3-1-1989

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DETERMINATION OF SULFUR AND IRON VALENCE BY MICROPROBE

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Abstract

SKα, SKβ and FeKβ valence related wavelength changes are large enough to be measured with microprobe spectrometers. The relative difference between S^{2-} and S^{6+} is measured as 1.27 eV for the SKα line and 1.66 eV for the SKβ line. This SKα and SKβ peak shift is function of the valence. Accurate microprobe measurement of the peak shift allows the determination of the sulfur valence in a microarea. The relative difference between Fe^{2+} and Fe^{3+} for the FeKβ line is 0.94 eV. Considering the achieved accuracy of measurements, this peak can only be used for an approximate determination of the iron valence in a microarea.

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Introduction

Elements below atomic number 18 have unfilled 3p orbitals. Since the Kβ line arises from a transition from this level, the wavelength of the Kβ line for these elements is coordination/valence dependent (Jenkins & De Vries, 1975). The same is true to a lesser extent for the Kα_1 and Kα_2 lines of these elements, which arise from 2p transitions. Sulfur is an element which occurs in 5 valence stages : -2, 0, $+2$, $+4$ and $+6$. The wavelength difference for the SKα line in sulfide and sulphate was found by X-ray spectrometry to be 1.37 eV (Lehr et al., 1980). The wavelength difference corresponding to the SKβ shift between sulfide and sulphate is larger. It was found by X-ray spectrometry to be about 2 eV (Jenkins & De Vries, 1975) or 3.3 eV using a modified NaCl spectrometer (Birks & Gilfrich, 1978) or even 6.5 eV as determined by a rather more sensitive technique of electron spectroscopy (Hagstrom et al., 1964, see Jenkins and De Vries, 1975). The value of the sulfide-sulphate shift in X-ray spectrometry depends on the type and quality of the applied crystals. Fine structure of SKβ lines reveals the presence of satellites on both sides of the sulfide Kβ peak and only one but stronger satellite on the sulphate Kβ peak (Birks & Gilfrich, 1978). In thiosulphate a double peak, corresponding to S^{2-} and S^{6+} is revealed (Jenkins & De Vries, 1978).

The SKβ peak is also coordination dependent. This was demonstrated in synthetic MnS polymorphs by Kβ emission and absorption spectra (Sugiura et al., 1972), and in sulfur minerals by microprobe (Lovering et al., 1968). However, the SKβ peak position difference of 0.09 eV between cubic and orthorhombic FeS_2 stays within the error of measurement of the JEOL 733 probe used in this study.

Wavelength shifts were also observed in Kβ lines of the transition elements. Since these elements have only partially filled 3d orbitals the Kβ wavelengths are also coordination/valence dependent (Jenkins & De Vries, 1975).

The K X-ray emission spectra of cations with 2p valence electrons are also suitable to

study the energy relationships between the outer electronic shells in ionic crystals (Best, 1971).

Changes in X-ray emission spectra caused by oxidation of metals are most extensively studied using the L lines. The related wavelength shifts are small, but the $L\beta/L\alpha$ intensity ratio increase is considerable for the oxides compared to the metals (Fisher, 1965). A systematic increase of the $FeL\beta/L\alpha$ intensity ratio occurs in the Fe^{2+} and Fe^{3+} oxides : magnetite-ulvite and hematite-ilmenite and in the anhydrous silicates (Albee and Chodos, 1970). However, in more complex minerals the $L\beta/L\alpha$ ratio can provide only qualitative information concerning Fe^{2+}/Fe^{3+} (O'Nions and Smith, 1971). More recently it has been indicated that the $L\beta/L\alpha$ may provide quantitative information on the iron valence within one mineral series (Jasienska and Nowak, 1987).

However, the use of the $FeL\alpha$ and $L\beta$ lines in EPMA has some serious inconveniences : i) the intensity variation with accelerating voltage, ii) the low intensities of the L lines, iii) the rapid variation of the absorption related to the change in λ makes it difficult to distinguish spectral change due to a valence/bond association or due to the self absorption phenomena. It is the aim of this study to discuss an application of a microprobe to determine the S and Fe valence in a microarea of samples containing oxidation-reduction products of metalsulfides and -sulphates.

Materials and methods of investigation

Valence related shifts were measured with a commercial JEOL 733 probe automated with a Tracor Northern software package. Spectrometer and stage movements are motor driven. After a rough peak location an accurate peak scan was performed. Peak position was calculated by least squares data fitting. After peak position calculations, the specimen stage was moved for 30 µm and the peak calculation was repeated up to 7 times. The repeated measurements were used to calculate the standard deviation. The peak structure and surrounding area was scanned using steps of 0.02 L units with a dwell time of 5 seconds. The peak top was scanned using steps of 0.01 L units with a dwell time of 5 seconds, where

$$L = \frac{2R}{2d} \cdot n\lambda \qquad (1)$$

2R – diameter of Rowland circle, JEOL :
    R = 140 mm
2d – spacing of analyzing crystal (Å)
    (PET : $2d_{002}$ = 8.742 Å)
λ – wavelength (Å)
n – order of reflection

Synthetic FeS_2, ZnS, S, $Na_2S_2O_3$, Na_2SO_3, $CaSO_4$, $BaSO_4$, Fe_2O_3 and Fe_3O_4 were used as standard specimens. All samples were freshly

polished, except $Na_2S_2O_3$ and Na_2SO_3 where crystal surfaces have been obtained by cleavage. To provide a good surface conductivity the standards and the samples were covered with a carbon film of 200 Å thickness. Using an accelerating voltage of 20 kV a good peak to background ratio was obtained; e.g, for FeS_2 $SK\alpha$ ca 250:1, $SK\beta$ ca 20:1 and $FeK\beta$ ca 50:1. To prevent heat damage and decomposition of the samples a beam diameter of 25 µm has been used.

All the measurements were performed using a FeS_2 standard as sulfur and iron zero reference point. The spectrometer was recalibrated after each 3 to 5 measurement sets because of time drift of the zero reference point. The composition of melnikovite was determined with a Camebax probe at 20 kV using following spectral lines and synthetic standards : $SK\alpha$ and $FeK\alpha$ (FeS_2), $MnK\alpha$ ($MnSiO_3$), $NiK\alpha$, $ZnK\alpha$ (ZnS), $AsL\alpha$, $TlM\alpha$, $PbM\alpha$ (PbS). The oxygen content was determined by difference, and was checked using a Fe_2O_3 standard. A partition of sulfur for stoichiometric calculations was based on the $SK\alpha$ and $SK\beta$ valence shifts, the presence of valence characteristic satellites and the presence or absence of a double peak on fine $SK\beta$ scans. Fe bound to sulfur was assumed to be Fe^{2+}. The rest of the iron, according to X-ray diffraction measurements, was calculated as goethite (FeOOH) where iron is in the form of Fe^{3+}. H was calculated to balance the FeOOH formula.

A poor selection of standards for sulfur concentration measurement may be an important source of error. For example, with the FeS_2 standard the measured sulfur concentration in $CaSO_4$ falls 2.5 wt% short of the real value because the used ZAF correction program does not include corrections for the valence related shifts.

Sulfur valence determination from the $SK\alpha$ shift

The $SK\alpha$ line has a high intensity and is free of coincidences (table 1). The components α_1 and α_2 cannot be resolved with the PET crystal used. A measured difference between the sulfidic and sulphatic $K\alpha$ line is 1.27 eV, and agrees within an error of measurement with the value of 1.37 eV obtained by X-ray spectrometry (Lehr et al., 1980). A relationship between the S valence and the $SK\alpha$ shift can be approximated by a straight line (figure 1). This type of relationship allows one to perform a relatively accurate determination of an average sulfur valence (table 2). A double $SK\alpha$ peak cannot be resolved in thiosulphate.

Sulfur valence determination from the $SK\beta$ shift

The relationship between the shift and the valence for the $SK\beta$ line can also be approximated by a straight line (figure 2). The accuracy of the measurements on the $SK\beta$ line is less good than on the $SK\alpha$ line (table 2). Yet, the $SK\beta$ line has some important advantages over

Table 1

X-ray emission wavelengths and L-value table of SKα, SKβ, SKβ satellites in sulphate, sulfite and thiosulphate, and overlapping Pb and Ba spectral lines (after JEOL).

Spectral line	N	Intensity	keV	n λ (Å)	L (PET)
SKα$_{1,2}$	1	150	2.307	5.37309	172.1000
SKα$_3$	1	45	2.321	5.34077	171.0600
SKα$_4$	1	45	2.324	5.33415	170.8500
SKβ$_1$	1	7	2.464	5.03160	161.1600
SKβ$_x$	1	7	2.468	5.02330	160.8900
S^{6+}Kβ satellite		2.5			161.9
S^{4+}Kβ satellite		1.2			161.1 and 160.65
$S^{2-,6+}$Kβ satellite		0.7			162.1
PbM$_4$–O$_2$	1	1	2.477	5.00400	160.2700
BaLβ$_3$	2	6	4.926	5.03280	161.2000
PbLβ$_4$	5	4	12.304	5.03750	161.3500
PbLγ$_1$	6	10	14.762	5.03838	161.3800
PbMβ	1	60	2.442	5.07600	162.5800

N – order of reflection
L – peak position on JEOL spectrometer

Table 2

Effect of valence state on sulfur Kα and Kβ emission energy, calculated as a difference from FeS$_2$ standard (JEOL spectrometer – PET crystal).

| Sulfur Compound	Valence	ΔL SKα	δ	ΔeV	ΔL SKβ	δ	ΔeV
FeS$_2$	–2	0.0000	±0.0050	0.00	0.0000	±0.0060	0.00
ZnS	–2	0.0000	±0.0050	0.00	0.0021	±0.0053	0.03
S	0	0.0110	±0.0045	0.13	0.0100	±0.0143	0.15
Na$_2$S$_2$O$_3$	–2,+6	0.0352	±0.0073	0.47	0.0408	±0.0133	0.63
Na$_2$SO$_3$	+4	0.0750	±0.0079	1.00	0.0747	±0.0092	1.14
CaSO$_4$	+6	0.0953	±0.0082	1.27	0.1082	±0.0142	1.66
BaSO$_4$	+6	0.0903	±0.0096	1.21	0.1179	±0.0198	1.80
Spectrometer step		0.01		0.13	0.01		0.15

δ – standard deviation

$$L = \frac{2R}{2d} \cdot n\lambda$$

2R – diameter of Rowland circle (mm), JEOL spectrometer : R = 140
2D – spacing of analysing crystal (Å), PET : 2d$_{002}$ = 8.742
λ – wavelength (Å)
n – order of reflection
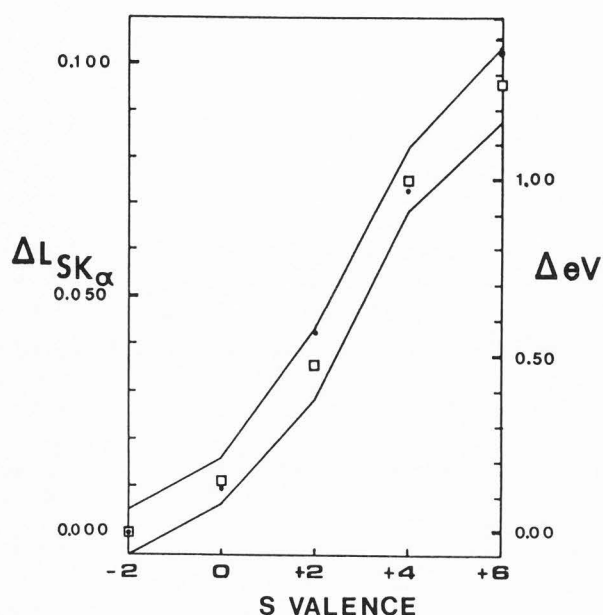
•Lehr et al.(1980)
□This study

Fig. 1. SKα shift plotted against sulfur valence. The vertical scale is in eV and L values of JEOL spectrometer with PET crystal. The two solid lines show one standard deviation.
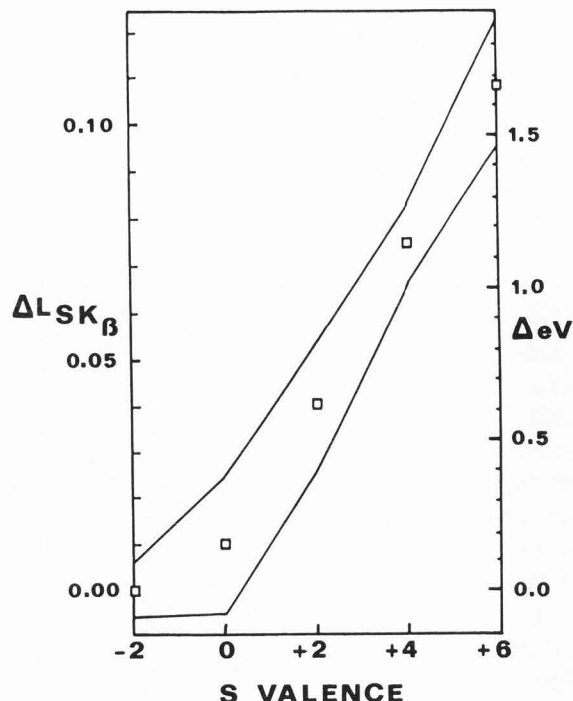

Fig. 2. SKβ shift plotted versus sulfur valence. The vertical scale is in eV and the L values of JEOL spectrometer with PET crystal. The two solid lines show one standard deviation.

the SKα peak : i) the shift between S^{2-} and S^{6+} is larger (table 2), ii) sulphate has one strong satellite, sulfite has two on both sides of the main peak, and thiosulphate has one (table 1, figure 3), and iii) two peaks can be resolved on fine SKβ scans of thiosulphate. Compounds containing the sulfidic sulfur have a very weak satellite marked as S^{2-} (figure 3). This satellite is also seen in elemental sulfur (figure 3). The nature of this weak satellite requires further study using a larger number of standards with sulfidic sulfur. Despite important advantages the SKβ line has a lower intensity than the SKα and may suffer from coincidences with Ba and Pb (table 1). A Pb content higher than 2 wt% hides the SKβ satellites and affects the main SKβ peak. The determination of both the SKα and SKβ lines is recommended for the study of the sulfur valence states.

Iron valence determination from the FeKβ shift

The difference between Fe^{2+} and Fe^{3+} on the FeKβ line was measured as 0.94 eV (table 3). The relationship between the iron valence and the FeKβ shift is not linear as shown in figure 4 by the Fe_3O_4 position. The relation-

ship seems to be controlled by both the valence and the coordination number. This problem, however, requires a further study using a wider range of different, reliable iron standards. Considering the level of precision achieved (table 3) a microprobe can be used for a rough estimation of the Fe valence in a microarea by measuring the FeKβ shift.

Table 3

Effect of valence state on iron FeKβ emission energy calculated as a difference from FeS_2 standard (JEOL spectrometer – LiF crystal, 2d = 4.0267 Å)

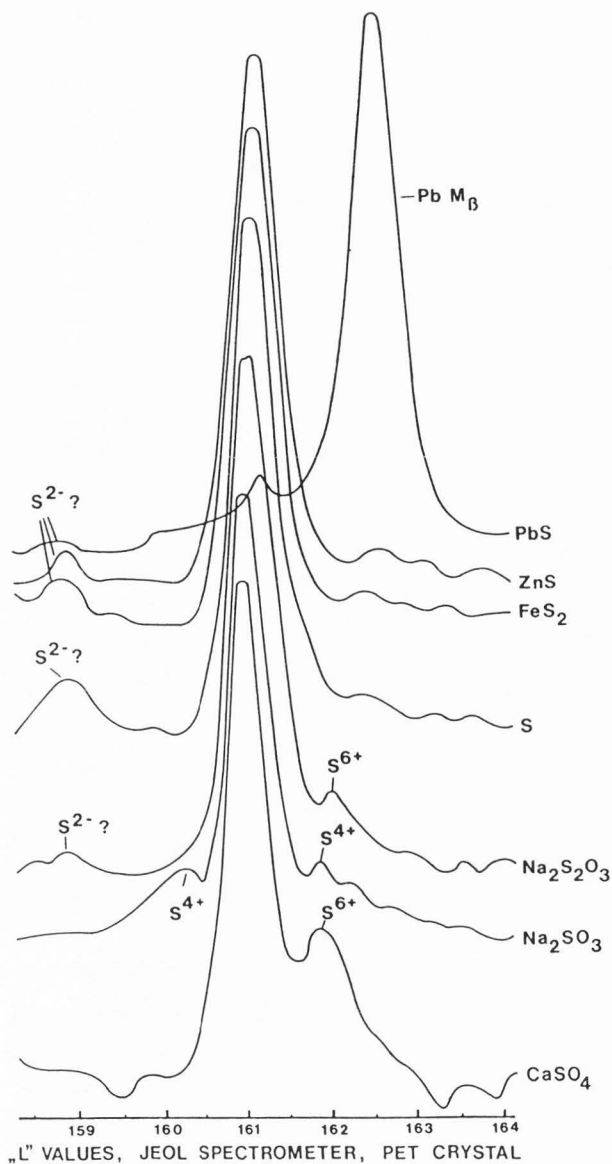| Iron com-pound	Valence	L	δ	eV
FeS_2	+2	0.0000	±0.0039	0.00
Fe_3O_4	0.333 +2	0.0223	±0.0033	1.28
	0.667 +3			
Fe_2O_3	+3	0.0253	±0.0035	1.46
Spectrometer step		0.01		0.58

"L" VALUES, JEOL SPECTROMETER, PET CRYSTAL

Fig. 3. Scans of the SKβ line in different synthetic compounds. Sulphate has one satellite, sulfite two on either side of the main peak, thiosulphate one satellite related to the S^{6+} and another weak one probably related to the S^{2-}. A weak S^{2-} satellite is also shown by sulfides.

Fig. 4. FeKβ shift plotted versus iron valence. The vertical scale is in eV and the L values of a JEOL spectrometer with LiF crystal. The two solid lines show one standard deviation.

starting measurements. The use of a microprobe with a stabilized beam current, or a continuous beam current printout will improve the accuracy of the measurements.

The specimen/standard positioning in the Z-axis. A deviation of the specimen from the standard position in the vertical Z-axis can cause shifts of the measured X-ray peaks. To avoid such an error standards were mounted side by side in a metal ring and polished together. In the analysis of melnikovite a FeS_2-reference standard was mounted in a metal ring next to the melnikovite and both were polished together.

Acceleration voltage. Small changes in the SKβ peak shape were noticed when the acceleration voltage was changed from 15 to 20 kV. The phenomenon is probably of the same origin as in the case of Al (Maruno and Fujii, 1970). It suggests that recalibration of the spectrometer is necessary if accelerating voltage is changed.

Thermal drift of the crystal. A PET crystal is particularly temperature sensitive (Jenkins and De Vries, 1975) and requires a frequent recalibration of the zero reference point. Measurements over an extended period of time on the FeS_2 standard indicate that results are reproducible within 30 minutes. This enables us to perform a set of 3-time repeated measurements on 3 to 5 microareas before recalibration is necessary. The use of another analysing crystal may improve the measurement accuracy.

Chemical decomposition of samples caused by heat produced by electron bombardment. This negative effect can be avoided by using an electron beam of 25 μm diameter instead of a submicron focused spot. Using a 25 μm beam no side effects were observed even over an extended period of time, with the exception of the native sulfur crystals.

Accuracy, reproducibility and method limitation

The main factors affecting measurement accuracy are :

Beam intensity drift. Drift can almost be excluded by a careful and precise recentering of the electron filament with respect to the Wehnelt cap and by a filament preheating of about 0.5 hour on a low current and of about 1 hour on the normal emission current before
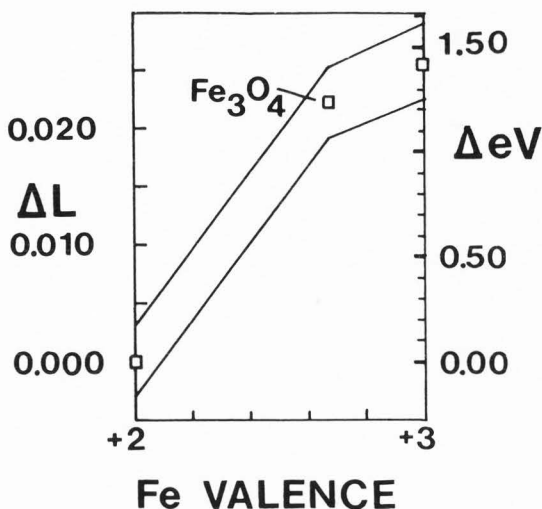
Table 4   Chemical composition of concentrically banded sphere (fig. 7) composite of melnikovite-pyrite, wt%.

Sample	S	Mn	Fe	Ni	Zn	As	Pb	Total	O (Diff.)
EMP9/D1	4.40	0.10	49.08	0.08	2.15	0.19	1.20	57.19	42.81
EMP9/D2	10.46	0.05	49.13	0.14	2.01	0.20	1.36	63.34	36.66
EMP9/D3	5.15	0.10	48.33	0.06	2.44	0.19	1.16	57.42	42.58
EMP9/D4	6.93	0.04	48.38	0.09	2.47	0.16	1.55	59.62	40.38
EMP9/D5	13.17	0.04	49.59	0.12	1.88	0.19	1.39	66.34	33.66
EMP9/D6	16.94	0.04	49.83	0.20	1.69	0.19	1.30	70.14	29.86
EMP9/D7	19.00	0.04	48.99	0.16	1.48	0.14	2.21	71.97	28.03

Table 5   Iron and sulfur valence determined in melnikovite by measuring the shift of $FeK\beta$ and $SK\alpha$ lines using FeS_2 as a zero reference point, and using relationships shown in figures 1 and 4.

	$FeK\beta$	ΔL	Valence by chemical shift Fe^{2+}	Fe^{3+}	$SK\alpha$	ΔL	S valence by chemical shift (average)	S valence by chemical composition
D1	122.1348 ±0.0054	0.0270	0.0	1.0				
D2	122.1395 ±0.0099	0.0222	0.1	0.9	172.2718 ±0.0108	0.0575	+3	+4
D3	122.1534 ±0.0114	0.0084	0.7	0.3	172.2084 ±0.0125	0.1209	+6	+6
D4	122.1400 ±0.0093	0.0217	0.1	0.9	172.3070 ±0.0081	0.0223	+1.3	+1 (−2,+6)
D5	122.1415 ±0.0085	0.0203	0.2	0.8	172.2966 ±0.0035	0.0327	+2	+2 (−2,+6)
D6	122.1492 ±0.0069	0.0125	0.5	0.5	172.3176 ±0.0042	0.0117	+1.3	+2 (−2,+4)
D7	122.1462 ±0.0074	0.0156	0.4	0.6	172.3000 ±0.0063	0.0293	+1.8	+1.8 (−2,+4)
FeS_2	122.1617 ±0.0097	0.0000	1.0	0.0	172.3293 ±0.0011	0.0000	−2	

Table 6   A partition of sulfur and iron between different valence states deduced from chemical composition (Table 4); upper figure wt%, lower figure atomic proportions

	S^{2-}	S^{4+}	S^{6+}	Fe^{2+}	Fe^{3+}	Ni	Zn	As*	Pb	H	O
D2		10.46 0.2611		16.00 0.2611	33.14 0.4750	0.14 0.0019	2.01 0.0246	0.20 0.0024	1.36 0.0054	0.60 0.4750	34.74
D3			5.15 0.1495	6.52 0.1086	41.81 0.6970	0.06 0.0010	2.44 0.0347	0.19 0.0023	1.16 0.0052	0.76 0.6970	34.35
D4	3.47 0.0955	3.47 0.0955		9.47 0.1497	38.91 0.6154	0.09 0.0013	2.47 0.0334	0.16 0.0019	1.55 0.0066	0.70 0.6154	27.54
D5	6.58 0.1534		6.58 0.1534	20.83 0.2787	28.76 0.3847	0.12 0.0015	1.88 0.0215	0.19 0.0019	1.39 0.0050	0.52 0.3847	29.68
D6	5.64 0.1206	11.30 0.2416		27.93 0.3429	21.90 0.2689	0.20 0.0023	1.69 0.0127	0.19 0.0017	1.30 0.0043	0.40 0.2689	29.52
D7	7.34 0.1519	11.66 0.2411		31.08 0.3691	18.17 0.2158	0.16 0.0020	1.48 0.0150	0.14 0.0013	2.21 0.0071	0.32 0.2128	27.76

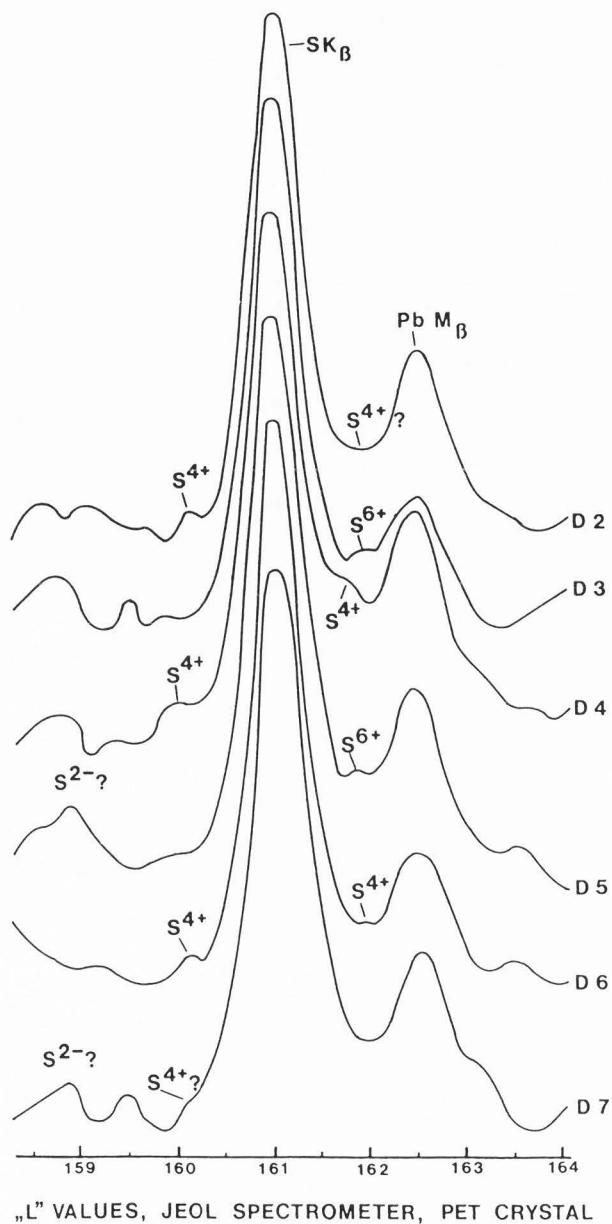* as As_2O_3 Fe^{2+}, Ni, Zn, Pb – bound to sulfur Fe^{3+} as FeOOH (goethite by X-ray diffraction)

Fig. 5. Scans of the SKβ line in melnikovite (fig. 7). Spectra are partly obscured by the PbMβ line, but in most cases the S^{4+} and the S^{6+} satellites are resolved.

„L" VALUES, JEOL SPECTROMETER, PET CRYSTAL

Fig. 6. Fine structure of the SKβ line in thiosulphate and melnikovite. Double peak is resolved in melnikovite in points D4 and D5.

Chemical composition limitations. The main limitations of the method are due to the instrumentation as discussed above and to coincidences of spectral lines with Pb. Lead at higher concentrations seriously disturbs the SKβ use.

A sulfur valence determination using only the straight line approximation (figures 1,2) is applicable when one sulfur valence is present. If two sulfur valences are present in the sample, their presence may be detected by a detailed scan of the SKβ line 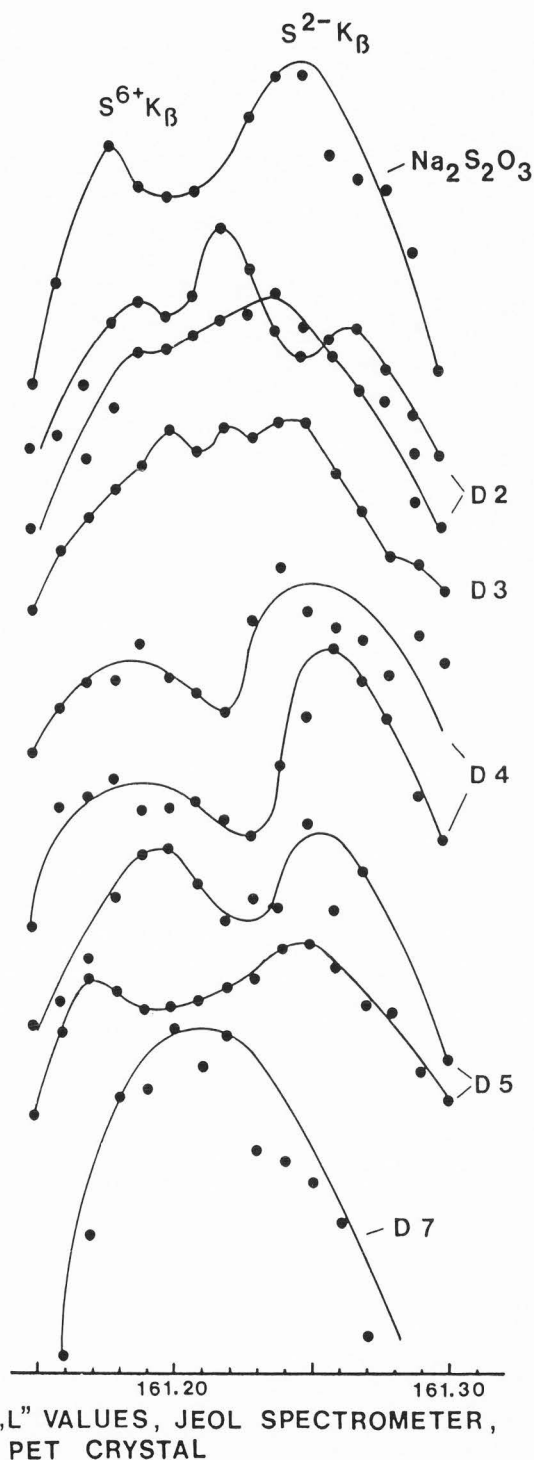(figures 3,6). In thiosulphate a double SKβ peak is resolved (figure 6), while sulphate and sulfite have different satellites (figure 3), table 1). However, these satellites are weak and therefore sulfur with a second valence cannot be detected if the amount is less than 1/5 of the total
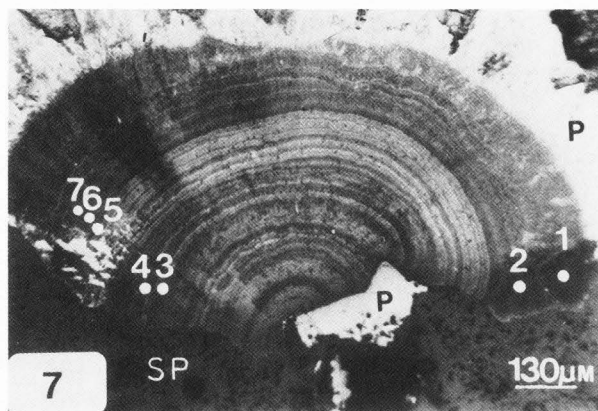
Fig. 7. Photomicrograph of melnikovite composed of recurrent darker and brighter spheres by reflected light in a Zn-Pb ore from Engis, Belgium. Arabic numerals 1 to 7 represent spots of microprobe measurements D1 to D7 (Table 4). P - pyrite, SP - sphalerite.

sulfur content. Despite the discussed limitations the method may be useful in studying the mechanisms of oxidation of sulfides, reduction of sulphates and corrosion of metals in environments rich in SO_2 and SO_4.

An example of application

The valence related shift of SKα and SKβ lines has been used to study melnikovite (figure 7). Melnikovite is composed of recurrent darker and brighter spherical layers.

The darker layers have a reflectivity in air of 16.6-17.6 %, the brighter of 51-53 %. X-ray diffraction data indicate the presence of goethite FeOOH, cubic and orthorombic FeS_2 and lines of an unknown phase. Despite the fact that melnikovite is a very common mineral substance that has been studied for over 50 years no exact chemical formula has been given to it (Ramdohr, 1969). FeS_2, FeS and H_2O are usually reported as major mineral constituents of melnikovite with minor amounts of Pb and As.

The melnikovite studied is composed mainly of Fe, O and S with minor amounts of Pb and Zn (table 4). Oxygen calculated by difference and determined with a Fe_2O_3-standard give similar values.

The iron valence was measured with the FeKβ line, the sulfur valence with the SKα (table 5) and the sulfur satellites with the SKβ line (figure 5). The presence of the S^{6+} and S^{2-} split in thiosulphates was checked using fine scans of the SKβ line (figure 6).
A comparison between values derived from a shift measurement (table 5) and deduced from the measured chemical composition (tables 4,6) show rather good compatibility for sulfur. The deduced sulfur valence is also in good agreement with a fine SKβ peak structure (figure 6) and with the observed SKβ satellites (figure 5).

Poor results for the Fe valence measurements are related to the Fe standards which are probably inadequate in this case. The use of FeOOH, though to be more reliable, instead of Fe_2O_3 or Fe_3O_4 may give better results. This problem requires further study.

Taking into account the observed optical properties (figure 7), the results of X-ray powder diffraction, the measured chemical composition (table 4) and the SKα and SKβ spectra (table 5, figures 5,6) the melnikovite studied is composed of syntaxial intergrowths of goethite, pyrite, Fe-sulfite and Fe-thiosulphate.

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Discussion with reviewers

R.H. Packwood : If memory serves me correctly, the JEOL 733 on which $\Delta\lambda$ was determined does not have column isolation windows on the spectrometer ports and as a result has a rather high contamination rate.   Did you experience any difficulty with carbon contamination ?

Authors : The JEOL 733 used for this study is equipped with a liquid nitrogen trap and baffle. With an accelerating potential of 20 kV and with the beam in spot mode the carbon contamination is measured on a freshly polished pure Fe standard over 2 hours.   A contamination rate of 0,0025 wt% C/min is observed.