

A natural ferrous substituted saléeite from Arcu su Linnarbu, Capoterra, Cagliari, Sardinia

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Abstract

Ferrous substituted saléeite is a new variety of saléeite from Arcu su Linnarbu, Sardinia. It is tetragonal with $a = 6.982(2)$ $c = 19.660(2)$ Å, $Z = 2$; the ideal formula is $(\text{Mg}, \text{Fe}^{2+})(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. The strongest lines in the X-ray powder diffraction pattern are: 3.473(100)(114), 4.95(50)(110), 4.91(40)(004), 4.443(40)(112), 2.200(30)(118), 2.193(30)(303) and 2.178(30)(009). The mineral is light-yellow in colour and is dull fluorescent. The measured density is 3.242 g/cm^3 and $Z = 2$. There is a prominent (001) cleavage. Refractive indices are: $\alpha = 1.572(2)$ $\beta = 1.577(2)$ $\gamma = 1.581(2)$ and $2V = 48^\circ(2)$. The pleochroism is very weak and the elongation is positive parallel to Y. The mineral occurs as subparallel crystal aggregates with a quadratic outline.

KEYWORDS: saléeite, ferrous substitution, uranyl phosphate group, Arcu Su Linnarbu, Sardinia.

Introduction

THE prospecting area of Arcu su Linnarbu is located in the Monte Arcosu, near the village Capoterra in the province of Cagliari, Sardinia. The Monte Arcosu granites are bounded by metamorphic rocks with a northeast-southwest contact. These rocks consist of two distinct types, a sericite-muscovite schist and a cornubianitic, slightly micaceous, quartzite. Uranium mineralization occurs in the contact zone, consisting predominantly of secondary uranium minerals. In late 1950 exploration for uranium began, with the last mining activity between 1980 and 1983. The mining operations included open pit and underground working. Most of the secondary uranium minerals belong to the group of the uranyl phosphates; a number of these minerals have been described by Garavelli *et al.* (1959); Ippolito *et al.* (1956); Pietracaprina (1963); Ravagnani (1974) and Vochten *et al.* (1984).

The minerals reported are: meta-autunite, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 2-6\text{H}_2\text{O}$; bassetite, $\text{Fe}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$; parsonsite, $\text{Pb}_2(\text{UO}_2)(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$; phosphuranylite, $\text{Ca}(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_4 \cdot 6\text{H}_2\text{O}$; sabugalite, $\text{HAl}(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$; saléeite, $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$; and meta-torbernite, $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$.

Recently a ferrous-bearing saléeite was found at this locality. Up till now no data on this variety have ever been reported, although ferrian (Fe(III)) saléeite has been reported from two localities in Portugal (Lencastre, 1964–5).

The crystals are opaque, light yellow in colour and dull fluorescent under long and short wave ultraviolet radiation. Saléeite is transparent with a deep olive green colour and fluoresces strongly. In this paper some data are given for this ferrous-bearing saléeite.

Chemical composition

Chemical analyses were carried out with a Cameca electron microprobe type Microsonde SX-50 using the following standards: uranium dioxide (U), apatite (P), olivine (Mg), hematite (Fe) and leucite (K). Since insufficient material was available, the water content was obtained by difference from the data of the microprobe analysis. The analyses were carried out on three different crystals with twenty data points on each. By a separate microchemical test with α, α' -Dipyridyl (Feigl, 1972) only the presence of Fe^{2+} ions could be detected.

The analytical results are: P_2O_5 16.95 (± 0.20), FeO 1.35 (± 0.20), K_2O 0.10 (± 0.02), MgO 3.99 (± 0.20), UO_3 69.27 (± 0.5), H_2O 8.35. The

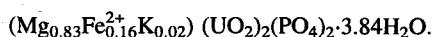
TABLE 1. X-ray powder diffraction data of ferrous substituted saléeite from Capoterra

d_{obs}	d_{calc}	I_{meas}	h	k	l
9.96	9.83	10	0	0	1
6.64	6.58	5	1	0	1
6.57	6.55	10	0	0	3
4.95	4.94	50	1	1	0
4.91	4.92	40	0	0	4
4.76	4.78	20	1	0	3
4.443	4.412	40	1	1	2
3.473	3.484	100	1	1	4
3.318	3.292	20	2	0	2
3.275	3.277	20	0	0	6
3.091	3.084	20	2	1	1
3.011	2.976	10	2	1	2
2.837	2.846	15	2	0	4
2.824	2.819	10	2	1	3
2.775	2.809	5	0	0	7
2.734	2.731	5	1	1	6
2.642	2.636	5	2	1	4
2.467	2.469	20	2	2	0
2.412	2.394	20	2	2	2
2.2	2.2	30	1	1	8
2.193	2.193	30	3	0	3
2.178	2.185	30	0	0	9
2.15	2.154	25	3	1	2
2.109	2.104	5	3	0	4
2.013	2.014	5	3	1	4

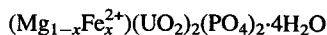
+ 27 additional indexed lines

Guinier-Hägg camera, 100 mm, Cu-K α_1 radiation, 40 kV, 20 mA.

empirical formula calculated from the analysis on the basis of 12 oxygen atoms is



This mineral is to be considered as a member of an isomorphic series between saléeite and bassetite with the general formula:



with $x < 1$.

The water content of this variety is relatively small in comparison with the end members of this series, and a natural dehydration must be accepted which is reflected in the opacity of the crystals.

Compatibility calculations using the Gladstone-Dale relationship yield $K_p = 0.1778$ and $K_c = 0.1711$ for the analytical formula using constants reported by Mandarino (1981) hence $1 - (K_p/K_c) = -0.039$, indicating an excellent compatibility.

X-ray diffraction data

Since the specimens consist of subparallel and fractured crystals, no reliable single crystal studies

were possible. For this reason the only source of information on the lattice parameters was obtained from X-ray powder diffraction data. These data have been obtained at 40 kV and 20 mA with Cu-K α_1 radiation ($\lambda = 1.5406 \text{ \AA}$) using a Philips PW-1140 generator.

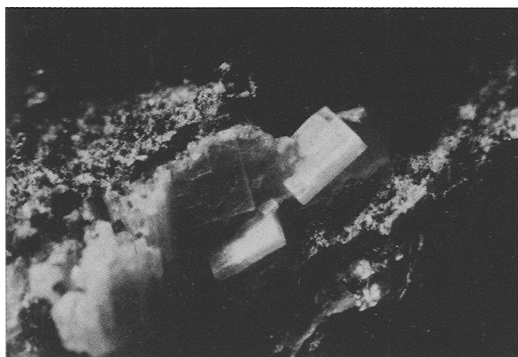


FIG. 1. Micrograph of ferrous substituted saléeite from Capoterra on Agfacolor XRG-200. Width of field is 2.9 mm.

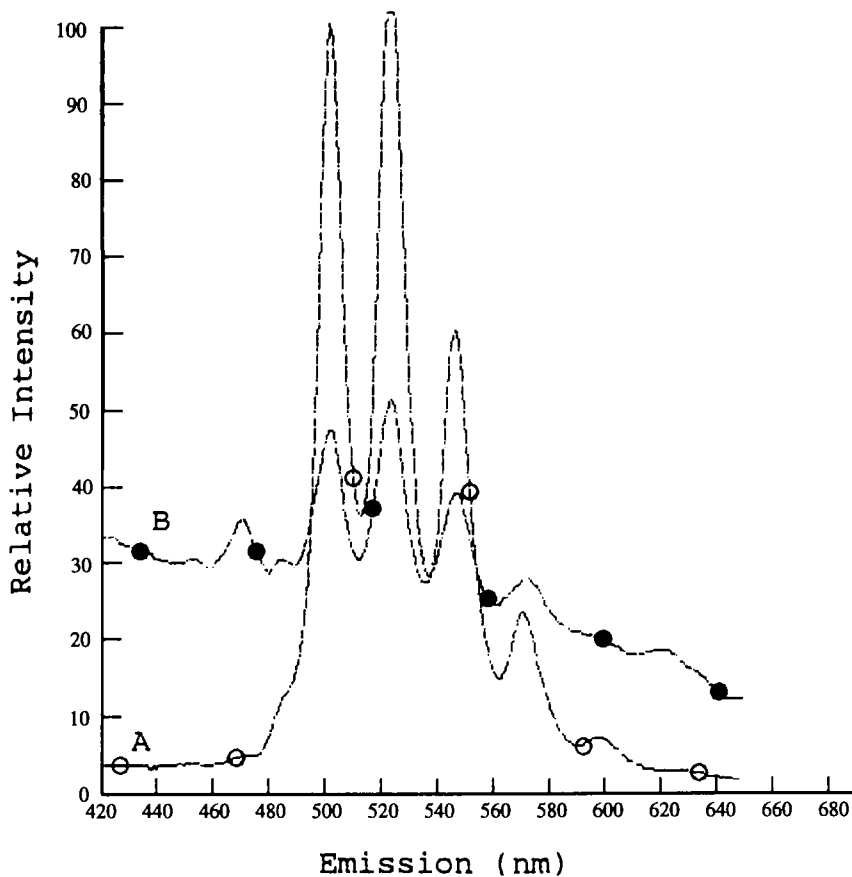


FIG. 2. Luminescence spectra of saléeite (A)(amplification 0.3) and ferrous substituted saléeite from Capoterra (B)(amplification 3.0) at 298 K with an excitation wavelength of 380 nm.

The photographs were recorded by means of a Guinier-Hägg camera with a diameter of 100 mm and an exposure time of 20 min. Silicon powder (NBS-640) was used as an internal calibrant for an accurate determination of the camera constant as a function of the glancing angle. The relative intensities of the diffraction lines were measured with a Carl Zeis Jena MD-100 microdensitometer.

Since the powder diffraction data of saléeite and the ferrous substituted saléeite are identical, the lattice parameters of saléeite, $a = 6.98$ and $c = 19.71$ Å with space group $P4/nmm$ (Hoffmann, 1972), were used for indexing and refinement with the NCRVAX program (Gabe *et al.*, 1989). All the recorded diffraction lines are indexed and the refined parameters for ferrous substituted saléeite are: $a = 6.982(5)$ and $c = 19.663(5)$ Å. This implies that

partial substitution of Mg^{2+} by Fe^{2+} ions does not affect the structure of saléeite. Table 1 summarizes the X-ray diffraction data for ferrous substituted saléeite from Capoterra.

The density of ferrous saléeite, measured at 25°C by means of the floating method is 3.242 g/cm^3 , whereas that for synthetic saléeite is 3.200 g/cm^3 (JCPDS; 29-874). The value of Z for both minerals is 2.

Crystal morphology

The crystals of ferrous substituted saléeite occur as opaque light-yellow aggregates. Figure 1 shows a micrograph from which it is clear that the habit is tabular-quadratic ($\{100\}$, $\{010\}$ and $\{001\}$). The crystals consist of relatively subparallel aggregates (0.4–1.5 mm) and display irregular fractures.

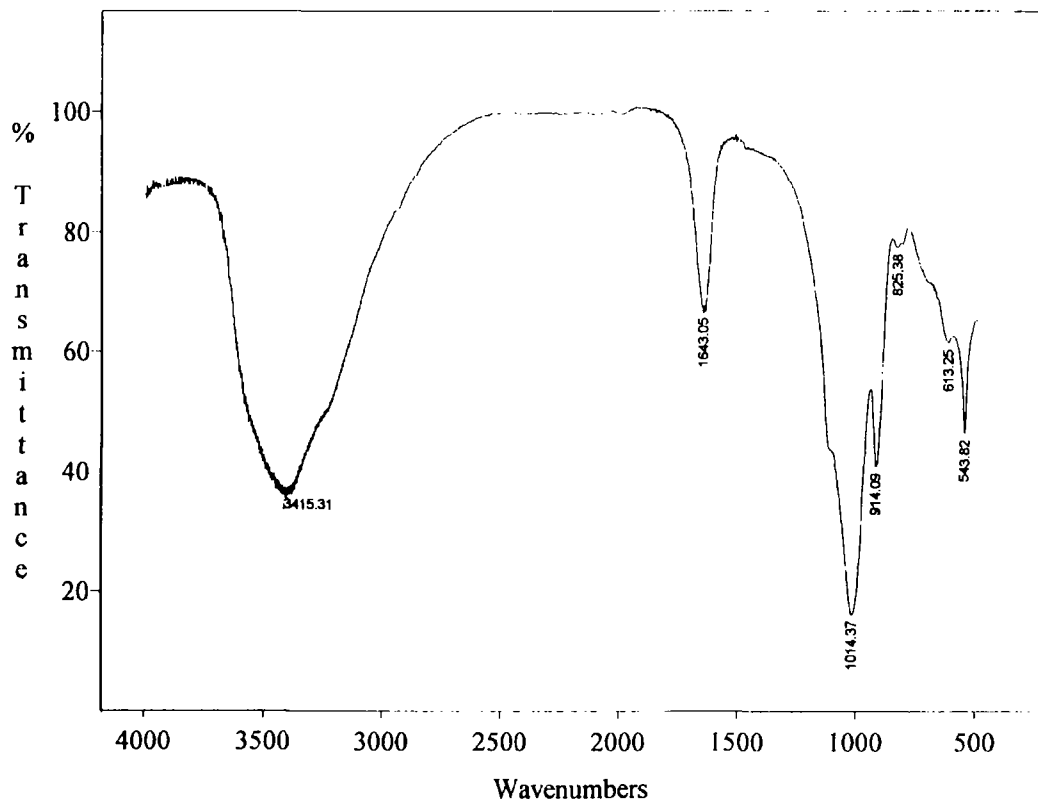


FIG. 3. Infrared spectrum of ferrous substituted saléite from Capoterra, recorded in KBr pellets.

Optical properties

The mineral is biaxial negative with $\alpha = 1.572(2)$, $\beta = 1.577(2)$, $\gamma = 1.581(2)$ determined at 589 nm and $2V$ is calculated as $48^\circ(2)$. The orientation corresponds with $X(\alpha)$, $Y(\beta)$ and $Z(\gamma)$ and the elongation is positive parallel to $Y(\beta)$.

The pleochroism is very weak with a slight yellow colour. The refractive indices lie between those of saléite and bassetite (Fron del, 1958). The slight differences from saléite may be attributed to partial substitution and dehydration as well.

Luminescence spectrum

Ferrous substituted saléite fluoresces dull green under both short and long wave ultraviolet radiation whereas saléite fluoresces very strongly. The fluorescence spectrum of synthetic saléite and the ferrous substituted saléite were recorded by means of a Perkin-Elmer MPS-44B spectrofluorimeter at 298 K with an excitation wavelength of 380 nm and a scan

speed of 120 nm/min. The samples were prepared as a thin layer on a gelatine strip. The two spectra are represented in Fig. 2 from which it is clear that the two samples are characterized by four uranyl bands: 501, 523, 546 and 570 nm. Taking into account the applied amplification for saléite (0.3) and ferrous substituted saléite (3.0), it is clear that saléite fluoresces more intensively than the Fe-substituted variety. It is obvious that the presence of Fe acts as a fluorescence quencher. Just as some activators can be effective in small amounts, deactivators can also be effective in very small amounts.

Infrared spectrum

The infrared spectrum of the ferrous substituted saléite was recorded by means of the KBr technique (1 mg/300 mg KBr) with an Ati-Wattson Genesis FTIR-spectrometer covering the range $400\text{--}4000\text{ cm}^{-1}$.

The infrared spectrum, represented in Fig. 3 is simple and can be interpreted by considering the

vibrations of OH^- , PO_4^{3-} and UO_2^{2+} groups, in addition to the vibrations of water molecules. According to Gonzalez-Diaz *et al.* (1978) the vibrational modes of the PO_4^{3-} groups are: ν_1 PO-stretching (940 cm^{-1}); ν_2 OPO-bending (420 cm^{-1}); ν_3 PO-stretching (1020 cm^{-1}); and ν_4 OPO-bending (560 cm^{-1}). The recorded values for ν_3 and ν_4 are 1014 and 544 cm^{-1} respectively. The absorption bands at about 3415 , 1643 and 613 cm^{-1} are thought to be due to water, corresponding to stretching, deformation and vibrational modes respectively. The ν_2 of the UO_2^{2+} group probably coincides with the ν_1 of the PO-stretching vibration of the PO_4^{3-} group at 914 cm^{-1} . Only the ν_1 of the UO_2^{2+} group at 825 cm^{-1} is not well pronounced.

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