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Rodolicoite and grattarolaite, two new phosphate minerals from Santa Barbara Mine, Italy

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Abstract: Grattarolaite and rodolicoite, two new anhydrous iron phosphates, were found at Santa Barbara lignite mine as reddish-brown nodules. They occur as small crystallites (< 1000 Å), associated in fine-scale intergrowth that prevent the measurement of physical properties.

Grattarolaite is trigonal, with space group $R3m$; rodolicoite is also trigonal, but with space group $P3_121$. Cell dimensions, calculated from X-ray powder patterns, are: grattarolaite $a = 7.994(4)$, $c = 6.855(4)$ Å, $V = 379.4$ Å^3, $Z = 3$; rodolicoite $a = 5.048(3)$, $c = 11.215(8)$ Å, $V = 247.5$ Å^3, $Z = 3$.

The chemical data, obtained by transmission electron microscope microanalysis, give the composition $Fe_{2.99}P_{1.01}O_{7.00}$ for grattarolaite and $Fe_{1.04}P_{0.96}O_{4.00}$ for rodolicoite. Infrared spectroscopy and thermal analysis confirm the anhydrous nature of both minerals.

Key-words: phosphates, rodolicoite, grattarolaite, Santa Barbara, Italy.

Introduction

Occurrence and geological features

The specimens come from the Santa Barbara lignite mine in the Upper Arno River Valley lignitiferous basin, 30 km southeast of Florence.

The Upper Arno River Valley (Upper Valdarno) is an asymmetric tectonic basin, elongated NW-SE, situated between the Chianti hills and Pratomagno mountains. Normal faulting (Lazzarotto & Liotta, 1991) allowed the deposition of more than 500 m of fluvial-lacustrine sediments, in three stages. Initial distension (stage 1) began in the Upper Pliocene and led to sedimentation of the Castelnuovo Series. Tectonic movements led to subsidence of the area and established suitable conditions for the accumulation of organic vegetable matter, thus giving rise to the lignite beds. Owing to rising water-levels, the Meleto clays (200 m thick) and San Donato sands (80 m thick) were then deposited (Sagri & Magi, 1992). Flora and fauna remains found in stage-1 sediments suggest a tropical humid climate (Azzaroli, 1984). In the Upper Pliocene-Lower Pleistocene, uplift of the Chianti and Pratomagno ridges led to deposition of the stage-2 sediments (Montevarchi Series), consisting mainly of paludal-lacustrine deposits (Terranova silts, Torrente Ascione clays, Oreno silts and sands) and alluvial fan deposits (Billi *et al.*, 1991). Finally, in the Middle Pleistocene (stage 3), the Monticello fluvial deposits completely filled the basin.

Since 1867, the Santa Barbara mining area has yielded a considerable amount of lignite, used in recent times to fuel a local thermoelectric power plant. In the past 20 years, samples of vivianite, anapaite and hartite have been discovered in this area. However, the mines have recently been closed and will shortly be used for waste disposal. Before the deposits become inaccessible, we decided to undertake a review of the mineralogy of this area.

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Specimen description

Several brown earthy nodules were examined in order to determine their chemical and mineralogical composition and to shed some light on their origin and significance.

X-ray diffraction patterns show that most of the nodules are composed of amorphous materials, probably derived from the thermal alteration of vivianite (Billi, 1980; Pratesi, 1993). A few samples, more reddish than the others, attracted our attention because their powder diffraction patterns suggested the presence of new mineral species.

The analytical techniques employed to characterize these specimens (X-ray and electron diffraction, scanning and transmission electron microscopy, electron probe microanalysis, infrared and Mössbauer spectroscopy, thermogravimetry) showed them to consist of a fine intergrowth of two new species, of anhydrous iron phosphate, for which we propose the names grattarolaite (Fe_3PO_7) and rodolicoite ($FePO_4$), in honour of Giuseppe Grattarola (1844–1907) and Francesco Rodolico (1905–1988), both professors of mineralogy at the University of Florence. These minerals and their names have been approved by the I.M.A. Commission on New Minerals and Mineral Names. The type specimen is kept at the Museum of Natural History (mineralogical section) of the University of Florence, under catalogue number 2087/RI.

Grattarolaite and rodolicoite occur as little reddish-brown earthy nodules, about 1 cm in diameter, exhibiting cavities lined with aggregates up to 1 mm in length. Only three samples have been found to date. These nodules come from the Castelnuovo Mine and lie within a brick-like matrix (Capacci, 1909). The thermal alteration of the matrix suggests that "self-burning" was involved in the formation of nodules. Because of the fine-grained nature of the intergrowths, grattarolaite and rodolicoite being optically indistinguishable; only a general description is given here. The reddish-brown aggregates are brittle, having a greasy lustre and brown streak; they are not translucent. There is no evidence of cleavage. Owing to the size, the crystallite morphology was observed only by transmission electron microscopy. Consequently, physical properties such as optical behaviour and hardness were not measured. The calculated densities of grattarolaite and rodolicoite are 4.08 and 3.04 g/cm^3, respectively.

X-ray diffraction data

The X-ray powder diffraction data (Table 1) were obtained with a Philips PW-3710 automated diffractometer, using Co$K\alpha$ radiation, 0.02° 2θ step, a counting time of 1 second per step and NaF as internal standard.

The observed pattern closely matches a mixture of synthetic Fe_3PO_7 (JCPDS 37-61) and synthetic $FePO_4$ (JCPDS 29-715); peak indexing was carried out using XPOW software (Downs *et al.*, 1993). The following unit-cell data were obtained by least-squares refinement. Grattarolaite (Fe_3PO_7) is trigonal, with space group $R3m$; the unit-cell parameters are: $a = 7.994(4)$, $c = 6.855(4)$ Å, $V = 379.4$ Å^3, Z = 3. Rodolicoite ($FePO_4$) is also trigonal, with space group $P3_121$; the unit-cell parameters are: $a = 5.048(3)$, $c = 11.215(8)$ Å, $V = 247.5$ Å^3, Z = 3.

A full-profile Rietveld analysis of the observed pattern, performed by means of the software Wyriet 3.0 (Schneider, 1989), converged to a mineralogical composition of 80% rodolicoite and 20% grattarolaite. The diffraction lines of the two phosphates are wider than normally found. FWHM is in the order of 0.45° for rodolicoite, and of 0.35° 2θ for grattarolaite. By using the Scherrer equation, we estimate a coherent grain size of 260 Å for rodolicoite and 380 Å for grattarolaite.

In the absence of single-crystal data, it is convenient here to summarize the basic data on synthetic analogues of grattarolaite and rodolicoite. The structure of Fe_3PO_7 (Modaressi *et al.*, 1983) is similar to that of graftonite (Calvo, 1968) and consists of isolated PO_4 tetrahedra and FeO_5 distorted trigonal bipyramids. Since three polyhedra share two edges and form a Fe_3O_{10} cluster, the formula might be better written as $Fe_3O_3(PO_4)$. According to Korinth & Royen (1961), only Fe_3PO_7 exists between Fe_2O_3 and $FePO_4$. At 1100 °C, Fe_3PO_7 decomposes to Fe_2O_3 and $FePO_4$. The structure of $FePO_4$ was first solved by Hok Nam Ng & Calvo (1975) and successively refined by Arnold (1986) using neutron powder diffraction. The structure is isomorphous with berlinite and thus similar to α-quartz, but with a doubling of the c lattice parameter because of the ordering of the tetrahedral Fe and P cations.

Microprobe data

Initial chemical data, obtained with a JEOL 8600 electron microprobe, indicated an overall Fe/P ra-

Table 1. X-ray powder diffraction data of grattarolaite and rodolicoite.

Observed X-ray powder diffraction pattern		**Grattarolaite**				**Rodolicoite**			
d_{obs}(Å)	I_{obs}	d_{JCPDS}	I_{JCPDS}	d_{calc}(Å)	*hkl*	d_{JCPDS}	I_{JCPDS}	d_{calc}(Å)	*hkl*
4.87	20	4.86	10	4.871	101				
4.38	25					4.360	19	4.372	100
4.08	7					4.066	2	4.073	101
3.99	2	3.98	2	3.997	110				
3.74	1					3.750	2	3.738	003
3.45	100					3.445	100	3.448	102
3.08	100	3.09	100	3.090	021				
2.857	3					2.843	<1	2.841	103
2.527	5					2.518	7	2.524	110
						2.458	1	2.462	111
				2.445	211				
2.437	20	2.446	16						
				2.436	202				
2.362	20					2.362	14	2.360	104
2.304	15	2.305	6	2.308	300				
2.295	10					2.298	7	2.302	112
		2.280	2	2.285	003				
2.190	15					2.180	10	2.186	200
						2.142	<1	2.146	201
						2.090	<1	2.092	113
2.077	30	2.078	20	2.080	122				
						2.0335	3	2.0366	202
1.995	10	1.997	13	1.998	220	1.9986	2	1.9957	105
1.983	10	1.980	5	1.984	113				
								1.8870	203
1.877	20					1.8846	12		
								1.8759	114
1.846	15	1.845	11	1.849	131				
1.724	10					1.7221	6	1.7239	024
1.676	3	1.676	4	1.675	312	1.6772	1	1.6766	115
1.662	5	1.661	5	1.663	104				
						1.6304	1	1.6347	211
1.622	20	1.623	23	1.624	303				
1.587	10					1.5814	8	1.5850	212
1.545	15	1.545	12	1.545	042				
1.538	10	1.534	7	1.536	024				
		1.509	3	1.511	410	1.5081	3	1.5113	213
1.506	10	1.501	3	1.504	223			1.5043	017
						1.5035	2	1.5021	116
		1.440	16	1.441	232				
1.437	20								
		1.433	8	1.434	214				
								1.4235	124
1.426	15					1.4214	10		
								1.4206	206
						1.4068	4	1.4104	302
1.357	2			1.357	051				
1.335	15			1.332	330	1.3376	3	1.3349	108
						1.2912	2	1.2930	304
1.284	2			1.284	502				
1.274	2			1.275	205				
1.2595	1					1.2588	<1	1.2619	220
1.2396	1					1.2375	2	1.2380	216
1.2231	3					1.2273	2	1.2255	118
1.2143	2			1.214	125				
						1.2093	2	1.2125	310

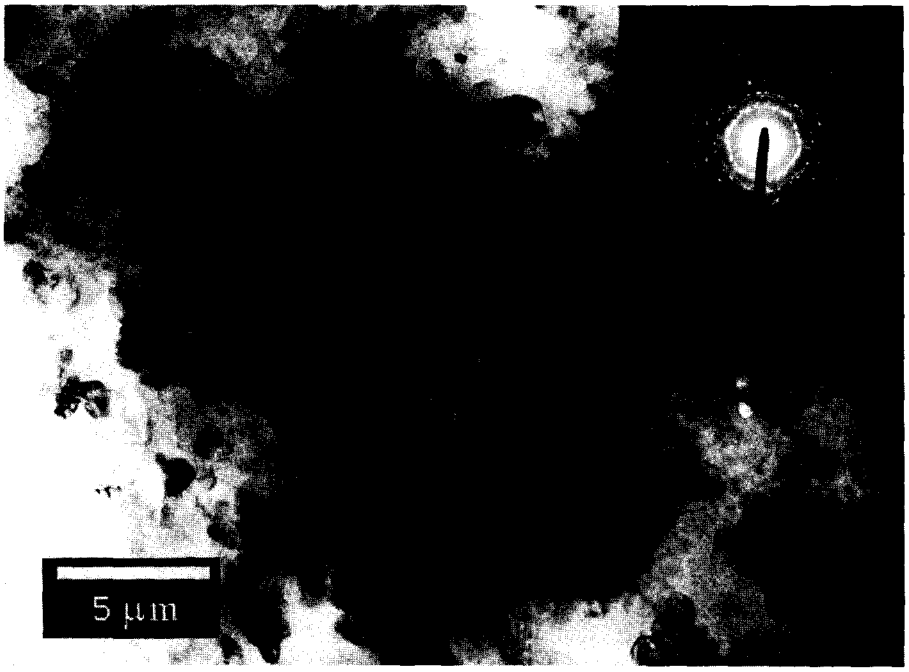

Fig. 1. TEM image showing the typical intergrowth of rodolicoite and grattarolaite; the corresponding electron diffraction pattern is also shown.

tio close to 1.3; however, the electron microprobe analysis was completely unable to resolve individual data points corresponding to rodolicoite (Fe/P = 1) or grattarolaite (Fe/P = 3), because the individual particle size was much smaller than the excited volumes.

From the ratio Fe/P = 1.3, we estimate a rodolicoite content close to 85%; this appears to be in good agreement with the previous estimate by Rietveld analysis.

Transmission electron microscopy

The specimens were investigated using a Philips 400T transmission electron microscope (TEM) operating at 120 kV and equipped with an energy-dispersive X-ray detector (EDS). The main purpose was to obtain spatially resolved chemical data; both ground powders and ion-thinned sections were investigated.

Chemical data were gathered using a spot-size of 800–1000 Å, and corrected using the thin-film approximation of Cliff & Lorimer (1972, 1975), using a vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$ standard for the determination of the proportionality factor and the general analytical approach described by Mellini & Menichini (1985). J_{FeP} was determined to be 0.78. As no beam broadening occurred in the thin film used for TEM observations, we expected to record EDS spectra with a resolution of 800–1000 Å, sufficient to achieve chemical resolution of rodolicoite from grattarolaite.

This objective was not immediately attained, however, as the grain size was generally smaller than the spot size. Fig. 1 is a typical image of the grattarolaite and rodolicoite mixture, showing that the specimen is almost homogeneously composed of a fine intergrowth of irregularly shaped crystallites, typically less than 1000 Å in size and showing variable contrast features. The observed compositions are compatible with a formula of $Fe_{1.04}P_{0.96}O_{4.00}$ for rodolicoite and $Fe_{2.99}P_{1.01}O_{7.00}$ for grattarolaite; in the following, these compositions are assumed as representative of the two phases.

A final comment regards the sporadic occurrence of heterosite (polymorph of rodolicoite) within the mixture. Heterosite appears as large lamellae, 1–2 μm in size; its identification was confirmed by EDS analysis and by electron diffraction meas-

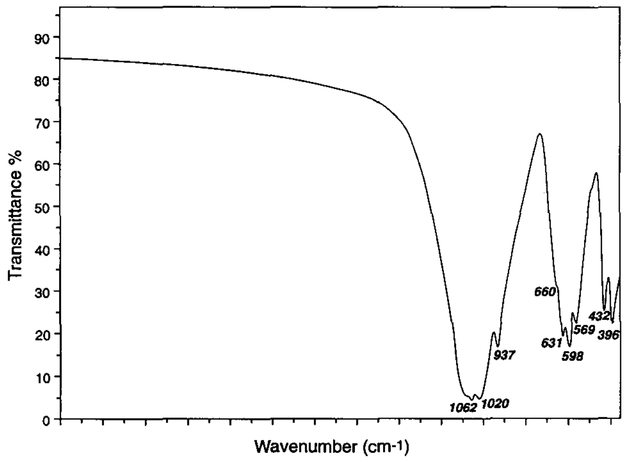

Fig. 2. Infrared spectrum of the grattarolaite-rodolicoite mixture.

urement of interplanar spacings. These heterosite crystals commonly show structural modulations, as shown by the appearance of satellite spots in the electron diffraction patterns and of irregular lattice fringes in the TEM lattice images.

Infrared spectroscopy and thermal analysis

The infrared spectrum (Fig. 2) was collected with a Perkin-Elmer 1710 FTIR spectrometer, from 4000 to 400 cm^{-1}; approximately 2 mg of the rodolicoite-grattarolaite mixture were mixed with KBr and pressed into a disk. The main absorption bands occur at 1062, 1020, 937 (P-O stretching vibrations), 660(s), 631, 598, 569, 432, 396 cm^{-1} (P-O-P bending and Fe-O stretching and bending vibrations). Minor bands were observed also at 1631 and 1462 cm^{-1}, possibly indicative of a P-O double-bond contribution. The absence of absorption bands in the O-H stretching region matches the completely anhydrous nature of the mixture.

The anhydrous nature is confirmed also by D.T.A. and T.G. analysis (data collected up to 900 °C); furthermore, no phase transition was observed in this temperature range.

Mössbauer spectroscopy

An attempt was made to discriminate rodolicoite and grattarolaite on the basis of Mössbauer spectroscopy. The pattern was collected with an instrument equipped with a CMTE driver and a CANBERRA acquisition device.

Fig. 3 shows the spectrum obtained at 170 K. It consists of a single doublet, with spectral parameters of 0.33(1) (chemical shift, δ), of 0.99(2) (quadrupole splitting, Δ) and 0.60(4) mm/sec (line broadening, Γ). The features fit well those previously reported by Modaressi *et al.* (1983) for Fe_3PO_7, namely $\delta = 0.34$, $\Delta = 1.13$ and $\Gamma = 0.28$ mm/sec. Clearly, the wider line of the natural specimen may be related to its composite nature.

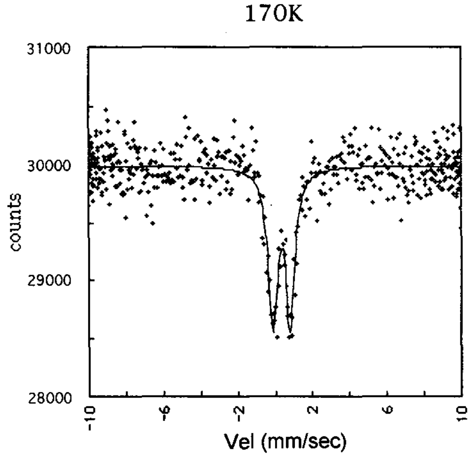

Fig. 3. Mössbauer spectrum of rodolicoite-grattarolaite mixture.

The Mössbauer data on the rodolicoite-grattarolaite mixture confirm the occurrence of ferric iron, but do not succeed in resolving the tetrahedral iron doublet (rodolicoite) from the five-fold coordinated iron (grattarolaite). This difficulty in dealing with iron compounds has been previously commented by Bancroft *et al.* (1967) and Hawthorne (1988).

Discussion and conclusions

Rodolicoite and grattarolaite are two new anhydrous iron phosphate minerals. Although the fine-scale intergrowth prevented us from obtaining a complete set of data, the results obtained demonstrate that the two phosphate minerals are the natural analogues of previously known synthetic compounds.

By comparison with their synthetic analogues, it is possible to point out the most important crystalchemical feature of these two minerals, namely their unusual iron coordinations. In fact, the occurrence of iron phosphates with trivalent iron is well established (Alluaud, 1825), but iron normally occurs in six-fold coordination. An example is heterosite, the other known iron anhydrous orthophosphate always containing Mn^{III}. However, iron occurs in the unusual four-fold coordination in rodolicoite and in the still less common five-fold coordination in grattarolaite.

These unusual coordinations are in good agreement with the formation conditions of the two minerals. In particular, the low coordination numbers fit rather high temperature conditions, in agreement with the general crystal chemical behaviour. In fact, grattarolaite and rodolicoite are the last phases produced during the progressive thermal alteration of hydrated phosphate minerals, according to the sequence:

vivianite → metavivianite → amorphous phase →
Fe^{VI} → Fe^{VI} → ... →

grattarolaite + rodolicoite → rodolicoite → molten phase
Fe^{V} + Fe^{IV} → Fe^{IV} → ...

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