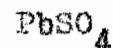


### Minerals of secondary origin.

Although this thesis is concerned mainly with the primary ore and gangue minerals of the Zeehan ore-bodies, the secondary minerals associated with the ores are discussed briefly.

Many of the secondary minerals have not been observed by the present author but were recorded by Petterd in a detailed review of Tasmanian minerals (1910). The majority of Petterd's identifications are regarded as correct but there are some examples which may be open to doubt. In the absence of samples of the minerals in question, little can be said on the validity of these identifications.

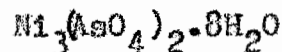
#### Anglesite



According to reports by Waller (1903) and Twelvetreces and Ward (1910), anglesite was found in the oxidized zone of both the east and west lodes of the Susannite (Britannia Ext.) Mine.

Petterd (1910) quoted a communication from L. K. Ward stating that anglesite had been found in this locality as "clear, colourless, tabular crystals up to 2 inches in length and  $\frac{1}{4}$ -inch in depth—".

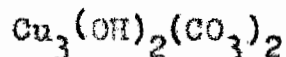
#### Annabergite



The only report of annabergite in the Zeehan area is that of Williams (1958), who identified it as a thin coating, due to oxidation, on two specimens of nickel ore from the Central Balstrup Mine.

Atacamite

Petters (1910) reported that atacamite occurred in small amounts in "mixed oxidized ore" in the Zeehan Queen workings.

Azurite

Copper carbonates are not common in the Zeehan area, and have been reported in the workings of only two mines, viz. Silver Stream and Fahey's Tribute of the South King workings.

Waller (1903) described a lode south-west of the main Silver Stream workings as consisting of "kaolin, steatite and gossan, much stained with copper carbonate", but did not specify whether the carbonate was azurite or malachite, or both.

A specimen (X.5176/P.227) of the gossanous material from Fahey's Tribute contains azurite in association with malachite, covellite and chalcocite.

Petters (1910) included Zeehan in a list of the occurrences of azurite in Tasmania, but did not state any specific locality at Zeehan.

Bindheimite

According to Petters (1910), bindheimite was known as "canary" or "picos" ore in the mining fields of western Tasmania. Petters recorded that bindheimite occurred in the oxidized zone of the Silver (Zeehan) Queen Mine.

Tilley (1891) recorded "canary ore" at Balstrup's Mine (Manganese Hill); this was probably largely bindheimite but

may also have contained massicot, a yellow lead oxide which occurred in some of the Zeehan mines.

### Cerargyrite

AgCl

Cerargyrite was an important constituent of several argentiferous gossan formations in the Zeehan field. Reports indicate that these occurred mainly in the central and eastern parts of the field, and the localities include Sylvester, Spray, Florence, Obnah, Junction, Balstrup's and Zeehan Queen mines, and the "Chloride Lode" in the Colonel North area.

The halide was occasionally reported to be the bromian variety of cerargyrite known as embolite. This variety was recorded at the Sylvester, Junction and Zeehan Queen mines and near Balstrup's Mine.

Native silver was often associated with the halides in these gossan formations, and silver assays up to 2,000 ozs. per ton were recorded.

### Cerussite

PbCO<sub>3</sub>

Cerussite was reported to be a constituent of the oxidized zone of several ore-bodies in the Zeehan area. Petterd (1910, p.40) recorded that cerussite was mined "in fairly large quantities ... at the Silver (Zeehan) Queen, Sylvester, Austral and other mines at Zeehan ...". Tilley (1891) and Jack (1963) reported small amounts at Balstrup's Mine (Manganese Hill).

Specimen no. X.2169 from the Tasmanian Museum collection, labelled "Leadhillite, Silver (Zeehan) Queen Mine,

Zeehan", has been identified as cerussite by means of X-ray diffraction.

### Cervantite



According to Petterd (1910), small quantities of cervantite were found at several of the silver-lead mines at Zeehan. Although Petterd does not give specific localities, it is likely that the cervantite occurred at mines containing a high proportion of antimony-bearing sulphides in the ore (e.g. Spray, Grubb's) since cervantite is an oxidation product of minerals such as boulangerite and bournonite. The related mineral stibiconite has been reported at the Spray Mine (Petterd, 1910).

### Chalcocite



The only occurrence of chalcocite noted in this study was that in gossanous material from the South King (Fahey's Tribute) workings. In this material small amounts of secondary chalcocite occur with covellite in malachite, azurite and earthy iron oxides.

### Covellite



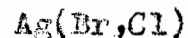
Covellite is a rare mineral in the Zeehan district, having been observed as trace amounts only in ores from some of the mines in the eastern part of the area. All of the covellite observed is probably of secondary origin.

Small amounts of covellite are associated with chalcocite in malachite, azurite and earthy iron oxides from the South King (Fahey's Tribute) workings.

Traces of fine covellite have also been noted in

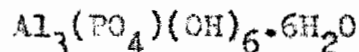
chalcopyrite from the Zeehan Bell and Oonah mines, in argentite from the Spray Mine, and in tetrahedrite from the Zeehan-Western Mine.

Embolite



See under "cerargyrite" (p. 228).

Evansite

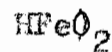


Smith (1893) reported on the composition of a specimen of botryoidal evansite from the Mount Zeehan Mine. The following analysis was published by Smith.

$\text{P}_2\text{O}_5$	18.11%
$\text{Al}_2\text{O}_3$	40.19%
$\text{H}_2\text{O}$	41.23%

Petters (1910, p. 70) also referred to evansite at Zeehan, but gave no locality details other than stating that it occurred "in a silver-lead lode with galena and sphalerite".

Goethite



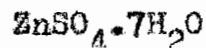
The limonite gossan formations associated with several lodes in the Zeehan area are presumed to contain goethite as the main iron oxide constituent. The identity of the iron oxide has not been investigated in detail.

Several of these gossans returned high silver assays (up to 2000 ozs. of silver per ton), with the silver present in the form of cerargyrite, embolite and native silver. More rarely, copper carbonates and supergene copper sulphides are associated with the iron oxide.

The black botryoidal variety of limonite known as

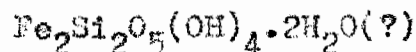
stilpnosiderite was recorded by Petterd (1910) as occurring at the Central Balstrup Mine (Austral Valley), and is represented in the Tasmanian Museum collection by a large hand specimen (X.2350) from this locality.

Goslarite



Petterd (1910) recorded the occurrence of goslarite at the Comstock Mine, but gave no details of abundance.

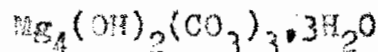
Hisingerite



Waller (1903, p.13) reported the presence of hisingerite, of secondary origin, at the Comstock Mine and described it as occurring in "amorphous masses associated with pyritic ore.....exposed in the lower tunnel....".

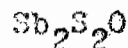
One specimen (X.1847) of hisingerite from this locality is represented in the Tasmanian Museum collection.

Hydromagnesite

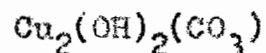


The only record of hydromagnesite in the Zeehan field is that by Petterd (1910, p.97) who reported "solid, almost white, radiating bunches" of hydromagnesite at the Comstock Mine.

Kermesite



Petterd (1910, p.102) recorded that kermesite had been found "in extremely limited quantity implanted in the fractures of jamesonite at the British Zeehan Mine". As described earlier (p.194) the mineral referred to as "jamesonite" is, in fact, boulangerite. The name "British Zeehan Mine" was sometimes used for the Spray Mine.

Malachite

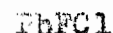
The occurrence of copper carbonates at Zeehan has been described under "azurite" (p. 227).

Petterd's (1910) list of minerals in Tasmania did not include any occurrences of malachite.

Massicot

Massicot was recorded by Petterd (1910, p. 113) as occurring "in limited quantity at several of the.... Zeehan silver-lead mines", but no particular mines were mentioned.

Bindheimite and "canary ore" have been recorded at the Zeehan Queen and Balstrup's mines (Petterd, 1910; Tilley, 1891) and "lead oxide" was reported at Balstrup's mine (Montgomery, 1893). It is probable that massicot constituted at least part of the materials referred to in these reports.

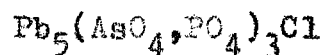
Matlockite

The only report of matlockite at Zeehan is that by Petterd (1910).

According to Petterd (p. 113), matlockite was found "in tabular crystals of a greenish-grey colour, apparently rare, associated with mixed sulphide and carbonate ores of lead at the Sylvester Mine"; and "in small patches of a honey-yellow colour attached to galena at the Montana Mine, Zeehan".

Melanterite

Petterd (1910) recorded the occurrence of melanterite at the Silver (Tasmanian) Crown Mine, and suggested that it had formed as the result of decomposition of pyrite in the abandoned workings.

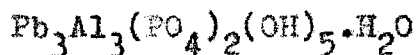
Mimetite

Mimetite occurred in oxidized ore from the Susannite (Britannia Ext.) Mine and the Britannia Mine.

The mimetite found at the Susannite Mine was originally thought to be the leadhillite variety known as susannite, hence the name of the mine. Later it was shown by W. F. Petterd and W. A. McLeod (in Twelvetrees, 1901a) to be campylite, a variety of mimetite. Campylite was also found at the Britannia Mine.

Some of the mimetite from the Britannia Mine was described by Twelvetrees (1901b) as a new mineral, which he called "petterdite". However, Anderson (1908) found it to be a variety of mimetite. Anderson questioned the chemical analysis published by Twelvetrees and published two further analyses, the mean of which is shown below.

PbO	77.14%
As <sub>2</sub> O <sub>5</sub>	17.95%
P <sub>2</sub> O <sub>5</sub>	2.50%
Cl	2.46%

Plumbogummite

Petterd (1901, p.139) recorded plumbogummite as having been found "attached to partially decomposed galena" at the British Zeehan (Spray) Mine.

The only specimen of plumbogummite from Zeehan in the Tasmanian Museum collection is specimen no.X.2083, from the Zeehan-Montana Mine. The specimen consists of galena which has been partially altered to pyromorphite, which has, in



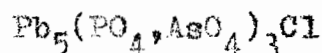
turn, been partially altered to plumbogummite (see also Baker, 1963).

### Pyrolusite



The only reported occurrence of pyrolusite in the Zeehan field is at Manzanese Hill, where it is associated with limonite in the manganiferous gossan capping the hill. Jack (1963) has suggested that the gossan was derived from the oxidation of pyrite and manganiferous siderite.

### Pyromorphite



Pyromorphite was found in abundance at the Sylvester Mine ("pyromorphite lode") and, according to Petterd (1910), there were other minor occurrences in the Zeehan area. Petterd did not name any of these other localities, but one small specimen (X.3278) of pyromorphite from the Zeehan Queen Mine is present in the Tasmanian Museum collection.

Petterd (op. cit., p.139) also recorded the occurrence of the calcium-rich variety of pyromorphite, known as polysphaerite, at the Sylvester Mine.

### Silver

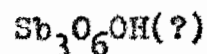


Native silver of secondary origin has been recorded in the oxidized zones of several ore-bodies in the Zeehan area.

The silver occurred in the limonite gossan formations along with the silver halides cerargyrite and embolite, and very high silver assays (up to 2000 ozs. of silver per ton) were recorded. Gossanous formations carrying high silver values have been reported in the upper workings of the Oonah,

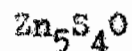
Spray and Balstrup's mines, near the Florence Mine, and in the Colonel North area (Chloride Lode).

Stibiconite



Stibiconite was recorded by Petterd (1910, p.171) as having been found in small quantities in the British Zeehan (Spray) mine at Zeehan.

Voltzite



Petterd (1910, p.197) recorded voltzite at the Silver (Tasmanian) Crown Mine as rare globular and lamellar inclusions.

GEOLOGICAL THERMOMETRY

An investigation into the composition of sphalerite from the Zeehan area has been made in an attempt to obtain information on temperatures of formation of the ores and to see if there is any evidence of temperature gradients having existed during deposition of the ores. Published temperature data for other sulphide systems have also been examined and compared with the results of the sphalerite study.

Fe - Zn - S system.

The application of the system Fe - Zn - S in geological thermometry has followed the experimental work of Kullerud (1953), who determined the phase relations and mix-crystal compositions in the system FeS - ZnS. Where pyrrhotite and sphalerite have formed in equilibrium, the iron content of the sphalerite can be used to determine the temperature of formation of the sphalerite. Examples of the application of this system in geological thermometry are provided by the work of Kullerud et. al. (1955), Edwards (1956), Edwards and Lyon (1957), Coleman (1957), and Benson (1960).

Attempts have also been made to use the system pyrite-sphalerite as a geological thermometer where pyrrhotite is either scarce or absent. Examples of the use of this system are found in the work of Fryklund and Fletcher (1956), Temple (1956), and Sims and Barton (1961).

It is the system pyrite-sphalerite which is of interest in the Zeehan ores, since pyrrhotite occurs in only minor to trace amounts in ores from the western and central parts of

the area and is absent elsewhere.

In this study of the Zeehan ores, the composition of the sphalerite has been investigated for all mines in the area from which suitable samples could be obtained. As described earlier in this thesis, the majority of the mines in the Zeehan area are now inaccessible and most of the samples were, therefore, collected from the dumps of the mines. Although it would be of interest to investigate the variation in composition of sphalerite within individual ore bodies, this is not possible for the Zeehan ores.

Growth zoning was observed in some specimens of sphalerite from the district, but measurements of the iron content were not made on these specimens.

#### Analytical methods and results.

The samples of sphalerite were investigated by two different methods, viz. electron-probe micro-analysis and X-ray powder diffraction.

The analyses with the electron-probe micro-analyser were kindly carried out for the author by Mr. P. Schultz of the Australian Mineral Development Laboratories, Adelaide, South Australia. Elements determined were iron, cadmium and manganese. Results of these analyses are shown in Table 11. For these determinations the samples were submitted as polished sections mounted in cold-setting polyester resin, and the following notes on analytical technique were supplied by Mr. Schultz.

The samples were used as received without carbon coating. Some charging effects were experienced. The electron-probe was 1.5 microns in diameter, produced by an accelerating voltage of 25kV, and yielding a specimen current of 0.35 $\mu$ A.

In each instance one accurate spot analysis was made for Fe, Cd and Mn, with several approximate analyses as checks. Pure metals were used as standards and mass absorption corrections were applied to all values quoted.

Values quoted are accurate to  $\pm 30\%$  of the amount present.

One obvious disadvantage of the electron-probe technique used in these measurements is the range of analytical uncertainty, but the total spread of iron values in sphalerite from Zeehan is sufficiently large for the method to provide significant results. The great advantage in this method is the ability to carry out analyses on extremely small quantities of material, and in several of the Zeehan samples sphalerite is not sufficiently abundant to enable analysis by any other method.

It is interesting to note that Adler and Barton (1963) have reported that measurement made by them of the iron contents of sphalerite, using the electron-probe technique, were accurate to  $\pm 4\%$  of the amount present, in the range 15 to 55 mole percent FeS. No details of the method were given in this abstract report, but Mr. K.L. Williams of the Australian National University has recently succeeded in applying correction procedures to electron-probe micro-analyses of sphalerite and has advised the author (pers. comm.) that the majority of analyses by the technique can be quoted as accurate to  $\pm 4\%$  of the amount present. The correction procedures have been outlined briefly by Williams, (1965).

The results shown in Table 11 were considered to be sufficiently interesting to warrant the analysis of further samples from the area. As it was not possible to have further analyses carried out by the electron-probe method, the X-ray powder diffraction method was employed.

Kullerud (1953), Skinner et al. (1959) and Skinner (1961) have demonstrated that accurate measurements of the unit-cell edge of sphalerite provide sensitive measurements of the composition. Skinner (1961) reported the following relationship between unit-cell edge and composition of sphalerite.

$$a = 5.4093 + 0.000456 X + 0.00424 Y + 0.00202 Z$$

Where X, Y, and Z are the contents of FeS, CdS and MnS (in mole per cent) and a is the unit-cell edge of the sphalerite (in Angstroms).

The unit-cell edge measurements of sphalerite samples from Zeehan have been made by taking X-ray powder diffraction photographs in cameras of 114.6mm. in diameter, using manganese filtered iron K $\alpha$  radiation. In each case the values of  $a_0$  calculated for each of the lines measured were plotted against the Nelson and Riley function (Nelson and Riley, 1945), and the curve extrapolated to give the unit-cell edge value at  $180^\circ 2\theta$ . The uncertainty in these measurements was  $\pm 0.0005\text{\AA}$ , this uncertainty being the deviation obtained from the numerical average of several measurements of the same photograph.

TABLE 11.

Electron-probe micro-analyses of sphalerite, Zeehan\*.

Mine	Polished section number	Element, weight per cent			FeS mole per cent
		Fe	Cd	Mn	
Oceana	P.254	1.7	0.6	0.1	3.0 4
Oonah	P.255	2.5	0.22	0.02	4.3 6
Austral Valley	P.256	0.6	0.5	0.2	0.9 1
Zeehan Bell	P.258	5.0	0.3	0.01	8.5 9
Sunrise	P.259	0.04	0.25	0.07	0.06 1
Sunrise	P.221	1.5	0.25	<0.01	2.6 4
Silver King	P.260	1.1	0.25	0.03	1.9 2
Montana S.L.	P.261	1.1	<0.01	0.02	1.9 2
Tasmanian Crown	P.262	3.1	0.4	0.04	5.4 6
Junction	P.263	0.8	0.2	<0.005	1.4 2
No. 4 Argent	P.264	7.8	0.3	0.05	13.4 13
Stormsdown	P.265	8.2	0.3	<0.005	14.0 14
Silver Stream	P.266	13.3	0.25	1.7	22.6 24
Comstock	P.267	11.2	0.2	0.15	19.1 20
Swansea	P.268	1.6	0.27	<0.005	2.7 4
T. L. E.	P.269	5.3	0.3	0.6	9.1 10
Spray	P.270	7.7	0.27	0.03	13.2 13

\* Analyses by P. Schultz, Australian Mineral Development Laboratories, Adelaide, South Australia.

The above relationship between unit-cell and composition demonstrates that the cell edge is dependent on the presence not only of iron, but also on other components in solid solution. Therefore, in order to calculate the iron content from unit-cell edge measurements it is necessary to know at least the cadmium and manganese contents. In these calculations it has been assumed that the cadmium and manganese contents of the sphalerite samples are equivalent to the average values obtained from the seventeen electron-probe analyses. The average CdS value is 0.24 mole per cent, and the average MnS value is 0.31 mole per cent. Table 11 demonstrates that the cadmium content of sphalerite shows little variation in the Zeehan area, but the variation in manganese content is somewhat higher and introduces an additional source of error into the calculations.

Measurements of the unit-cell edges of eleven sphalerite samples, and the calculated FeS values are listed in Table 12. The last two samples listed in Table 12, i.e. sphalerite from the Comstock and Spray mines, have been included to provide a comparison with the electron-probe micro-analyses. Three figures are shown for each of these samples, these are (1) the FeS value calculated on the basis of the average values for cadmium and manganese, (2) the FeS value calculated using the actual cadmium and manganese values for these samples measured by electron-probe (see Table 11) and (3) the FeS value from electron-probe measurement (see Table 11). The two calculated values for each sample are in



reasonable agreement with the electron-probe micro-analyses, and are within the range of analytical uncertainty of the electron-probe measurements.

TABLE 12.

Measured unit-cell edge values and calculated iron contents of sphalerite, Zeehan.

Mine	Corresponding Polished section number.	Unit-cell edge* (Å)	Calculated FeS, mole per cent.
Doric	P.333	5.4190	17.8
Sylvester	P.320	5.4203	20.6
Boss	P.325	5.4180	15.6
Britannia	P.332	5.4178	15.1
Stonehenge	P.352	5.4130	4.6
Grubbs	P.335	5.4145	7.9
Colonel North (Tramway Formation)	P.345	5.4132	5.0
Despatch	P.310	5.4150	9.0
Sweeney's	P.368	5.4205	21.1
Comstock	P.267	5.4196	19.1(17.7 <sup>**</sup> , 19.1 <sup>***</sup> )
Spray	P.196	5.4175	12.3(15.6 <sup>**</sup> , 13.2 <sup>***</sup> )

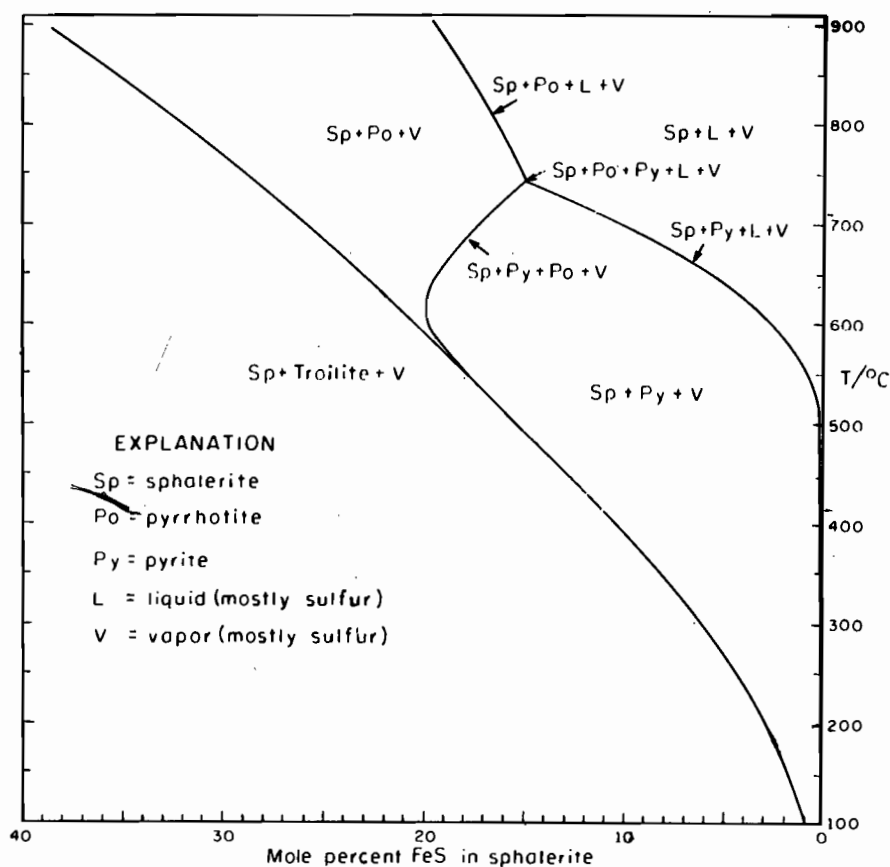
\* Measured to within  $\pm 0.0005\text{\AA}$ .

\*\* Calculated value on basis of actual Cd and Mn content of these samples.

\*\*\* Values obtained by electron-probe micro-analysis.

### Interpretation of results.

The variations in iron-content of sphalerite in the Zeehan area may be interpreted by means of Figure 3 (from Sims and Barton, 1961) in conjunction with the theoretical and experimental work of Kullerud (1953, 1959), Barton and Kullerud (1958), and Sims and Barton (1961).



**FIGURE 3.** Composition of sphalerite in equilibrium with various phases in the system Fe - Zn - S (from Sims and Barton, 1961).

The factors controlling the iron content of sphalerite in equilibrium with pyrite are (a) other elements present in the structure of the sphalerite (b) total pressure

(c) temperature, and (d) activity of sulphur.

In addition to iron, small amounts of other elements may substitute for zinc in sphalerite. The most important of these other elements are cadmium and manganese, but bismuth, cobalt, copper, gallium, indium, lead, mercury, molybdenum, silver and tin also may be capable of substituting for zinc. Previous investigations (e.g. Fryklund and Fletcher, 1956; Sims and Barton, 1961) have shown that pure samples of sphalerite contain very low amounts of these elements.

According to Kullerud (1959), experimental work has shown that the presence of 2 per cent or less of cadmium and/or manganese has no significant effect on the solubility of iron in sphalerite.

The effects of total pressure, temperature and activity of sulphur are interrelated, and have been considered by Sims and Barton (1961). According to Sims and Barton, calculations have shown that total pressure has little effect on the iron content of sphalerite in equilibrium with pyrite for a given temperature and activity of sulphur. If these conclusions are ~~correct~~, it can be assumed that the variations in iron content in sphalerite at Zeehan are due to the combined effects of temperature and activity of sulphur.

Sims and Barton have also calculated that at constant temperature within the pyrite-sphalerite stability field (see Figure 3), an increase in the activity of sulphur by two orders of magnitude decreases the molecular percentage of FeS in sphalerite by one order of magnitude. Sims and

Barton have pointed out that since the range in composition of FeS in sphalerite is only about one order of magnitude (39 mole percent at 894°C to about 3 mole percent at 200°C) whereas the possible range of activity of sulphur is many orders of magnitude, activity of sulphur is a very important variable in pyrite-sphalerite assemblages.

The iron content of sphalerite, formed in equilibrium with pyrite, provides a minimum temperature of formation of the sphalerite-pyrite assemblages, when the FeS-ZnS solvus curve (lower curve in Figure 3) is used as a temperature indicator. Similarly a maximum temperature is obtained by using the curve which shows the composition of sphalerite existing in equilibrium with pyrite + liquid + vapour (Figure 3). The actual temperature, within these limits, at which the sphalerite-pyrite assemblage was formed, cannot be specified without further knowledge regarding the activity of sulphur at the time of formation.

The question of equilibrium between pyrite and sphalerite is clearly of critical importance in the application of the system Fe-Zn-S in geological thermometry. Equilibrium in natural mineral assemblages is difficult to prove, but it is often assumed for coexisting minerals.

Sims and Barton (1961) have suggested that if sphalerite is deposited in the presence of an earlier generation of pyrite, then the sphalerite is in equilibrium with the surface of the pyrite. The term "surface equilibrium" was used by Sims and Barton to describe the extent of equilibrium

between the minerals in such a situation. Since it is the sphalerite which is in equilibrium with the surface of the pyrite, the requirements for the application of the Fe-Zn-S system in geological thermometry would be satisfied.

The conventional interpretation of the textural relationship between pyrite and sphalerite in the Zeehan area indicates that the sphalerite occupies a later position than pyrite in the paragenetic sequence. If this is so, then the sphalerite would be in surface equilibrium with the pyrite.

It is essential that sufficient pyrite was present for the sphalerite to have become saturated with iron at the temperature at which it was deposited. Pyrite is not abundant in all mines in the Zeehan area, but care was taken to measure the iron content of only those sphalerite samples containing associated pyrite.

The sphalerite samples listed in Table 13, and also shown in Figure 4, have iron contents ranging from 0.06 mole percent FeS (Sunrise Mine) up to 22.6 mole percent FeS (Silver Stream Mine). Sims and Barton (1961, p.1230) have reported that the maximum amount of iron found in sphalerite with pyrite in synthetic runs was 19.5 to 20.0 mole percent FeS at 620°C. The value of 22.6 mole percent FeS for the sample from the Silver Stream Mine is, therefore, higher than the maximum figure possible for a pyrite-sphalerite assemblage but is within the range of analytical uncertainty. Similarly the values of 20.6 and 21.1 mole percent FeS for sphalerite from Sylvester and Sweeney's mines are slightly

higher than would be expected but are again within the range of analytical uncertainty. The temperatures of formation of these three samples are shown in Table 13 as  $620^{\circ}\text{C}$ .

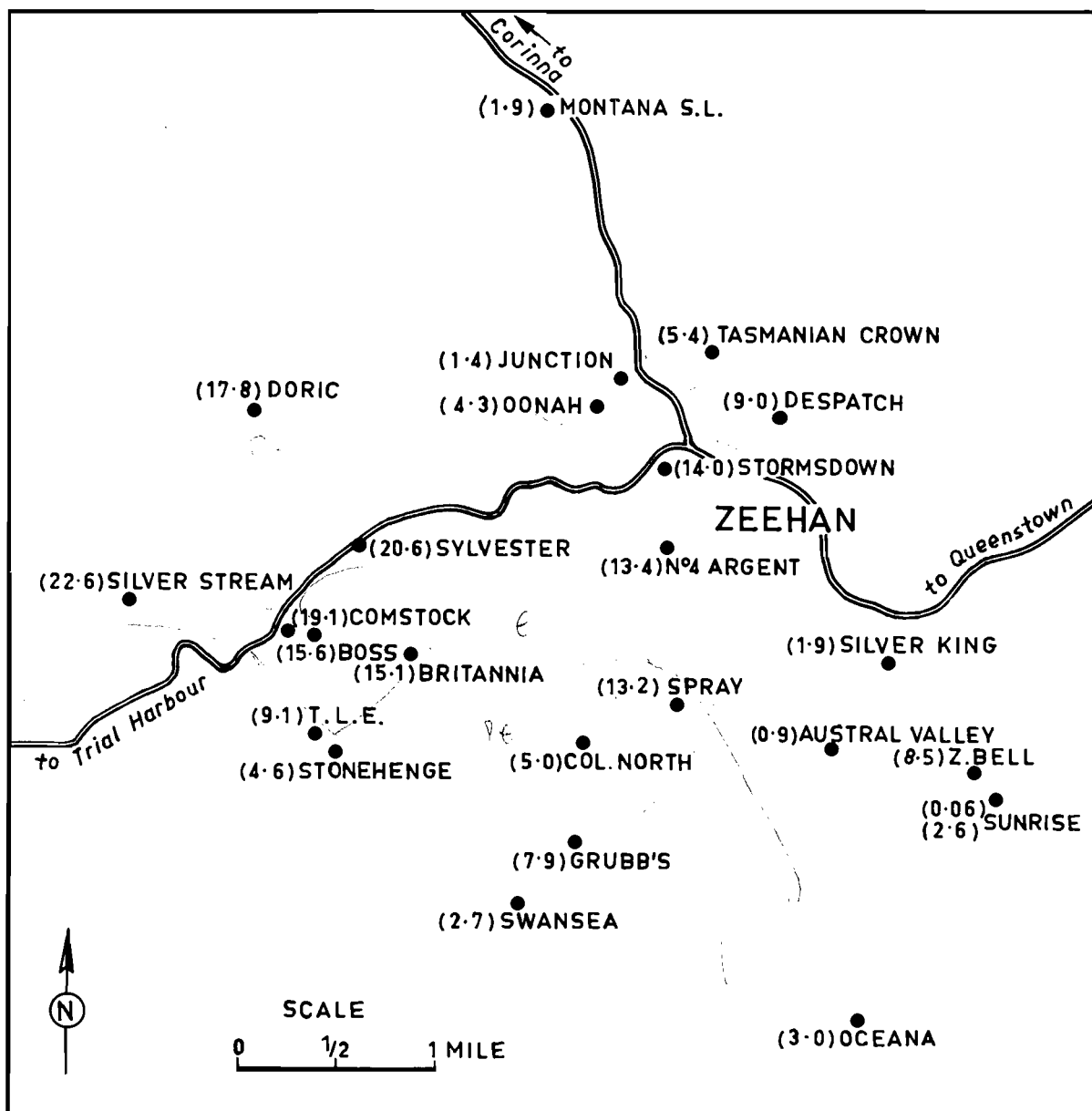
The temperatures obtained from Figure 3 for other samples are less specific, and show a considerable range between the maximum and minimum temperatures for each sphalerite sample (eg. sphalerite from the Britannia Mine, containing 15.1 mole percent FeS, could have formed at any temperature between  $490^{\circ}$  and  $740^{\circ}\text{C}$ , depending on the activity of the sulphur.) The possible temperature ranges for the various samples are listed in Table 13. It must, however, be realised that these temperatures are based on the measured values of FeS and, if allowance were made for the margin of analytical uncertainty, the possible ranges of temperature would be increased even further for each sample. The uncertainty of the temperature data is again further increased by the statement of Toulmin and Barton (1964, p.668) that the FeS-ZnS solvus curve of Kullerud (1953) could be in error and is in need of further investigation. If this is so, then the "minimum" temperatures listed in Table 13 could be subject to revision when further experimental work is carried out for the FeS-ZnS solvus.

TABLE 13.

Iron contents and estimated temperatures of formation of sphalerite, Zeehan.

Mine	Polished section number	FeS content (mole percent)	Estimated temperature of formation (°C)*	
			Minimum	Maximum
Oceana	254	3.0	190	605
Oonah	255	4.3	245	630
Austral Valley	256	0.9	<100	560
Zeehan Bell	258	8.5	355	680
Sunrise	259	0.06	<100	400
Sunrise	221	2.6	190	595
Silver King	260	1.9	155	590
Montana S.L.	261	1.9	155	590
Tasmanian Crown	262	5.4	280	640
Junction	263	1.4	125	570
No. 4 Argent	264	13.4	460	730
Stormsdown	265	14.0	475	735
Silver Stream	266	22.6	620	620
Comstock	267	19.1	580	660
Swansea	268	2.7	180	600
T.L.E.	269	9.1	370	685
Spray	270	13.2	455	730
Doric	333	17.8	550	685
Sylvester	320	20.6	620	620
Boss	325	15.6	505	730
Britannia	332	15.1	490	740
Stonehenge	352	4.6	255	630
Grubb's	335	7.9	340	675
Colonel North (Tramway Formation)	345	5.0	265	635
Despatch	310	9.0	370	685
Sweeney's	368	21.1	620	620

\* Not corrected for pressure.



**Figure 4.** Map of ZEEHAN AREA showing location of mines and iron contents (in mole percent Fe S) of sphalerite samples.



The iron contents of the sphalerite exhibit a pattern which is generally systematic with respect to the geographic location of the mines (see Figure 4), although there are some local irregularities. Sphalerite samples from mines in the western part of the field (Silver Stream and Comstock Mines ) are high in iron content, while sphalerite samples from mines in the north-eastern, eastern and southern margins of the field are low in iron content. The mines with sphalerite containing intermediate values are located in a region occupying the central part of the field and extending east to include mines in the Queen Hill-Argent Flat area. The variation within this region of intermediate values also shows a pattern which is generally systematic. The only sphalerite sample representing a mine within the Heemskirk Granite is that from Sweeney's Mine (located approximately 2 miles north-east of Trial Harbour). The iron content of this sample was measured at 21.1 mole percent FeS.

Because each iron content does not, in most cases, indicate a specific temperature of formation but instead provides a range between maximum and a minimum values, it is difficult to interpret the results from the point of view of temperature gradients. The total possible range of temperature of formation for sphalerite in the Zeehan area is  $100^{\circ}$  (or less) up to  $740^{\circ}\text{C}$ . Without some knowledge of prevailing sulphur vapour pressures it is not possible to make a precise interpretation of the thermal pattern of the ores.

It is useful at this stage to consider the work of

McKinstry and Kennedy (1957), Sims and Barton (1961), and Markham (1963).

McKinstry and Kennedy (op.cit.) studied natural mineral assemblages in the systems Cu-Fe-S, Fe-O-S, Cu-As-S, Pb-As-S and Pb-Sb-S and constructed phase diagrams on the basis of observed sequences of mineral assemblages in various mineral deposits. The phase diagrams of McKinstry and Kennedy demonstrated that the trend of crystallization of the mineral assemblages was indicative of an increase in the chemical potential of sulphur in the systems. McKinstry and Kennedy suggested that the most reasonable explanation for this would be a simultaneous decline in both temperature and partial pressure of the sulphur.

Sims and Barton (op.cit.), in a detailed study of sphalerite-bearing assemblages in ores from the Central City district of Colorado, showed the presence of a correlation between iron content of the sphalerite and the zonal arrangement of the ores in the area. Although Sims and Barton were also dealing with sphalerite-pyrite assemblages giving a considerable range of temperature for each sphalerite sample, they were able to place more restrictive limits on these ranges by consideration of other minerals present in the assemblages, and also by some measurements of temperatures of formation from fluid inclusions in the sphalerite. The presence, in many samples, of tennantite which has a melting point of  $640^{\circ}\text{C}$ , was used to place an upper limit of  $640^{\circ}\text{C}$  on the temperature of formation of the

sphalerite in these samples. By consideration of the dissociation curve for the enargite  $\rightleftharpoons$  tennantite + S<sub>2</sub> reaction, Sims and Barton were able to place further restrictive limits on some of the temperature ranges and were also able to obtain information on prevailing sulphur activity. This dissociation curve provides the approximate relationships between temperature and activity of sulphur for the enargite-tennantite reaction. Where the pyrite-sphalerite assemblages were accompanied by enargite or tennantite, the possible temperature range provided by the pyrite-sphalerite assemblage was reduced by consideration of the enargite-tennantite curve. As a result of their investigations, Sims and Barton concluded that the sphalerite in the Central City district was deposited over a temperature range of approximately 620°C, in the inner zone, to approximately 150°C, at the margins of the outer zone, and they also inferred a decrease in activity of sulphur from the central to outer zones.

Markham (1963) studied sulphide mineral assemblages in the ores at Mount Lyell, Tasmania, and suggested that the trend of crystallization of the assemblages was one of declining sulphur vapour pressure and temperature.

The work of McKinstry and Kennedy, Sims and Barton, and Markham should be considered when making an interpretation of the variation in composition of sphalerite in the Zeehan district. The most reasonable interpretation is that the decrease in iron content of the sphalerite, from west to east, was controlled by a simultaneous decline in both temperature and activity of sulphur.

A much more detailed investigation of the variations in composition of sphalerite from the Zeehan area is at present being carried out by Mr. K. L. Williams of the Australian National University. Mr. Williams is employing the electron-probe and atomic absorption techniques and is applying correction procedures to obtain results of greater accuracy than those quoted by the present author. Although Mr. Williams' study is not yet complete, the results to date have apparently confirmed the overall pattern demonstrated herein (pers. comm. K.L.W.). It is anticipated that Mr. Williams' results will provide a more detailed pattern and could lead to interesting geochemical considerations.

### Trace elements in sphalerite

There is no apparent correlation between the iron content and cadmium or manganese contents of the sphalerite in the Zeehan area.

The solubility of cadmium and manganese in sphalerite both increase with increasing temperatures, and approximate correlations between iron and manganese have been demonstrated by Fryklund and Fletcher (1956, Star Mine in Coeur d'Alene district, Idaho) and Sims and Barton (1961, Central City district, Colorado). Edwards (1955) showed that the cadmium content of sphalerite from Broken Hill, N.S.W., decreases with increasing zinc content.

The cadmium content of the Zeehan sphalerite is essentially uniform (see Figure 5). The manganese content is generally low and shows little variation, with the exception of sphalerite from the Silver Stream and T.L.E. Mines (see Figure 6). It can, therefore, be concluded that, with the possible exception of manganese in the Silver Stream and T.L.E. Sphalerite, cadmium and manganese did not reach equilibrium concentrations and the distribution of these elements in sphalerite in the area was not controlled by temperature.

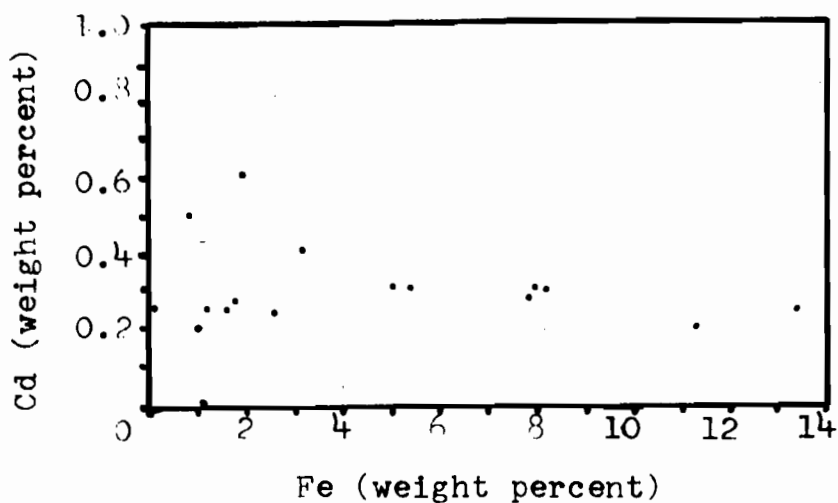


FIGURE 5. Cd content v  
Fe content of sphalerite, Zeehan.

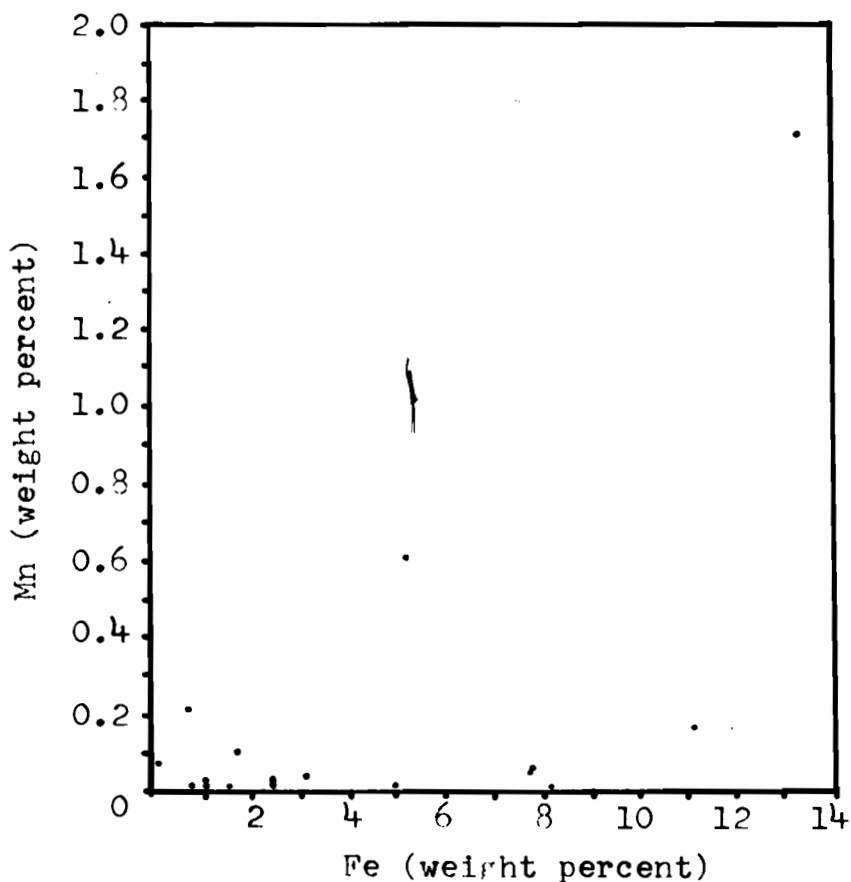


FIGURE 6. Mn content v  
Fe content of sphalerite, Zeehan.

Other sulphide mineral assemblages

As described above, Sims and Barton (1961) used the melting point of tennantite ( $640^{\circ}\text{C}$ ) to place an upper limit on the temperature of formation of assemblages of sulphide minerals containing tennantite. The melting point of tetrahedrite is given by Wernick and Benson (1957) as  $555^{\circ}\text{C}$ , but it is not known to what extent this figure varies as a result of substitution of elements such as iron, zinc and silver in the tetrahedrite lattice.

It would normally be difficult to rule out the possibility that tetrahedrite or tennantite could have crystallized from a sulphide melt. Sims and Barton regarded the occurrence of tennantite in the form of well-developed crystals projecting into vugs as evidence that the tennantite in the Central City district, Colorado, formed below  $640^{\circ}\text{C}$ . Tetrahedrite is common as a minor constituent in ore samples from the majority of the mines in the Zeehan area, but it is not possible to preclude the possibility of solidification from a melt. Dr. N. L. Markham, of the University of New South Wales, has informed the author (pers. comm.) that tetrahedrite in samples of ore from Broken Hill, N.S.W., shows no textural evidence of melting, yet these ores are generally accepted as having formed above  $600^{\circ}\text{C}$  (Edwards, 1956; Kullerud, 1959).

It would, therefore be dangerous to attempt to place limits on the possible temperatures of formation of Zeehan ores on the basis of the melting point of tetrahedrite.

Temperature data for other sulphide mineral assemblages have also been considered, to see if it is possible to define more precisely the temperatures of formation of the Zeehan ores. Most of these considerations have not provided satisfactory information, for reasons which are discussed below.

Clark (1959, 1960) reported that experimental work in the Fe - As - S system has shown that the maximum temperature for stability of the assemblage arsenopyrite-pyrite is  $491^{\circ} \pm 12^{\circ}\text{C}$ . Above this temperature, pyrrhotite is produced according to the reaction arsenopyrite + pyrite  $\rightarrow$  pyrrhotite + liquid. The assemblage arsenopyrite - pyrite has been observed in samples from several of the mines represented in Table 13 and Figure 4, viz. Comstock, Sylvester, Britannia, Spray, Oonah, Stormedown and Zeehan Bell mines.

Comparing the temperature given by Clark with the possible temperature ranges in Table 13 for the pyrite-sphalerite assemblages, an upper limit of  $491^{\circ} \pm 12^{\circ}\text{C}$  would be possible for all except the Comstock and Sylvester ores, for which there is a serious conflict. The pyrite-sphalerite assemblage indicates a possible temperature range of  $580^{\circ} - 660^{\circ}\text{C}$  for the Comstock Mine sphalerite (19.1 mole percent FeS), and a temperature of approximately  $620^{\circ}\text{C}$  for the Sylvester Mine sphalerite (20.6 mole percent FeS). There is no textural evidence of instability in these arsenopyrite-pyrite assemblages (eg. no reaction rims of pyrrhotite were observed). According to the conventional interpretation of



the textural relationships between the minerals, arsenopyrite and pyrite formed approximately contemporaneously, with sphalerite being later in the paragenetic sequence.

The reasons for the conflict between the temperature data provided by the Fe-Zn-S and Fe - As - S systems are not clear. The experimental work of Clark (op.cit.) showed that increased confining pressure resulted in only a relatively small rise in the upper temperature of stability of the arsenopyrite - pyrite assemblage. The effect of other elements, such as cobalt, nickel, bismuth or antimony, has not been investigated and could possibly provide a partial explanation for the difference in the temperatures.

The analytical uncertainty in the iron analyses of the Zeehan sphalerite samples may account for at least a part of the observed difference in temperatures. If allowance is made for the stated uncertainty of  $\pm 30\%$  in the electron-probe micro-analyses, then the minimum possible temperature for the Comstock sphalerite is  $480^{\circ}\text{C}$ , for a value of 14.4 mole percent FeS. But in view of the close agreement between the electron-probe result and the unit-cell measurement (see Table 12) it is unlikely that the true iron content is as low as this.

It is also possible that the conflict of temperature data is partly explained by the observation of Toulmin and Barton (1964, p.668) that the FeS - ZnS solvus curve may be in error and in need of further calibration.

Attempts have been made by some workers to use "unmixing"

temperatures of solid solutions to set lower limits to the temperatures of formation of the mineral assemblages concerned. The assemblage sphalerite-chalcopyrite has often been used in these estimates of minimum temperatures of formation. Buerger (1934) carried out heating experiments with samples of sphalerite from Bingham Canyon, Utah, and reported that the temperature of unmixing of chalcopyrite from the sphalerite for these samples was in the range  $350^{\circ} - 400^{\circ}\text{C}$ . The presence of exsolution bodies of chalcopyrite in sphalerite is sometimes used to indicate that the sphalerite was deposited at a temperature of at least  $350^{\circ}\text{C}$  (eg. Edwards, 1954).

Edwards (1954), Lyon (1959) and Edwards and Lyon (1957) have reported on heating experiments on ore from Pine Vale, Queensland, and the Aberfoyle Mine, Rossarden, Tasmania. In the experiments on the ore from Pine Vale, where chalcopyrite, bornite and tetrahedrite occur in oriented exsolution intergrowths, samples of the ore were homogenized by heating for about 100 hours at  $480^{\circ} - 500^{\circ}\text{C}$ . Edwards and Lyon found that the original lamellar textures could be reproduced only by cooling the homogenized ore rapidly. If slower cooling was allowed, an equigranular mosaic of chalcopyrite and tetrahedrite resulted. The original textures were obtained only by quenching from  $480^{\circ}\text{C}$  to below  $250^{\circ}\text{C}$ , and Edwards and Lyon concluded that the mineralizing fluids were introduced at a temperature of at least  $500^{\circ}\text{C}$  and cooled to about  $250^{\circ}\text{C}$  in a matter of minutes. Similar heating

experiments were performed by Edwards and Lyon (1957) on ore from the Aberfoyle Mine. This ore contains exsolution intergrowths of chalcopyrite, stannite and sphalerite, and the results of heating experiments were interpreted as indicating that these sulphides were deposited at a temperature of about  $600^{\circ}\text{C}$  and cooled rapidly to less than  $400^{\circ}\text{C}$ . According to Edwards and Lyon this rapid chilling caused the unmixing of the solid solutions to be arrested.

The conclusions of Edwards and Lyon for the Pine Vale and Aberfoyle ore have recently been disputed by Brett (1964), who has carried out extensive controlled cooling experiments on solid solutions in the system  $\text{Cu} - \text{Fe} - \text{S}$ . Brett has demonstrated in these experiments that exsolution lamellae can form by slow as well as by rapid cooling. According to Brett, care should be taken in the interpretation of temperatures of formation of mineral assemblages on the basis of rehomogenization experiments. Brett (p.1268) states that "considering the difficulties in interpretation of results, the only geothermometric information that can result from such rehomogenization experiments is a minimum temperature of formation, obtained by homogenizing lamellae within single grains".

The only mineral assemblages present in the Zeehan ores showing exsolution relationships, for which unmixing temperature data exist, are the assemblages chalcopyrite-sphalerite and chalcopyrite - stannite. The former is a widespread assemblage, and the latter occurs at the Oonah Mine

and in the nearby Clarke's Lode of the Zeehan Queen Mine. As mentioned above, Buerger (1934) reported the unmixing temperature of chalcopyrite from sphalerite as  $350 - 400^{\circ}\text{C}$ . According to Edwards (1954) the unmixing temperature of chalcopyrite from stannite is  $500^{\circ}\text{C}$ . These figures could represent minimum temperatures of formation for the assemblages concerned, and as such, they would not conflict with the temperatures obtained from the pyrite-sphalerite assemblages. But in view of the experimental work of Brett (op. cit) it would be unwise to attempt to place restrictive limits on the pyrite - sphalerite temperature data by use of these unmixing temperatures.

Conclusions concerning temperatures of formation.

It is apparent that there is no suitable geological thermometer to enable determination of temperatures of formation of the Zeehan ores. Although analyses of the sphalerite have shown significant variations in the iron content, temperatures indicated by the pyrite-sphalerite assemblages are not of any quantitative use in establishing temperature trends.

The only other sulphide assemblage to provide useful information on the temperatures of formation is the arsenopyrite-pyrite assemblage. This mineral pair places an upper limit of approximately 500°C on the temperature of formation of many of the ore-bodies in the Zeehan field.

If the work of McKinstry and Kennedy (1957), Sims and Barton (1961) and Markham (1963) is considered when interpreting the conditions under which these ores were formed, it is possible to make the following suggestions concerning the ores:-

1. Sphalerite in the western part of the Zeehan area formed at temperatures in the vicinity of 500°C and at moderate sulphur vapour pressure.
2. The decrease in iron content of the sphalerite from west to east was controlled by a decline in both temperature of formation and sulphur activity.
3. The deposits in the Zeehan field were formed from solutions which moved eastwards from the granitic body.

It should be emphasized that this interpretation, although considered to be geologically and chemically reasonable, must be regarded as tentative. Further experimental information regarding the various mineral assemblages is required before a more satisfactory interpretation is possible. Further knowledge of the famatinite-tetrahedrite dissociation curve could be particularly useful. Sims and Barton (1961) were able to use the enargite-tennantite relationship successfully and it is possible that a similar treatment of the corresponding famatinite-tetrahedrite relationship would assist in a better approximation of the temperatures and activity of sulphur during formation of the Zeehan ores. Barton and Toulmin (1964) have reported that preliminary work on the variation of the fugacity of the sulphur with temperatures for the system tetrahedrite-famatinite, by means of the electromotive force method, has yielded promising results. The relationships have not yet been published as Barton and Toulmin considered that further investigation was required before publication.

## SULPHUR ISOTOPE COMPOSITION

### Introduction

In recent years the applications of isotope studies in ore genesis have received considerable attention. In particular, sulphur isotopes have been widely used as a tool in the investigation of the origin of many sulphide mineral deposits, and in several cases sulphur isotope studies have proved useful in differentiating between opposing theories on the origin of the deposits concerned.

Professor M. L. Jensen, of Yale University, has kindly carried out analyses of the sulphur isotopic composition of several samples of ore from the Zeehan district.

Before the results of these analyses are discussed, a brief summary of the basic principles of sulphur isotope studies is presented.

The isotopes of interest in the study of ore deposits are  $S^{32}$  and  $S^{34}$ , since these are the most abundant isotopes of sulphur. Variations in the relative abundances of these two isotopes can be discussed in terms of  $S^{32}/S^{34}$  ratio values, or in terms of  $\delta S^{34}$  per mil (‰) values. The  $\delta S^{34}$  values represent variations from a standard value, according to the following relationship.

$$\delta S^{34}(\text{‰}) = \frac{(S^{34}/S^{32})_{\text{sample}} - (S^{34}/S^{32})_{\text{standard}}}{(S^{34}/S^{32})_{\text{standard}}} \times 10^3$$

The standard used in almost all sulphur isotope studies is troilite from the Canyon Diablo meteorite, with a ratio value of  $S^{32}/S^{34} = 22.220$  and  $\delta S^{34} = 0.00\%$ . (Ault and Jensen,

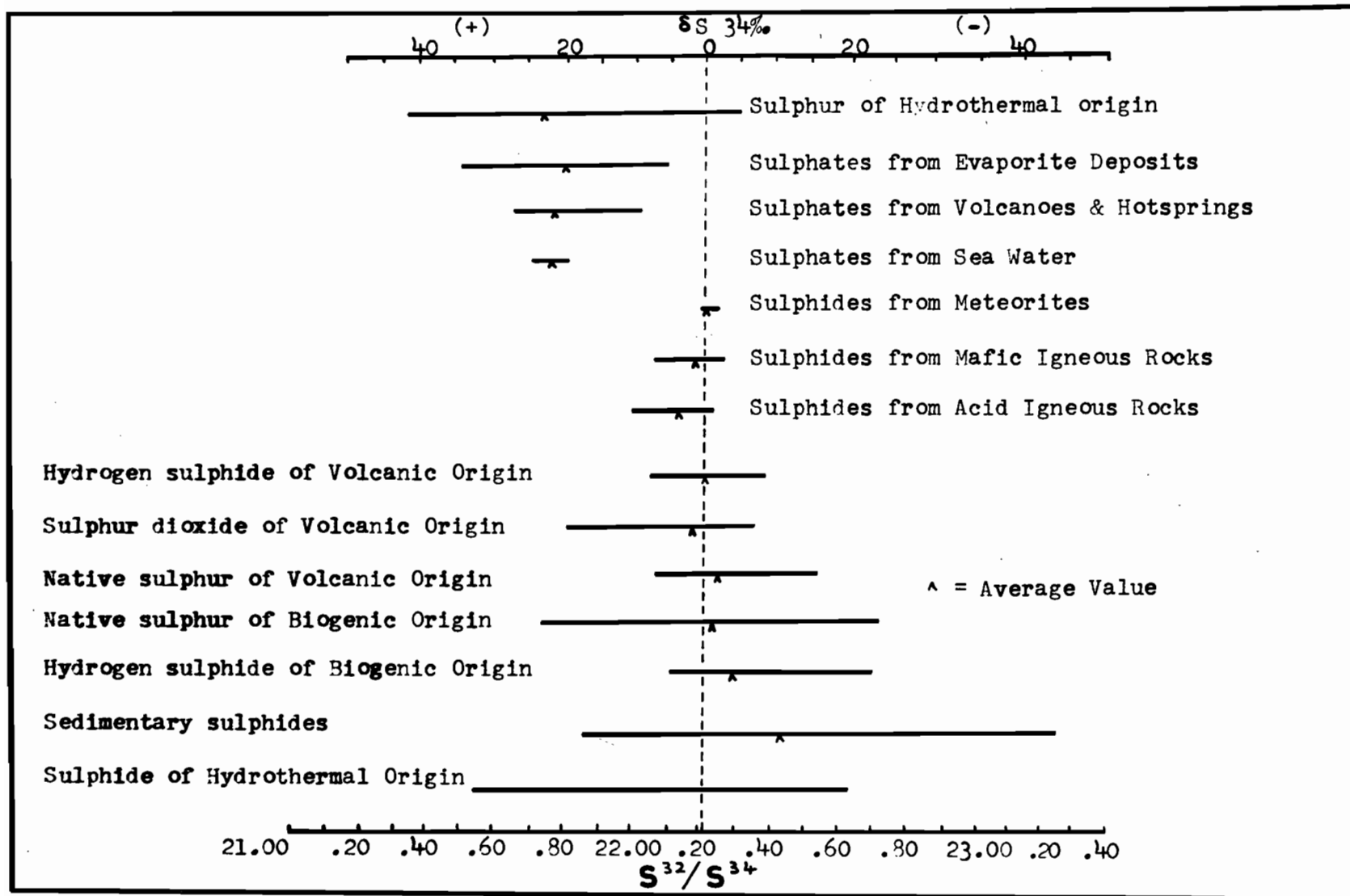
1962). The value of  $\delta S^{34} = 0.00\%$  is also generally accepted as representing the average composition of terrestrial sulphur (Macnamara and Thode, 1950).

The observed variations in relative proportions of  $S^{32}$  and  $S^{34}$  in various sources in nature are shown in Figure 7.

The most useful criteria in sulphur isotope studies of mineral deposits are (a) the total spread of  $\delta S^{34}$  values shown by the sulphide minerals in a given deposit or group of related deposits, and (b) the difference between these  $\delta S^{34}$  values and the terrestrial average of  $\delta S^{34} = 0\%$ .

If the sulphide minerals from a deposit exhibit a narrow range of  $\delta S^{34}$  values with an average close to  $\delta S^{34} = 0\%$ , this is normally regarded as good evidence of a magmatic hydrothermal origin for the deposit, i.e. the deposit is regarded as having been deposited from hydrothermal solutions of magmatic origin (Jensen, 1959). Such an origin would involve a homogeneous source of sulphur, and available evidence suggests that the processes leading up to the formation of these ores do not cause significant fractionation of sulphur isotopes between the sulphide minerals (Ault and Kulp, 1960).





**FIGURE 7.** Sulphur isotope variations in nature. Compiled by Tupper (1960).

A broad spread of  $\delta S^{34}$  values is often indicative of a biogenic origin, with the sulphides having been deposited as the result of reduction of soluble sulphates to insoluble sulphides by the action of sulphate - reducing bacteria. Experimental work by several groups (e.g. Thode et al., 1951; Jones et al., 1956; Feely and Kulp, 1957; Harrison and Thode, 1958) has demonstrated that fractionation of the sulphur isotopes takes place during reduction of sulphates by the bacteria Desulphovibrio desulphuricans. During this reduction, which involves a change in valence of sulphur from + 6 to - 2, the lighter isotope ( $S^{32}$ ) is concentrated in the sulphide phase, leaving the sulphate enriched in  $S^{34}$ .

The literature on sulphur isotopes is extensive and for comprehensive accounts of the causes of fractionation of sulphur isotopes and the interpretation of sulphur isotopic composition of mineral deposits, the reader is referred to Jensen (1959, 1962), Ault (1959), Ault and Kulp (1960), and Stanton (1960).

### Results

Of the fourteen samples analysed for the author by Professor Jensen, twelve were selected from mines in the Zeehan field and two from mines in nearby related areas. One of these two samples was collected from Sweeney's Mine, within the Heemskirk Granite, and the other from Mayne's Mine, which is situated south-west of the Zeehan field and is a short distance south of the southern margin of the Heemskirk Granite. The twelve samples from the Zeehan field were selected to provide a reasonable geographic coverage of the field, and also to provide analyses of the sulphur isotopes in several different sulphide minerals.

The results of the analyses are shown in Table 14 and are presented diagrammatically in Figure 8.

TABLE 14.

Sulphur isotopic composition of ore minerals, Zeehan. \*

Sample No.**	Mine	Mineral	$\delta S^{34}(\text{‰})$
X.5239	Comstock	Sphalerite	+6.9
X.5254 <sub>45</sub>	T.L.E.	"	-0.7
X.2587	Swansea	"	+6.5
X.4911	Oonah	Stannite	+1.5
X.5251	Spray	Boulangerite	+4.9
X.5236	Montana S.L.	Galena	-3.6
X.5198	Oceana	"	+1.2
X.5205	Zeehan Bell	Pyrite	+1.7
X.5210	Silver King	Galena	+2.2
X.5221	No.2 Argent	"	+1.5
X.5226	Stormsdown	Pyrite	+1.3
X.5252	Grubb's	Galena	+7.1
X.3162	Mayne's	Pyrite	+5.8
X.5283	Sweeney's	Sphalerite	+15.1

\* Isotope analyses by M.L. Jensen, Yale University.

\*\* Tasmanian Museum accession numbers.

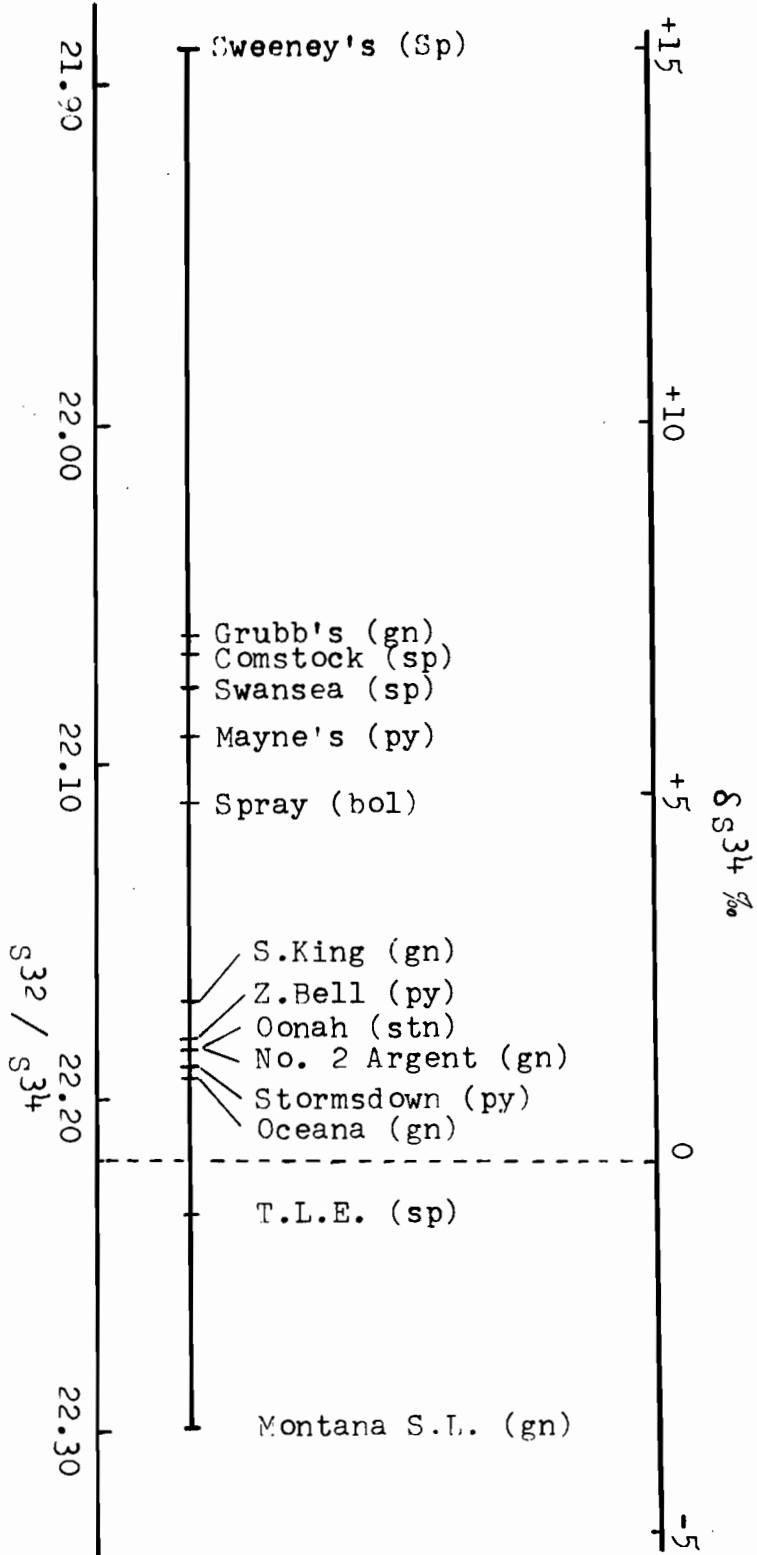


FIGURE 3. Sulphur isotopic composition of ore minerals, Zeehan.

bol = Boulangerite  
gn = Galena  
py = Pyrite

sp = Sphalerite  
stn = Stannite

### Interpretation of results

The analyses do not show any correlation between sulphur isotopic content and mineral species, nor is there any apparent relationship with the host rocks for the mines concerned. Similarly there is no consistent relationship, as far as can be judged, with probable temperatures of formation. The analyses with  $\delta S^{34}$  values of the order of + 5%, or greater, represent mines located in the western and south-western part of the area, but this is not a consistent feature since the T.L.E. mine ( $\delta S^{34} = -0.7\%$ ) is also located in this region.

The total spread of  $\delta S^{34}$  values for the samples is - 3.6 to + 15.1%, with an average value of + 3.7%. This range is considerably greater than would be expected for deposits of magmatic hydrothermal origin in accordance with the ideas discussed by Jensen (1959).

If the analysis for Sweeney's Mine is excluded the range becomes - 3.6 to + 7.1%, for which the average is + 2.8%. This range is still somewhat greater than would be expected for deposits formed by sulphur derived from a homogeneous source, as required for a magmatic hydrothermal origin. Deposits formed by such a process are not expected to show variations greater than approximately 5% from the zero value.

Many of the Zeehan analyses are well within the range of  $0.00 \pm 5\%$ , and it is suggested that the ores represented by these analyses were formed by normal magmatic hydrothermal

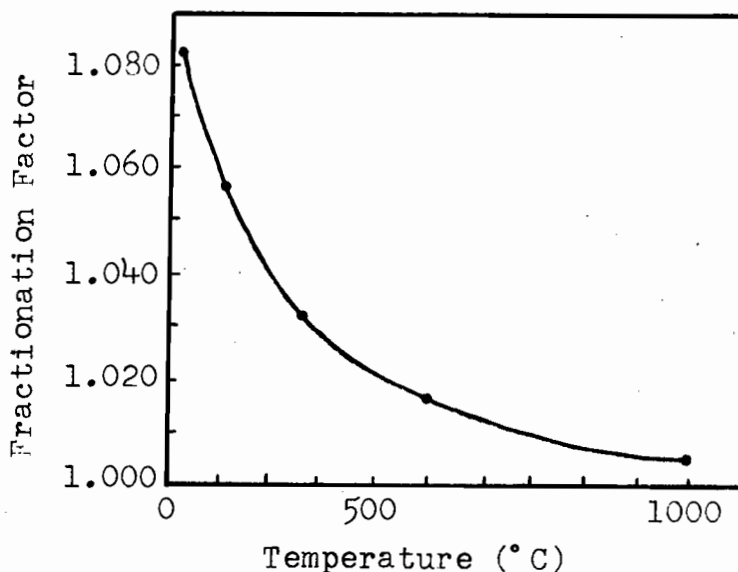
processes with the sulphur having been derived from a homogeneous source, such as the upper mantle, by selective volatilization. The analyses outside this range are enriched in  $S^{34}$ , which strongly suggests contamination by a source rich in sulphate.

The sulphur isotope analyses can, therefore, be interpreted as indicating that the sulphur in these ores was derived from two sources. If this is so, the most likely explanation would be that sediments, containing sedimentary sulphate, were assimilated by the magma during emplacement of the Heemskirk Granite, and that the sulphate was reduced to sulphide during the assimilation process.

The data of Tudge and Thode (1950) and Sakai (1957) has demonstrated that reduction of sulphate to sulphide at temperatures in excess of  $500^{\circ}\text{C}$  will cause very little fractionation of the sulphur isotopes. Figure 3 (from Sakai, 1957) illustrates the decrease in the fractionation factor with increasing temperature.

According to the above hypothesis, the sulphur of magmatic origin would have become contaminated by sulphur from a sulphate-rich source, giving rise to the observed variations in  $\delta S^{34}$  values.

There are, however, alternative interpretations which could be made for the analyses. It could, for example, be argued that the analyses indicate that the ores in the Zeehan field are unrelated to the Heemskirk Granite, in view of the analysis of + 15.1‰ from Sweeney's Mine compared



**FIGURE 9.** Variation of fractionation factor with temperature for  $S^{2-}/SO_4^{2-}$ . (From Sakai, 1957).

with + 7.1‰ as the highest  $\delta S^{34}$  value from the Zeehan field. Another alternative interpretation would be that most of the ores in the western and south-western part of the Zeehan field are related to the Heemskirk Granite whereas those in the eastern part of the field are related to some other source.

The first of these interpretations is not favoured by the author because several samples show an enrichment in  $S^{34}$  by more than 5‰. This suggests that these ores contain some sulphur derived, as explained above, from a sulphate-rich source.

It is not possible to conclusively reject the second alternative, but it is considered to be less likely than the hypothesis outlined above. One factor not in favour of two completely separate sources for the ore deposits is the mineralogical zoning of the ores with respect to the



Heemskirk Granite, as described in a subsequent section. The systematic pattern shown in the iron contents of the sphalerite (as discussed in the previous section) also suggests a relationship with the granite body.

Independent evidence which assists in the interpretation of the origin of the sulphur is provided by recent work of members of the Department of Geophysics, Australian National University. This work has been concerned with the composition and origin of the Heemskirk Granite, and will be outlined in two forthcoming papers by Brooks and Compston (in press) and Heier and Brooks (in press). The investigations of the granite have involved field mapping, petrological studies, and measurements of the Rb, Sr, Th and U compositions. Mr. C. Brooks has informed this author (pers. comm.) that the combined data of these two papers strongly suggest that two periods of activity were involved in the formation of the granite. According to the theories proposed by the above authors, the first phase of the magma was accompanied by incorporation of Precambrian sediments, but the second phase was a more normal magmatic intrusion, with far less accompanying volatiles than the first phase, and did not involve significant assimilation of crustal material.

This theory for the origin of the granite mass is compatible with the sulphur isotope data and provides a mechanism for the derivation of sulphur from two sources. If this theory is correct, then it indicates that the ores

of the Zeehan field are genetically related to the first phase of the granite magma.

Another approach which provided some further evidence on the origin of the sulphur is the selenium content of the sulphides. This is discussed in the following section.

A discussion of the sulphur isotopic composition of the Zeehan ores would not be complete without some reference to isotopic analyses of other ores from the west coast region in Tasmania. Dr. M. Solomon, of the University of Tasmania, has kindly supplied the author with unpublished sulphur isotope analyses of ores from the Mount Lyell, Renison Bell, and Rosebery deposits. These analyses were carried out by Professor Jensen, and ranges of  $\delta S^{34}$  values and the respective average values are shown in Table 15. The range and average of the Zeehan analyses are included for comparison.

While it is not possible to discuss these results in detail without going well beyond the scope of this thesis, it is nevertheless, interesting to note that there is an apparent tendency for all sulphide deposits in western Tasmania to show an enrichment in  $S^{34}$ . This is of particular interest in view of the possibility that more than one type of origin is represented by these deposits. Whereas the Renison Bell cassiterite-pyrrhotite ores are accepted as magmatic hydrothermal, the origins of the Mount Lyell copper ores and the Rosebery galena-sphalerite ores are not clear.

TABLE 15.

Summary of sulphur isotopic composition of ores from  
western Tasmania.

Locality	Minerals analysed	Range of $\delta S^{34}$ values(‰)	No. of analyses	Average $\delta S^{34}$ (‰)
Mount Lyell	Pyrite, sphalerite, chalcopyrite, bornite	- 2.8 to + 8.6	18	+ 4.6
Renison	Pyrrhotite,	+ 2.2 to	10	+ 6.3
Bell	pyrite,galena	+ 8.1		
Rosebery	Sphalerite chalcopyrite, galena,pyrite	+ 9.2 to +13.8	11	+11.7
Zeehan-	See Table 14	- 3.6 to	14	+ 3.7
Heemskirk		+15.1		

Recent investigations by Dr. M. Solomon (University of Tasmania) and Dr. N. L. Markham (University of New South Wales) suggest that these ores may be, at least in part, related to Cambrian volcanic activity (Solomon, 1964; Solomon and Elms, 1965; Markham, pers. comm.).

Further work is needed to explain the apparently consistent enrichment in  $S^{34}$  in the ores in western Tasmania.

S U L P H U R : S E L E N I U M R A T I O S

Edwards and Carlos (1954) investigated the selenium content of ores from many mineral provinces in Australia and included in their results are four analyses from the Zeehan and Heemskirk areas. It is of interest to briefly review some aspects of the work of Edwards and Carlos, and to discuss the selenium content of the Zeehan ores, since the S:Se ratios offer a possible correlation with the sulphur isotope analyses.

The primary objective of the work by Edwards and Carlos was to test the use of S:Se ratios as a method for distinguishing sulphide mineral deposits of hydrothermal origin from those of sedimentary origin. Goldschmidt and Strock (1935) had found that pyrite of sedimentary origin had S:Se ratios of the order of 200,000 or more, while pyrite of hydrothermal origin had a S:Se ratio of 10,000 to 20,000.

Goldschmidt and Strock (1935) and Goldschmidt (1958) have explained that the low selenium content of sedimentary pyrite is due to the breakdown in the partnership between sulphur and selenium during the weathering cycle. The selenium content of sea water is very low, since most of the selenium is precipitated with bottom sediments. Minerals such as gypsum and anhydrite in evaporite deposits contain very little selenium.

Edwards and Carlos (op. cit.) measured the sulphur and selenium contents, and calculated the S:Se ratios, of

sulphide minerals from various Australian mineral deposits. As a result of their investigations, Edwards and Carlos concluded that a high selenium content, with a S:Se ratio of the order of 10,000, is positive evidence of hydrothermal origin. A low selenium content, giving high S:Se ratios, was considered by Edwards and Carlos to be indicative of sedimentary origin; but, according to Edwards and Carlos, hydrothermal sulphide deposits could be low in selenium content if formed in a selenium-poor province. The results of Williams and Byers (1934) are in essential agreement with these conclusions.

It should be noted that the pyrite deposits at Nairne, South Australia, were found to have S:Se ratios ranging from 9,950 to 13,400 for pyrite samples and from 20,600 to 37,400 for samples of pyrite-pyrrhotite concentrate. On the basis of these results Edwards and Carlos concluded that the Nairne deposits are of hydrothermal origin, but it is generally considered that these deposits are of sedimentary origin (Skinner, 1958; Mirams, 1965).

The four analyses reported by Edwards and Carlos for the Zeehan - Heemskirk region are listed in Table 16. Three of the analyses represent sulphide minerals from mines in the Zeehan field and the fourth refers to a sample of pyrite from the Heemskirk Granite.

TABLE 16.

Sulphur and selenium content of ore minerals,  
Zeehan and Heemskirk (Edwards and Carlos, 1954).

Mineral	Locality	S(%)	Se(%)	S:Se
Sphalerite	Swansea Mine	29.77	0.0005	59,940
Stannite	Oonah Mine	27.76	0.0019	14,600
Boulangerite	Spray Mine	17.82	0.0008	22,275
Pyrite	Heemskirk Granite (precise locality not stated)	31.75	—	

The S:Se ratios of the stannite from Oonah Mine and boulangerite from Spray Mine are compatible with the expected values for hydrothermal ores, but the ratio for sphalerite from Swansea Mine is not conclusive. The selenium content of the pyrite sample from the Heemskirk Granite was below the level of detection for the method employed by Edwards and Carlos. This sample was reported to consist of "a number of loose cubes of pyrite encrusted with minute crystals of cassiterite" and had such obvious magmatic associations that Edwards and Carlos concluded that the Heemskirk area represented a selenium-poor province.

It is interesting to compare the S:Se ratios in Table 16 with the sulphur isotope analyses in Table 14. Although the number of samples is limited there is a clear correlation between the two sets of data. The S:Se ratio of the pyrite from the Heemskirk Granite and the  $\delta S^{34}$  value of sphalerite

from Sweeney's Mine, within the granite, are both incompatible with the respective expected values for sulphur of magmatic origin.

Whereas Edwards and Carlos interpreted the low selenium content of this pyrite as indicating an association with a selenium-poor province, the  $\delta S^{34}$  value of the sphalerite sample strongly suggests that the sulphur in this pyrite and the sphalerite has been derived largely from sedimentary sulphate by the processes outlined in the previous section.

On the same basis the S:Se ratio and the  $\delta S^{34}$  value of the sphalerite from Swansea Mine both suggest a mixture of magmatic and sedimentary sulphur.

It can, therefore, be said that the sulphur isotope analyses and the sulphur - selenium analyses of ores in the Zeehan and Heemskirk areas are in good agreement and provide supporting evidence for theories on the origin of the sulphur in the ores.

These results indicate that S:Se ratios of ore minerals may be of more value in studies on the origin of ore deposits than has been previously acknowledged. However, the above results also emphasise that care is needed in the interpretation of S:Se ratios. It would obviously be interesting to have both sulphur isotope and sulphur-selenium analyses carried out for a comprehensive and representative suite of sulphide samples from the Heemskirk Granite. Such a project could provide further information of the validity of the ideas expressed in this and the previous section.