - 0.31%) was detected, the large spot size did not allow a careful investigation; thus only average values are represented here.

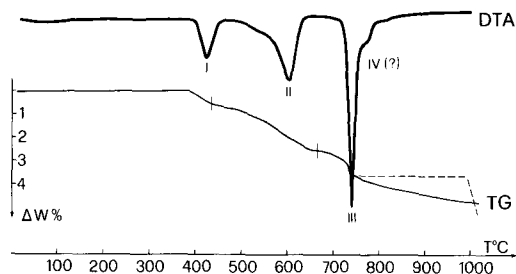


FIG. 1. DT and TG traces for cesanite. Note: the dotted TG line was obtained by rapid heating.

A separate analytical problem concerns the volatile content. Apatite-group minerals may contain O, OH, F, Cl anions in the A site (assuming the general formula  $X_5[Al(ZO_4)_3]$ ), whereas in the Z site other volatile elements (particularly C) can be present. The total volatile loss of cesanite, determined by low-speed TGA followed by a continuous heating at 1000°C for 60 min., is 4.75%. However this loss occurs stepwise (fig. 1): the DTA curve exhibits three major endothermic peaks at 425°, 605° and 740°C, plus a shoulder at about 760–70°C. While the first two effects involve well-defined losses (about 0.5% and 2.0% respectively) the third one reaches a maximum at 740°C, to continue slowly up to 1000°C (the final temperature of the experiment). The volatile loss involved at 740°C is 1.1%, bringing the total loss up to 3.6%. The interpretation of the TGA curve is not straightforward. Adding the total of the microprobe analysis to the final loss (4.75%) or to the loss at 740°C (3.6%) gives an analytical sum within the limits of the microprobe analyses (100.27 and 99.12 respectively). It is likely that the final TGA heat-loss may reflect volatilization of sodium; moreover we are aware that at 740°C and 760°C two phase changes take place as discussed elsewhere (D. Andretta and S. Deganello, personal communication).

The IR spectrum of cesanite is shown in fig. 2. Most of the absorption bands can be referred to modes involving  $[\text{SO}_4]^{2-}$  ions. However the broad band at  $3440 \text{ cm}^{-1}$  is due to adsorbed water, and

TABLE II. *Cesanite microprobe analysis, representing the mean of three determinations. Cl and F by colorimetry*

	% oxide	$\epsilon$	Formula	
			8 metals	S = 3
CaO	18.9	0.25	1.54	1.54
SrO	0.72	0.08	0.03	0.03
Na <sub>2</sub> O	23.3	0.31	3.42	3.43
K <sub>2</sub> O	0.21	0.03	0.02	0.02
SO <sub>3</sub>	52.6	0.74	2.99	3.00
Cl	0.44	—	0.06	0.06
F	0.25	—	0.06	0.06
H <sub>2</sub> O	2.91	0.20	1.47	1.48
	99.33		9.59	9.62
O $\equiv$ Cl, F	-0.21			
	99.12			

$\epsilon$  = maximum error for the 95% confidence level.

the smooth band at 1615 to water bonding vibrations. The 3570 cm<sup>-1</sup> band, typical of structural OH, is very faint and interfered with by the H<sub>2</sub>O band. Other data on the volatiles present in the cesanite were obtained by colorimetry (Cl, F) or optical spectrography (B < 10 ppm) on single samples. There is no CO<sub>2</sub> present in the structure.

The comprehensive chemical analysis is given in Table II.

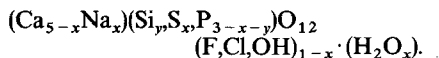
**Discussion.** The apatite-group minerals are often (e.g. Ramdohr and Strunz, 1978) described according to the general formula  $X_5[A](ZO_4)_3$  where X = Ca, Pb, Sr (and minor amounts of REE, Ba, K, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Mg, Th); A = F, Cl, OH,  $\frac{1}{2}$ O; Z = P, As, V, S, Si, C, Cr. The formulae are computed on the basis of 13 (or 26) anions.

In the case of cesanite, such a procedure is not

possible, since the volatile (anion) content constrains the accuracy of the analysis. Therefore two alternative ways of computing the formula may be used.

On a cation basis of 8 (or 16) following the analyses obtained by electron microprobe techniques (Neumann, 1976; Stern, 1979); or on the basis of S = 3 (i.e. assuming no substitution of [CO<sub>3</sub>]<sup>2-</sup> for [SO<sub>4</sub>]<sup>2-</sup>, as suggested by chemical evidence).

As far as the major elements are concerned, both procedures, when applied to cesanite, lead to almost identical results, and to anionic contents in good agreement with the amount required to balance the formula. Given the presence of (Na + K) substituting for (Ca + Sr) in excess of 3, i.e. the amount required to balance the complete substitution of S<sup>6+</sup> for P<sup>5+</sup>, some H<sub>2</sub>O is needed to substitute for (OH + Cl + F) in order to fully balance the formula. Thus, in order to account for the newly found cesanite, the general formula for the natural apatite-group of minerals, suggested by Harada *et al.*, 1971, as Ca<sub>5</sub>(Si,S,P)<sub>3</sub>O<sub>12</sub>(Cl,F,OH) should be expanded to



This general formula will account not only for the existence of wilkeite, ellestadite and hydroxylellestadite (here the balanced substitution Si<sup>4+</sup>S<sup>6+</sup> for P<sup>5+</sup>P<sup>5+</sup> does not affect the Ca occupancy), but also for the present coupled substitution Na<sup>+</sup>S<sup>6+</sup> for Ca<sup>2+</sup>P<sup>5+</sup>, which involves changes in the X group. It is therefore suggested to restrict the name 'sulphate-apatite' only to those minerals in the apatite group containing substantial sulphate where the main X cation is predominantly Ca (or another divalent cation), and to use the new name 'cesanite group' for those sulphates, isostructural with apatite, where the monovalent cation (mostly Na) plays a dominant role in the X position.

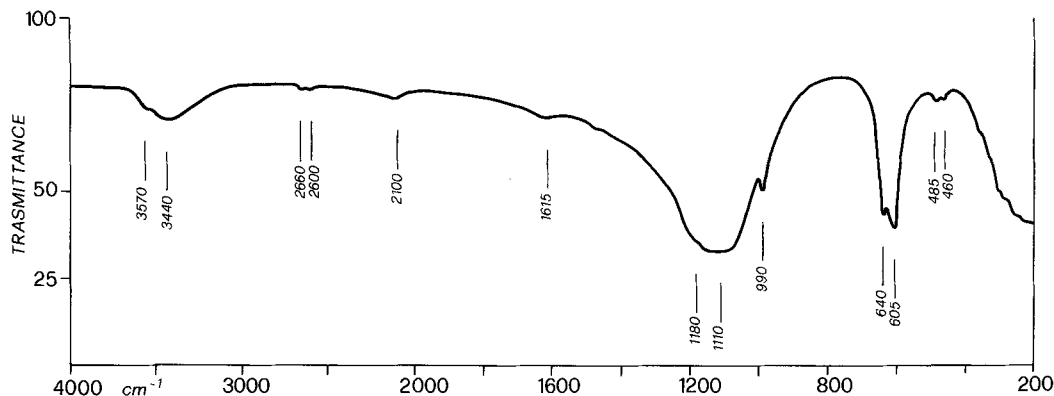


FIG. 2. IR spectrum of cesanite.

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## REFERENCES

- Appleman, D. F. and Evans, H. T. (1972). Nat. Techn. Inf. Serv. U.S. Dep. Commerce, Springfield, Virginia, PB-216, 188.
- Baldi, P., Civitelli, G., Fucicciello, R., Lombardi, G., Parotto, M., and Serva, L. (1976a). *Intern. Congr. on Thermal Waters, Geothermal Energy and Volcanism of the Mediterranean Area*, Athens, Proc. Geoth. Energy, **1**, 71-86.
- Fucicciello, R., Locardi, E., and Parotto, M. (1976b). *Ibid.* **1**, 43-55.
- Calamai, A., Cataldi, R., Dall'Aglio, M., and Ferrara, G. C. (1975). *UN Symp. on Geothermal Energy*, S. Francisco, Cal., USA **1**, 305-13.
- Chapell, B. W. and White, A. J. R. (1968). *Am. Mineral.* **53**, 1735-8.
- Dihn, P. and Klement, R. (1942). *Z. Elektrochem.* **48**, 331-3.
- Eakle, A. S. and Rogers, A. F. (1914). *Am. J. Sci.* **37**, 262-7.
- Fletcher, L. (1889). *Mineral. Mag.* **8**, 172.
- Fucicciello, R., Locardi, E., and Parotto, M. (1976). *Boll. Soc. Geol. It.* **95**, 831-49.
- Mariotti, G., Parotto, M., Preite-Martinez, M., Tecce, F., Toneatti, R., and Turi, B. (1979). *Geothermics*, **8**, 55-73.
- Harada, K., Nagashima, N., Nakao, K., and Kato, A. (1971). *Am. Mineral.* **56**, 1507-18.
- Klement, R. (1939). *Die Naturwiss.* **27**, 568.
- Lovering, J. F. and Widdowson, J. R. (1968). *Lithos*, **1**, 264-7.
- McConnell, D. (1937). *Am. Mineral.* **22**, 977-86.
- Maras, A. (1979). *Per. Mineral.* **48**, 195-203.
- Neumann, E. R. (1976). *Norsk Geol. Tidsskr.* **56**, 1-6.
- Ramdohr, P. and Strunz, H. (1978). *Klockmanns Lehrbuch der Mineralogie* 16th edn., F. Enke Verlag, Stuttgart.
- Schneider, W. (1967). *Neues Jahrb. Mineral., Monatsh.* **284-9**.
- (1969). *Ibid.* 58-64.
- Stern, W. B. (1979). *Schweiz. Mineral. Petrogr. Mitt.* **59**, 75-82.
- Vasilieva, Z. V., Litzarev, M. A., and Organova, N. I. (1958). *Dokl. Akad. Nauk SSR*, **118**, 577-80. (In Russian.)
- Websky, M. (1886). *Sitzg-Ber. Berlin. Akad. Wiss.* 1045.

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