

## The $^{57}\text{Fe}$ Mössbauer parameters of pyrite and marcasite with different provenances

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**Abstract**—Eighteen pyrite and twelve marcasite samples which have different provenances have been investigated to determine the systematics of the influence of mineralogical and geological factors on the  $^{57}\text{Fe}$  Mössbauer spectra at 298 K. The following results have been obtained: there is no ambiguity in distinguishing single phase pyrite from single phase marcasite by means of  $^{57}\text{Fe}$  Mössbauer spectroscopy at 298 K. At 298 K the average electric quadrupole splitting,  $\langle\Delta E_Q\rangle$ , and average isomer shift,  $\langle\delta\rangle$ , with respect to Fe metal, are  $0.6110 \pm 0.0030 \text{ mm s}^{-1}$  and  $0.313 \pm 0.008 \text{ mm s}^{-1}$ , respectively, for the 18 pyrites;  $\langle\Delta E_Q\rangle = 0.5030 \pm 0.0070 \text{ mm s}^{-1}$  and  $\langle\delta\rangle = 0.2770 \pm 0.0020 \text{ mm s}^{-1}$  for the 12 marcasites. At 77 K,  $\Delta E_Q$  is  $0.624 \text{ mm s}^{-1}$  for pyrite and  $0.508 \text{ mm s}^{-1}$  for marcasite. In distinguishing pyrites from marcasites, spectra obtained at 77 K are not warranted.

The Mössbauer parameters of pyrite and marcasite exhibit appreciable variations, which bear no simple relationship to the geological environment in which they occur but appear to be selectively influenced by impurities, especially arsenic, in the pyrite lattice. Quantitative and qualitative determinations of pyrite/marcasite mechanical mixtures are straightforward at 298 K and 77 K but do require least-squares computer fittings and are limited to accuracies ranging from  $\pm 5$  to  $\pm 15$  per cent by uncertainties in the parameter values of the pure phases. The methodology and results of this investigation are directly applicable to coals for which the presence and relative amounts of pyrite and marcasite could be of considerable genetic significance.

### INTRODUCTION

THERE have been several reports of  $^{57}\text{Fe}$  Mössbauer investigations of pyrite as a synthetic compound (Vaughan and Drickamer, 1967; Nishihara and Ogawa, 1979) as a pure mineral (Temperley and Lefevre, 1966; Morice *et al.*, 1969) and as a component of assemblages of iron-containing phases in coals (Huffman and Huggins, 1978; Saporoschenko *et al.*, 1980). The Mössbauer parameters reported thus far have a spread in values ( $0.59 \text{ mm s}^{-1} \leq \Delta E_Q \leq 0.65 \text{ mm s}^{-1}$ ) far greater than that of  $\pm 0.01 \text{ mm s}^{-1}$  expected for a pure, stoichiometric,  $\text{FeS}_2$ , pyrite phase. Because the systematics of the Mössbauer parameters for well-defined pyrites from ore deposits have not been established at the present time, it is not clear whether this spread in values of the Mössbauer parameters is due to variations in composition, conditions of formation for natural samples, or differences in Mössbauer spectroscopic techniques. Very little is known about the systematics of the  $^{57}\text{Fe}$  Mössbauer parameters of the morphologically unique varieties of pyrite and marcasite found in coals (Boctor *et al.*, 1976).

Some investigations have demonstrated that both the morphology (Boctor *et al.*, 1976; Sergeeva and Eremin, 1978) and chemical composition of pyrite and marcasite are dependent on the mode of formation, *e.g.*, the occurrence of genetically related framboidal and euhedral pyrite with high arsenic concentrations. Consequently, consideration must be given to the possibility that the above-mentioned

spread in the  $^{57}\text{Fe}$  Mössbauer parameters of pyrite results from (1) differences in texture, size, morphology, etc., which are characteristic of the process by which the pyrites were formed, (2) differences in chemical composition, or (3) different combinations of effects due to (1) and (2).

A similar situation exists for marcasite as a synthetic and mineral phase, although less data are available, but in no  $^{57}\text{Fe}$  Mössbauer investigation of coal has an unambiguous detection of marcasite been reported thus far despite numerous microscopic and X-ray diffraction determinations of marcasite in coals (Sergeeva and Eremin, 1978; King and Renton, 1980).

Therefore, a definitive body of Mössbauer parameters for pyrite and marcasite is needed before the systematics of the relationship between texture, composition and the Mössbauer spectrum can be established for pyrite and marcasite in coals. Furthermore, precise determinations of the Mössbauer parameters of pyrite and marcasite are critical in quantitative analysis of pyrite and marcasite Mössbauer spectra both among themselves and with those of other iron-containing phases in coals, for example, illite and melanterite (Huffman and Huggins, 1978).

As pyrite and marcasite occur together in some coals, it is necessary to determine their relative concentrations for a complete characterization of the inorganic minerals in such coals. The relative proportions of pyrite and marcasite are also believed to be of considerable importance in questions relating to the genesis and paragenesis of coals. For example,

the association of marcasite with framboidal pyrite in Seelyville Coal III is considered to be unique to framboids in coal and is sufficient to distinguish pyrite framboids in the Seelyville coal from sedimentary pyrite framboids which are not associated with marcasite (Boctor *et al.*, 1976). Further, even though it is generally believed that the majority of the pyrite in coal was formed during the coal deposition stage, it is also clear that some of the pyrite is detrital and that some of it is formed epigenetically (Minkin *et al.*, 1980). Provided the  $\text{FeS}_2$  phases are sufficiently sensitive to variations in composition arising from different depositional processes, the result of this investigation should be useful, at least, in assessing the importance of detrital pyrites in coal since detrital pyrites would have been derived from sources similar to those of the pyrites employed in this study.

In order to devise a quantitative  $^{57}\text{Fe}$  Mössbauer spectroscopic technique for the analysis of pyrites and marcasites in coals, the range over which the Mössbauer parameters might be expected to fall for naturally occurring samples from a variety of different environments must be determined, as there are likely to be several morphologically and genetically distinct varieties of pyrite and marcasite in coals. Data from an early  $^{57}\text{Fe}$  Mössbauer study of pyrites and marcasites of different provenance are too imprecise for comparisons with data of recent studies (Vaynshteyn *et al.*, 1967). Therefore, 18 pyrite and 12 marcasite samples, many from well-known localities, have been investigated by means of  $^{57}\text{Fe}$  Mössbauer spectroscopy. The Mössbauer spectra of *laboratory-prepared*, mechanical mixtures of selected marcasite and pyrite samples have also been obtained.

The spread in the electric quadrupole splitting among different samples of pyrite and marcasite has been found to be greater than the experimental error by at least an order of magnitude. The ranges of values for the Mössbauer parameters of pyrite and marcasite do not, however, overlap and the ability to distinguish pyrite from marcasite by means of Mössbauer spectroscopy is unequivocal in the absence of interfering absorptions from other phases. The quantitative determinations of either mineral in a mixture of the two can be routinely performed with accuracies of  $\pm 5$  to  $\pm 15$  per cent. Preliminary indications are that the magnitude of the electric quadrupole splitting for pyrite is correlated with the arsenic concentration and has significant implications for coal petrologic studies.

These results may serve as norms in establishing whether the pyrite and marcasite in coal have crystal-chemical structures different from those in ore deposits.

## EXPERIMENTAL

Samples, which were obtained from a variety of sources, are listed in Tables 1 and 2 along with information, where available, on their geological setting. Qualitative, energy-

dispersive X-ray fluorescence analysis was performed on all of the pyrite samples; those samples showing appreciable concentrations of impurity elements were further analyzed by means of quantitative, emission-spectrographic analyses. Pyrite samples 11P and 13P were especially free of impurities showing only trace amounts of zinc and aluminum which are probably not present in the pyrite phase (Ramdohr, 1969). Wet-chemical analyses for iron and sulfur were performed on sample 13P with the following results: 46.2 weight per cent iron and 53.6 weight per cent sulfur. The ideal values for  $\text{FeS}_2$  are 46.55 weight per cent iron and 53.44 weight per cent sulfur. Samples 12P and 15P contained copper impurities at levels of about 1 per cent; again, it is not clear whether the copper is contained in the pyrite lattice. Arsenic was the only non-metallic element present at significant concentration levels in more than two samples as determined by emission spectrographic analysis, and the results are presented in a later table.

An automated powder diffractometer, using  $\text{Cu K}\alpha$  radiation, was used to characterize the samples by means of X-ray diffraction. The samples, with a small amount of  $\text{Al}_2\text{O}_3$  as an internal standard, were ground under alcohol with a boron carbide mortar and pestle, mixed into a slurry with collodion, and mounted on a glass slide. The intensities and  $d$ -values of the pyrite lines were in good agreement with those on JCPDS-powder-diffraction file card No. 24-0076. The  $d$  value for the (321) line of the natural samples used in this study is in excellent agreement with that reported on the JCPDS card which is based, however, on the pattern of a synthetic sample (Brostigen and Kjekshus, 1969).

Some additional lines resulted from other phases present. For example, sample 9P was known to contain minor amounts of quartz, and quartz was indeed detected in the X-ray powder diffraction pattern. These additional lines suggest that many of the trace elements in Table 1 are not in pyrite but rather in accessory minerals. Sample 2P is exceptional inasmuch as a sufficient number of additional lines were present to permit an attempt at identifying the accessory phases. Even though a definitive assignment has not proven possible, the presence of westerveldite ( $\text{FeAs}$ ), xanthosite ( $\text{Ni}_3\text{As}_2\text{O}_8$ ), or playfairite [ $\text{Pb}_{16}(\text{Sb,As})_2\text{S}_{10}$ ] cannot be ruled out. Sample 2P contains 1200 ppm As, 35 ppm Ni and 76 ppm Pb.

The Mössbauer spectra were obtained in a standard transmission geometry utilizing a 25 millicurie  $^{57}\text{Co}/\text{Pd}$  source, an electromechanical velocity transducer and 512 channels of a 1024 channel, multichannel analyzer, operated in the multiscaling mode. The velocity waveform was a sawtooth and calibrations were performed utilizing an Fe-metal foil and sodium nitroprusside (sodium pentacyanonitrosylferrate (III) dihydrate). Spectra of all samples were obtained at 298 K; additional spectra of pyrite, marcasite and pyrite/marcasite mixtures were obtained at 77 K. The source was maintained at 298 K for all spectra. The isomer shifts,  $\delta$ , are reported relative to an iron metal absorber at 298 K.

Absorbers were prepared using two methods: for the comparative studies of pyrite and marcasite, absorbers were prepared by mixing 20 mg quantities of samples that had been finely ground under acetone with an acetone/Duco<sup>R</sup> cement solution to form a slurry and forming the slurry into a 12 mm circular disk on aluminized mylar foil. After permitting the slurry to dry, the absorber and mylar backing were encased in a sheath of transparent, plastic, adhesive tape. This procedure was adopted to avoid any changes in the samples that might accompany encapsulating the samples in thermosetting plastics. Absorbers of the marcasite/pyrite mixtures were prepared by mixing the mineral powders with a thermosetting plastic and forming the mixtures into discs at 423 K and 4200 psi. This procedure was adopted in order to obtain a homogeneous dispersion of the two phases throughout the volume of the absorber.

TABLE 1. Pyrite sample provenance

Sample number	Locality	Type of deposit, crystal habit, etc.	Impurity elements detected in qualitative XRF analysis <sup>a</sup>
1P	OH Vein, Creede, Colorado	Hydrothermal, late, vein deposit; fine-grained, massive	As(s); Tl, Rb, Mo(w)
2P	Mine Lamotte, Missouri	Hydrothermal-magmatic (Tri-State), small single-crystals	As(s); Pb(vw)
3P	OH Vein, Creede, Colorado	Hydrothermal, early, vein deposit; fine-grained, massive	As(s); Zn
4P	Leadville, Colorado	Hydrothermal, mesothermal vein replacement deposit; low-grade ore	Zn, Cu, Pb, As(m)
5P	Fukazawa Mine, Japan	Hydrothermal, marine; fine-grained, massive	Ni, Zn, Ti, Zr (all w)
6P	Ambasaquas, Spain	Large single-crystal	
7P	Alden, New York	Sedimentary; fossiliferous concretion, Devonian shale	Zn(s), K, Ca, Rb(w); Si, Al, Mn, Ni, Zn(vw) As(vvw)
8P	Galena, Illinois	Hydrothermal-magmatic-meteoric; fibrous crystals	
9P	Bingham Canyon, Utah	Hydrothermal copper porphyry; with minor quartz	Pb(s), As, Se, Rb(w)
10P	Shakanai Mine, Japan	Hydrothermal marine, "kuroko" ore; crystalline, massive	Zn, Cu, Se(w)
11P	Butte, Montana	Hydrothermal vein deposit; small single crystals	Al, Cu, Zn(vw)
12P	Shakanai Mine, Japan	See 10P	Zn, Cu(m) Si, Ca, K(w)
13P	Shakanai Mine, Japan	See 10P	Zn (vw)
14P	OH Vein, Creede, Colorado	Hydrothermal, vein deposit; pyritohedral crystals	Pb(s); Zn(m); Rb, Ca, Zn, Al, Si(w)
15P	No Provenance	USGS analytical standard	Cu, Pb, As, Rb(w-m)
16P	No Provenance		Cu, Zn, Pb, Rb, Sr(w-m)
17P	No Provenance		Cu(s); Zn, As, Bi(w)
18P	Mineral Gap, Virginia		

<sup>a</sup> (s), (m), (w), (vw), etc. denote qualitative intensity of estimate of characteristic X-ray lines of element in question. For example, for sample 12P, the Zn: Fe and Cu: Fe lines had raw intensity ratios of 1:10 and 1:15, respectively.

The data were analyzed by means of computer-assisted least-mean-squares fitting procedures. A Lorentzian line-shape was assumed in all cases. The details of the computer program have been published elsewhere (Evans and Amthauer, 1980). The spectra of the pure phases were fitted to a single quadrupole doublet pattern in which the two

TABLE 2. Marcasite sample provenance

Sample number	Locality	Type of deposit, crystal habit
1M	Illinois-Kentucky Fluorite District	Hydrothermal
2M	No Provenance	
3M	Illinois-Wisconsin Pb-Zn District	Sedimentary; small crystals
4M	Tri-State District	Hydrothermal; single crystal
5M	Tri-State District	Hydrothermal; single crystal, cockscomb
6M	No Provenance	
7M	No Provenance	—; single crystal, cockscomb, tarnish
8M	No Provenance	—; single crystal, cockscomb, tarnish removed
9M	Baxter Springs, Kansas	Hydrothermal; single crystal
10M	No Provenance	
11M	Rensselear Quarry, Indiana	—; single crystal, cockscomb
12M	Tri-State District	Single crystal, cockscomb

lines were constrained to have equal integrated intensities (areas) but the widths,  $\Gamma_i$ , and intensities,  $I_i$ , were not constrained to be separately equal. Thus, the constraint was such that  $I_i\Gamma_i = I_j\Gamma_j$  where  $i$  and  $j$  refer to the two components of a quadrupole doublet. Previous investigations (Guettinger and Williamson, 1979) have demonstrated the absence of any asymmetry in the  $^{57}\text{Fe}$  Mössbauer spectrum of oriented, single crystals of pyrite and no asymmetry is expected in the spectra of polycrystalline samples. Unconstrained fits of two independent lines to the spectra of se-

lected samples have confirmed that such is the case for the samples reported on here. The spectra of the pyrite/marcasite mixtures were fitted according to a number of different assumptions, which included a fit to (1) two independent lines, (2) a single, area-symmetric quadrupole doublet, (3) the patterns of marcasite and pyrite with all parameters, except the relative intensities, constrained to those of the pure phases, and (4) two, area-symmetric, quadrupole doublets with all parameters being free variables. Fits made under assumptions (3) and (4) led to phys-

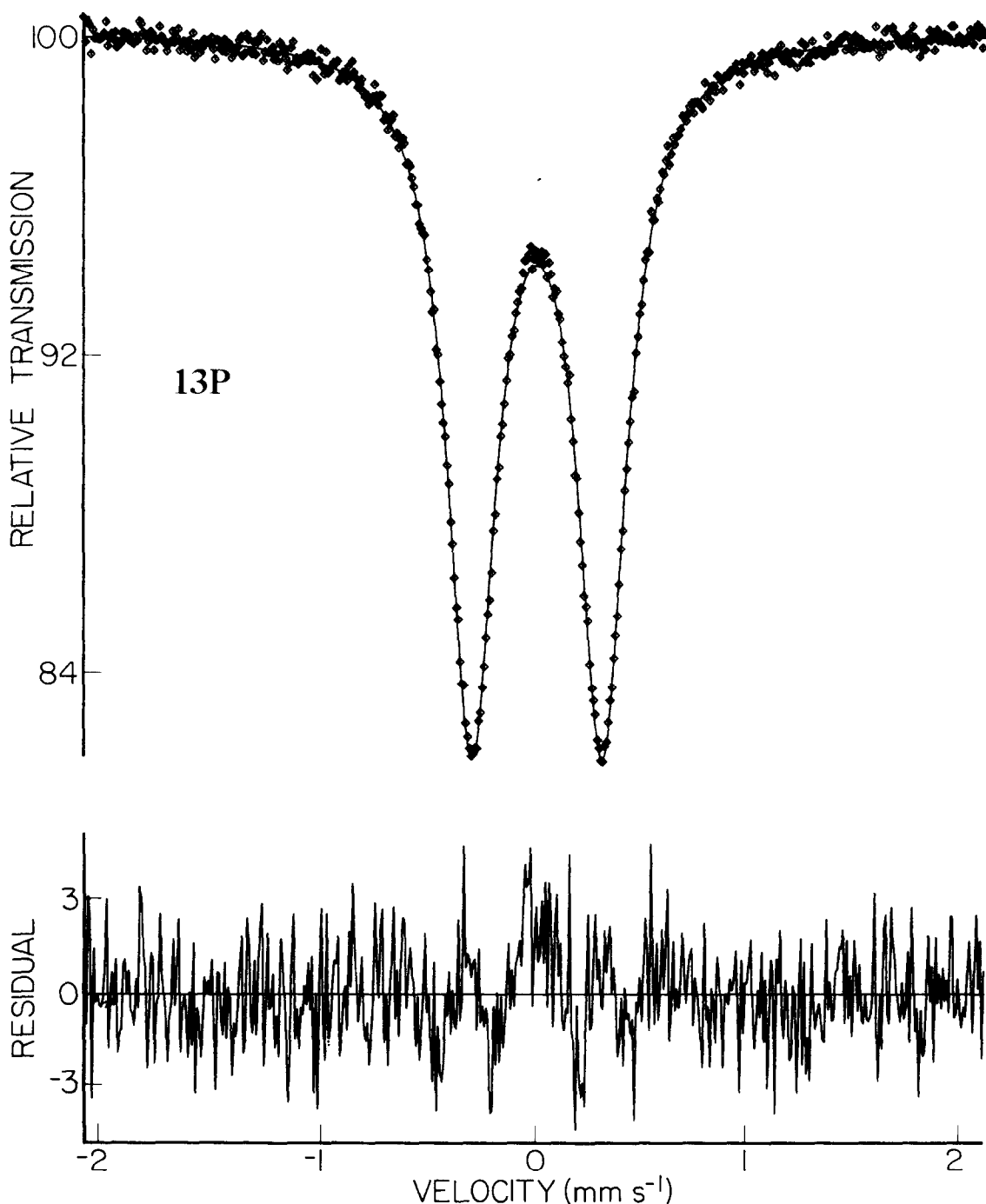


FIG. 1.  $^{57}\text{Fe}$  Mössbauer spectrum of pyrite sample 13P (Table 1) at 298 K. The points are the experimental data, as in all subsequent figures; and the solid line is the result of fitting a single quadrupole doublet to the spectrum. The residual plotted below the spectrum is the difference (normalized at each point to be in units of  $\sqrt{N_{\text{exp}}}$ ) between the fitted spectrum and experimental data.

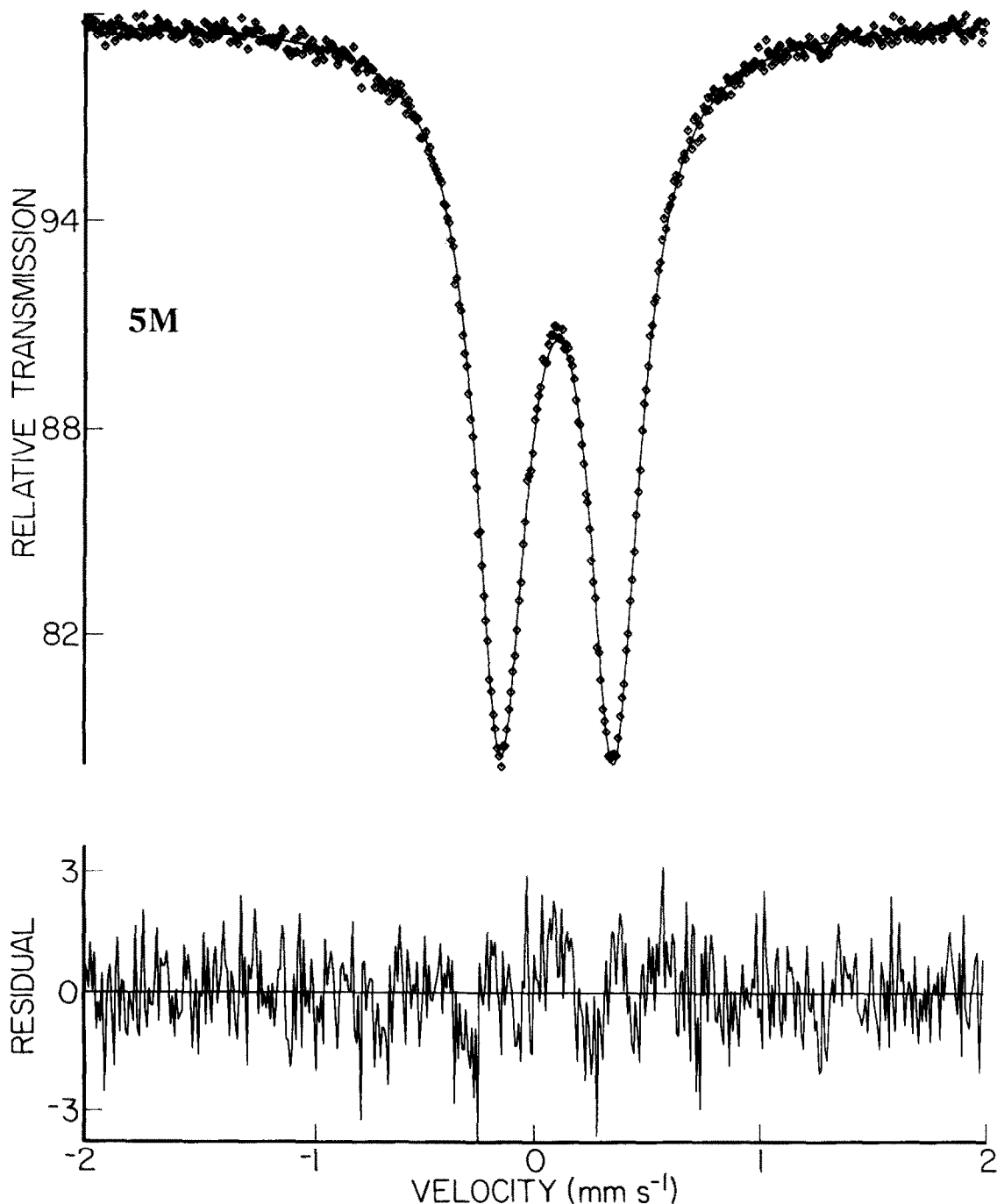


FIG. 2.  $^{57}\text{Fe}$  Mössbauer spectrum of marcasite sample 5M (Table 2) at 298 K.

ically unreasonable parameters and our attention will be focused on the results obtained from fits made according to (1) and (2).

### RESULTS

Typical spectra of pyrite and marcasite are shown in Figs. 1, 2, and 3. The spectrum of sample 13P in Figure 1 is an example of a good fit of a quadrupole doublet to a pyrite spectrum. It is noteworthy that sample 13P was one of those having especially low levels of impurities (*cf.* Table 1). The spectrum of

marcasite sample 5M is shown in Fig. 2. The spectrum of a (tarnished) iridescent marcasite was also obtained before and after the removal of the surface oxidation products constituting the tarnish. A comparison of the two spectra showed such surface oxidation to have no detectable influence on the Mössbauer spectrum when obtained in *transmission geometry*.

The spectra of the different samples were quite similar in qualitative appearance except for sample 2P from Mine LaMotte, Missouri, which is shown

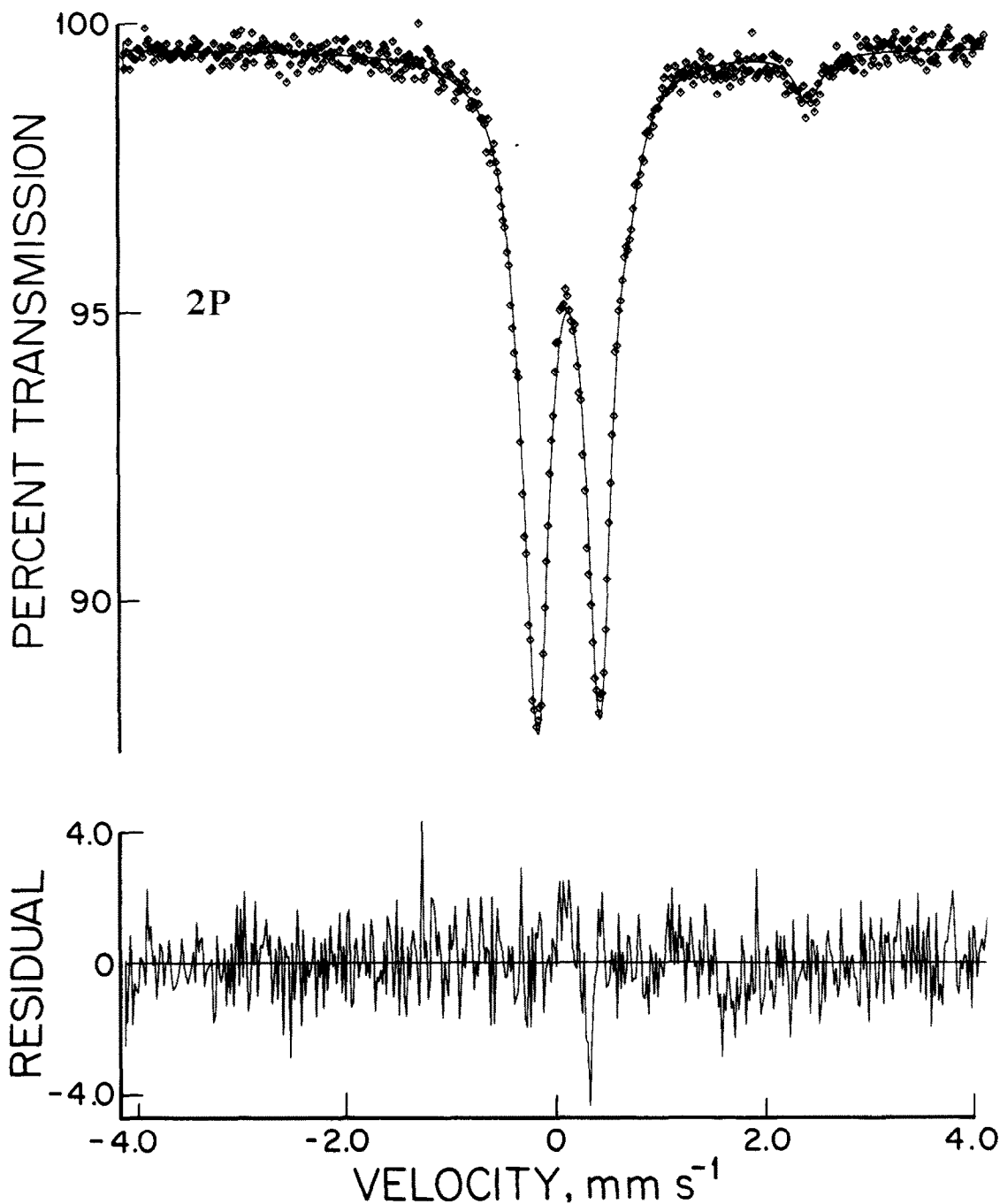


FIG. 3.  $^{57}\text{Fe}$  Mössbauer spectrum of pyrite sample 2P (Table 1). The widely split low-intensity component is tentatively attributed to  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ . The low velocity member of this quadrupole doublet is unresolved from the principal pyrite component and is the cause of the apparent asymmetry in the more intense, pyrite spectrum.

in Fig. 3. The presence of a non-pyritic, iron-containing phase is clearly demonstrated by the weak absorption near  $\sim +2.5 \text{ mm s}^{-1}$ , which is the positive component of a quadrupole doublet. The solid line in the spectrum is the result of fitting two quadrupole doublets to the spectrum. The parameters for the more intense doublet, which accounts for 92 per cent of the total absorption, are listed in Table 3 and are attributable to a pyrite that contains arsenic, *vide*

*infra*. The second doublet has a  $\Delta E_Q$  of  $2.54 \text{ mm s}^{-1}$  and a  $\delta$  of  $1.38 \text{ mm s}^{-1}$  and accounts for the remaining 8 per cent of the total intensity of the spectrum. Although the more unusual Fe containing phases suggested by the X-ray diffraction analysis cannot be ruled out, these parameters are very similar to those of szomolnokote,  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  (Huffman and Huggins, 1978; Saporoschenko *et al.*, 1980).

The results of fitting the spectra of the samples

listed in Table 1 and 2 to quadrupole doublet patterns are given in Table 3. The statistical parameters of the fits are also listed (Ruby, 1973) and are observed to be well within the reproducibility of the data as shown by the parameters of duplicate runs (entries 10P, 12P and 13P, respectively) and the consecutive entries 4M, 4M, respectively, and 5M, 5M, respectively. A comparison of Tables 1, 2 and 3 demonstrates that no simple relationship exists between the type of deposit in which the pyrite or marcasite is formed and their Mössbauer parameters. None-

theless, the range of variation in the parameters, although smaller than those already in the literature, is well outside the experimental errors of this investigation and must be attributable to mineralogical and/or geological factors.

Furthermore, the data clearly show that, as pure phases, pyrite and marcasite are easily distinguishable on the basis of their Mössbauer parameters. In principle, the determination of the FeS<sub>2</sub> phase in coals as pyrite or marcasite should be straightforward. However, many coals do not contain pure py-

TABLE 3. <sup>57</sup>Fe Mössbauer parameters of pyrites and marcasites at 298 K

Phase	Sample number	$\Delta E_Q^1$ (mm s <sup>-1</sup> )	$\delta^2$ (mm s <sup>-1</sup> )	$\Gamma^3$ (mm s <sup>-1</sup> )	$I_L/I_H^4$	MISFIT <sup>5</sup> (%)	$\chi^2$ <sup>6</sup>
Pyrite	1P	0.619 (1)	0.329 (1)	0.303 (2)	0.998	0.07 (3)	536
	2P	0.621 (1)	0.311 (1)	0.297 (3)	1.019	0.13 (3)	632
	3P	0.614 (1)	0.312 (1)	0.284 (1)	1.008	0.06 (1)	812
	4P	0.614 (1)	0.313 (1)	0.282 (1)	0.998	0.01 (1)	496
	5P	0.614 (1)	0.311 (1)	0.284 (1)	0.995	0.03 (1)	706
	6P	0.614 (1)	0.312 (1)	0.264 (1)	0.990	0.02 (1)	793
	7P	0.613 (1)	0.310 (1)	0.290 (1)	1.010	0.03 (1)	743
	8P	0.613 (1)	0.312 (1)	0.279 (2)	1.001	0.03 (1)	702
	9P	0.602 (2)	0.314 (2)	0.290 (3)	0.974	0.19 (3)	623
	10P	0.610 (1)	0.310 (1)	0.290 (1)	1.000	0.03 (1)	1035
	11P	0.610 (1)	0.310 (1)	0.262 (2)	1.002	0.03 (1)	551
	12P	0.609 (1)	0.310 (1)	0.280 (1)	1.002	0.04 (1)	805
	13P	0.609 (1)	0.310 (1)	0.272 (1)	0.999	0.02 (1)	578
	14P	0.609 (1)	0.310 (2)	0.272 (1)	1.000	0.03 (1)	700
	15P	0.608 (1)	0.310 (1)	0.280 (1)	0.996	0.04 (1)	679
	16P	0.607 (1)	0.311 (1)	0.283 (1)	0.998	0.03 (1)	685
	17P	0.604 (1)	0.312 (1)	0.273 (2)	0.993	0.04 (1)	657
	18P	0.615 (2)	0.315 (1)	0.252 (2)	1.026	0.25 (7)	576
Marcasite	1M	0.515 (1)	0.282 (1)	0.297 (1)	0.987	0.064 (6)	1016
	2M	0.515 (1)	0.276 (2)	0.303 (2)	0.959	0.040 (10)	672
	3M	0.510 (1)	0.278 (1)	0.295 (1)	0.996	0.040 (3)	1092
	4M	0.509 (1)	0.282 (1)	0.350 (2)	0.992	0.010 (20)	624
	5M	0.505 (1)	0.276 (1)	0.276 (1)	0.989	0.020 (2)	713
	5M	0.502 (1)	0.276 (1)	0.276 (1)	0.989	0.010 (40)	583
	6M	0.502 (1)	0.277 (1)	0.290 (1)	0.982	0.050 (10)	747
	7M	0.500 (1)	0.277 (1)	0.271 (1)	0.988	0.020 (2)	849
	8M	0.500 (1)	0.277 (1)	0.272 (1)	0.986	0.020 (2)	785
	9M	0.499 (1)	0.277 (1)	0.261 (1)	0.985	0.100 (10)	984
	4M	0.499 (1)	0.277 (1)	0.262 (2)	0.995	0.020 (10)	509
	4M	0.498 (1)	0.274 (1)	0.262 (2)	0.995	0.020 (10)	509
	10M	0.495 (2)	0.277 (1)	0.325 (2)	0.990	0.020 (10)	562
	11M	0.491 (1)	0.274 (1)	0.282 (1)	0.982	0.030 (10)	652
12M	0.504 (1)	0.277 (1)	0.256 (2)	1.021	0.110 (30)	593	

<sup>1</sup>  $\Delta E_Q$  is the quadrupole splitting and is the magnitude of the separation between the two absorption maxima.

<sup>2</sup>  $\delta$  is the isomer shift and corresponds to the center-of-gravity of the two absorption maxima, measured relative to the center-of-gravity of an iron metal absorber.

<sup>3</sup>  $\Gamma$  is the linewidth which is the full width of the absorption line measured at half of the maximum intensity.

<sup>4</sup>  $I_L/I_H$  is the ratio of the absorption amplitude of the lower velocity line,  $I_L$ , to that of the higher velocity line,  $I_H$ .

<sup>5</sup> MISFIT (Ruby, 1973) is defined as:

$$M = \left[ \sum_{i=1}^N \left[ \left( \frac{YC(i) - YD(i)}{\sqrt{YD(i)}} \right)^2 - 1 \right] \right]^{1/2} / \left[ \sum_{i=1}^N \left[ \left( \frac{YO - YD(i)}{\sqrt{YD(i)}} \right)^2 - 1 \right] \right]^{1/2}$$

where  $M$  is MISFIT;  $YC(i)$  is the calculated count at velocity  $i$ ;  $YD(i)$  is the experimental count at velocity  $i$ ;  $YO$  is the off-resonant count and  $N$  is the total number of data points.

<sup>6</sup> Chi-squared,  $\chi^2$ , is the usual goodness-of-fit criterion and is defined as:

$$\chi^2 = \frac{1}{(N - n)} \sum_{i=1}^N \left( \frac{YC(i) - YD(i)}{\sqrt{YD(i)}} \right)^2$$

where  $n$  is the number of constrained parameters and the other variables are defined as in the equation for MISFIT.

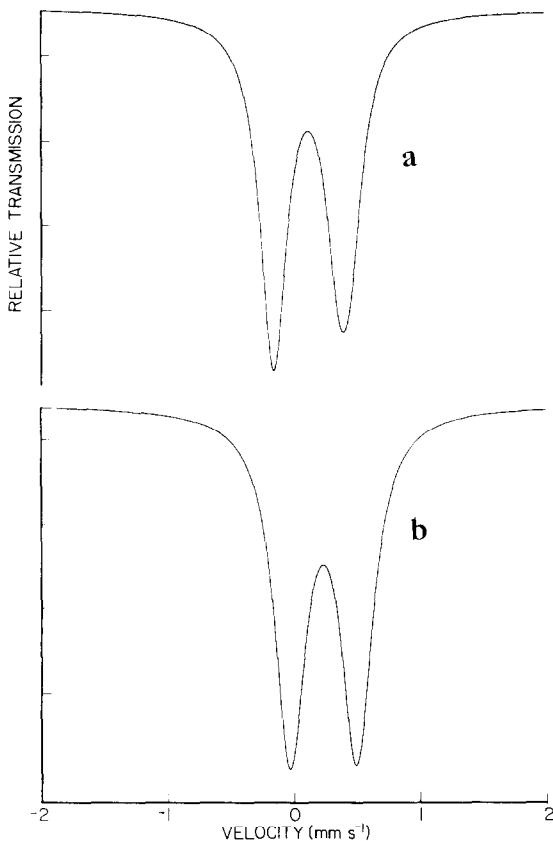


FIG. 4. Simulated  $^{57}\text{Fe}$  Mössbauer spectra for a 50:50 molar ratio pyrite:marcasite mechanical mixture (a) at 298 K. Parameters of samples 1P and 11M at 298 K were used to compute the spectra (b) at 77 K. The weakness of the asymmetry of this spectrum is noteworthy.

rite or marcasite but rather mixtures of the two and it is not obvious from these or other published spectra that mixtures of the two can be analyzed either qualitatively or quantitatively by means of Mössbauer spectroscopy. Therefore, preliminary to the analysis of the spectra of laboratory-prepared mixtures of pyrite and marcasite, the spectra of 75:25, 50:50 and 25:75 molar ratio mixtures of pyrite sample 1P and marcasite sample 11M have been simulated on the basis of the data in Table 3 (assuming equal recoilless fractions). As an example of these simulations, simulated spectra for a 50:50 molar ratio mixture are shown in Fig. 4.

From the available heat capacity data (Gronvold and Westrum, 1976), Debye temperatures,  $\theta_D$ , of 638°K and 615°K are calculated for pyrite and marcasite, respectively. Previous investigations have shown that for pyrite  $\theta_D$  derived from heat capacity data is in excellent agreement with that resulting from  $^{57}\text{Fe}$  Mössbauer spectroscopic measurements (Nishihara and Ogawa, 1979). The values of  $\theta_D$  leads to recoilless fractions for pyrite and marcasite that differ by only a few per cent at 300°K. Therefore, the assumption of equal recoilless fractions for the spectra of the pyrite/marcasite mixtures introduces

errors that are small compared to the precision of the data analysis and that would have no observable influence on the appearance of the simulated spectra.

Some features of the spectra in Fig. 4 are visually obvious. First, the spectra of mixtures of pyrite and marcasite at 298 K should be asymmetric quadrupole doublets with the low velocity line having the larger intensity and smaller line width. This general appearance is independent of whether pyrite or marcasite is the dominant phase. In addition, the apparent quadrupole splitting of a pyrite/marcasite mixture is less than that of the pure pyrite. The absence of any pronounced structure in the spectra is noteworthy and suggests that despite the ease of distinguishing single-phase pyrite from single-phase marcasite on the basis of their Mössbauer parameters, quantitative analyses of such mixtures by means of Mössbauer spectroscopy would require computer analysis of the data.

The qualitative conclusions based on the simulated spectra shown in Fig. 4 are verified by the spectra of mechanical mixtures of 12M and 18P for which the spectrum at 298 K for a 51:49 molar ratio pyrite:marcasite mixture is shown in Fig. 5. The solid lines in Fig. 5a represent fits of a single area-symmetric quadrupole doublet and in 5b of two independent lines. The fits of two independent lines were employed to allow for the asymmetry in the spectra of the mixtures as the isomer shifts for pyrite and marcasite are not identical. The parameters of the fits of two, independent lines are presented in terms of quadrupole doublets for the sake of comparisons with the pure phases. Both fits are equally satisfactory and lead to the same parameter values within experimental error as shown in Table 4. A comparison of the Mössbauer parameters and goodness-of-fits parameters for the two different fitting schemes is given in Table 5.

Attempts to fit two quadrupole doublets, with parameters corresponding to those of pure pyrite and pure marcasite, with variable intensities, failed to give relative intensities which were in reasonable agreement with the known compositions of the mixtures. For the 298 K spectra, fits of two quadrupole doublet patterns, in which all of the parameters were varied, led to reasonable relative intensities as shown in Table 6, but the  $\Delta E_Q$  values are erratic varying well outside the ranges shown in Table 3 and, therefore, rendering the fits unacceptable in terms of their deconvolution into a pyrite and a marcasite component. Because of the success of fitting either two independent lines or a single area-symmetric quadrupole doublet to the spectrum, it is not surprising that the two quadrupole doublets fits failed.

These results are consistent with those reported in a detailed study of the fitting of overlapping patterns in Mössbauer spectra (Dollase, 1975). For overlapping lines with equal widths and intensities and separations less than 0.6 of the value of the line width, it was found that the errors in all peak parameters



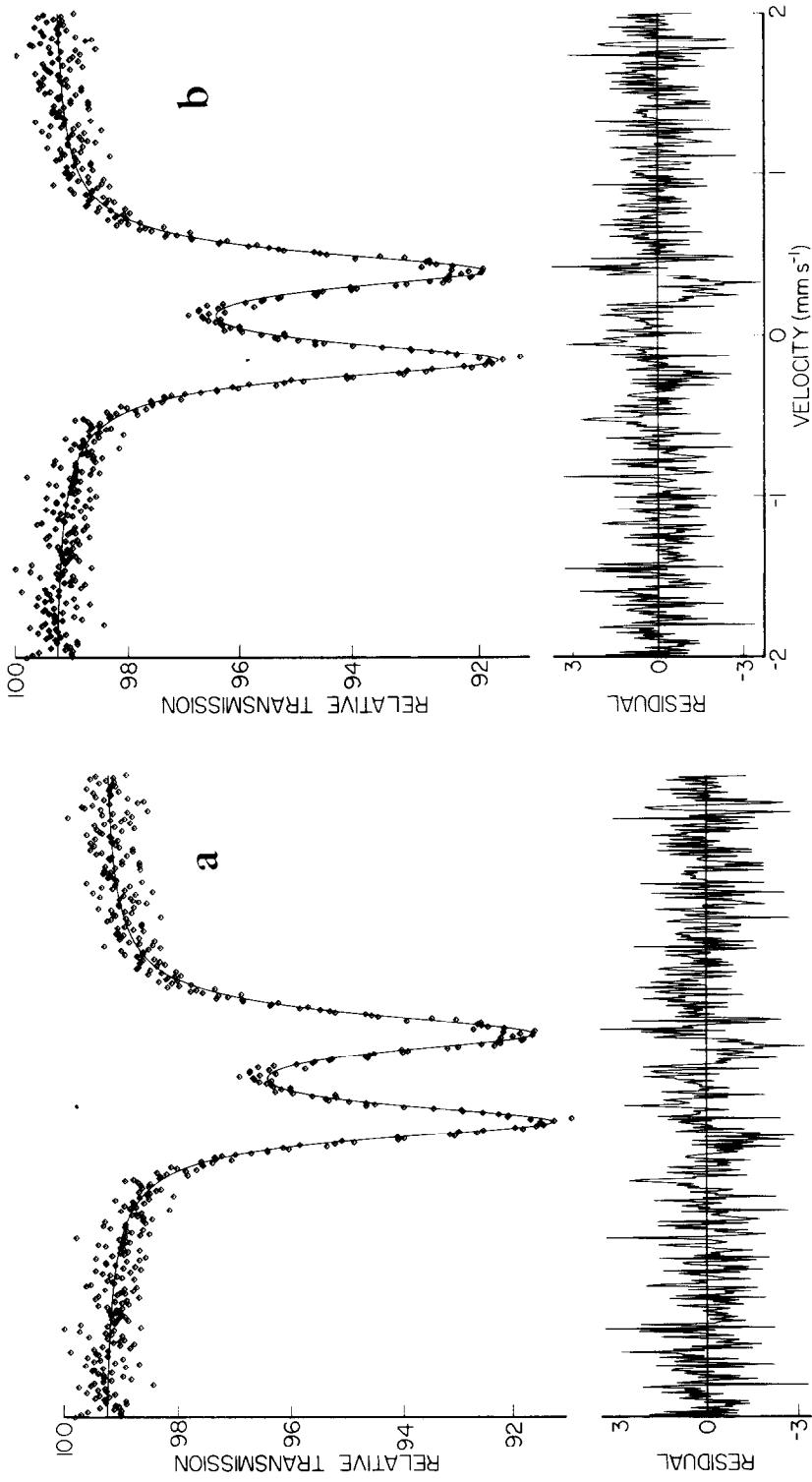


FIG. 5.  $^{57}\text{Fe}$  Mössbauer spectrum of a 51:49 molar ratio, pyrite: marcasite mechanical mixture at 298 K. (a) Fit of two independent lines, and (b) fit of an area-symmetric quadrupole doublet.

TABLE 4. Comparison of  $\Delta E_Q$  and  $\delta$  values for alternative fits to the spectra of pyrite/marcasite mixtures

Temperature (°K)	$X_{Py}/X_M^1$	$\Delta E_Q$ (mm s <sup>-1</sup> )		$\delta$ (mm s <sup>-1</sup> )	
		Two independent lines	One quadrupole doublet	Two independent lines	One quadrupole doublet
298	0.891/0.109	0.605 (1)	0.605 (1)	0.312 (1)	0.312 (1)
	0.783/0.217	0.591 (1)	0.591 (3)	0.309 (1)	0.309 (1)
	0.688/0.312	0.575 (2)	0.575 (1)	0.302 (2)	0.304 (1)
	0.509/0.493	0.554 (2)	0.554 (1)	0.298 (2)	0.299 (1)
	0.365/0.635	0.540 (1)	0.541 (1)	0.289 (1)	0.290 (1)
77	0.891/0.109	0.618 (1)	0.618 (1)	0.442 (2)	0.442 (1)
	0.783/0.217	0.610 (2)	0.606 (2)	0.424 (3)	0.422 (1)
	0.688/0.312	0.582 (1)	0.582 (3)	0.374 (2)	0.375 (1)
	0.507/0.493	0.566 (2)	0.566 (2)	0.367 (3)	0.368 (1)
	0.365/0.635	0.550 (2)	0.550 (2)	0.380 (3)	0.381 (1)

<sup>1</sup>  $X_{Py}$  and  $X_M$  are the mole fractions of pyrite and marcasite, respectively.

are remarkably high. For the two, apparent peaks in a marcasite/pyrite mixture, the separations between the two, component pyrite and marcasite lines are 0.12 mm s<sup>-1</sup> for the higher velocity lines and 0.01 mm s<sup>-1</sup> for the lower velocity lines; both of these separations are much less than the 0.19 mm s<sup>-1</sup> required for a reliable deconvolution of the spectrum.

Spectra of mechanical mixtures of pyrite and marcasite were also obtained at 77 K (as shown in Figs. 4 and 6). First of all, we note in the simulated spectrum of Fig. 4b that the averaging of the pyrite and marcasite spectral components is even more complete at 77 K than at 298 K, inasmuch as the asymmetry in the spectrum is no longer visually obvious. The spectrum of a mechanical mixture shown in Fig. 6 is in good agreement with the simulated spectrum. The solid lines represent the fit of a single, area-symmetric quadrupole doublet. Fits of two independent lines are also satisfactory and results of a data-analysis procedure similar to that used for the spectra at 298 K are given in Tables 4 and 5. The improved

agreement between the fits of two independent lines and a single quadrupole doublet on going from the 298 K to 77 K is in accord with the decreasing difference in isomer shifts.

The two quadrupole doublet fits to the 77 K spectra are poorer than those to the 298 K spectra in good accord (Dollase, 1975) with the poorer resolution of the component pyrite and marcasite spectra at 77°K. The maximum deviation between the lines of pyrite and marcasite contributing to a given, convoluted line in the spectrum of the mixture has been reduced from 0.12 mm s<sup>-1</sup> at 298 K to 0.07 mm s<sup>-1</sup> at 77°K. A reversal in the relative intensities of the two quadrupole doublet fits compared to the known amounts of pyrite and marcasite present is noteworthy, cf. rows eleven and twelve in Table 6.

The above results clearly show that the two <sup>57</sup>Fe Mössbauer spectral components in mixtures of pyrite and marcasite are strongly averaged in the composite spectrum and a deconvolution is ambiguous. It follows that the Mössbauer parameters of the composite

TABLE 5. Goodness-of-fit parameters for alternative fits to the spectra of marcasite/pyrite mixtures

Temperature	$X_{Py}/X_M$	Two independent lines		One quadrupole doublet		Two quadrupole doublet	
		$\chi^2$	MISFIT (%)	$\chi^2$	MISFIT (%)	$\chi^2$	MISFIT (%)
298	0.891/0.109	594	0.17 ± .04	596	0.17 ± .04	570	0.14 ± .04
	0.783/0.217	657	0.33 ± .06	659	0.34 ± .06	633	0.30 ± .06
	0.688/0.312	607	0.23 ± .05	617	0.24 ± .06	577	0.18 ± .06
	0.507/0.493	655	0.29 ± .05	675	0.32 ± .06	614	0.23 ± .05
	0.365/0.635	644	0.15 ± .03	655	0.15 ± .03	553	0.07 ± .03
77	0.891/0.109	519	0.04 ± .02	524	0.04 ± .02	497	0.02 ± .01
	0.783/0.217	577	0.08 ± .02	574	0.08 ± .02	527	0.05 ± .02
	0.688/0.312	658	0.07 ± .01	661	0.06 ± .01	577	0.04 ± .01
	0.507/0.493	675	0.17 ± .03	700	0.19 ± .03	629	0.14 ± .03
	0.365/0.635	619	0.20 ± .04	625	0.20 ± .04	565	0.13 ± .04

TABLE 6. Mössbauer parameters for the two quadrupole doublet fits to the spectra of pyrite/marcasite mixtures

Temperature (°K)	$X_{py}/X_M$	"Pyrite" Component			Rel. <sup>1</sup> integ. inten.	"Marcasite" Component			Rel. integ. inten.
		$\Delta E_Q$ (mm s <sup>-1</sup> )	$\delta$ (mm s <sup>-1</sup> )	$\Gamma$ (mm s <sup>-1</sup> )		$\Delta E_Q$ (mm s <sup>-1</sup> )	$\delta$ (mm s <sup>-1</sup> )	$\Gamma$ (mm s <sup>-1</sup> )	
298	1.00/0.00	0.619 (1)	0.329 (1)	0.303 (4)	1.00	—	—	—	—
	0.891/0.109	0.624 (2)	0.316 (1)	0.260 (10)	0.906	0.450 (20)	0.291 (6)	0.210 (40)	0.093
	0.783/0.217	0.616 (5)	0.314 (1)	0.258 (2)	0.857	0.460 (10)	0.286 (2)	0.210 (10)	0.142
	0.688/0.312	0.624 (5)	0.309 (2)	0.260 (10)	0.700	0.480 (10)	0.286 (5)	0.210 (10)	0.300
	0.507/0.493	0.639 (5)	0.315 (4)	0.250 (10)	0.434	0.485 (5)	0.286 (4)	0.250 (10)	0.566
	0.365/0.635	0.660 (4)	0.303 (3)	0.232 (4)	0.330	0.481 (3)	0.284 (1)	0.241 (3)	0.670
	0.00/1.00	—	—	—	—	0.504 (1)	0.274	0.256 (2)	1.00
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77	1.00/0.000	0.624 (2)	0.407 (1)	0.278 (4)	1.000	—	—	—	—
	0.891/0.109	0.616 (2)	0.425 (1)	0.272 (3)	0.881	0.620 (7)	0.523 (3)	0.17 (1)	0.119
	0.783/0.217	0.630 (10)	0.458 (4)	0.47 (1)	0.679	0.520 (10)	0.320 (10)	0.43 (5)	0.320
	0.688/0.312	0.590 (4)	0.428 (6)	0.357 (6)	0.504	0.575 (3)	0.300 (7)	0.36 (1)	0.496
	0.506/0.493	0.603 (4)	0.394 (3)	0.280 (10)	0.552	0.523 (4)	0.338 (4)	0.31 (2)	0.448
	0.365/0.635	0.589 (5)	0.442 (3)	0.230 (10)	0.292	0.538 (3)	0.351 (2)	0.30 (3)	0.708
		0.000/1.00	—	—	—	—	0.508 (1)	0.402 (1)	0.294 (3)

<sup>1</sup> Relative integrated intensities, i.e. the relative areas of the fitted patterns.

spectrum are, themselves, weighted averages of those of pyrite and marcasite and could be used to determine the relative amounts of pyrite and marcasite in the mixture. We have, therefore, adopted an approach for analyzing pyrite/marcasite mixtures in which the spectrum is treated as a single quadrupole doublet whose Mössbauer parameters are the weighted averages of those of the pure phases.

At 77 K, a least squares analysis of the relationship between the mole fraction,  $X_{py}$ , of pyrite and the electric quadrupole splitting of the mixture,  $\Delta E_Q^M$ , provided by the data in Table 4, results in the following equation for the dependence of  $\Delta E_Q^M$  on the pyrite concentration:

$$\Delta E_Q^M = 0.121X_{py} \text{ (mm s}^{-1}\text{)} + 0.507 \text{ (mm s}^{-1}\text{)} \quad (1)$$

for which the multiple correlation coefficient squared,  $R^2$ , is 0.984. If we use the data in Table 6 for pure pyrite and pure marcasite, the equation expected on the basis of the above-mentioned assumption of an averaged spectrum is

$$\Delta E_Q^M = 0.116X_{py} \text{ (mm s}^{-1}\text{)} + 0.508 \text{ (mm s}^{-1}\text{)} \quad (2)$$

The fitted equation for the data at 298 K for which  $R^2$  is 0.99 is given below:

$$\Delta E_Q^M = 0.114X_{py} \text{ (mm s}^{-1}\text{)} + 0.500 \text{ (mm s}^{-1}\text{)} \quad (3)$$

The equation expected on the basis of the parameters for pure pyrite and pure marcasite listed in Table 3 is the following:

$$\Delta E_Q^M = 0.111X_{py} \text{ (mm s}^{-1}\text{)} + 0.504 \text{ (mm s}^{-1}\text{)} \quad (4)$$

### DISCUSSION

A comparison of the Mössbauer parameters of this investigation with those reported previously for pyrite

provides some insight into the difficulties occasioned by measurements on small suites of samples. The average values for  $\langle \Delta E_Q \rangle$  and  $\langle \delta \rangle$  at 298 K for pyrite computed from the data in Table 3, excluding the first four entries, are  $0.6110 \pm 0.0020 \text{ mm s}^{-1}$  and  $0.3130 \pm 0.0070 \text{ mm s}^{-1}$ , respectively.  $\langle \Delta E_Q \rangle$  and  $\langle \delta \rangle$  at 298 K for marcasite are  $0.5030 \pm 0.0070 \text{ mm s}^{-1}$  and  $0.2779 \pm 0.0020 \text{ mm s}^{-1}$ , respectively. The most detailed investigation (Huffman and Huggins, 1978) of the Mössbauer spectra of pyrite in coals results in a range of values for  $\Delta E_Q$  from  $0.59 \text{ mm s}^{-2}$  to  $0.63 \text{ mm s}^{-1}$ , clearly outside of the range of values found in this study for relatively pure samples of pyrite. The "best" values obtained in the above-mentioned study (Huffman and Huggins, 1978) of  $0.614 \text{ mm s}^{-1}$  for  $\Delta E_Q$  and  $0.303 \text{ mm s}^{-1}$  for  $\delta$  are in good agreement with the results obtained in this study. These "best" values were, however, chosen primarily on statistical grounds regarding the quality of the spectrum and not on an independent analysis of the mineralogy and chemistry of the pyrite samples themselves.

An earlier report of a Mössbauer investigation of a sample from the same locality as pyrite 6P resulted in a  $\Delta E_Q$  of  $0.634 \text{ mm s}^{-1}$  and  $\delta$  of  $0.299 \text{ mm s}^{-1}$  (Finklea *et al.*, 1976). These parameters values are not only in poor agreement with those of an apparently similar specimen, *e.g.*, sample 6P, but are also outside of the range of parameters reported in Table 3. The magnitude of the electric quadrupole splitting is higher and the isomer shift smaller, respectively, than any of those determined in this investigation. The present results on the suite of samples demonstrate that such large values of  $\Delta E_Q$  are to be expected for samples having high concentrations of impurities, which does not appear to be the case for the specimen from Ambasaquas, Spain. A recent report

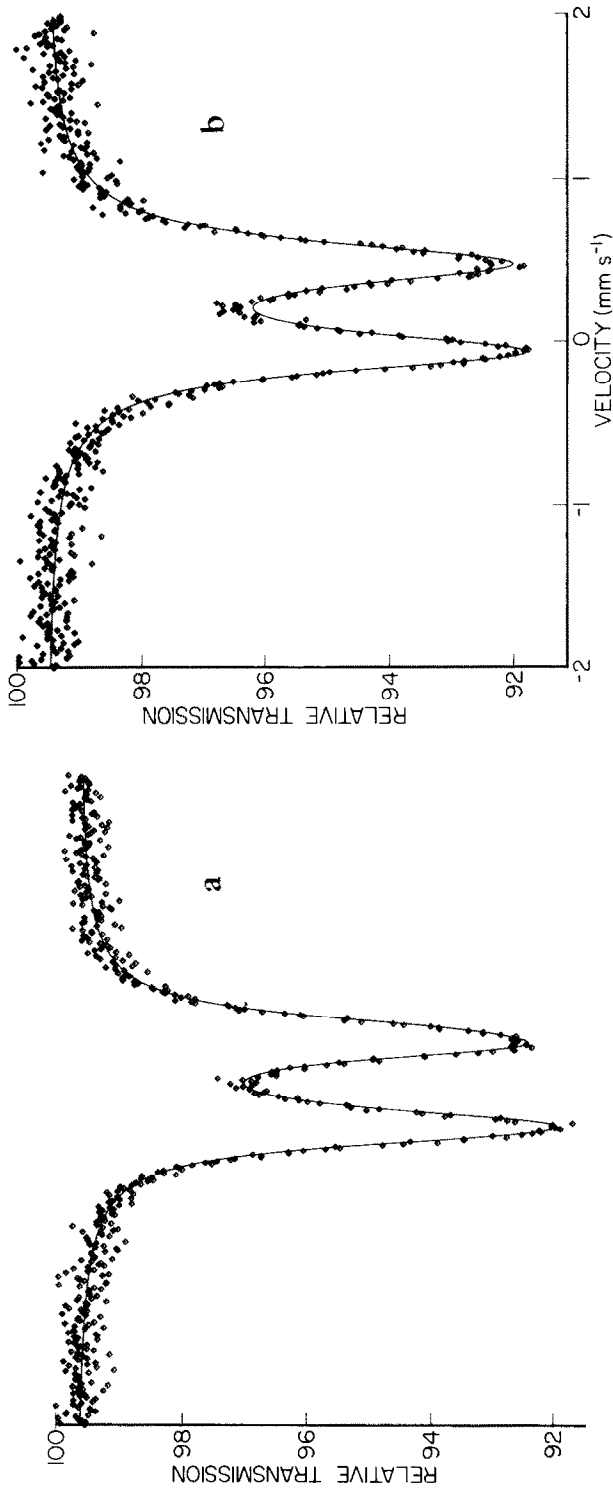


FIG. 6.  $^{57}\text{Fe}$  Mössbauer spectrum of a 37:63 molar ratio, pyrite:marcasite mechanical mixture at (a) 298, and (b) 77 K. The change in the asymmetry of the spectrum on going from 298 K to 77 K is in excellent agreement with the simulated spectra in Figure 4.

of  $0.652 \text{ mm s}^{-1}$  for  $\Delta E_Q$  of a pyrite in a coal slurry clearly warrants further confirmation (Saporoschenko *et al.*, 1978), for either the Mössbauer parameters are in error or they suggest a very unusual chemistry or texture for the pyrite in question.

Pyrite and marcasite, as pure phases, can, with little question, be distinguished from each other by means of <sup>57</sup>Fe Mössbauer spectroscopy at 298 K almost without regard for the nature of the deposit in which they are found. A definitive statement cannot be made for pyrite and marcasite in coals at this time because adequate comparative data are lacking. However, unless the pyrites and marcasites in coals are indeed different in their crystal/chemical structures, a determination of whether the FeS<sub>2</sub> phase in coals is pyrite, marcasite, or a mixture of the two should be straightforward.

The range of values observed in this investigation for the Mössbauer parameters of pyrite and marcasite of different provenances is rather large. For pyrite, the range of values is  $0.619 \text{ mm s}^{-1}$  to  $0.604 \text{ mm s}^{-1}$  for  $\Delta E_Q$  and  $0.329 \text{ mm s}^{-1}$  to  $0.310 \text{ mm s}^{-1}$  for  $\delta$  at 298 K. For marcasite at 298 K, the range of values is  $0.515 \text{ mm s}^{-1}$  to  $0.491 \text{ mm s}^{-1}$  for  $\Delta E_Q$  and  $0.282 \text{ mm s}^{-1}$  to  $0.274 \text{ mm s}^{-1}$  for  $\delta$ . When considered in the light of other iron-containing phases in coals, this spread in hyperfine parameters for pyrite and marcasite can, in principle, pose difficulties to a complete, nondestructive determination of the distribution of iron among different phases. The mineral contained in coal whose Mössbauer spectrum overlap most with those of the FeS<sub>2</sub> phases is illite (Huffman and Huggins, 1978). There are several components in the <sup>57</sup>Fe Mössbauer spectrum of illites but only one presents significant difficulties to deconvolution of the spectra of coals. This component has been reported to have isomer shifts ranging from  $0.32 \text{ mm s}^{-1}$  to  $0.36 \text{ mm s}^{-1}$  and quadrupole splittings ranging from  $0.49 \text{ mm s}^{-1}$  to  $0.63 \text{ mm s}^{-1}$  (Ericsson *et al.*, 1977; Saporochensko *et al.*, 1980). A definitive Mössbauer investigation of well-characterized illites has not been reported and it is yet possible that the spectra of coals containing both illite and pyrite may be analyzed quantitatively. For the moment, however, dilute hydrofluoric acid is effective in removing the component in the spectrum attributable to illite and an analysis of the pyrite/marcasite component is possible even when illite is present (Evans *et al.*, unpub. results).

With some limitations, quantitative analysis of pyrite and marcasite in mixtures of the two is feasible with a time investment similar to that required for traditional X-ray diffraction analysis. The precision of the analyses is limited by the accuracy and precision with which the Mössbauer parameters of the pyrite and marcasite, as pure phases, are known. For these analyses, the electric quadrupole splitting is the more useful parameter. The variations in the electric quadrupole splitting caused by small differences in composition and other less-well defined mineralogi-

cal/geological parameters limit the acquisition of quantitative data with errors less than approximately  $\pm 5$  per cent. Nonetheless, determinations of acceptable accuracy can be obtained. If we consider various combinations of extreme values of the quadrupole splittings for pyrite and marcasite, the maximum error for a 50:50 marcasite/pyrite mixture would be  $\pm 15$  per cent. If the pyrite and marcasite are known to contain low concentrations of impurities, for example,  $<1000$  ppm of arsenic, then the error in the determination of the relative amounts of marcasite and pyrite in a mixture from a single quadrupole doublet fit to the spectrum would not exceed  $\pm 5$  per cent. The extent to which the unusual textures of pyrite and marcasite in coals would influence these results is not known. The spectrum of a synthetic vapor-deposited film has been published and parameters close to those of bulk pyrite samples were obtained (Seehra *et al.*, 1979); on the other hand, a preliminary report also suggested that the influence of particle size on the Mössbauer spectrum was significant (Williamson *et al.*, 1979); but definitive <sup>57</sup>Fe Mössbauer spectra of framboidal and other morphologically unusual pyrite and marcasite specimens have not been reported.

Examination of the data in Tables 1, 3, and 7 shows that those samples which have abnormally high quadrupole splittings also contain significant concentrations of arsenic. In the absence of such impurities, the range of values for the <sup>57</sup>Fe Mössbauer parameters of pyrite is considerably reduced; we have excluded the Mössbauer parameters of such samples, as noted above, from the computation of  $\langle \Delta E_Q \rangle$  and  $\langle \delta \rangle$  for the suite of pyrite samples. The increase in the electric quadrupole splitting associated with the relatively high arsenic contents is of potential importance as it suggests that <sup>57</sup>Fe Mössbauer spectroscopy of pyrite can be used to monitor the extent of arsenic solid solution in the pyrite lattice.

Appreciable concentrations of arsenic in pyrite have been shown to be associated with low formation temperatures (Ramdohr, 1969) and have been observed in pyrite framboids with the arsenic being incorporated into the pyrite lattice during its primary crystallization (Ostwald and England, 1979). In a recent investigation of the distribution of arsenic in an Upper Freeport Coal, it was concluded that the

TABLE 7. Arsenic contents and electric quadrupole splittings in pyrites

Sample number	Arsenic Concentration (ppm)
1P	3700 (0.619 mm s <sup>-1</sup> )
2P	1200 (0.615 mm s <sup>-1</sup> )
3P	7600 (0.614 mm s <sup>-1</sup> )
4P	1500 (0.614 mm s <sup>-1</sup> )
5P	— (0.614 mm s <sup>-1</sup> )
6P	— (0.614 mm s <sup>-1</sup> )
7P	— (0.613 mm s <sup>-1</sup> )

arsenic-containing pyrites were epigenetic (Minkin *et al.*, 1980). The occurrence of arsenic in pyrite therefore has important implications for the processes by which pyrite is emplaced in coal and a definitive confirmation of the influence of arsenic on the Mössbauer parameters of pyrite would be highly desirable.

Even though further, systematic studies of arsenic-containing pyrite and marcasite are warranted, the observed tendency for  $\Delta E_Q$  to increase as the arsenic content increases is supported by other available data. Both arsenopyrite, FeAsS, and (synthetic) loellingite, FeAs<sub>2</sub>, have <sup>57</sup>Fe quadrupole splittings appreciably larger than that of pyrite (Nishihara and Ogawa, 1979; Goncharov *et al.*, 1970).  $\Delta E_Q$  for FeAsS is  $\sim 1.1 \text{ mm s}^{-1}$  and for FeAs<sub>2</sub>  $\sim 1.68 \text{ mm s}^{-1}$  at 298 K. A strict correlation of the magnitude of the quadrupole splitting with the arsenic content of pyrite is not expected to be valid as the structures of pyrite, arsenopyrite, and loellingite are not the same. However, at the low concentrations of arsenic considered here, a linear perturbation approach to the effect of arsenic on the Mössbauer parameters of pyrite is probably justified. Assuming, therefore, that the  $\Delta E_Q$  for an arsenic-containing pyrite is the weighted mean of the  $\Delta E_Q$  values for pyrite and loellingite, we calculate that  $\Delta E_Q$  should increase by approximately  $0.01 \text{ mm s}^{-1}$  for each 10,000 ppm of arsenic present. This estimate is in good agreement with the results in Table 7. For this calculation, we have used the  $\Delta E_Q$  value of sample 13P, one of the purest pyrite samples used in this investigation, which leads to the following equation for the relationship between the electric quadrupole splitting of an arsenic-containing pyrite, and the arsenic content:

$$\Delta E_Q(py - As) = \Delta E_Q(l) + \frac{0.8335 - 1.1 \times 10^{-6} X_{As}}{0.8335 - 4.8 \times 10^{-7} X_{As}} [\Delta E_Q(p) - \Delta E_Q(l)] \quad (5)$$

where  $\Delta E_Q(py - As)$  is the quadrupole splitting of an arsenic-containing pyrite.  $\Delta E_Q(l)$  is the electric quadrupole splitting of loellingite;  $\Delta E_Q(p)$  is the electric quadrupole splitting of pure pyrite and  $X_{As}$  is the concentration in ppm of arsenic. We also note that  $\Delta E_Q$  for FeAsS is surprisingly close to the average value of  $\Delta E_Q$  for pyrite and loellingite though the linear perturbation model used here is certainly not expected to be valid at such high arsenic concentrations.

For pyrites in coals having arsenic concentrations in the higher range of those reported thus far (about 2 per cent) (Ostwald and England, 1979) the increase in the electric quadrupole splitting would be  $\sim 0.02 \text{ mm s}^{-1}$ . This change in  $\Delta E_Q$  is well within the experimental error with which the quadrupole splitting can be determined and indicates that the arsenic contents of pyrites can be estimated with an accuracy of  $\pm 10$  per cent on the basis of the Mössbauer parameters. Comparisons between the measured quad-

rupole splittings of pyrites in arsenic-containing coals and those calculated using Equation (5) would provide important insights into the distribution of arsenic among the various phases. This datum is very important and otherwise difficult to obtain (Minkin *et al.*, 1980).

The effects of impurities, such as selenium and tellurium are expected to be much smaller than those of arsenic as the  $\Delta E_Q$  values of the pure, end-member compositions do not differ greatly from those of pyrite; for instance,  $\Delta E_Q$  is  $0.649 \text{ mm s}^{-1}$  for FeTe<sub>2</sub> and  $0.667 \text{ mm s}^{-1}$  for FeSe<sub>2</sub> (Nishihara and Ogawa, 1974). The isomer shifts for these two phases,  $0.447 \text{ mm s}^{-1}$  and  $0.527 \text{ mm s}^{-1}$ , respectively, unlike those of FeAs<sub>2</sub> and FeAsS, are substantially different from that of pyrite, indicating significant differences in electronic structure. Metallic impurities such as nickel and cobalt would lead to quadrupole splittings of smaller magnitudes and larger isomer shifts than those in pure pyrite (Nishihara and Ogawa, 1979). Therefore, the quantitative estimates of the arsenic content of pyrites having low levels of metallic impurities should be straightforward. Complications arising from impurities such as nickel, cobalt, selenium, and tellurium would be readily indicated by an asymmetric spectrum at 298 K and proper care in analyzing the data could result, even in this case, in meaningful results. Verification of the above extrapolations by systematic measurements on arsenic, selenium, tellurium, nickel, and copper substituted pyrites prior to applying this methodology to coals would be desirable.

## CONCLUSIONS

The <sup>57</sup>Fe electric quadrupole splittings of pyrite and marcasite show variations well outside of the range of experimental error and for pyrite appear to reflect variations in the concentration of impurity elements. As expected, the variations in the isomer shifts for both pyrite and marcasite are smaller than those for  $\Delta E_Q$ . Preliminary results indicate that Mössbauer spectroscopy can be used to monitor the arsenic content of pyrite and, because of the special circumstances under which arsenic exhibits an appreciable solubility in pyrite, can provide critical insights into genetic investigations of coal deposits. Results of this investigation also demonstrate that <sup>57</sup>Fe Mössbauer spectroscopy can provide determinations of moderate accuracy of the relative amounts of pyrite and marcasite in mixtures of the two. The application of the above results to coals will, however, require further improvements in methodology because of the extreme overlap with the pyrite/marcasite pattern of the <sup>57</sup>Fe spectra resulting from clays and other more poorly defined iron-containing phases in coals.

Recent experiments on samples of Waynesburg coals, however, demonstrate that the relative concentrations of pyrite and marcasite in coal are readily

determined using the methodology developed here, provided the non- $\text{FeS}_2$  iron is removed by HF leaching (Evans *et al.*, unpub. results). In these experiments, the pyrite/marcasite ratio is readily determined using  $^{57}\text{Fe}$  Mössbauer spectroscopy even though the presence of marcasite is not obvious in the X-ray diffraction pattern.

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