

Detection of elemental sulphur on galena oxidized in acidic solution

I. Kartio ^{a,*}, G. Wittstock ^b, K. Laajalehto ^a, D. Hirsch ^c,
J. Simola ^a, T. Laiho ^a, R. Szargan ^b, E. Suoninen ^a

^a *Laboratory of Materials Science, Department of Applied Physics, University of Turku, Vesilinnantie 5,
FIN-20014 Turku, Finland*

^b *Institute of Physical and Theoretical Chemistry, University of Leipzig, Linnéstrasse 2, D-04103 Leipzig,
Germany*

^c *Institute of Surface Modification, Permoser Str. 15, D-04138 Leipzig, Germany*

Accepted 14 April 1997

Abstract

Galena (PbS) oxidation on potentiostatically treated specimens in acetate buffer was investigated by atomic force microscopy (AFM) and by X-ray photoelectron spectroscopy (XPS). Elemental sulphur was detected as an oxidation product by XPS. To minimize the evaporation of elemental sulphur during the XPS experiments in ultra high vacuum, sample cooling was required before the evacuation was started. Decreasing the pressure to 1 torr for 5 min, before the sample was cooled, removed the elemental sulphur almost completely from the surface. In addition, when an electrochemically oxidized sample was exposed to air at ambient pressure for about 2 h, the relative intensity of the S2p component of elemental sulphur was observed to decrease to about half of the value achieved by instant cooling and measuring. AFM images showed elemental sulphur to be present on galena surface as local accumulations rather than as a uniform layer. The sulphur formation is highly localized, but does not seem to occur preferentially at steps. © 1997 Elsevier Science B.V.

Keywords: galena (PbS) oxidation; elemental sulphur; sulphide flotation; atomic force microscopy (AFM); photoelectron spectroscopy (XPS)

* Corresponding author. Tel.: +358 2 3335967; fax: +358 2 3336254; e-mail: ikartio@utu.fi

1. Introduction

Oxidation of galena in air and in aqueous solutions has been the subject of many investigations utilizing various experimental techniques (e.g. Gardner and Woods, 1979; Buckley and Woods, 1984; Laajalehto et al., 1993; Richardson et al., 1994; Fornasiero et al., 1994; Kim et al., 1995). One of the reasons for the particular interest in oxidation of galena is to identify the species making the surface hydrophobic without a collector under oxidizing conditions (Guy and Trahar, 1984; Hayes et al., 1987). It is generally acknowledged that the hydrophobic product is rich in sulphur, but the exact chemical nature of this species is still under debate. Elemental sulphur, metal-deficient sulphide and polysulphides have all been proposed to be the oxidation product on galena slightly oxidized under acidic conditions (e.g. Richardson and Maust, 1976; Gardner and Woods, 1979; Buckley and Woods, 1984; Kartio et al., 1996a).

The pioneering XPS studies of Buckley and Woods (1984, 1985a) on oxidation of sulphides have shown that sample cooling is required for detecting elemental sulphur on a sample surface. In the case of galena (Buckley and Woods, 1984), it was shown that elemental sulphur is formed when a galena sample was oxidized in hydrogen peroxide solution. The potential of the sample was estimated to be about +450 mV/SHE (Buckley and Woods, 1985b). The same authors also found polysulphides or severely metal-deficient sulphide on galena oxidized in dilute acetic acid for several weeks at open circuit potential of about +250 mV/SHE. No elemental sulphur was found on this sample. However, a significant enrichment of copper and antimony complicated the interpretation.

A recent study utilizing synchrotron radiation excited photoelectron spectroscopy (SR-XPS) showed new sulphur states on galena in acetate buffer pH 4.6 already at potentials above +50 mV/SHE (Kartio et al., 1996a). The new S2p components were concluded to originate from a chain of sulphur atoms, attached to Pb or impurity cations on the surface, e.g. polysulphides. This interpretation was based on the clearly discrete nature of the new components. Furthermore, the S2p binding energies determined for them agreed well with those measured for sulphur atoms in compounds with similar nearest-neighbour bindings as in the suggested polysulphide chains. Finally, the relatively low volatility of the new species, suggested by the small attenuation of their emission upon evacuation, can be understood on the basis of the anchoring of the chains to Pb (or impurity) ions. Since the samples were not cooled during the measurement, the possibility of parallel formation of elemental sulphur species (e.g. S₈) cannot be excluded, since they would have been almost completely lost during the evacuation of the sample chamber.

In this report, new results are presented on galena oxidation in acidic solution at potentials around +250 mV/SHE, which is the most interesting potential region from flotation view point (Buckley and Woods, 1994). Because of the phenomenon described above, special attention was paid to the sample handling and cooling prior to insertion into the ultra high vacuum of the XPS spectrometer. The possibility to preserve a thin layer of elemental sulphur on galena surface was tested by exposing a preoxidized galena sample to air at ambient pressure and to nitrogen atmosphere at 1 torr for different time periods before cooling and measuring.

2. Experimental

Natural galena (PbS) originating from Brushy Greek, MO, USA, provided by Wards Natural Science Establishment (USA) was used in all experiments. It was analyzed by XRF to be 98.9% pure (by mass). The other elements found were Si (0.5%), Ga (0.3%) and Fe (0.08%). Si was probably present as a silica inclusion in the sample. Deionized (18 M Ω cm) water was used in buffer solutions and for rinsing the samples. Analytical grade acetic acid and sodium acetate were used for making the pH 4.9 buffer solution for all electrochemical experiments. Purified nitrogen gas (99.999%) was used for deoxygenation of the electrolyte.

The AFM work was carried out with a Nanoscope III instrument (Digital Instruments (DI)), an in-house constructed sample holder and an electrochemical cell (DI) in a three-electrode configuration and potentiostatic working mode. This cell used a platinum counter electrode and a chlorinated silver wire as reference electrode. The reference electrode was experimentally determined to have a potential of +180 mV against saturated calomel electrode, SCE, in the acetate buffer used. This value corresponds to +421 mV/SHE. Further details have been described elsewhere (Wittstock et al., 1996).

The samples for XPS measurements were prepared *ex situ* in a three-electrode electrochemical (EC) cell with a platinum counter electrode and Ag/AgCl/KCl reference electrode. The potential of the reference electrode was experimentally measured to be +221 mV/SHE in acetate buffer solution. Prior to each experiment, a fresh acetate buffer solution was purged with nitrogen gas for at least 20 min to remove most of the oxygen from solution. Compact galena pieces were cleaved in air and subsequently attached to a sample holder of the working electrode. In the XPS experiments reported in Section 3.1., a potential of -89 mV/SHE was applied to the samples for 5 min before sweeping to the desired potential at a rate of 2 mV/s. No reducing-potential pretreatment was carried out with the sample discussed in Section 3.2. The treatment time of each sample at the final potential was 15 min. After the treatment, the sample was removed from the EC cell maintaining its potential, rinsed and transferred into the introduction chamber of the spectrometer.

The XPS experiments were performed with a Perkin-Elmer PHI 5400 spectrometer using monochromated AlK $_{\alpha}$ (1486.6 eV) excitation. The photoelectrons were collected at 45° take-off angle with a hemispherical analyzer having a constant pass energy of 89.45 eV for wide scans and 35.75 eV for narrow scans. The spectrometer was calibrated by using the Au4f $_{7/2}$ (BE = 84.0 eV) and Cu2p $_{3/2}$ (BE = 932.7 eV) lines of sputtered pure metal surfaces as a reference. The pressure inside the analysis chamber never exceeded 5 \times 10 $^{-8}$ torr during the measurements. To minimize evaporation of any volatile species from the sample surface in ultra high vacuum, a special sample introduction chamber, equipped with a cold finger, nitrogen gas inlet and a vacuum gauge was utilized to cool the samples under controlled conditions before evacuation. Technical details of this pre-cooling chamber can be found elsewhere (Kartio et al., 1992). The sample temperature was maintained below 130 K during the transfer to the analyzing stage and throughout the measurement.

3. Results and discussion

3.1. Identification of the oxidation product remaining at the surface

In situ AFM images of a galena surface recorded at different potentials in acetate buffer pH 4.9 are presented in Fig. 1. After recording the image in Fig. 1a at +21 mV/SHE, the potential of the sample was raised to +221 mV/SHE before capturing the next image. After that, images were obtained at 15 mV potential increments. Here three selected images are presented from a larger series. As can be seen in Fig. 1b, fairly large accumulations of surface species with mutual distances of typically hundreds of nanometres and dimensions of 200–300 nm (width) \times 50–200 nm (height) were formed at +251 mV/SHE. The first changes in surface morphology could be observed already at +236 mV/SHE, where the accumulations, clearly visible in Fig. 1b, were just discernible. They seem to have formed at random locations on the surface and their position did not change during image recording, as indicated by the subsequent images. The growth of these accumulations slowed down with increasing potential. At +266 mV/SHE new accumulations started to form which can be seen clearly at +296 mV/SHE (Fig. 1c).

XPS measurements on pre-cooled samples were conducted to identify the species formed and retained at the surface during anodic treatment and observed as accumulations in AFM images. Selected S2p spectra of galena treated at different potentials for 15 min in pH 4.9 acetic buffer are shown in Fig. 2. No other S2p doublets than that of PbS (S2p_{3/2} component at 160.7 eV) can be observed on the sample treated at +91 mV/SHE (Fig. 2a). This is in good agreement with the AFM image recorded at +21 mV/SHE showing no changes in morphology of the surface. At higher potentials (Fig. 2b,c), a new sulphur doublet is evident and increases with potential. The S2p_{3/2} binding energy (BE) of the new doublet is 163.9 eV, which is a value characteristic of elemental sulphur (Mycroft et al., 1990; Szargan et al., 1992). If the samples were allowed to warm up to room temperature inside the spectrometer vacuum and re-measured subsequently, the component at 163.9 eV could not be observed any more. This finding supports the conclusion that the new sulphur species observed at slight overpotentials (at +211 mV/SHE and above) is elemental sulphur. The Pb4f spectrum showing only the component of PbS (BE(Pb4f_{7/2}) = 137.5 eV) does not change as a function of potential which is consistent with the general notion that all the oxidized lead species are dissolved at low pH.

It can be concluded that the accumulations observed by AFM are deposits of elemental sulphur formed in the oxidation process of galena at slightly anodic potentials. The sulphur formation is highly localized and does not occur preferentially at steps discernible with the height scale used (Fig. 1). It probably starts at point-type defects in the surface atomic layer, such as impurities or vacancies. To the knowledge of the present authors, this is the first spectroscopic evidence for the formation of elemental sulphur at such low anodic potentials on galena surface at a pH around 5. Possible co-existence of small amounts of less volatile species, such as polysulphides or metal-deficient sulphide in the surface layer, could not be detected with conventional XPS technique used here. Evidence of formation of these species in quantities less than

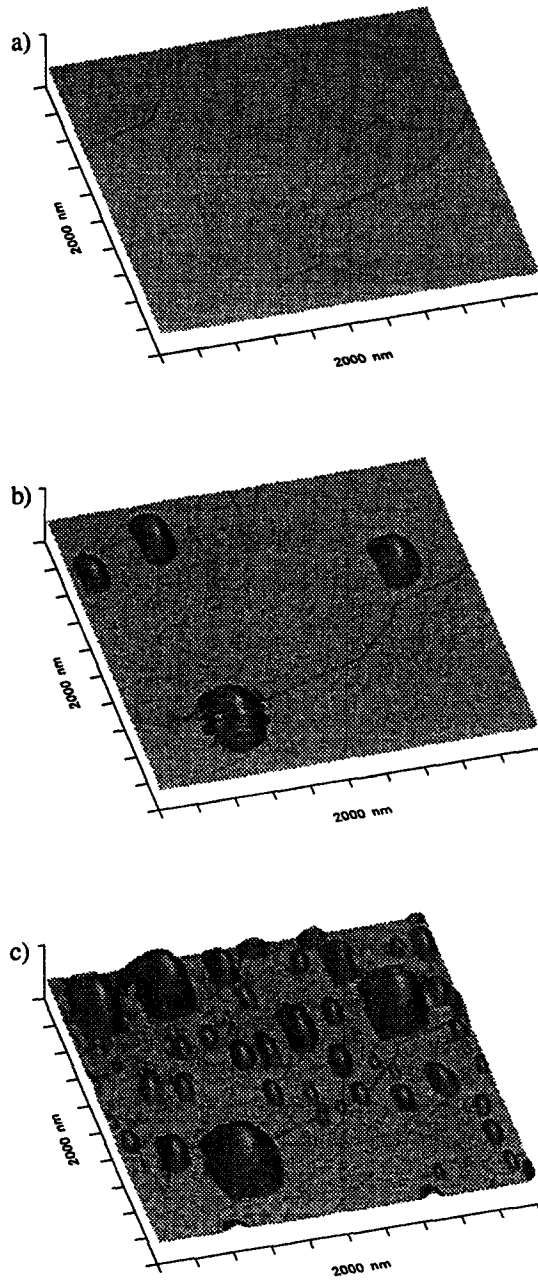


Fig. 1. In situ AFM images of a galena surface at different potentials in acetate buffer pH 4.9: (a) +21 mV; (b) +251 mV; (c) +296 mV/SHE. The height scale of the images is 450 nm. Adapted from Wittstock et al. (1996).

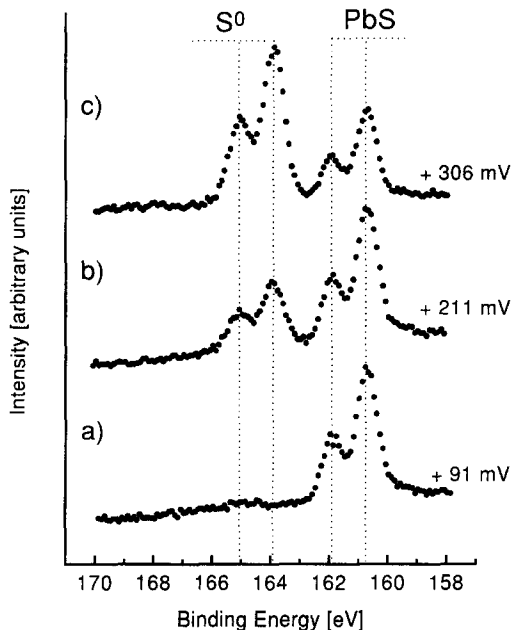


Fig. 2. S_{2p} spectra of galena potentiostatically pretreated at different potentials in acetate buffer pH 4.9 for 15 min. The potentials indicated in each spectrum are referred to SHE scale. Adapted from Wittstock et al. (1996).

a nominal monolayer has indeed been observed with other techniques at similar conditions (Kartio et al., 1996a; Wittstock et al., 1996; Buckley and Woods, 1996). However, enrichment of impurity cations on the surface complicated the interpretation of those results.

3.2. Stability of elemental sulphur in air and at reduced pressure

Experimental requirements for detecting low amounts of elemental sulphur on galena surface by XPS were studied in more detail on oxidized galena. The aim was to identify conditions under which elemental sulphur formed on galena can be retained between the electrochemical sample preparation and the spectroscopic measurement.

A freshly cleaved galena sample was oxidized for 15 min at +291 mV in acetate buffer solution and subsequently cleaved into two pieces to divide the treated surface into two samples. One of them was introduced immediately in the introduction chamber and subsequently cooled down in the same manner as the samples describe in Section 3.1. The S_{2p} spectrum of this sample is shown in Fig. 3a. The comparison of Fig. 3a and Fig. 2c shows a good reproducibility of the S_{2p} spectrum of oxidized PbS for similar sample treatment and handling.

The other half of the oxidized sample was kept in air at room temperature for 2 h, after which it was cooled and measured. The resulting S_{2p} spectrum is shown in Fig. 3b. It can be observed clearly that the relative intensity of the signal from elemental sulphur

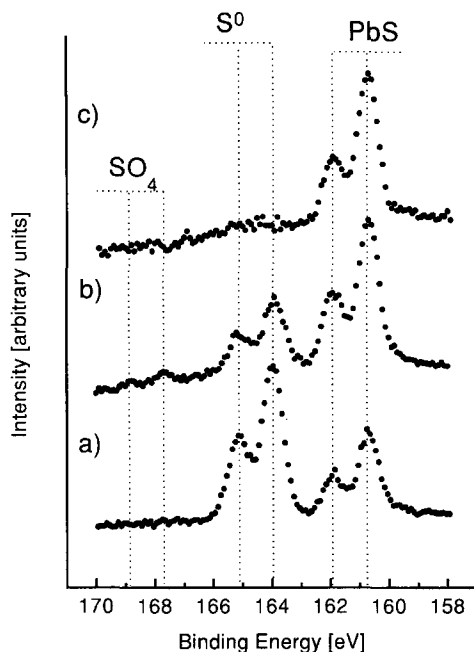


Fig. 3. Galena potentiostatically pretreated at +291 mV/SHE in acetate buffer pH 4.9 for 15 min: (a) cooled to 130 K and measured immediately after the treatment; (b) stored 2 h in air at room temperature and atmospheric pressure, cooled to 130 K and measured; (c) sample (a) warmed up to room temperature at atmospheric pressure in 10 min. The pressure was then reduced to 1 torr for 5 min, after which the sample was cooled to 130 K again, evacuated and measured.

is much lower than in the spectrum of the surface, which was cooled and measured immediately after sample preparation (Fig. 3a). Because the solution treatment of both pieces was the same, it is clear that the amount (or coverage) of elemental sulphur on galena was reduced extensively during storage in air. Since the laboratory atmosphere is an open system with continuous air exchange and the partial pressure of sulphur in the vicinity of the sample is initially expected to be many orders of magnitudes lower than the vapour pressure of sulphur at room temperature (about 10^{-5} torr for bulk material; Honig, 1962), it seems plausible that the observed decrease in sulphur signal was due to loss of elemental sulphur from the sample surface by evaporation. It should be emphasized here that the absolute quantity of sulphur lost is very small, probably of the order of few monolayers.

The minor doublet with the $S2p_{3/2}$ component at 167.7 eV in the spectrum 3b can be assigned to sulphate or basic sulphate species (Buckley and Woods, 1984; Kartio et al., 1996b) probably formed by oxidation of sulphur in air. This doublet is very weak and cannot correspond to all the observed decrease in the amount of elemental sulphur. However, this indirectly indicates that oxidation of elemental sulphur to SO_2 and its subsequent evaporation in air could have taken place as well.

Surface diffusion of sulphur to form thicker clusters with lower surface coverage could also explain at least partly the reduction of the relative intensity of the elemental

sulphur component. However, as observed in the AFM images in Fig. 1, the elemental sulphur on the surface is already highly accumulated in the first place and it seems unlikely that the accumulates could further grow in height on the expense of lateral dimensions. Nevertheless, the surface diffusion is also expected to slow down at low temperatures. Hence, regardless of the reason for the decrease of the sulphur signal during air exposure, this experiment evidently emphasizes the requirement of rapid sample cooling already at atmospheric pressure, when sulphide–liquid interfaces are studied by XPS.

The sample in Fig. 3a was transferred back to the pre-cooling chamber, which was subsequently filled with nitrogen gas to atmospheric pressure maintaining the low sample temperature. The sample was then warmed up to room temperature in 10 min by heat conducted from a copper block at room temperature. After this treatment, most of the elemental sulphur detected in Fig. 3a was expected to have remained on the sample surface. The pressure was then reduced to 1 torr for 5 min, after which the sample was cooled and returned to the measuring stage. As can be seen in Fig. 3c, all elemental sulphur had disappeared from the surface during the procedure described above. Hence it can be concluded that the volatility of elemental sulphur on the galena surface is so high that there is no way to preserve small quantities of it, if the pressure is lowered from atmospheric value by only about two decades before cooling. This raises doubts on the merits of traditional cooling systems in XPS measurements, in which cooling of the sample is started simultaneously with evacuation. In such measurements, elemental sulphur, if originally present on the sample surface, is probably lost before the sample reaches a sufficiently low temperature. Cooling of the sample first after it has been transferred to the measuring stage of the spectrometer is, of course, even less efficient and useless from this point of view.

4. Summary and conclusions

(1) Elemental sulphur was found on galena surface as accumulations of 10–200 nm height after treatment in solution of pH 4.9 at potentials above 200 mV/SHE.

(2) The sulphur signal detected by XPS was found to decrease, if the sample was kept in air before cooling and measuring.

(3) If pre-cooling of the sample was conducted after keeping the sample for 5 min at a pressure of 1 torr, the sulphur had been evaporated from the surface and could not be detected any more.

(4) These results demonstrate the importance of careful and rapid sample cooling when investigating oxidation of sulphides with XPS.

Acknowledgements

This work has been supported by the European Community under contract No. BRE2-CT94-0606. Travel grants from the Academy of Finland (I. Kartio, K. Laajalehto

and E. Suoninen) and the German Academic Exchange Office (D. Hirsch, R. Szargan and G. Wittstock) are gratefully acknowledged.

References

- Buckley, A.N., Woods, R., 1984. An X-ray photoelectron spectroscopic study of the oxidation of galena. *Appl. Surf. Sci.* 17, 401–414.
- Buckley, A.N., Woods, R., 1985a. X-ray photoelectron spectroscopy study of oxidised pyrrhotite surfaces, II. Exposure to aqueous solutions. *Appl. Surf. Sci.* 20, 472–480.
- Buckley, A.N., Woods, R., 1985b. An X-ray photoelectron spectroscopic investigation of the surface oxidation of sulfide minerals. In: Richardson, P.E., Srinivasan, S., Woods, R. (Eds.), *Proc. Int. Symp. Electrochemistry in Mineral and Metal Processing*. Electrochemical Society, Pennington, pp. 286–302.
- Buckley, A.N., Woods, R., 1994. On the characterization of sulfur species on sulfide mineral surfaces by X-ray photoelectron spectroscopy and Raman spectroscopy. *J. Electroanal. Chem.* 370, 295–296.
- Buckley, A.N., Woods, R., 1996. Relaxation of the lead-deficient sulfide surface layer on oxidised galena. *J. Appl. Electrochem.* 26, 899–907.
- Fornasiero, D., Li, F., Ralston, J., Smart, R.St.C., 1994. Oxidation of galena surfaces, I. X-ray photoelectron spectroscopic and dissolution kinetics studies. *J. Colloid Interf. Sci.* 164, 333–344.
- Gardner, J.R., Woods, R., 1979. A study of the surface oxidation of galena using cyclic voltammetry. *J. Electroanal. Chem.* 100, 447–459.
- Guy, P.J., Trahar, W.J., 1984. The influence of grinding and flotation environments on the laboratory flotation of galena. *Int. J. Miner. Process.* 12, 15–38.
- Hayes, R.A., Price, D.M., Ralston, J., Smith, R.W., 1987. Collectorless flotation of sulfide minerals. *Miner. Process. Extractive Metall. Rev.* 2, 203–234.
- Honig, R.E., 1962. Vapor pressure data for the solid and liquid elements. *RCA Rev.* 23, 567–586.
- Kartio, I., Laajalehto, K., Suoninen, E., Karthe, S., Szargan, R., 1992. Technique for XPS measurements of volatile adsorbed layers: application to studies of sulphide flotation. *Surf. Interface Anal.* 18, 807–810.
- Kartio, I., Laajalehto, K., Kaurila, T., Suoninen, E., 1996a. A study of galena (PbS) surfaces under controlled potential in pH 4.6 solution by synchrotron radiation excited photoelectron spectroscopy. *Appl. Surf. Sci.* 93, 167–177.
- Kartio, I., Laajalehto, K., Suoninen, E., 1996b. Recent progress in applications of SR-XPS to surface studies of sulfide minerals. In: Doyle, F., Richardson, P., Woods, R. (Eds.), *Proc. 4th Int. Symp. Electrochemistry in Mineral & Metal Processing*. The Electrochemical Society, Pennington, in press.
- Kim, B.S., Hayes, R.A., Prestidge, C.A., Ralston, J., Smart, R.St.C., 1995. Scanning tunneling microscopy studies of galena: the mechanisms of oxidation in aqueous solution. *Langmuir* 11, 2554–2562.
- Laajalehto, K., Smart, R.St.C., Ralston, J., Suoninen, E., 1993. STM and XPS investigation of reaction of galena in air. *Appl. Surf. Sci.* 64, 29–39.
- Mycroft, J.R., Bancroft, G.M., McIntyre, N.S., Lorimer, J.W., Hill, I.R., 1990. Detection of sulphur and polysulphides on electrochemically oxidized pyrite surfaces by X-ray photoelectron spectroscopy and Raman spectroscopy. *J. Electroanal. Chem.* 292, 139–152.
- Richardson, P.E., Maust, E.E. Jr., 1976. Surface stoichiometry of galena in aqueous electrolytes and its effect on xanthate interactions. In: Fuerstenau, M.C. (Ed.), *Flotation. A.M. Gaudin Memorial Volume, Vol. 1*. American Institute of Mining, Metallurgical and Petroleum Engineers, New York, pp. 364–392.
- Richardson, P.E., Yoon, R.-H., Woods, R., Buckley, A.N., 1994. The photoelectrochemistry of galena. *Int. J. Miner. Process.* 41, 77–97.
- Szargan, R., Karthe, S., Suoninen, E., 1992. XPS studies of xanthate adsorption on pyrite. *Appl. Surf. Sci.* 55, 227–232.
- Wittstock, G., Kartio, I., Hirsch, D., Kunze, S., Szargan, R., 1996. Oxidation of galena in acetate buffer investigated by atomic force microscopy and photoelectron spectroscopy. *Langmuir* 12, 5709–5721 in press.