

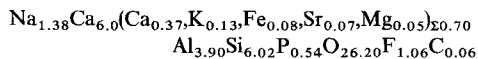
Fluorine in sarcolite: additional history and new chemical data

A. LIVINGSTONE

Department of Geology, Royal Scottish Museum, Chambers Street, Edinburgh, Scotland

ABSTRACT. The historical background leading to the discovery of sarcolite by Thomson is reviewed. Many mineralogical reference works quote *Thompson* (1807) but no paper on sarcolite by *Thomson* has been found; also the spelling of Thomson is incorrect on numerous occasions. The history of sarcolite from its original discovery is reviewed. Chemically, sarcolite is inadequately characterized in spite of a structural study by Giuseppetti *et al.* (1977). All known chemical analyses are collated and discussed. Two new analyses, using a combination of gravimetric, colorimetric, atomic absorption, and electron probe methods, are presented which show sarcolite to contain 2 wt. % fluorine. The presence of this element in sarcolite was reported in 1860 but no quantitative data given; the new determinations cast some doubt over certain aspects of the sarcolite structure.

Measured densities of sarcolite range from 2.93 to 2.96 (mean 2.95) gm/cm³; the tetragonal unit cell of *a* 12.32 and *c* 15.48 Å leads to a calculated density of 2.925 gm/cm³ using the empirical formula. Empirically sarcolite may be expressed as:



and ideally



and suggests 27 (oxygen and fluorine) atoms in the quarter unit cell.

Details are given of the mineralogical assemblage, optical properties, infra-red and thermal behaviour of sarcolite which, after 176 years, is still known from only one locality—Monte Somma.

MANY mineralogical reference works refer to the discoverer of sarcolite as *Thompson*, 1807; however, there are two incorrect aspects associated with this statement. First, evidence exists which unequivocally indicates the spelling should be *Thomson*. Secondly, it is believed Thomson died in 1806 (Waterston, 1965). In addition, no paper by Thomson (or Thompson) in 1807 has been found and nobody has quoted an actual publication in 1807. With regard to the spelling there is compelling evidence to show that *Thomson* is correct, for within the Edinburgh University Library is lodged a

collection of William Thomson's books, and many are inscribed with his signature. Also, an attested copy of his will is likewise lodged in Edinburgh and again the copy of his signature leaves no doubt that the correct spelling is without *p*. The original description of sarcolite is attributed to Vauquelin (1807) who actually used the name *Tompson* (no *h*) whereas Haüy (1809) refers correctly to 'M. Thomson à qui la découverte en est due, leur a donné le nom de sarcolithe'. It is quite clear from the paper by Vauquelin that his material, which came from Montecchio Maggiore, Northern Italy, was not Thomson's sarcolite but gmelinite found in lavas by M. Faujas-Saint-Fond.

Dana (1837, 1844, 1850, and 1854) all spell *Thomson* correctly whereas the fifth edition (1868) contains the error *Thompson*, which is perpetuated to modern times in numerous mineralogical reference works. (The Vauquelin variant does not seem to have been repeated.) Dana's (1868) erroneous emendation would appear to stem from Faujas-Saint-Fond (1808) who assumed the Montecchio Maggiore mineral was the same as Thomson's. He wrote to Naples for Vesuvian material, for he knew in 1808 that Thomson was dead. He noted that the 'Montecchio-Maggiore' (one *c*) material received from the Dolomieu collection resembled 'beaucoup à celle que Thompson avoit reconnue auparavant dans une ancienne lave du Vésuve, et à laquelle il avoit donné, à cause de sa couleur d'un rouge pâle, le nom impropre de sarcolite.'

Dana (1837) has sarcolite as a variety of analcime 'separated by the late Dr Thomson, of Naples, as a distinct species, under the name of Sarcolite. This, however, is unwarranted until analysis shall manifest a dissimilar composition. Their crystalline forms are not inconsistent with the idea of their identity.' Clearly, Thomson considered sarcolite to be a separate species whereas Dana (1837) also details, correctly, Vauquelin's sarcolite under gmelinite. In the 1844 edition, under analcime, is added, 'The cubo-octahedral variety, or sarcolite,

occurs among the ancient lavas of Vesuvius, associated with Wollastonite, hornblende. . . . The sarcolite of Vauquelin is now mentioned under chabazite, and also as a synonym of humboldtilite (Sarcolite, Bondi, no reference). This union with humboldtilite was due to Breithaupt (1841) whereas DesCloizeaux (no reference, Dana, 1850) doubts the identity with this phase. The first analysis of sarcolite (see Table I, and anal. 1) from Vesuvius is given by Scacchi (1842) although Dana (1850) still persists in grouping sarcolite under analcime and humboldtilite. Four years later (Dana, 1854) sarcolite attains independent species status and is no longer included as a variety of analcime or gmelinite.

Haüy (1822) pronounced sarcolite to be cubic for in 1809 he examined some of Thomson's sarcolite and noted 'Il est du moins certain que les faces

principales font entre elles des angles droits . . . j'ai présumé qu'ils étaient une variété de l'analcime.' This may well have given rise to some confusion in the early literature for red analcime (and red gmelinite) have been referred to as sarcolite. Brooke (1831) showed the mineral to be tetragonal and hemihedral. His crystal drawing is reproduced in fig. 1 and was based on a specimen given by Mr Heuland, and a crystal fragment donated by Dr Donati. Sarcolite morphology is discussed in detail by Zambonini (1910) who also lists additional references to the mineral.

The hemihedral nature was confirmed by Giuseppetti *et al.* (1977) in their crystal structure studies of sarcolite, though Brooke's work was not referred to. Giuseppetti *et al.* (1977) in their references refer to *G. Thompson* (1818) whereas the text

TABLE I. *Chemical composition of sarcolite*

	1	2†	3	4	5	6	7	8	9	10
SiO ₂	42.11	40.51	39.34	36.05	40.27	36.5	38.26	36.7	34.70	34.4
Al ₂ O ₃	24.50	22.15	21.63	22.20	23.81	17.8	19.42	19.9	19.07	18.4
Fe ₂ O ₃	—	—	—	—	0.29	—	1.06	—	—	—
FeO	—	—	—	—	—	0.31	—	—	0.58	0.6
MgO	—	—	0.36	tr	0.28	0.26	—	—	0.20	0.3
CaO	32.43	32.36	33.70	35.03	32.34	32.35	32.36	32.9	34.25	32.7
SrO	—	—	—	—	0.08	—	—	—	0.74	0.8
BaO	—	—	—	—	0.23	—	—	—	n.d.	—
MnO	—	—	—	—	—	0.04	—	—	0.03	0.05
Na ₂ O	2.93	3.30	4.43	3.88	2.05	4.05	n.d.	5.1	4.10	4.4
K ₂ O	—	1.20	—	2.98	0.87	0.54	0.66	—	0.60	0.5
Li ₂ O	—	—	—	—	0.008	—	—	—	n.d.	—
SO ₃	—	—	—	—	n.d.	—	0.12	—	n.d.	—
CO ₂	—	—	—	—	0.30	—	—	2.0	0.29	—
P ₂ O ₅	—	—	—	—	—	—	1.52	1.7	3.69	2.9
Cl	—	—	—	—	0.04	—	0.02	0.1	0.01	0.04
H ₂ O ⁺	—	—	—	—	—	—	—	1.6‡	0.01	—
F	—	—	—	—	—	—	—	—	1.94	2.0
	'101.96'	99.52	99.46	100.14	100.57	91.85	93.42	100.0	100.26*	97.09
								Less O ≡ F	0.82	0.84
									99.44	96.25

n.d. = not determined; ‡ assumed to be H₂O⁺

1. Scacchi (1842); 2. Rammelsberg (1860); 3. Pauly (1906); 4 and 5. Zambonini and Caglioti (1931).

6. Electron probe microanalysis (analyst G. Kurat), quoted from Giuseppetti *et al.* (1977).

7. X-ray fluorescence analysis (analyst L. Leoni), quoted from Giuseppetti *et al.* (1977).

8. Calculated composition derived from the structure, quoted from Giuseppetti *et al.* (1977).

9. Clear, glassy sarcolite; H₂O⁺ and CO₂ determined using a Perkin Elmer 240 elemental analyser (analyst C. J. Elliott). *Includes 0.05% TiO₂.

10. Electron probe microanalysis (analyst P. Hill). Same material as for analysis No. 9.

† For this analysis SiO₂ is the average of three separate determinations, CaO of two determinations, Na₂O and K₂O only one determination each. Al₂O₃ was determined three times although the average value (21.54) is not quoted by Rammelsberg but by subsequent authors.

$P,a1 = 157^{\circ} 19'$
 $P,a2 = 128 \ 33$
 $P,d = 90$
 $P,c = 138 \ 25$
 $M,b1 = 153 \ 20$
 $M,a2 = 123 \ 34$
 $M,b2 = 102 \ 28$
 $M,e = 153 \ 26$
 $M,d = 135$

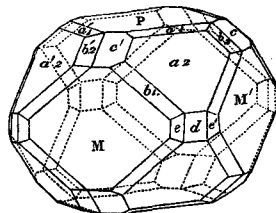


FIG. 1 Crystal drawing of sarcolite reproduced from Brooke (1831).

mentions Thompson (1807) as the discoverer. The 1818 publication is by Breislak, and Giuseppetti *et al.* quote volume iii. In this volume Breislak refers to 'La sarcolite ou l'analcime trapezoidale... a été encore reconnue par Thomson dans les laves erratiques du mont Somma, et dans celle de Cape di Bove' (material from the latter locality is probably a zeolite).

Considerable confusion arises, however, due to the introduction of G. Thomson (see above); some of William Thomson's books in the Edinburgh University Library are also inscribed *G. Thomson*. When W. Thomson left Britain (see below) he changed his name to Guglielmo. The two signatures are indisputably in the same handwriting and the identity of G. Thomson with W. Thomson was Gunther's (1939) main discovery. William Thomson's connections with Edinburgh stem from his medical studies at the university in the years 1780-2. He was elected a member of the Royal

Medical Society of Edinburgh in November 1781; by this time his interest in mineralogy had already nucleated. He later went to Oxford to continue his medical career and became a physician at the Radcliffe Infirmary. Thomson suddenly terminated his scientific career in Britain and eventually settled in Naples, and finally in Sicily (Waterston, 1965).

As an active mineralogist and geologist Thomson avidly studied the Naples volcanic environment and within the ejected blocks of Monte Somma discovered the mineral which he named sarcolite from the Greek *σαρξ* flesh, and *λιθος* stone, in allusion to the pink colour. The extensive Thomson collection arrived in Edinburgh from Palermo in 1808 after a hazardous sea journey during which the convoy was chased by two French frigates. A very small portion of the mineralogical collection survives and is housed in the Royal Scottish Museum. No documentary evidence exists to substantiate five sarcolite-bearing specimens in the collection as being those of William Thomson, although they probably originate from the Thomson collection. The whole, or a considerable portion of Thomson's volcanic minerals collection, reached Lady Hippisley in 1807 (Gunther, 1939) at Ston Easton, near Bath. A small part of the collection was rescued by Arthur Kingsbury and is now in the British Museum (Natural History) (Hey, pers., comm.), and includes the type specimen of sarcolite (BM 1960, 629).

Mineralogy. Thomson studied mineralogical transformations within ejected blocks of limestone, which ultimately led to the discovery of sarcolite.

TABLE II. Empirical formulae on the basis of 27(O,OH,F)

	1	2	3	4	5	6	7	8	9	10
Si	6.88	6.88	6.72	6.30	6.73	6.84	6.85	6.07	6.02	5.97
Al	4.72	4.42	4.36	4.56	4.68	3.93	4.10	3.88	3.90	3.76
Na	0.92	1.08	1.46	1.30	0.66	1.47	—	1.63	1.38	1.48
Ca	5.68	5.89	6.00	6.00	5.78	6.00	6.00	5.83	6.00	6.00
Ca	—	—	0.18	0.55	—	0.49	0.21	—	0.37	0.08
Ba	—	—	—	—	0.01	—	—	—	—	—
Sr	—	—	—	—	0.01	—	—	—	0.07	0.08
Fe ²⁺	—	—	—	—	—	0.05	—	—	0.08	0.08
Fe ³⁺	—	—	—	—	0.04	—	0.14	—	—	—
Mn	—	—	—	—	—	—	—	—	—	0.01
K	—	0.26	—	0.64	0.18	0.13	0.15	—	0.13	0.11
Mg	—	—	0.09	—	0.07	0.07	—	—	0.05	0.08
P	—	—	—	—	—	—	0.23	0.23	0.54	0.42
F	—	—	—	—	—	—	—	—	1.06	1.09
Cl	—	—	—	—	—	—	—	—	—	0.01
S	—	—	—	—	—	—	0.01	—	—	—
C	—	—	—	—	0.07	—	—	0.45	0.06	—
(OH) (?)	—	—	—	—	—	—	—	1.76	—	—

Sarcolite-bearing specimens in the Royal Scottish Museum certainly demonstrate strong affinities with contact metamorphosed limestones; diopside and a grossular-andradite garnet are common matrix minerals. *In toto* eleven minerals have been identified on these specimens by X-ray powder diffraction and optics: aegirine, calcite, diopside, garnet (as above), gehlenite, microsommite, nepheline, olivine (Fo_{84}), phlogopite, wollastonite, and sarcolite; the latter is optically positive and has refractive indices ω 1.600 and ϵ 1.615.

The five sarcolite-bearing specimens are medium size (up to 7 cm) with sarcolite occurring either as clear, glassy, flesh-pink irregular masses up to 2 cm long or as distinct crystals in cavities. In the latter case, the imperfect crystals range up to 2.5 cm and may, or may not, be glassy in appearance. Most crystals are very thinly coated with greyish gehlenite, which occurs either as a mosaic of minute, radiating prismatic crystals and characteristic square-shaped basal sections, or as a general featureless coating. Sarcolite does not show a particular affinity for any one mineral, or group of minerals.

Chemistry. Table I presents all the known chemical analyses of sarcolite, together with a new analysis (no. 9) determined by gravimetric, colorimetric, and atomic absorption methods and an electron probe analysis (no. 10). By far the most important aspect of these two new analyses is the presence of 2 wt. % fluorine. Rammelsberg (1860) first reported fluorine in sarcolite, 'Der S. scheint überdiets eine Spur Fluor zu enthalten', and Zambonini (1910) comments 'la sarcolite sembra contenere una traccia di fluoro: con gli acidi gelatinizza: al cannello fonde in uno smalto bianco.' The latter author discusses the chemistry of sarcolite on the basis of two analyses (Scacchi, 1842, and Rammelsberg, 1860) but does not present an analysis by Pauly (1906) although he mentions the reference. The presence of fluorine seems to have been overlooked by Giuseppetti *et al.* (1977) for it is mentioned by Zambonini (1935)—a paper they quote.

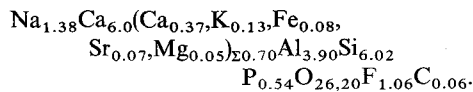
The tenor of fluorine raises some serious doubts concerning the validity of certain aspects of the sarcolite structure determined by Giuseppetti *et al.* This premiss is based on the summation of F, CO_2 , and H_2O^+ less $\text{O} \equiv \text{F}$ in the new analysis (1.42%) being similar to the weight loss determined by Giuseppetti *et al.* They noted that their weight loss of 2.2% was greater than the H_2O^+ (1.6%) derived from their structural formula but was also lower than combined H_2O^+ and CO_2 (3.6%) derived from sarcolite heated at 1100 °C for four days. Water was not determined by Giuseppetti *et al.* nor did they present any direct evidence for its existence in their analysed sarcolite, for infra-red showed

only the presence of CO_3^{2-} ions. It is conceivable that fluorine was not considered by them during their structural studies for they *assumed* water to be present from an ignition loss and decreased occupancy of O(8) which may well be fluorine and not oxygen, as their electron clouds are similar.

Two noteworthy features of the new analysis (no. 9) are strontium and phosphorus contents considerably higher than published values. Zambonini and Caglioti (1931) showed sarcolite to contain Ba, Sr, Li, CO_2 , and Cl; although Ba and Li were sought they were not found during the new analysis. Phosphorus is over twice the highest value previously reported and as will be shown later plays an important role, for PO_4^{3-} ions occupy cavities in the tetrahedral framework in a partially disordered way.

The analyses in Table I display considerable variation in sarcolite chemistry, only Ca shows consistency. Si/Al ratios exhibit marked changes throughout the analyses for as silica decreases alumina does not increase but likewise decreases. Available evidence suggests that deficiencies are made good by increases in total alkali and phosphorus contents. Examination of the empirical formulae (Table II) given for all the analyses in Table I indicates clearly some of the above trends.

The chemical analysis derived from the structure (no. 8) by Giuseppetti *et al.* yields 28 oxygens in the unit cell using the method of Hey (1939), whereas the recently analysed sarcolite suggests 27 (oxygen + fluorine) atoms in the empirical unit cell. This is based on tetragonal cell edges of $a = 12.32$ and $c = 15.480$ Å determined from X-rayed analysed material and a mean density of 2.95 gm/cm³. Sixteen grains (14–30 mg) yielded a range of 2.93–2.96, mean 2.95 gm/cm³, using a Berman balance. Suspension in bromoform–methylene iodide gave 2.94 gm/cm³. Giuseppetti *et al.* observed a density of 2.92 gm/cm³. Using the above cell parameters and empirical formula given below, the calculated density of the analysed material is 2.925 gm/cm³. On the basis of 27 (oxygen + fluorine) atoms the empirical unit-cell contents from analysis No. 9 are:



This leads to the ideal formula



or



The (Ca–Mg) grouping results from an atomic site designated *Me* by Giuseppetti *et al.* for the site characteristics are such that it is suitable for small

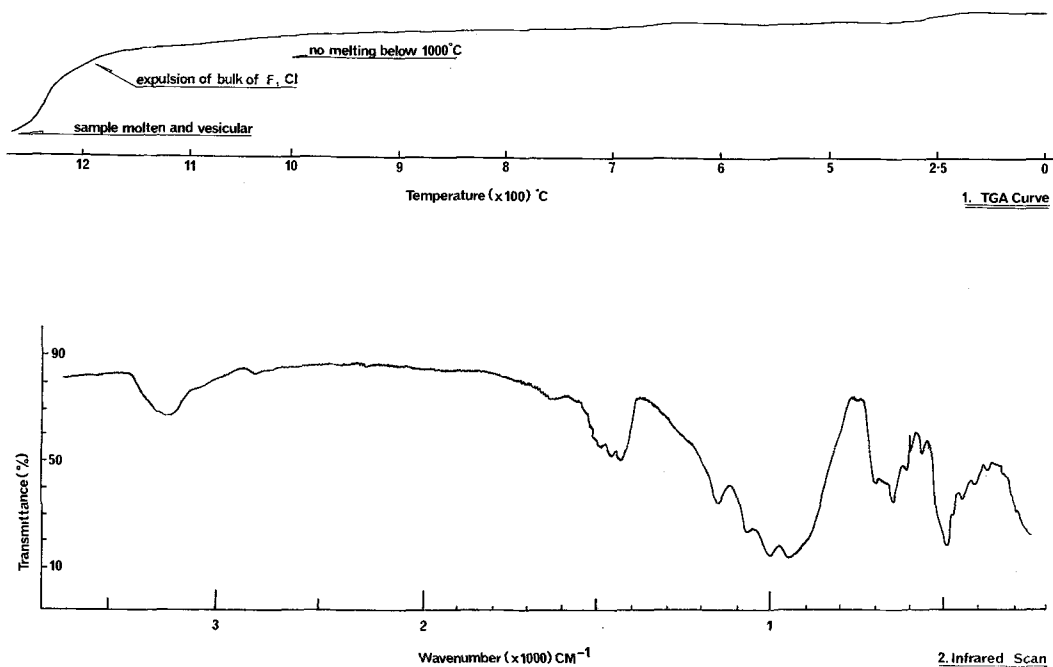


FIG. 2 Thermogravimetric analysis curve (1) and infra-red scan (2) of analysed sarcolite.

amounts of the heaviest atoms in sarcolite, and the formula demonstrates the site is approximately three-quarters filled. Another site identified by the authors forms large cavities in the tetrahedral framework into which $(\text{Si,P})\text{O}_4$ partially enters with some degree of disorder. The new analysis demonstrates that the site is fully occupied by P to the half-occupancy predicted. A major difference exists between the new chemical analysis and that derived from the structure. From the former it can be established that F completely fills the site at 1 atom per unit whereas the latter leads to the assumed presence of $(\text{OH}, \text{H}_2\text{O})$ and to be < 2 in the site.

Thermogravimetric and infra-red curves are presented in figures 2.1 and 2.2. The former curve was obtained on -100 mesh material using a Stanton-Redcroft TG 700 thermobalance, and a gas flow rate of 10 ml/min. This flow rate was thought desirable in order to prevent volatiles from condensing on the cooler parts of the sample crucible. A featureless curve is obtained up to about 1000°C , thereafter melting and release of chlorine, and especially fluorine, occurs. The latter element may have started slowly evolving at about 750°C but commenced rapid removal around 1100°C possibly after melting of the sample. The curve is totally devoid of features that could be attributed

to structural water, which is minimal. In this respect, and the fluorine content, the sarcolite would seem to differ from that of Giuseppetti *et al.*, although it is conceivable that their 'water' should be fluorine.

Infra-red spectra of scapolite, to which sarcolite is chemically but not structurally related, show some affinities to that of sarcolite. The absorptions between 1400 and 1500 cm^{-1} are assigned, very tentatively, to the CO_3^{2-} ions in sarcolite. Wehrenberg (1971) in his infra-red study of scapolite shows that a band about 1530 cm^{-1} decreased in wave number with increasing meionite content whereas the band at about 1420 cm^{-1} remains constant with change in composition. There is insufficient chemical data available for sarcolite to say whether the same phenomenon will be found for this mineral or whether a definite hydroxyl sarcolite has been previously analysed.

Acknowledgements. The author is indebted to Dr D. J. Morgan of the Institute of Geological Sciences for the thermal and infra-red analyses. Thanks are also due to Mr K. Smith and Mr P. Davidson of the Royal Scottish Museum for the preparation of figs. 1 and 2 respectively. The manuscript has benefited from reading and suggestions by Drs P. J. Dunn, J. A. Mandarino, and M. H. Hey.

REFERENCES

- Breislak, S. (1818) *Institutions Géologiques, Milan* **3**, 195.
- Breithaupt, A. (1841) *Annalen. Phys. Chem. Poggendorff*, **53**, 145.
- Brooke, H. J. (1831) *Phil. Mag.* **10**, 187.
- Dana, J. D. (1837) *A System of Mineralogy*, 1st edn., 279, 283, and 284.
- (1844) *Ibid.* 2nd edn., 337, 340, and 359.
- (1850) *Ibid.* 3rd edn., 311 and 343.
- (1854) *Ibid.* 4th edn., **2**, 200.
- (1868) *Ibid.* 5th edn., 317.
- Faujas-Saint-Fond (1808) *Annales Museum D'Histoire Naturelle, Paris*, **11**, 42-6.
- Giuseppetti, G., Mazzi, F., and Tadini, C. (1977) *Tschermaks Mineral. Petrog. Mitt.*, **24**, 1-21.
- Gunther, R. T. (1939) *Nature*, **143**, 667-8.
- Haüy, A. (1809) *Tableau Comparatif Des Résultats De La Cristallographie et de L'Analyse Chimique, Paris*, 199.
- (1822) *Traité de Minéralogie, Paris*, **3**, 173.
- Hey, M. H. (1939) *Mineral. Mag.* **25**, 402.
- Pauly, A. (1906) *Centralblatt für Mineral. Geol.* 266.
- Rammelsberg, C. F. (1860) *Annalen. Phys. Chem. Poggendorff*, **109**, 567.
- Scacchi, A. (1842) *Distrib. Sistem. Min. Naples*, 66.
- Vauquelin, L. N. (1807) *Annales Museum D'Histoire Naturelle, Paris* **9**, 241-50.
- Waterston, C. D. (1965) *Univ. Edinburgh J. Autumn*, 122-34.
- Wehrenberg, J. P. (1971) *Am. Mineral.* **56**, 1639-54.
- Zambonini, F. (1910) *Mineralogia Vesuviana*, **14**, ser. 2, no. 6, 247.
- (1935) *Ibid.* 2nd edn. Torino Rosenberg e Sellier, 215-20.
- and Caglioti, V. (1931) *Compt. Rend. Acad. Sci.* **192**, 967-70.

[Manuscript received 8 December 1982;
revised 7 June 1983]