

## Viaeneite, $(\text{Fe,Pb})_4\text{S}_8\text{O}$ , a new mineral with mixed sulphur valencies from Engis, Belgium

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**Abstract:** Viaeneite,  $(\text{Fe,Pb})_4\text{S}_8\text{O}$ , forms aggregates up to 4 mm in size. Associated minerals are pyrite, marcasite, melnikovite, sphalerite, galena, other Zn-Pb compounds with double sulfur valencies, goethite, zincian siderite, smithsonite and greigite. The mineral has a yellow colour, a distinct reflection pleochroism and is strongly anisotropic. Its  $R\%$  in air, for  $\lambda = 546$  nm, is 23.8-36.8 %,  $\text{VHN}_{200} = 252$  kg/mm<sup>2</sup> (range: 123-357),  $D_{\text{meas}} = 3.8 \pm 0.1$  g/cm<sup>3</sup>,  $D_{\text{calc}} = 3.65$  g/cm<sup>3</sup>. Microprobe analyses give (wt.%, average): Fe 42.37, Pb 4.02, Zn 0.05, Ni 0.20, As 0.17, S 49.74, O 3.69, total 100.24. The empirical formula (based on microprobe analyses) is:  $(\text{Fe}_{3.91}\text{Pb}_{0.10}\text{Ni}_{0.02})_4.03(\text{S}_{8.00}\text{As}_{0.01})_{8.01}\text{O}_{1.16}$ . The sulphur is present in two valency combinations: disulphide,  $\text{S}_2^{2-}$ , and thiosulphate,  $\text{S}_2\text{O}_3^{2-}$ , in the ratio 11:1.

Viaeneite is monoclinic :  $a = 9.717 \pm 0.008$ ,  $b = 7.280 \pm 0.006$ ,  $c = 6.559 \pm 0.007(\text{\AA})$  and  $\beta = 95.00^\circ \pm 0.03$ ,  $V = 462.2 \pm 0.8 \text{\AA}^3$ ,  $Z = 2$ . The cell is probably primitive. The strongest XRD powder reflections are 3.43(5), 2.709(10), 2.419(8), 2.323(7), 1.920(6), 1.758(8), 1.595(5), 1.162(5), 1.092(5), 1.035(5), 0.9911(5) and 0.9576(7)( $\text{\AA}$ ).

The name is given in honour of Prof. W. Viaene, Katholieke Universiteit Leuven, Belgium.

**Key-words:** new mineral, viaeneite, sulphur valency, thiosulphate, disulphide.

### Introduction

Two  $\text{FeS}_2$  polymorphs are known : cubic pyrite, with  $a = 5.41 \text{\AA}$ , and orthorhombic marcasite, with  $a = 4.45$ ,  $b = 5.42$  and  $c = 3.38 \text{\AA}$  (Ramdohr, 1980). Marcasite has usually nearly theoretical composition. Pyrite is mostly pure but sometimes contains high amounts of Ni and/or Co. The contents of Cu, Zn, Ag and Au are at trace level, while Se concentration may occasionally reach 3 wt.% and As content is usually low (Ramdohr, 1980). A mineral substance known as mel-

nikovite-pyrite, colloform pyrite or crystallized  $\text{FeS}_2$  etc. is usually mentioned in relation to pyrite proper (Ramdohr, 1980; Uytendogaardt & Burke, 1985). This substance is often so fine-grained that X-ray diffraction (XRD) photographs show hardly any lines. Melnikovite has distinctly lower density than pyrite proper, and it may be as soft as galena. In reflected light it is yellow-brown and appears much darker than pyrite. Varieties rich in As exhibit distinct anisotropy in reflected light. The properties of this compound change upon ageing (Ramdohr, 1980;

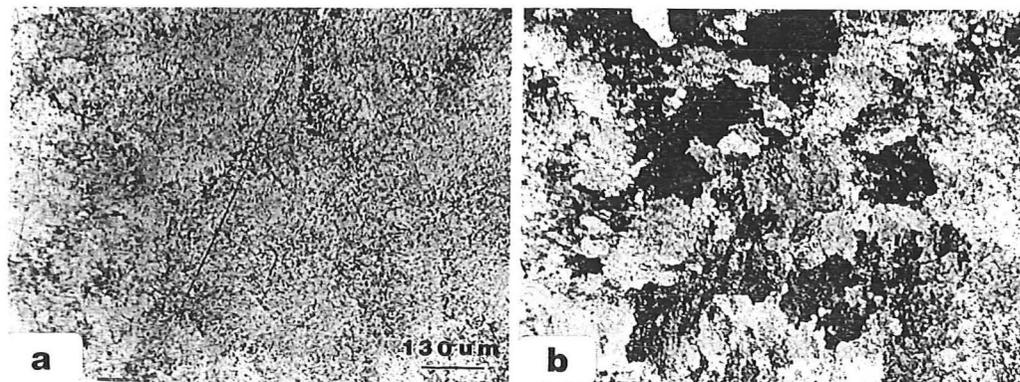


Fig. 1. Reflected light microphotograph of viaeneite. a - plane polarized light showing bireflectance visible at grain boundaries, b - between crossed nicols, showing strong anisotropy.

Uytenbogaardt & Burke, 1985). In modern terms melnikovite-pyrite may be described as a variable mixture of disulphide and compounds with intermediate sulphur valencies (Kucha *et al.*, 1989; Kucha & Viaene, 1993).

The stability of intermediate valency S in minerals is shown by many examples. Sulphur occurs in minerals in seven dominant valency states: -2, -1, 0, +2, +3, +4 and +6, in order of increasing valency. Monosulphides, such as ZnS and PbS, are common examples of compounds with a sulphur valency of -2. The ubiquitous natural disulphides are cubic or orthorhombic FeS<sub>2</sub> with an average valency of -1. Polysulphides

have valencies between -1 and 0. For example, a natural compound with stoichiometric S valence of -0.66 is BaS<sub>3</sub>·Ba(OH)<sub>2</sub>·2Al(OH)<sub>3</sub>·8H<sub>2</sub>O (Braithwaite *et al.*, 1993). The valency 0 is found in native sulphur. S<sup>2+</sup> is present in sulphoxylanes (Valensi *et al.*, 1963), and (Fe,Zn,Pb)(S,As)O<sub>2</sub> is a natural example (Kucha & Viaene, 1993). A valency of +3 occurs in subsulphites (Valensi *et al.*, 1963), as in (Fe,Pb)S<sub>2</sub>O<sub>4</sub>, a natural composition documented by soft X-ray spectroscopy (Kucha & Viaene, 1993). Sulphites have S as +4 and several compounds of this kind have been reported: scotlandite, PbSO<sub>3</sub> (Paar *et al.*, 1984), hannebachite, CaSO<sub>3</sub>·0.5H<sub>2</sub>O (Hentschel *et al.*,

Table 1. Physical properties of pyrite, marcasite and viaeneite.

MINERAL	R% IN AIR, λ = 546 nm	VHN (kg/mm <sup>2</sup> )	REFLECTION PLEOCHROISM IN AIR	ANISOTROPISM IN AIR
Pyrite	53.5	1165* 1027-1240* 1505-2315**	Not observed	Usually not observed, some pyrites may be distinctly anisotropic
Marcasite	49.0-56.0	1113* 941-1288* 915-1099**	Distinct, //a white to pinkish-brown, //b faint yellow, //c yellow-greenish	Very strong, colours: yellow, light-green, deep-green
Viaeneite	23.8-36.8	252 123- 357 n=10, σ=65	Distinct, greyish-brown, orange, orange-yellow	Very strong, colours: orange, yellow-orange, grey with green hue

σ - standard deviation, n - number of indentations  
Optical properties of pyrite and marcasite after Ramdohr (1980), VHN after Cameron (1966)\* and Criddle & Stanley (1993)\*\*,  
R% after Uytenbogaardt & Burke (1985).

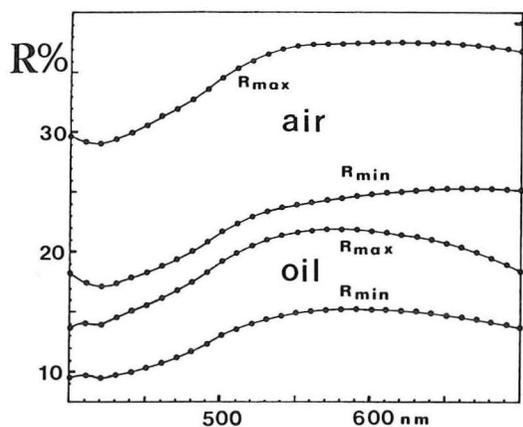


Fig. 2. Reflectance dispersion curves of viaeneite measured in air and in oil. Vertical axis - reflectance R%, horizontal axis - wavelength of incident light in nm.

1985), gravegliaite,  $MnSO_3 \cdot 3H_2O$  (Basso *et al.*, 1991),  $(Fe,Pb)SO_3$  (Kucha & Viaene, 1993),  $ZnSO_3$  (Kucha & Stumpfl, 1992) and  $BaSO_3$  (Braithwaite *et al.*, 1993). The highest reported oxidation state of sulfur in minerals, *i.e.* +6, is found commonly in sulphates.

Sulphur also readily forms compounds of mixed valency such as: i) polysulphides having two S valencies -2 and 0 with an average value of valence changing from -1 to 0, ii) polythionates with a general formula  $M^{2+}S_nO_6$ , where  $n = 2$  to 6 and average valency changes from +5 to +1.33, and iii) thiosulphates having one sulphur of -2 and one of +6, with an average valence of the ligand of +2. Bazhenovite,  $CaS_5 \cdot CaS_2O_3 \cdot 6Ca(OH)_2 \cdot 20H_2O$  (Chesnokov *et al.*, 1987),  $PbS_2O_3$  from Ballinalack (Kucha, 1988) and  $BaS_2O_3 \cdot BaF_2$  as well as  $BaS_2O_3 \cdot H_2O$  (Braithwaite *et al.*, 1993) are examples of naturally occurring thiosulphates.

## Occurrence

Viaeneite occurs in the carbonate-hosted La Mallieue lead-zinc deposit at Engis, about 40 km southwest of Liege, Belgium. It was found in samples containing massive sphalerite, pyrite, marcasite and minor galena. Other associated minerals are various Fe-Pb compounds with double sulphur valencies (Kucha & Viaene,

Table 2. Reflectance data of viaeneite in air and in oil ( $n=1.518$ ).

$\lambda$ (nm)	AIR $R_{min.}$	$R_{max.}$	OIL $R_{min.}$	$R_{max.}$
400	18.1	29.6	9.5	13.8
410	17.5	29.3	9.8	14.2
420	17.1	29.1	9.6	14.2
430	17.4	29.5	9.9	14.6
440	17.9	30.0	10.1	15.0
450	18.4	30.6	10.4	15.7
460	18.9	31.3	10.8	16.3
470	19.5	32.1	11.3	17.0
480	20.2	32.9	11.7	17.6
490	20.7	33.6	12.3	18.4
500	21.5	34.5	12.9	19.1
510	22.1	35.2	13.4	20.0
520	22.8	35.9	14.0	20.6
530	23.2	36.3	14.4	21.0
550	23.8	36.8	14.8	21.6
560	24.2	37.3	15.1	21.8
570	24.3	37.3	15.2	21.9
580	24.5	37.4	15.2	21.9
590	24.6	37.4	15.3	21.9
600	24.7	37.4	15.2	21.8
610	24.9	37.4	15.2	21.6
620	25.0	37.4	15.0	21.3
630	25.0	37.4	15.1	21.1
640	25.1	37.3	15.0	20.9
650	25.1	37.3	14.9	20.6
660	25.2	37.3	14.8	20.3
670	25.2	37.1	14.6	19.9
680	25.2	37.0	14.4	19.5
690	25.2	36.8	14.2	19.0
700	25.1	36.7	13.9	18.5

1993), goethite, zincian siderite, smithsonite, dolomite, ferroan dolomite, quartz, cerussite and anglesite. The fluid inclusion temperatures obtained from carbonate-hosted Zn-Pb deposits in Belgium are 50-190°C (Darimont, 1987). It has therefore been suggested that the minerals with mixed sulphur valencies formed by precipitation from medium- to low-temperature solutions containing sulphidic, sulphitic, sulphatic and thiosulphatic species (Kucha & Viaene, 1993).

## Appearance and physical properties

Viaeneite forms oval-shaped intergrown aggregates ranging in size from 0.05 to 0.5 mm, exceptionally up to 4 mm. The mineral occurs inside pyrite, pyrite-melnikovite, marcasite and sphalerite. The aggregates of viaeneite are made up of minute crystals with sizes usually ranging from a few  $\mu m$  to 30  $\mu m$  (Fig. 1a, b), exceptionally up to 80  $\mu m$ . When studied under high

Table 3. Microprobe composition of viaeneite; upper figure wt.%, lower figure atomic proportions.

SAMPLE	EMP9/B1	EMP9/B2	EMP9/B3	AVERAGE
S	49.97	49.38	49.87	49.74
	8.0000	8.0000	8.0000	8.0000
Fe	42.87	42.03	42.22	42.37
	3.9402	3.9096	3.8877	3.9127
Ni	0.23	0.22	0.16	0.20
	0.0205	0.0193	0.0144	0.0181
Zn	0.04	0.08	≤0.02	0.05
	0.0024	0.0060		0.0036
As	0.18	0.19	0.14	0.17
	0.0121	0.0133	0.0096	0.0120
Pb	3.90	4.39	3.76	4.02
	0.0966	0.1097	0.0937	0.1000
TOTAL	97.19	96.30	96.18	96.55
O <sub>diff</sub>	2.81	3.70	3.82	3.45
	0.9018	1.2011	1.2283	1.1119
O <sub>meas.</sub>	3.10	3.98	4.00	3.69
	0.9946	1.2013	1.2860	1.1606

Sought for but not detected: Mn ≤0.02, Co ≤0.02, Tl ≤0.05.

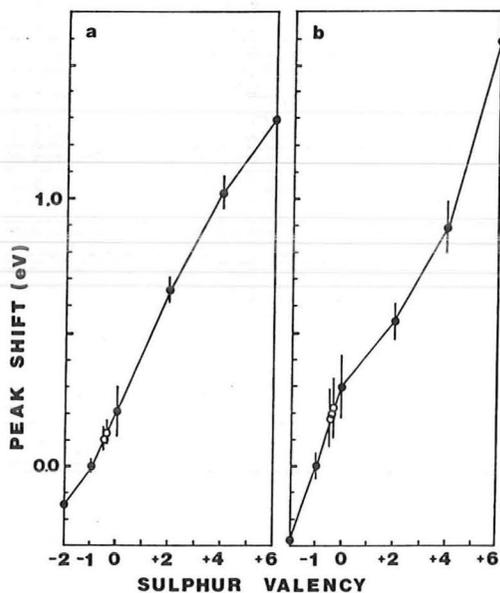


Fig. 3. a) Relationship between sulphur valency and the  $SK\alpha$  peak shift (eV). Heavy circles indicate standard specimens: FeS, FeS<sub>2</sub>, S<sup>0</sup>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub>, and CaSO<sub>4</sub>. Open circles show the analysed microareas of viaeneite (Table 4).

b) Relationship between sulphur valency and the  $SK\beta$  peak shift (eV). Heavy circles indicate standard specimens: FeS, FeS<sub>2</sub>, S, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub>, and CaSO<sub>4</sub>. Open circles show the analysed microareas of viaeneite (Table 4).

magnification in oil, or by scanning electron microscopy (SEM), viaeneite appears to be homogeneous and no inclusions of any second phase can be distinguished. Viaeneite may be replaced by pyrite, marcasite and sphalerite. The mineral shows a much lower polishing hardness than the above mentioned surrounding minerals.  $VHN_{200} = 252 \text{ kg/mm}^2$  (range 123-357) while Moh's hardness is 3. Although leavage was not observed by reflected light microscopy, it is clearly visible under TEM parallel to {110}. Density measured using a Berman balance  $D_{\text{meas}} = 3.8 \pm 0.1 \text{ g/cm}^3$ , while density calculated from X-ray data  $D_{\text{calc}} = 3.65 \text{ g/cm}^3$ . The density of viaeneite is therefore much lower than that of pyrite or marcasite, *i.e.* 5.1 and 4.8-4.9 g/cm<sup>3</sup>, respectively (Ramdohr, 1980).

Viaeneite is opaque with a metallic lustre. Its colour is yellow, similar to pyrite and marcasite. The streak is black. The physical properties of viaeneite thus differ notably from those of pyrite or marcasite.

### Optical properties

Viaeneite in polished section is yellow with a brassy hue, and is much darker than encompassing pyrite or marcasite (Table 1). The mineral shows distinct birefractance, changing from

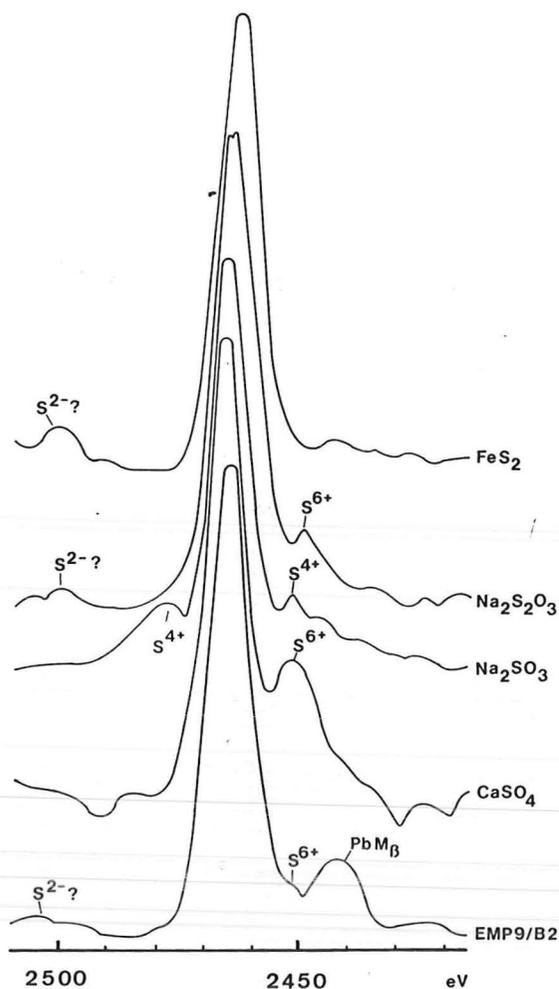


Fig. 4. Emission spectra of the SK $\beta$  line in standard specimens of FeS<sub>2</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub>, and CaSO<sub>4</sub>, and in viaeneite (Table 3) showing a S<sup>6+</sup> satellite near 2450 eV.

greyish-brown through orange to yellow-orange. Reflectance dispersion curves agree with the observed pleochroism showing maxima in the red part of the spectrum (Fig. 2, Table 2).

Under crossed nicols, viaeneite shows strong anisotropy with colours: orange, yellow-orange and greenish-grey. Reflectance values were measured on a freshly polished surface with an automated Opton reflectance set using a SiC standard in air and in oil with  $n = 1.518$ . The mineral is significantly darker than the associated pyrite or marcasite (Table 1). The lowest reflectance values are observed at 420 nm (Fig. 2, Table 2) both in air and in oil. The highest R % values appear in oil at 589 nm, but in air they appear as a very broad maximum in the red part of the spectrum.

When viaeneite is exposed to air it tarnishes within a few weeks. However, it remains unchanged when the mineral is kept in an air-tight container.

### Chemical data

The chemical composition of viaeneite was determined with a Cameca Camebax microprobe at CAMST (Centre d'Analyse par Microsonde pour les Sciences) of the Université Catholique de Louvain at 25 kV using the following X-ray lines, with synthetic compounds and pure element standards: SK $\alpha$  & FeK $\alpha$  (FeS<sub>2</sub>), MnK $\alpha$ , CoK $\alpha$ , NiK $\alpha$ , ZnK $\alpha$ , AsL $\alpha$ , TlL $\alpha$  and PbM $\alpha$  (PbS). Oxygen was analysed at 10 kV using Fe<sub>2</sub>O<sub>3</sub> as a standard.

Table 4. Sulphur valency measured in viaeneite by the  $SK\alpha$  and  $SK\beta$  shifts compared to the valency deduced from the chemical composition (VDCC).

SAMPLE	EMP9/B1	EMP9/B2	EMP9/B3	(Fe,Pb) <sub>4</sub> S <sub>8</sub> O	FeS <sub>2</sub>	CaSO <sub>4</sub>
SK $\alpha$ PEAK (eV)	2304.04	2304.06	2304.06		2303.94	2305.21
	$\pm 0.05$	$\pm 0.00$	$\pm 0.05$		$\pm 0.02$	$\pm 0.11$
SHIFT (eV)	+0.10	+0.12	+0.12		0.00	+1.27
VALENCY	-0.40	-0.30	-0.30		-1.00	+6.00
SK $\beta$ PEAK (eV)	2461.78	2461.79	2461.82		2461.69	2463.29
	$\pm 0.11$	$\pm 0.11$	$\pm 0.11$		$\pm 0.12$	$\pm 0.11$
SHIFT (eV)	+0.19	+0.20	+0.23		0.00	+1.60
VALENCY	-0.50	-0.40	-0.30		-1.00	+6.00
VDCC	-0.29	-0.25	-0.23	-0.29	-1.00	+6.00
S <sup>2-</sup> <sub>2</sub>	11.0054	10.7987	10.7140	11.0000	1.0000	0.0000
S <sup>2-</sup>	0.9946	1.2013	1.2860	1.0000	0.0000	0.0000
S <sup>6+</sup>	0.9946	1.2013	1.2860	1.0000	0.0000	1.0000

Viaeneite is composed of S, Fe, Pb and O as main elements. Ni, Zn and As are present in trace amounts (Table 3). The S concentration is very uniform, while Fe and Pb are anticorrelated. The oxygen contents calculated by difference and measured using a Fe<sub>2</sub>O<sub>3</sub> standard are very close, reflecting the good quality of the electron microprobe measurements. The empirical formula based on 8 sulphur atoms is: (Fe<sub>3.91</sub>Pb<sub>0.10</sub>Ni<sub>0.02</sub>)<sub>4.03</sub>(S<sub>8.00</sub>As<sub>0.01</sub>)<sub>8.01</sub>O<sub>1.16</sub>. The simplified formula is (Fe,Pb)<sub>4</sub>S<sub>8</sub>O. Lead is incorporated into the formula because it is always present in viaeneite (Table 3) as well as in other compounds with double sulphur valencies in amounts in excess of 3-4 wt.% (Kucha & Viaene, 1993). It seems that lead may stabilize the structure of the compounds discussed here.

### S and Fe valencies

Sulphur valency can be determined from valency-related shifts of the  $SK\alpha$  and  $SK\beta$  lines using X-ray fluorescence (XRF) (Faesler & Goehring, 1952; Lehr *et al.*, 1980) but it can also

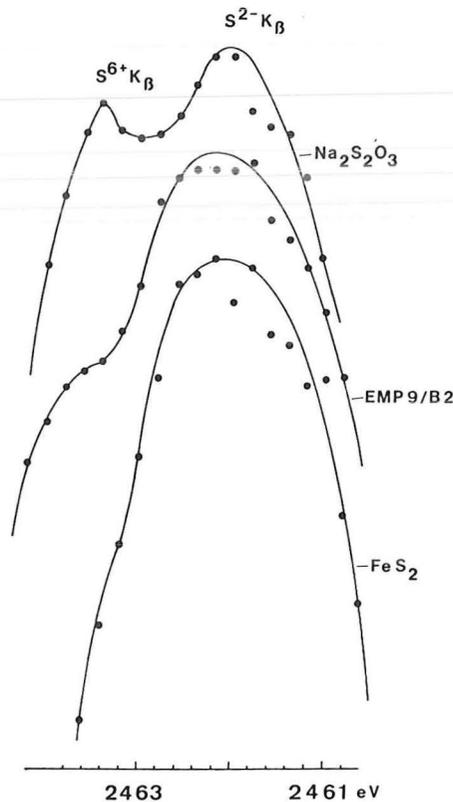


Fig. 5. Fine scans of the  $SK\beta$  peak top in standard specimens of FeS<sub>2</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and in viaeneite (EMP9/B2). A second  $SK\beta$  peak in viaeneite is apparent on a low-energy shoulder of the main peak.

Table 5. XRD pattern of (Fe,Pb)<sub>4</sub>S<sub>8</sub>O, CoK $\alpha$ , Fe filter ( $\text{\AA}$ ). (d-diffuse, bd-broad diffuse).

I	d <sub>meas</sub>	d <sub>calc</sub>	hkl
1d	4.82	4.84,4.86	200,011
3	4.22	4.23	111
1bd	3.80-3.60	3.74-3.65	201,020
5	3.43	3.41	120
1	3.26	3.27	002
2	3.03	3.02	102
10	2.709	2.711	221
8	2.419	2.420	400
7	2.323	2.323	122
2	2.230	2.230	131
3bd	2.08-2.05	2.076-2.054	113,203, 231,013
6	1.925	1.924	203
1	1.870	1.868	402
1	1.820	1.820	040
8	1.758	1.760,1.753	511,041
2	1.723	1.718	141
3	1.701	1.704	240
3	1.682	1.683	431
2bd	1.635	1.634,1.636	004,241
5	1.595	1.595	114,014
3	1.538	1.536	423
1	1.525	1.526	341
4	1.505	1.508	204
4	1.434	1.436	441
1	1.406	1.404	441
4	1.372	1.372	143,251
2bd	1.316	1.314,1.311	324,152
		1.322	243
2bd	1.303	1.304,1.302	442,404
3	1.215	1.216	044
2	1.210	1.210	800,060
3	1.193	1.194	153
5	1.162	1.161	244
2bd	1.111	1.110	405
5	1.092	1.089	006
2	1.072	1.072	435
3	1.058	1.059	444
1	1.046	1.049	354
5bd	1.035	1.037	226
2	1.015	1.014	454
3	1.009	1.008	840
5	0.9911	0.9904	913
4	0.9859	0.9852	841
6	0.9605	0.9609	922
7	0.9576	0.9574	535
3	0.9374	0.9374	173
2	0.9307	0.9306	246
2	0.9176	0.9172	645
3	0.9133	0.9125	571

be quantitatively measured using the electron microprobe (Kucha *et al.*, 1989). The SK $\alpha$  and SK $\beta$  emission wavelengths are valency-dependent (Fig. 3a, b). The SK $\alpha$  shift between sulphide, S<sup>2-</sup>, and sulphate, S<sup>6+</sup>, was found by XRF to be 1.33 eV (Faesler & Goehring, 1952), 1.37 eV (Lehr *et al.*, 1980) and 1.43 by microprobe (Kucha *et al.*, 1989). The SK $\beta$  wavelength difference between sulphide and sulphate was measured by XRF to be 2 eV (Jenkins & de Vries, 1975). A value of

1.78 eV was obtained by microprobe (Kucha *et al.*, 1989) compared with 1.88 eV in this study (Fig. 3b). The fine structure of the SK $\beta$  line reveals valency-related satellites (Faesler & Schmid, 1954) on either side of the sulphite K $\beta$  peak, but only one on the low-energy side of the sulphate K $\beta$  peak (Fig. 4). Thiosulphate shows a similar S<sup>6+</sup>-related satellite but half as intense as in sulphate (Kucha *et al.*, 1989). Taking into account valency-related shifts of the SK $\alpha$  and SK $\beta$  lines as well, sulphur valency can be determined quantitatively in sulphur compounds (Kucha *et al.*, 1989).

Sulphur valency was determined at the Institute of Material Sciences, Katholieke Universiteit Leuven, with a Jeol 733 microprobe automated with a Tracor Northern software package, using an accelerating voltage of 20 kV with a beam spot size of 15  $\mu\text{m}$ . The spectrometer with a PET crystal was calibrated using the following sulphur standards: CaSO<sub>4</sub>, CaSO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, S, FeS<sub>2</sub> and FeS. Cubic FeS<sub>2</sub> was used as a zero reference point determined directly before and after a given microarea was tested. When the drift of the zero reference point was smaller than one standard deviation (one  $\sigma$ ) the measurement was accepted. The sulphur valency was calculated by procedures developed for the electron microprobe (Kucha *et al.*, 1989).

Iron valency was determined by measurement of the FeK $\beta$  shift (Kucha *et al.*, 1989) with a Jeol 733 microprobe at 20 kV using a spectrometer with a LiF crystal, automated with a Tracor Northern software package. Cubic FeS<sub>2</sub> was used as a reference standard.

The presence of oxygen in viaeneite (Table 3) suggests the occurrence of a second sulphur valency or oxide. The SK $\alpha$  and SK $\beta$  emission peaks are shifted towards higher sulphur valencies as compared with the pyrite standard (Fig. 3a, b). The average SK $\alpha$  shift in viaeneite is +0.11 eV, corresponding to a S valence of -0.33 (Table 4). The SK $\beta$  peak shift +0.21 eV is equivalent to a S valency of -0.40 (Table 4). The theoretical S valency of (Fe,Pb)<sub>4</sub>S<sub>8</sub>O is -0.29 (Table 4). There is therefore a good agreement between the sulphur valency required by the ideal formula and the sulphur valency derived from valency-related shifts. In particular, this is true for the SK $\alpha$  shift, which systematically provides more accurate results than the SK $\beta$  shift (Kucha *et al.*, 1989).

A scan of the X-ray emission spectrum around the SK $\beta$  peak in viaeneite (Fig. 4) indicates the

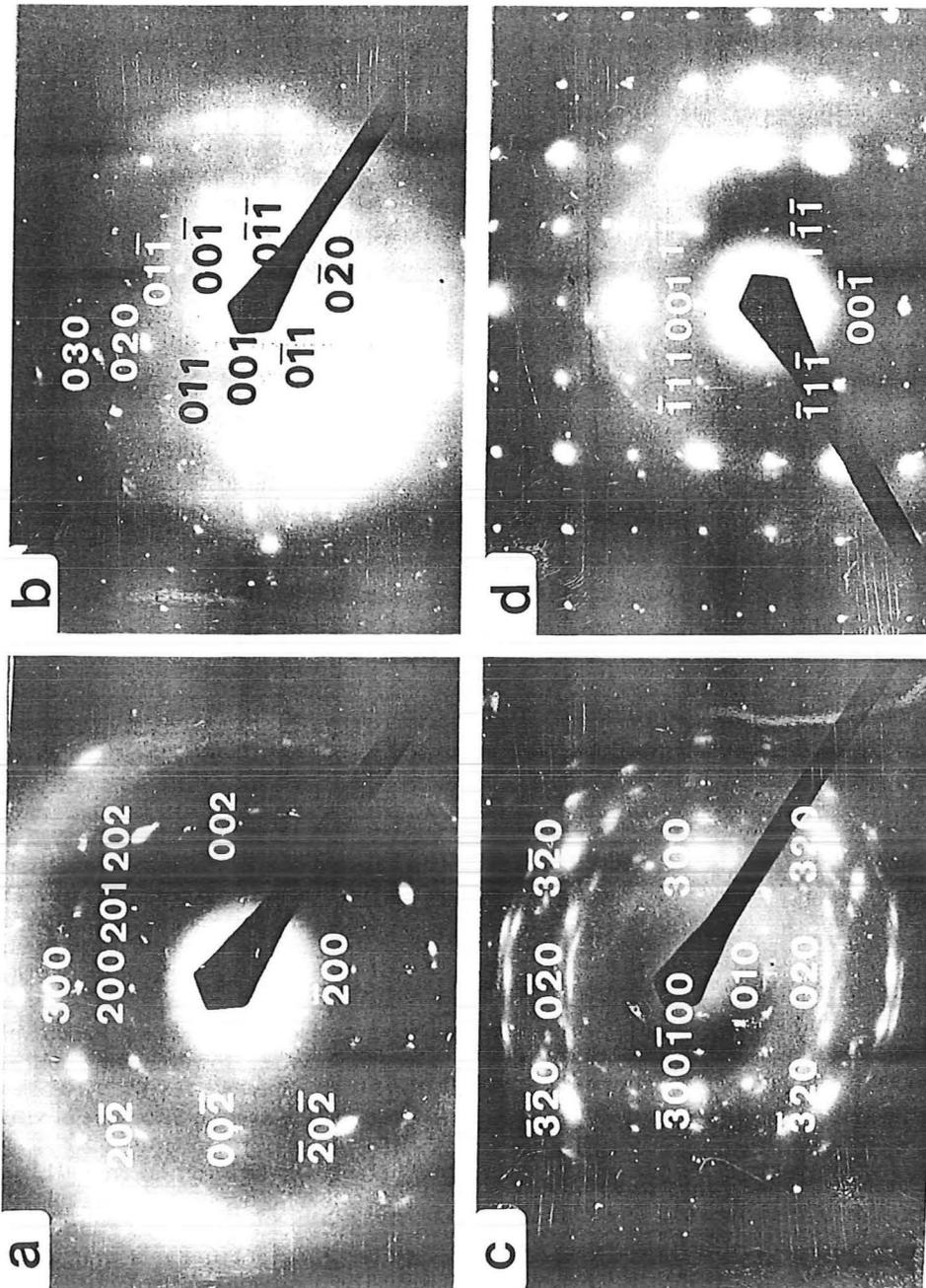


Fig. 6. Single crystal electron diffraction patterns of viaeneite: a) 010, b) 100, c) 001, d) 110.

presence of one satellite at the position of  $S^{6+}$ . A fine scan of the  $SK\beta$  peak top (Fig. 5) shows the main viaeneite peak coinciding with a position of

disulphide sulphur in pyrite. It also shows a second peak on the shoulder of the main  $SK\beta$  peak at the expected position of  $S^{6+}$ . This implies that

sulphur in viaeneite exists principally as disulphide (S<sup>2-</sup>) together with some sulphate (S<sup>6+</sup>).

The FeK $\beta$  peak position in viaeneite (7056.28  $\pm$  0.60 eV) is close to that observed in the pyrite standard (7055.93  $\pm$  0.56 eV), which demonstrates that iron valency in both minerals is identical (Kucha *et al.*, 1989). This conclusion enables a calculation of the cation-anion balance of viaeneite and may help to refine its chemical formula. Therefore, assuming that: i) Fe and Pb are divalent, and ii) S occurs mainly as S<sup>2-</sup> pair and less as S<sup>6+</sup>, the anions can only be balanced by cations if thiosulphatic sulphur is included in the formula. The formula meeting all established requirements is then (Fe,Pb)<sub>12</sub>(S<sup>2-</sup>)<sub>11</sub>(S<sub>2</sub>O<sub>3</sub>)<sub>1</sub> (Table 4), which is simplified as (Fe,Pb)<sub>4</sub>S<sub>8</sub>O.

### Crystallography

An X-ray powder pattern of viaeneite was obtained with Fe-filtered CoK $\alpha$  radiation from polycrystalline grains using a 57-mm-diameter Gandolfi camera. The particles were drilled off the polished surface under microscopic control from an area with a diameter of about 40  $\mu$ m.

Attempts to obtain readable X-ray single crystal patterns failed due to the polycrystalline composition of viaeneite extracted from the polished surface. Therefore, single crystal data were obtained using an electron diffraction technique (Kucha *et al.*, 1993). The study was carried on with a JEOL 100C transmission electron microscope (TEM) at 100 kV at the Academy of Mining & Metallurgy, Krakow, Poland. Particles for the TEM investigations were collected under an optical microscope from areas previously analysed by microprobe. The standard specimen was gold film put on one side of the viaeneite specimen on the same supporting electron grid. Such an arrangement provides d-values accurate to  $\pm$  0.5 % of the measured interplanar distance.

The X-ray powder pattern of viaeneite (Table 5) consists of 48 reflections, most of which are sharp and sufficiently intense to be measured accurately. The apparent absence of diffractions with d-values greater than 4.82  $\text{\AA}$  in the viaeneite pattern (Table 5) is due to the broad darkening of the film caused by scattering from fibre and glue. These missing reflections are, however, recovered from electron diffraction patterns (Fig. 6 abcd; Table 6).

The cell parameters of viaeneite were obtained from electron diffraction study using 51 recorded diffraction patterns out of which the basic 100, 010, 001, 110 *etc* (Fig. 6 abcd) were used to define the crystal system and cell parameters, subsequently refined from the indexed XRD pattern (Table 5) using a procedure developed for combined XRD-TEM data sets (Kucha *et al.*, 1993). The following refined cell parameters were obtained:  $a = 9.717 \pm 0.008$ ,  $b = 7.280 \pm 0.006$ ,  $c = 6.559 \pm 0.007$   $\text{\AA}$  and  $\beta = 95.00 \pm 0.03^\circ$ ,  $Z = 2$ . The cell is monoclinic. The space group is not known, but a lack of systematic extinctions observable on XRD and TEM diffraction patterns indicates that it is probably primitive. There is a very good match between the observed XRD pattern and calculated d-values (Table 5). Equally good compatibility exists between measured and calculated d-values of TEM diffraction patterns (Table 6), and between measured and calculated interplanar angles (Kucha *et al.*, 1993).

Table 6. The first 30 d values of viaeneite obtained from TEM ( $\text{\AA}$ ).

d <sub>meas</sub>	d <sub>calc.</sub>	hkl
9.73	9.68	100
7.33	7.28	010
6.46	6.53	001
5.84	5.82	110
5.70	5.65	10 $\bar{1}$
5.27	5.21	101
4.90	4.86	011
4.88	4.84	200
4.50	4.46	11 $\bar{1}$
4.25	4.23	111
4.06	4.06	20 $\bar{1}$
4.06	4.03	210
3.70	3.74	201
3.66	3.64	020
3.57	3.55	21 $\bar{1}$
3.40	3.41	120
3.33	3.32	211
3.28	3.27	002
3.25	3.23	300
3.20	3.18	10 $\bar{2}$ , 021
3.06	3.06	12 $\bar{1}$
3.04	3.02	10 $\bar{2}$
3.01	3.00	30 $\bar{1}$
3.00	2.98	012, 121
2.96	2.95	310
2.93	2.91	11 $\bar{2}$ , 220
2.81	2.82	20 $\bar{2}$
2.81	2.80	301
2.79	2.78	11 $\bar{2}$
2.70	2.71	22 $\bar{1}$

## Morphology

Viaeneite exhibits a tabular habit. No crystal forms could be identified due to the small size of crystallites. No twinning was observed on polished sections. However twinning was observed on some of the 101 electron diffraction patterns. The a:b:c ratio calculated from the cell parameters is 1.3348 : 1 : 0.9010.

## Mineral name

The name is from Prof. Willy Viaene, Katholieke Universiteit Leuven, Belgium, in recognition of his important contributions to the development of geological sciences in Belgium. Viaeneite has been approved by the IMA Commission on New Minerals and Mineral Names.

## Type material

Type material is deposited at the Museum of Natural History, Brussels; it is also preserved and catalogued in the Specimen Library of the Department of Geology KU Leuven under the number KUR32 ONB2 & ONB3; it is also stored at the Faculty of Geology, Academy of Mining & Metallurgy, Kraków, Poland under the number EMP9.

**Acknowledgements:** We acknowledge helpful discussions with Prof. G. King, as well as his grammatical improvements to the manuscript. The work was supported by KU Leuven grant F/86/9 (H.K.).

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Received 6 December 1994

Accepted 29 August 1995