

1-7987164c.2
CPUB

MRL 88-22 (OPJ)c.2

MRL 88-22 (OPJ)c.2

AN INVESTIGATION INTO THE RELATIONSHIP BETWEEN
THE EXPLOSIBILITY AND MINERALOGY OF SULPHIDE ORE
DUSTS

K.J. Mintz, J.P. Saindon, K.C. Wheeland and
B.J. Kieller

MRL 88-022(OPJ)

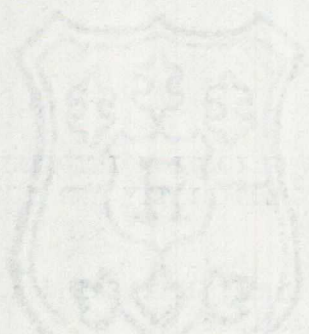


c.2
CPUB



W6T 88-93 (062) 5.3

5.0 (190) 56-88 JRM



© 1997 COTTON CANADA

SUPERFINE

LINEN RECORD

100% COTON / COTTON CANADA

Camnet Information
Centre
D'information de Camnet
 JAN 28 1997
 555, rue Booth ST.
 Ottawa, Ontario K1A 0G1

1-7987169c.2

CPUB
→

Article published in:

Sulphide Dust Explosions

Proceedings of the Special Session held at the
CIM Annual General Meeting, Edmonton, May 11, 1988

Edited by
Allan E. Hall
The University of British Columbia
Vancouver, Canada

Sponsored by the Metal Mining Division of
THE CANADIAN INSTITUTE OF MINING AND METALLURGY

c.2
CPUB →

H7987164 c.2
CPUB

AN INVESTIGATION INTO THE RELATIONSHIP BETWEEN THE EXPLOSIBILITY
AND MINERALOGY OF SULPHIDE ORE DUSTS

K.J. Mintz
Mining Research Laboratories,
CANMET, Energy, Mines and Resources,
Ottawa, Ontario.

J.P. Saindon and K.G. Wheeland
Noranda Research Centre,
Pointe-Claire, Quebec.

B.J. Kieller
Centre de Recherches Minérales,
Quebec, Quebec.

ABSTRACT

Twenty-one ore dusts of varying mineralogy, sulphur content and reputed in-mine explosibility were selected from eight mines. After chemical and mineralogical analysis and sieving into two size fractions (+45/ -63 microns and -45 microns), these samples and seven pure minerals were tested for explosibility in oxygen in a Hartmann chamber. The maximum explosion pressures and maximum rates of pressure do not correlate with sulphur content alone; the types of minerals are also important. Residues were analyzed to check the combustion reactions. Further comparisons between laboratory and mine results are planned to improve predictability.



C.2
CPUB

PURPOSE OF STUDY

The prediction of the risk of a secondary explosion of sulphide ore dust is an inexact science at present, and is usually based on the sulphur level in the ore and the previous history of blasting in the specific area of the mine. For example, a report in 1987 stated the following: "Samples from high-risk areas were >29% S, and no flame occurred at <23% S" (1).

It is generally not possible to predict occurrences with certainty except at very low and very high sulphur levels. Some of the factors involved include the mining method and blast design, as well as the characteristics of the ore and ore dust (homogeneity, chemical and mineralogical composition and friability).

This laboratory study was undertaken to evaluate the role of mineralogy.

OUTLINE OF OVERALL PROJECT

All sample selection and preparation was by Noranda Research, which is also coordinating the cooperative program.

A total of 28 samples of ground ore from high, medium and low explosibility risk areas were obtained from eleven mines. The samples were sized by wet screening into 45-63 micron and -45 micron fractions, and chemically analyzed for total sulphur. Polished sections were prepared from 21 samples for mineralogical examination by the Centre de Recherches Minérales (CRM). In addition, samples of 11 metal sulphide minerals (<106 microns) were submitted for explosivity testing.

Table 1 lists the samples and indicates the sulphur analyses and mineralogical results.

The mineral and ore dust samples (two screen sizes) were forwarded to CANMET for explosivity testing in a 1.2 L Hartmann tube and 20 L vessel. The minimum ignition temperature of the dust cloud was determined in a Godbert-Greenwald furnace. Samples of combusted solids from some of the explosivity tests were forwarded to CRM for mineralogical examination.

The experimental work and data review are incomplete at this stage. This paper presents and discusses some of the initial explosivity results, and indicates the course of further work.

TABLE 1 - DUST EXPLOSTIVITY SAMPLES

SAMPLE NUMBER	SOURCE	DESCRIPTION	SULPHUR %	MINERAL (AS % OF OPAQUE MINERAL)					
				PYRITE	PYRRHOTITE	SPHALERITE	CHALCOPYRITE	MAGNETITE	OTHER
1	WESTMIN	WM350	45.7	98.8	--	--	0.8	--	0.4
2	WESTMIN	WM356	44.0	72.0	--	24.0	3.0	--	1.0
3	WESTMIN	WM370	50.8	85.6	--	0.2	14.0	--	0.2
4	GECO	2-29-0	37.2	51.6	26.4	15.6	0.6	5.2	0.6
5	GECO	2-29-C	34.9	43.6	29.4	14.6	1.4	10.4	0.6
6	GECO	11-35-C	33.8	29.0	15.2	39.6	13.8	1.6	0.8
7	GECO	11-35-0	18.3	29.0	19.6	21.2	26.4	2.6	1.2
8	MATTABI	11-50-SILL	38.5	50.4	5.6	43.4	0.4	0.2	tr
9	MORITA	1039	31.5	53.2	8.0	18.0	0.8	12.0	tr
10	MORITA	1040	47.4	95.2	0.2	0.2	1.8	2.6	--
11	MORITA	1041	25.4	49.4	1.4	5.8	16.8	26.4	0.2
12	KIDD	9369	45.3	92.0	1.2	6.2	0.2	0.2	0.2
13	KIDD	9370	34.7	73.2	2.4	21.4	0.2	0.6	2.2
14	LOCKERBY	38-157	28.0	13.2	78.6	--	7.0	0.6	0.6
15	LOCKERBY	24-150	25.1	--	--	--	--	--	--
16	LOCKERBY	18-34	9.9	20.6	62.6	--	10.2	6.2	0.4
17	STRATHCONA	22-39-45	29.8	--	--	--	--	--	--
18	STRATHCONA	27-2-558	25.9	9.6	76.6	--	6.6	4.8	--
19	FRASER	34-1-274	30.2	13.4	82.0	--	11.8	2.8	--
20	FRASER	33-0-271	29.9	19.2	71.0	--	2.6	7.2	--
21	SULLIVAN	7-10	29.3						
22	SULLIVAN	3-75	25.2						
23	SULLIVAN	0-10-30	36.6						
24	MANISIVIK	1	30.7						
25	MANISIVIK	2	29.0						
26	MANISIVIK	3	43.6						
27	MANISIVIK	4	34.5						
28	HEMLO	--	--						
101	PYRITE	(See Note 2)	53.0						
102	PYRRHOTITE IMPURE		26.0						
103	PYRRHOTITE PURE		36.4						
104	CHALCOPYRITE		34.9						
105	GALENA		13.4						
106	ZNS		32.9						
107	SPHALERITE		32.9						
108	SPHALERITE LOW FE		32.5						
109	SPHALERITE HIGH FE		25.5						
110	TETRAHEDRITE		26.0						
111	ARGENTITE		10.0						

NOTES:

1. All -45 micron samples
2. Est'd for pure samples

EXPLOSIBILITY STUDIES

Procedures

The Hartmann apparatus for measuring the maximum explosion pressure, P_m , and the maximum rate of explosion pressure rise, $(dp/dt)_m$, was developed by the U.S. Bureau of Mines about 50 years ago, and is the subject of an ASTM Standard, E789-81. It was chosen for the first stage of this study because of its availability and its ability to generate data relatively rapidly. Although many dust explosion researchers have criticized it, primarily because of its small size, it can still provide useful relative data.

The apparatus consists essentially of a steel tube, into which dust is dispersed by a burst of air, a pair of electrodes to ignite the dust-air mixture and a pressure transducer to measure the pressure produced during the explosion. Using the CANMET equipment, the pressure was measured every 0.2 ms by a CEC 1000 strain-gauge transducer and stored in a Nicolet 4094 digital oscilloscope. Sulphide ore dusts, despite the problems that they have caused the mines, are relatively nonflammable. They are so insensitive that they cannot be ignited in air in the Hartmann tube. In order to increase the flammability of the sulphide dust clouds, pure oxygen was used in place of air. Although this may be considered an unrealistic condition, the relative explosibility values should still be valid.

The maximum explosion pressure is a function of the concentration of the dust, rising rapidly from the lower flammability limit to the optimum concentration, then decreasing slowly thereafter. For convenience, all the samples were tested at a concentration of 1.6 g/L, which is close to the optimum concentration.

The 20 L vessel is now widely used for dust explosion studies, but has not yet been adopted as a standard. It has a number of advantages: a more realistic size, a more reproducible dust dispersion system, a capacity to carry out tests employing atmospheres other than air, the capacity to sample the products of combustion and, most important for sulphide ore dusts, an ability to accommodate more powerful ignitors. CANMET has recently commissioned its 20 L vessel, which is based in the U.S. Bureau of Mines design (2). Preliminary tests have been carried out using the Sobbe 5 KJ chemical ignitor, which is much more powerful than the electrode discharge. Its use has allowed the

explosion tests to be carried out in ordinary air rather than in pure oxygen. The dust is placed in a tube at the bottom of the vessel, which is then completely evacuated. Then air at 1100 kPa contained in a 16 L pressure vessel is released through a solenoid valve and passes through the dust sample tube, thus dispersing it very effectively. After the dust is dispersed, the pressure is exactly one atmosphere. The ignitor is fired after a delay to decrease the turbulence arising from the initial dispersion. The timing of the events are controlled digitally to a millisecond. The dust dispersion and explosion can be observed through a window on the side of the vessel. After the explosion, the combustion gases can be drawn into a paramagnetic oxygen sensor to determine how much oxygen has not reacted, and a spectrometer to measure the gaseous products of combustion.

The major problem that mines experience with sulphide dust explosions is not usually the direct blast damage, but the SO_2 gas produced. In order to quantify the amounts produced, a Miran 80 infrared spectrometer with a 5 m variable path length Wilks spectrometer cell has been connected to the 20 L vessel to sample the atmosphere after an explosion test. Using known concentrations of SO_2 in air, the 9 micron wavelength absorption band has been shown to be linear in the range of concentrations involved. The other absorption bands of SO_2 have interference from CO_2 and H_2O absorption bands.

Another parameter of interest is the minimum ignition temperature (MIT), which is the lowest temperature at which a dust-cloud can self-ignite. The Godbert-Greenwald furnace, also developed by the U.S. Bureau of Mines (3), was used to determine the MIT's of some of the samples. In this test, a burst of air disperses dust from a sample holder into the top of a tubular furnace set at the desired test temperature. For most dusts, a flame emerging from the bottom of the furnace is taken to mean that the dust ignites at that temperature. The lowest temperature of the furnace at which a flame can be observed is taken as the minimum ignition temperature. For sulphide dusts, instead of a flame, individual sparks are observed. Note that these tests were done in air, not oxygen.

Results and Discussion

The mean values of P_m and $(dP/dt)_m$ for pure minerals and various ore

dust samples are presented in Table 2. The numbers given are averages of several tests. The standard deviation of P_m average 30% of the respective values; the standard deviation of $(dP/dt)_m$ average 48% of the respective values. P_m depends mainly on the formation of a dust cloud of appropriate characteristics, whereas $(dP/dt)_m$ depends on how the dust cloud is formed. Hence, the latter is more apparatus-dependent and produces more scattered data with higher standard deviations. In predicting damage from explosions, $(dP/dt)_m$ is usually considered more important than P_m , and is sometimes called the explosion severity. In the case of sulphide dust explosions, where the primary problem is usually the quantity of SO_2 produced, P_m , which is closely related to the amount of reaction, may be the more meaningful parameter. Figure 1 shows the relationship between $(dP/dt)_m$ and P_m for our sulphide dust tests. It appears to be of exponential type. The finer fraction shows a steeper dependence. It cannot be said with certainty at present whether this is caused by an apparatus effect or an actual characteristic of the samples. The points that are well above the -45 micron curve are the Sullivan mine samples. An image analyzer connected to an optical microscope was used to examine the size distribution of these samples: the average was about 10 microns, which would produce a higher rate of pressure rise than particles closer to 45 microns, and thus account for the discrepancies.

The minimum ignition temperature tests do not correlate well with the explosion tests. Pyrrhotite is interesting because of its very low MIT relative to pyrite. Sphalerite and tetrahedrite are interesting because their MIT's are in the same range as pyrite, yet they do not explode in the Hartmann chamber. Hence, the MIT measures a different characteristic of the dusts, most likely, their propensity for spontaneous combustion.

Figure 2, a plot of P_m vs. sulphur content for the pure minerals, shows that the explosibility of sulphide ores is not simply a function of the sulphur content. Pyrite, pyrrhotite and chalcopyrite can all be considered as explosible dusts, producing SO_2 . Sphalerite could not be made to explode in the Hartmann chamber. Galena is interesting, because it definitely explodes, even though it contains relatively little sulphur. After the explosion it produced a white powder and no SO_2 was detected indicating that the sulphate was probably produced. The reaction producing sulphate releases much more energy than the oxidation reaction. Thus, galena is potentially dangerous from the explosion viewpoint, but not from the toxic gas viewpoint.

Table 2 - Explosibility Tests on Sulphide Ore Dusts
In The Hartmann Apparatus

Sample	% S	45 - 63 microns Fraction		< 45 microns Fraction		MIT (°C)
		P_m (kPa)	$(dP/dt)_m$ (MPa/s)	P_m (kPa)	$(dP/dt)_m$ (MPa/s)	
1	45.7	300	3	430	16	510
2	44.0	250	2	320	4	530
3	50.8	320	3	450	21	520
4	37.2	210	1	420	11	---
5	34.9	270	3	410	12	470
6	33.8	110	0.5	90	0.3	---
7	18.3	no reaction		no reaction		---
8	38.5	220	1.3	410	10	---
9	31.5	230	1.3	320	5	550
10	47.4	440	9	470	24	---
11	25.4	20	0.09	130	1.4	540
12	45.3	380	6	470	36	---
13	34.7	210	1.4	250	3	---
14	28.0	80	0.4	60	0.6	---
15	25.1	no reaction		no reaction		---
16	9.9	no reaction		no reaction		730
17	29.8	8	---	90	---	---
18	25.9	220	2	20	---	---
19	30.2	290	3	330	5	---
20	29.9	8	0.04	no reaction		---
21	29.3	340	5	340	13	---
22	25.2	60	0.3	270	6	---
23	36.6	450	15	410	35	---
24	30.7	no reaction		no reaction		---
25	29.0	no reaction		290	5	---
26	43.6	360	5	490	50	---
27	34.5	110	0.8	150	2	---
28	---	---	---	no reaction		---
		< 106 microns Fraction		< 38 microns Fraction		
101	53.0	460	10	---	---	510
102	26.0	220	1.3	---	---	---
103	36.4	* 420	20	430	42	380
104	34.9	300	2	---	---	480
105	13.4	310	4	---	---	550
106	32.9	no reaction		no reaction		590
107	32.9	no reaction		---	---	560
108	32.5	---	---	no reaction		---
109	25.5	---	---	no reaction		---
110	26.0	no reaction		---	---	530
111	10.0	no reaction		---	---	780

* 38 - 75 microns fraction

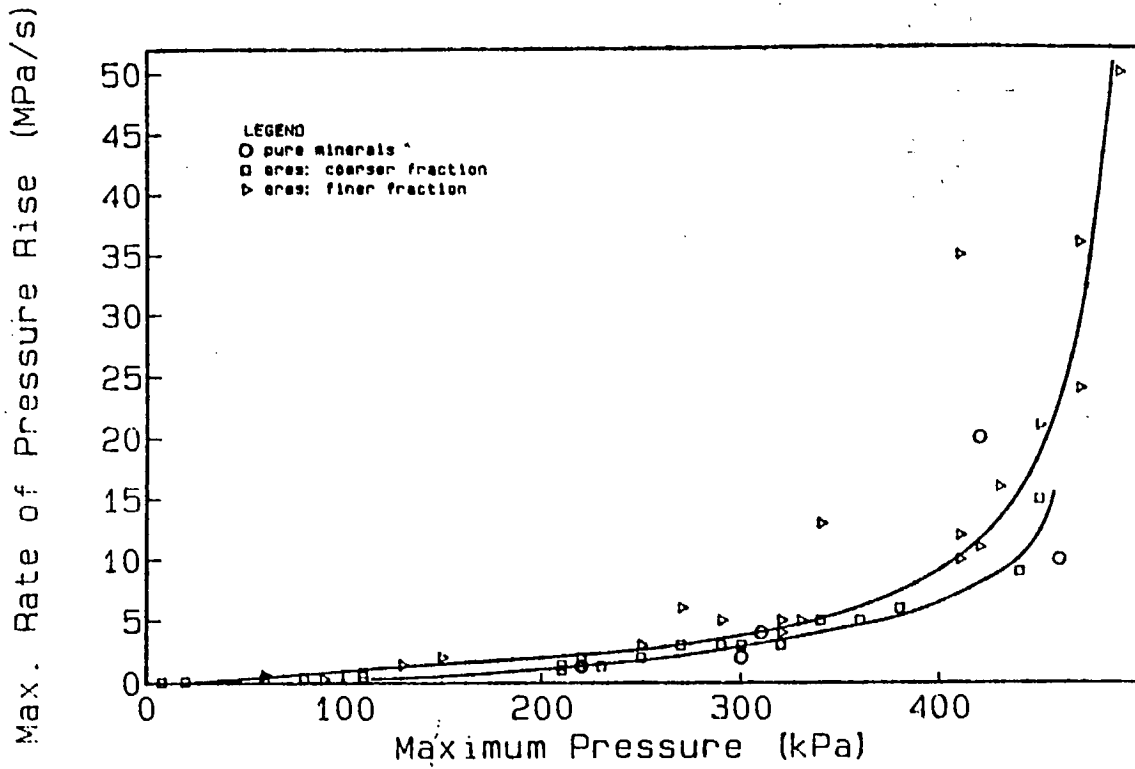


Fig. 1. Relationship between $(dP/dt)_m$ and P_m for sulphide dusts

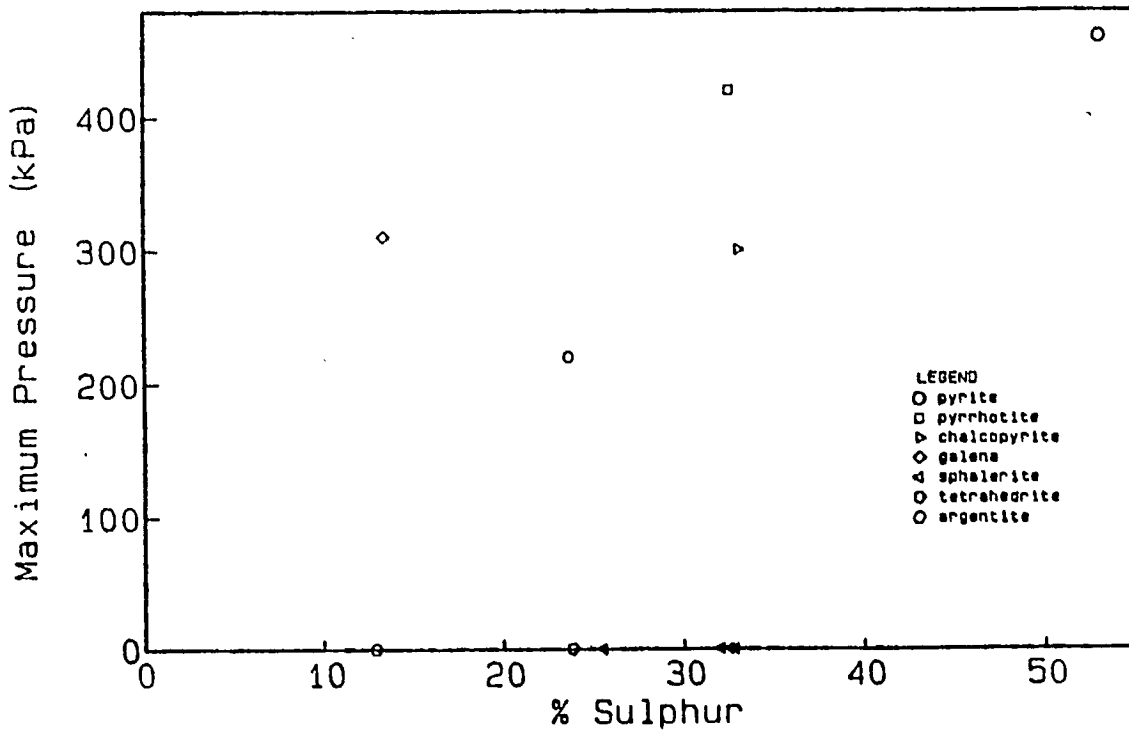


Fig. 2. Explosion pressure as a function of sulphur content for pure minerals

The pyrite produced only black powder (magnetite); the coarse fraction of pyrrhotite produced red powder (hematite), but the fine fraction of pyrrhotite produced either black powder or a mixture of black and red powder. On the basis of energy release, hematite is slightly favoured for both pyrite and pyrrhotite. However, thermodynamics may favour the less energetic reaction if the temperature is sufficiently high. Black powder was observed only for the tests generating the highest explosion pressures (and thus the highest temperatures), which lends credence to this hypothesis. Reaction of iron sulphides to the sulphates actually produce more energy, but ferric sulphate decomposes at the low temperature of 480°C, which accounts for the sulphate not being observed.

An analysis of the residue from the explosion tests was carried out at the CRM by scanning electron microscopy. Generally the quantity of spherical particles in the residue correlates with the explosibility as indicated by the maximum pressure. The details are given in Appendix A.

It is convenient to normalize the explosibility relative to pure pyrite, which should be the most explosible sulphide. Defining the relative explosibility of pyrite as 100, the relative explosibility of all the other samples is defined as:

$$\text{R.E. (actual)} = \frac{100 P_m (\text{sample})}{P_m (\text{pyrite})} \quad (1)$$

Figure 3 shows the relative explosibility as a function of the sulphur content of the ore. The curve shown is purely empirical. Although there is a general trend for the explosibility to increase with increasing sulphur content, the scatter about the line is very high.

An attempt has been made to derive a less empirical predictor of relative explosibility based on the relative explosibilities of the individual pure minerals. From equation 1, the relative explosibility of pyrrhotite is 90, chalcopyrite 65, galena 70 and sphalerite 0. Then, from the mineralogical analysis, the relative explosibility of the ore samples can be predicted from:

$$\text{R.E. (pred.)} = 1.0 \times \% \text{ Pyrite} + 0.9 \times \% \text{ pyrrhotite} + 0.65 \% \text{ chalcopyrite} + 0.7 \times \% \text{ galena} \quad (2)$$

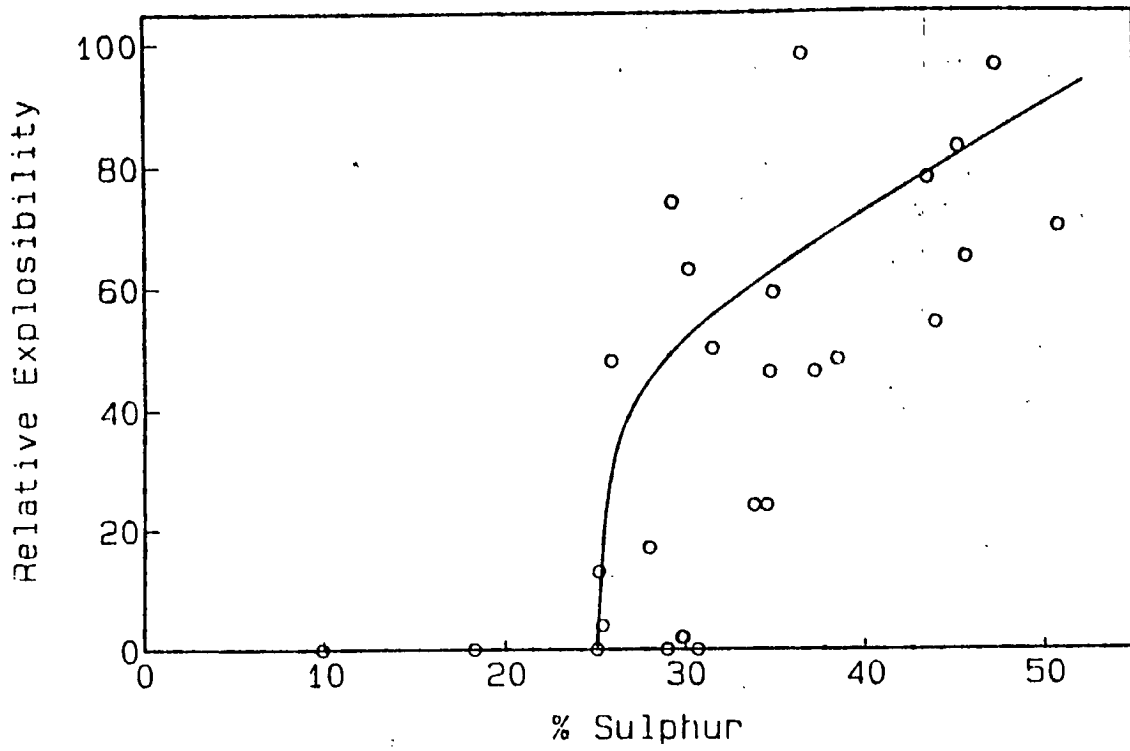


Fig. 3. Relative explosibility as a function of sulphur content for ores

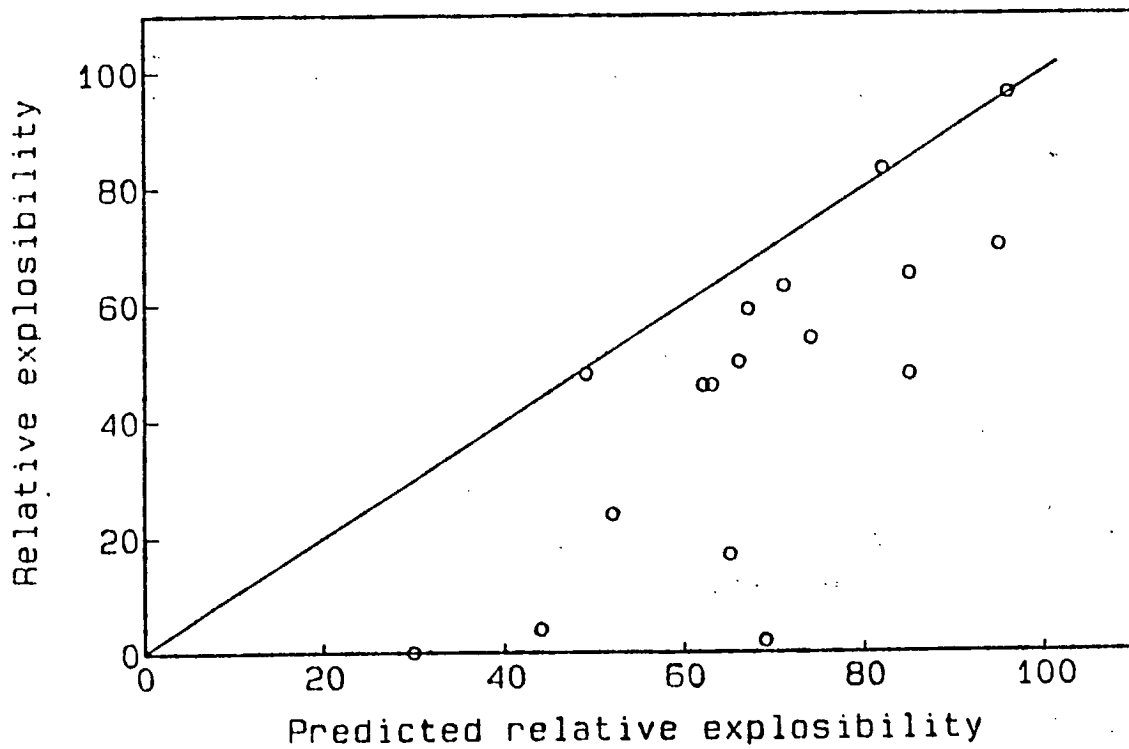


Fig. 4. Relative explosibility as a function of predicted relative explosibility

The ore compositions in Table 1 refer to the percentage of the total metallic minerals. Equation 2 requires knowledge of the percentage of metallics in the ore samples. This was estimated using the percent sulphur and the percentages shown in Table 1. This calculation yielded nonmetallics ranging from 1-53%. The predicted relative explosibilities are shown as a function of the actual relative explosibilities in Figure 4. The line shown is the theoretical line. Three points fall very close to this line, the others are below. It would appear that this line provides a prediction of the upper limit of the relative explosibility. Some of the deviation from this line may be due to the inerting effect of the nonmetallics, but certainly not all the data can be accounted for by this effect.

This approach of predicting explosibility using results obtained from the 20 L explosion vessel will be evaluated further. Mixtures of pure ore dusts will be used first so as to eliminate the complication of inerts. Then, inerts will be added systematically.

Three preliminary explosion tests were carried out in the 20 L vessel to determine whether the quantity of SO_2 can be measured. The results are shown in Table 3. In all three trials, only hematite was produced, unlike the Hartmann tests in which magnetite was produced. The difference is that the Hartmann tests were carried out in pure oxygen, which produced stronger reactions.

Table 3 - Explosion Tests in the 20 L Vessel

<u>Sample</u>	<u>Conc.</u> <u>(g/L)</u>	<u>SO₂ Concentration</u> <u>(mg/L)</u>	<u>Percent Reacted</u>
101 Pyrite	0.5	110	15
103 Pyrrhotite	0.5	25	7
1 Westmin	0.5	100	15

FURTHER WORK

Some additional mine samples will be tested, missing analyses and mineralogy will be obtained and the initial results will be reported in full.

The next laboratory phase will consist of a systematic study of the explosibility of pure and mixed minerals in the 20 L vessel, including the quantification of the SO₂ produced. Identification of the factors affecting the explosibility may lead to an improved prediction of explosibility. The effect of inerts will be measured using the 20 L vessel. The minimum explosible concentrations will be determined as a function of particle size. The minimum oxygen concentration required for explosions to occur will also be measured.

Further work will also be conducted directly with mine personnel to try to improve predictions on a site-specific basis.

REFERENCES

1. Wheeland, K.G. and McKinnon, D. in "Sulphide Dust Explosion", CANMET Report SP87-3, p. I/5.2; 1987.
2. Cashdollar, K.L. and Hertzberg, M., Rev. Sci. Instrum. 56, 596 (1985).
3. Dorsett, H.G. et al "Laboratory equipment and test procedures for evaluating explosibility of dusts", U.S. Bureau of Mines RI5624; 1960.

APPENDIX A

S.E.M. EXAMINATION OF PRODUCT OF COMBUSTION

Four of the eight samples investigated with a scanning electron microscope (S.E.M.) were sulphide minerals: pyrite, pyrrhotite, chalcopyrite and galena. The other four samples investigated were ore dust samples from specific mines. These samples are identified as follows: Westmin 350+45, Westmin 356+45/-63, Westmin 370+45 and 1135 Crushed.

A description of S.E.M. observations of the combustion test residues of the eight samples follows:-

Samples No. 101 and 1 (Pyrite and Westmin 350+45 samples)

The pyrite sample (see Figure 5) shows that the combusted dust contains a variety of virtually perfect spheres between 5 and 50 microns in diameter. Most of the fused particles appear to be composed of a single phase, apparently magnetite.

Sample Westmin 350+45, as shown in Figure 6, contains a majority of non opaque minerals. Pyrite composed ninety-nine percent of the opaque minerals as indicated in the table cited. Fused spherical particles are composed of more than one phase. Generally there are two phases. Hematite lamellae occur in the magnetite matrix but other phases are probably present as well.

In both samples unfused, oxidized pyrite particles occur. Pyrite still may occur in the core of such particles.

Sample No. 103 (Pyrrhotite sample)

This sample, as shown in Figure 7, contains angular and spherical particles. The former are composed of non-reactive pyrrhotite, although some of it may be oxidized, and non opaque minerals. The non opaque silicate minerals compose about twenty percent of the sample. The spherical grains seem to be composed of hematite.

Samples No. 16A and 2 (Chalcopyrite and Westmin 370+45 samples)

The chalcopyrite sample (see Figure 8) contains spheres which are less

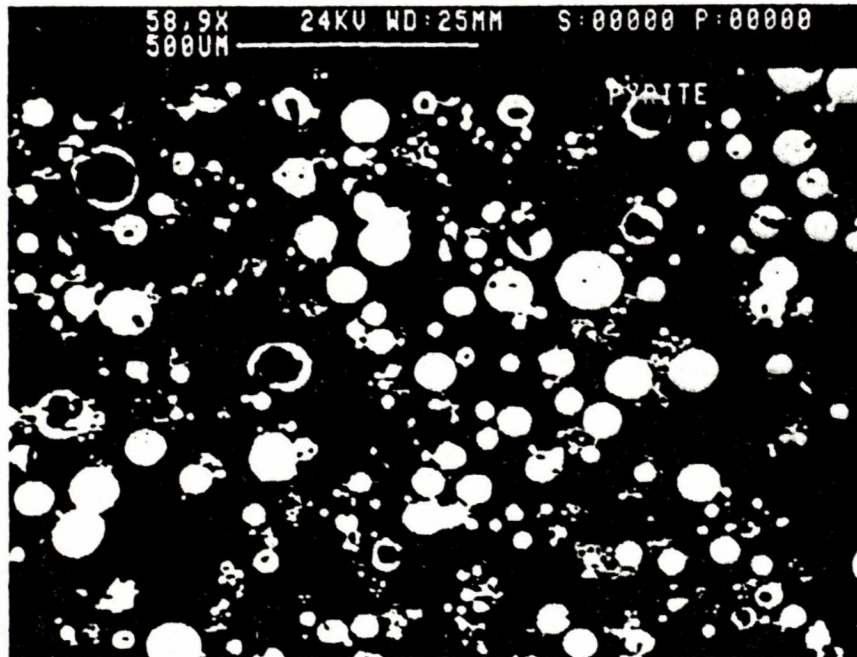


Figure 5 - S.E.M. photo of combusted residue from pyrite

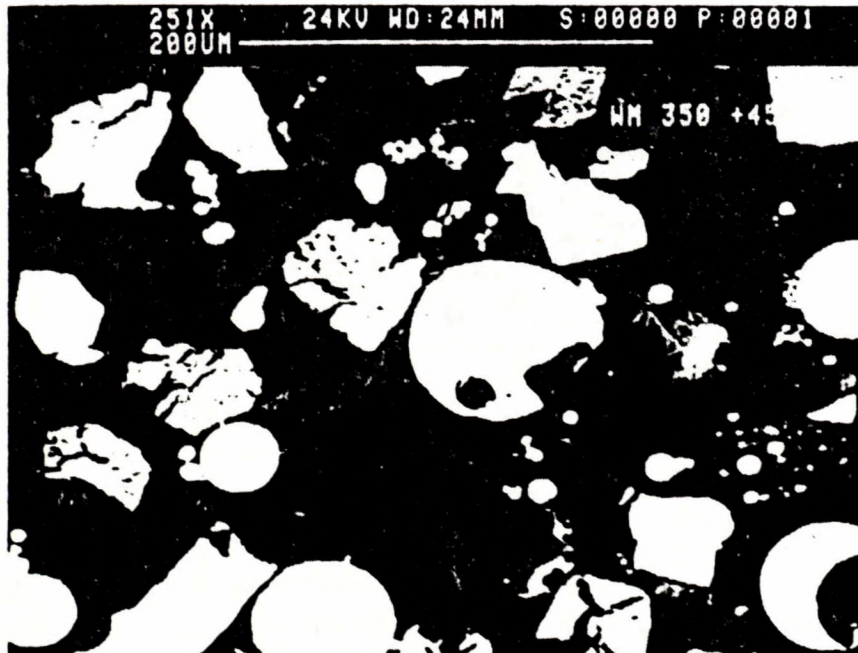


Figure 6 - S.E.M. photo of combusted residue from Westmin 350

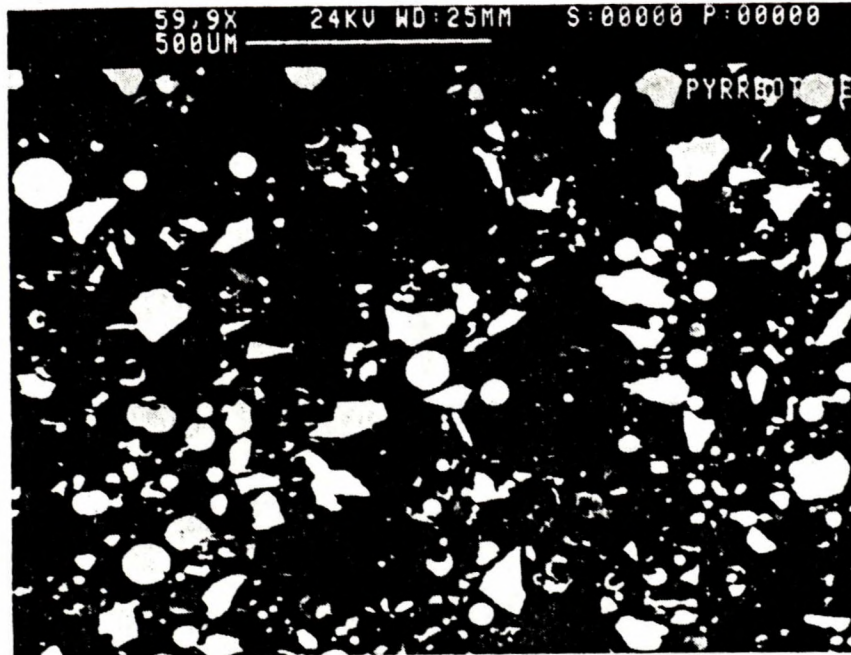


Figure 7 - S.E.M. photo of combusted residue from pyrrhotite

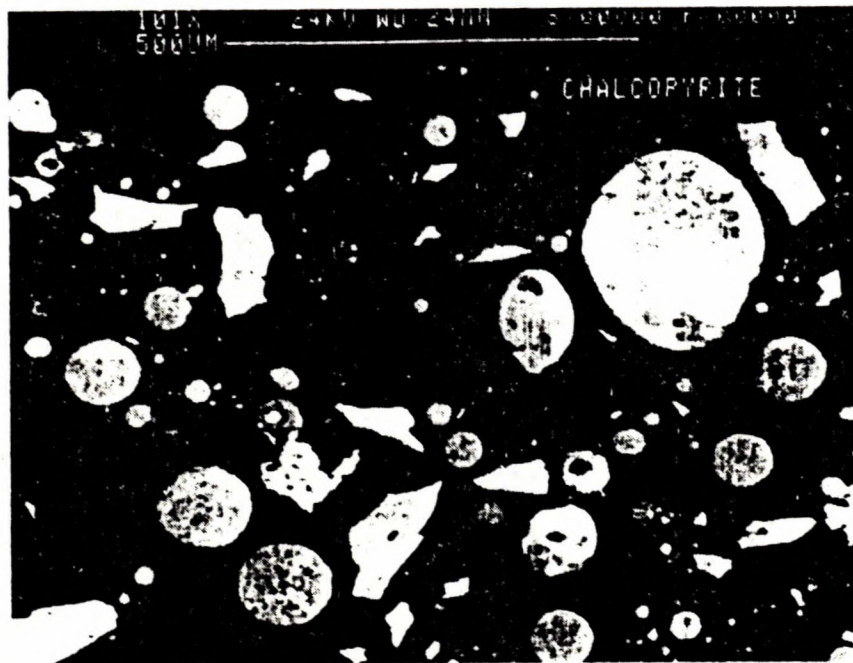


Figure 8 - S.E.M. photo of combusted residue from chalcopyrite

spherical than those seen in the pyrite and pyrrhotite samples. Microanalyses of some of these spherical particles shows that there is no more sulphur. The chalcopyrite has apparently been completely oxidized. Other particles of chalcopyrite show recrystallization with or without fusion. Several phases occur in such particles.

The opaque minerals in Westmin 370+45 samples (see Figure 9) contained 14% chalcopyrite. The remainder of the opaque minerals was mainly pyrite. Most analyzed spherical particles are composed of iron oxide with no copper. Most chalcopyrite particles have not been affected by the combustion. A few particles of chalcopyrite show that the mineral has fused with oxidation or crystallization to copper-iron sulphide compounds, such as chalcopyrite, bornite and covellite.

Sample No. 105 (Galena sample)

This sample, as shown in Figure 10, is almost entirely composed of spherical particles which are generally smaller than those observed in the other samples. Microanalyses show that the fused particles are composed of lead and sulphur. An optical microscope examination reveals that these particles are transparent. They are apparently composed of lead sulphate (anglesite).

Samples No. 2 and 6 (Westmin 356+45/-63 and Geco 1135 Crushed samples)

Twenty-four percent of the opaque minerals of Westmin 356, as shown in Figure 11, was composed of sphalerite. The remainder was pyrite. This sample contains few fused spherical particles. Most of the spherical particles are composed of iron oxide.

In sample 1135 Crushed, as shown in Figure 12, 40% of the opaque minerals was sphalerite before the combustion tests. The other opaque minerals were as follows: 29% pyrite, 15% pyrrhotite, 14% chalcopyrite and 2% of other minerals. As a result of the mixture, the composition of the particles which reacted is complex. Some are composed of iron oxide, others contain some unreacted sphalerite with iron oxide and still others are composed of different phases.

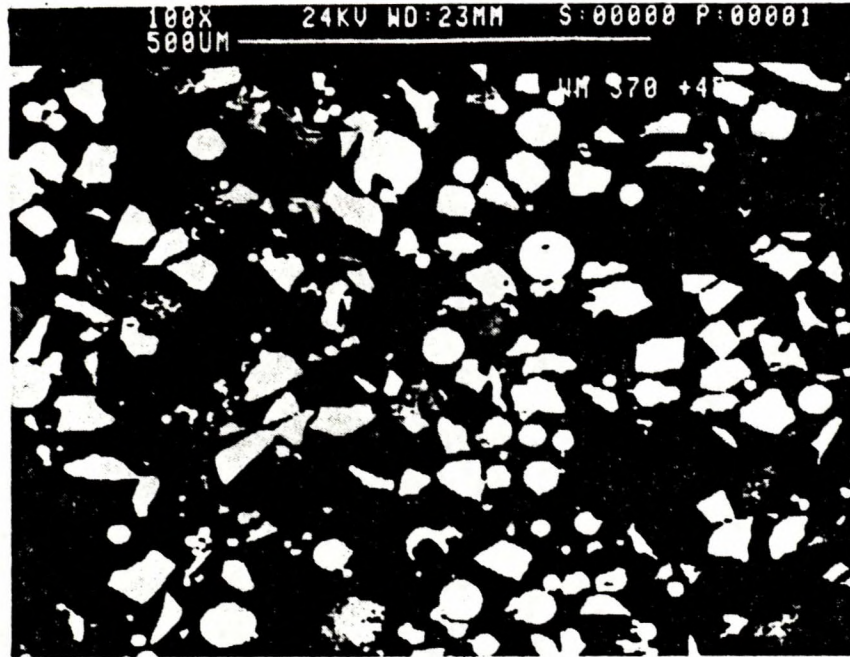


Figure 9 - S.E.M. photo of combusted residue from Westmin 370

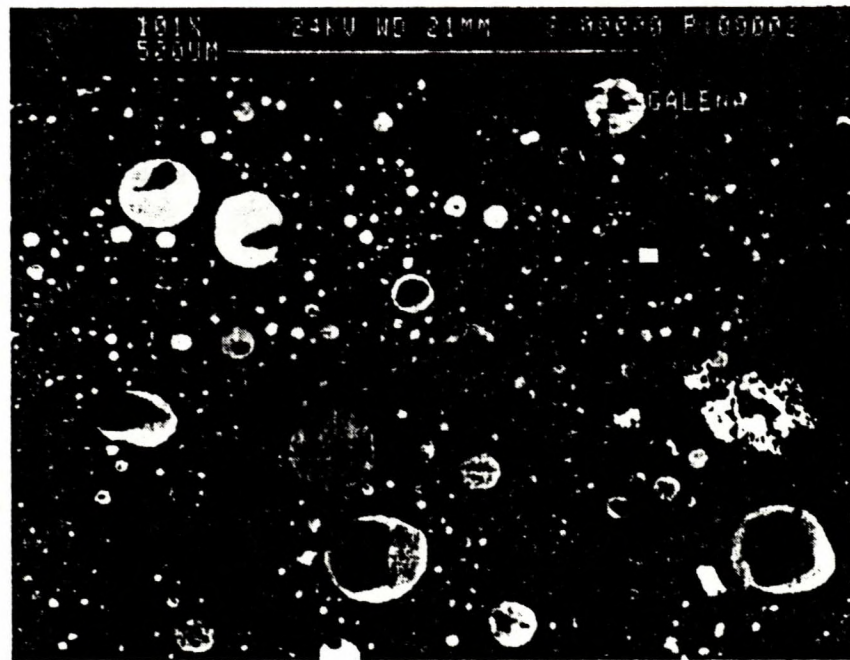


Figure 10 - S.E.M. photo of combusted residue from galena

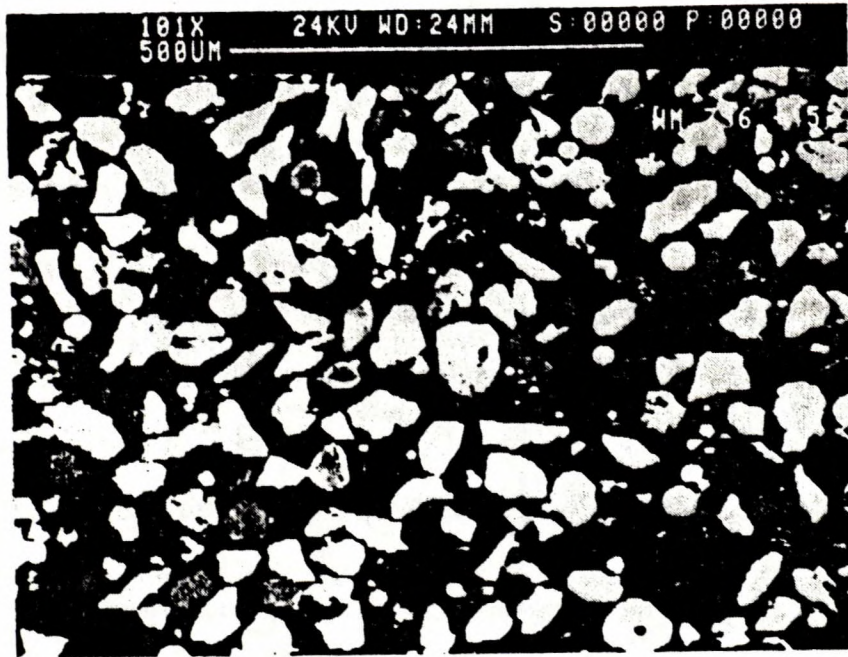


Figure 11 - S.E.M. photo of combusted residue from Westmin 356



Figure 12 - S.E.M. photo of combusted residue from Geco 1135

Interpretation of the reactions

The limited mineralogical examinations of samples tested for their combustibility permit certain interpretations as follows:

1) More particles of pyrite and pyrrhotite oxidize with fusion than chalcopyrite and sphalerite particles, indicating that the oxidation of the former two sulphides generated more energy than the latter two.

2) Pyrite particles seem to have generated more heat than pyrrhotite particles. The presence of magnetite in fused pyrite particles indicates that temperatures of 1388°C were reached where hematite was converted to magnetite.

3) Although galena did not oxidize to an oxide, its reactivity was high. Essentially all galena particles were transformed into a sulphate. Perhaps the galena particles were finer, due to their cleavability, than particles of the other sulphides.

10