Taolin Zn–Pb–fluorite deposit, People’s Republic of China: an example of some problems in fluid inclusion research on mineral deposits

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Abstract: The large Taolin zinc–lead–fluorite deposit in the People’s Republic of China was discovered 28 years ago, but whether its genetic affiliation is Mississippi Valley-type, epithermal, or mesothermal remains uncertain. Both the ore and gangue (cherty to coarse quartz, plus barite, chlorite and calcite) occur as open space filling in a major fault zone between granite and metasedimentary rocks. Following barren, pre-ore quartz, three stages of ore are recognized by Wang (1978) and Wang et al. (1981). Our studies on 400 fluid inclusions, from all 4 stages, show homogenization temperatures of 120–200 °C (av. ~160) and salinities of 0 to 14 wt% equiv. NaCl (av. 7.7). These results differ greatly from some previously published sulphur isotopic temperatures (221–344 °C), and data for five inclusions that are more saline (9.0–17.7 wt% equiv. NaCl) and much hotter (up to 345 °C).

This study provides good examples of a variety of problems that are encountered in the application of fluid inclusion data to mineral deposit research in general. These problems include mine sampling, inclusion sampling, inclusion measurement, changes in inclusions after trapping, disagreement with other data, genetic affiliation of the deposit, and possible application of the results to exploration.

The Taolin Zn–Pb–fluorite deposit (29°22′N, 113°27′E) is located near Linxiang in northeast Hunan Province, China. The deposit was discovered 28 years ago, but its genetic affiliation has remained uncertain. This study was undertaken originally to determine to which particular class of deposits it belongs, such as epithermal or Mississippi Valley-type (MVT). According to Wang (1958), Taolin is a mesothermal vein deposit, and Ding & Rees (1984), on the basis of δ34S studies, propose a formation temperature of c. 220–340 °C. Oxygen, hydrogen, and lead isotopes were investigated by Ding et al. (1986). Both papers also present fluid inclusion homogenization (T_H) data indicating similar high temperatures, as well as high salinities.

One of us (ER) visited the Taolin mine in 1985 and collected samples under the guidance of the mine geological staff. Our fluid inclusion data on these samples revealed much lower temperatures, and lower salinities, than those reported by Ding & Rees (1984) and by Ding et al. (1986). The reasons for these differences illustrate a variety of problems that are encountered in the application of fluid inclusion data to mineral deposit research in general.

Geological setting

The general geology at Taolin was discussed by Yen (1957) and Kappelle (1980), and formational processes were postulated by Wang (1958). The deposit occurs in a major fault, dipping 30–45 °N, between the Mofushan two-mica granitic batholith, (c. 3500 km²; age 136 Ma, Li et al. 1964), and metasediments (phyllites and quartzites) of the Proterozoic Lengjiaxi system (Fig. 1). The fault zone is 50–300 m wide and trends east–northeast for over 20 km (Ding et al. 1986). Mineralization is found mainly in the hanging wall side of the fault zone, along its length, but six separately-named ‘deposits’ occur along a 10 km section as large lenses, 500 to over 1000 m long, between 200 and 400 m in depth (Ding et al., 1986), and 20–30 m thick. Mineralization is developed as fissure-filling veins and as cementation of brecciated ore and country rock, in part concentrated at fault intersections. No other control on mineralization has been recognized.

The major ore minerals are sphalerite, galena, and fluorite. Minor amounts of chalcopyrite and pyrite are present. Current ore production is c. 106 ton a⁻¹ averaging 13 wt% fluorite and 3% sphalerite + galena, with Zn > Pb. Copper is low (c. 0.1%); silver (c. 10 g t⁻¹ of ore) is present in galena concentrate at c. 400 g t⁻¹; and gold is <1 g t⁻¹ in the sulphide concentrate. Sphalerite, particularly the late yellow sphalerite (Fe ≥ 0.1%) is high enough in Cd, Ge and In for their commercial recovery. Gangue is quartz (cherty to coarsely crystalline), barite, and minor chlorite and calcite. Ding & Rees (1984) report wall rock alteration consisting predominately of silification with lesser chloritization and sericitization, and minor carbonization (Wang et al. 1981), but just as with the ore minerals, these phases appear to occur only as open space filling, not replacement. Ore minerals are coarsely crystalline, with a few vugs. Barite blades up to 20 cm in length were seen.

Samples studied

Our studies were based on only eight samples, all collected by the senior author from the central section of the Shangtangchong mine (also transliterated ‘Shangtancen’ and ‘Shangtangchung’ in the literature), 120 m level, in or near the No. 9 (exploration) tunnel, about 800 m west of the shaft (Table 1). This tunnel crosses the orebody from the footwall (in Mofushan granite to the south) to the hanging wall (in Lengjiaxi metasediments to the north). Each sample was selected to be representative of one of the four paragenetic stages, as identified underground by the accompanying mine geological staff. These stages are as follows: Stage 0, barren pre-ore quartz plus minor pyrite;
Stage 1 is the first stage of a process observed in the Taolin ore deposit. It features the presence of quartz, galena, and sphalerite. The stage is characterized by the formation of quartz and galena within the ore body. This stage is described in detail in Table 1, which provides a comprehensive overview of the paragenetic sequence and the inclusion details.

**Table 1. Description and paragenetic details (where obtainable) on samples studied**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Description</th>
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<tbody>
<tr>
<td>Stage 0</td>
<td>Pre-ore, barren quartz plus trace of pyrite, near footwall (Lab. sample no. 1)</td>
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<tr>
<td>Stage 1</td>
<td>'Gel quartz', amethystine, fluorite and sphalerite, etc., from c. 200 m north of footwall. Sequence, recognized in one specimen: fluorite, quartz, minor chalcoprite and galena, then fluorite (Lab. sample no. 2)</td>
</tr>
<tr>
<td>Stage 2</td>
<td>Quartz, fluorite and sphalerite. Some fluorite crystals show inclusion-rich cores, followed by minor chalcoprite, and clear fluorite, then brecciation and quartz deposition. Some quartz may replace barite blades (Lab. sample no. 3) Sphalerite, galena, fluorite and quartz from c. 200 m east of north end of tunnel. Sequence: quartz, sphalerite, galena, quartz and fluorite (Lab. sample no. 6) Quartz and sphalerite, from c. 50 m east of north end of tunnel. Sphalerite masses are brown with yellow rims; quartz fills interstices between sphalerite crystals (Lab. sample no. 7)</td>
</tr>
<tr>
<td>Stage 3</td>
<td>Quartz, barite, and fluorite, from the earliest part of Stage 3, c. 20 m south of hanging wall. Quartz crystals nucleated on barite blades. Sphalerite, with minor chalcoprite and galena from the last part of Stage 3 (Lab. sample no. 4) Barite and fluorite from north end, at hanging wall. Fluorite fills interstices between barite blades (Lab. sample no. 5) Quartz, barite, sphalerite and galena from c. 230 m east of north end of tunnel. Some barite blades 20 cm long, with interstitial quartz, followed by sphalerite and galena, then fluorite (Lab. sample no. 8)</td>
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**Sample preparation, nature of inclusions, and inclusion methods used**

The process involves the preparation of samples, which includes the cutting of sections and the observation of inclusions. These inclusions are characterized by their size, shape, and content. The methods used to study these inclusions include optical microscopy and microthermometry.

All microthermometry was done on a Caiaxmea stage (Poyt et al. 1976). The temperature of homogenization ($T_h$) was measured using heating rates, near $T_h$, of c. 0.5-1.0 °C min⁻¹. Reproducibility was generally within ±1°C. All homogenizations were done to the liquid phase. Calibrations were run using standards in the form of synthetic fluid inclusions (Sterner & Bodnar 1984) made from the system NaCl–H₂O–CO₂ for below 0°C; for $T_h$, $p$-acetophenetide.

**Fig. 2. (a)** Section perpendicular to the axis of Stage 0 quartz crystal, diameter 12 mm, showing zones of abundant fluid inclusions. In crossed polars, this quartz is seen to consist of subparallel blades, all perpendicular to the visible growth zones, but of different extinction position. (b) Euhedral fluorite crystals having cores containing dense arrays of fluid inclusions. Left, Stage 1 fluorite, surrounded by later single crystal sphalerite; $T_e$ 130-150°C, $T_m$ - 8.6°C. Right, Stage 2 fluorite, embedded in brecciated ore and gangue, $T_e$ 170-192°C, $T_m$ - 6.7 to - 6.9°C. (c) Sphalerite, Stage 1, showing abundant primary inclusions in a crystallographically controlled array (presumably elongated perpendicular to the growing crystal faces). $T_e$ 130-146°C, $T_m$ -8.1 to -8.4°C. (d) Two primary inclusions in fluorite of Stage 3 that appear to have decrepitated (naturally), yielding halo of smaller inclusions. $T_e$ of primary inclusions 121°C, $T_m$ (decore) - 0.8°C.
(135 °C), tin (232 °C), NaNO₃ (307 °C) and K₂Cr₂O₇ (398 °C) were used. To avoid stretching, particularly in fluorite (Bodnar & Bethke 1984), the lower-\( T_h \) inclusions in any given chip were always run first.

The temperature of eutectic (i.e. first) melting (\( T_e \)) on warming a frozen inclusion was determined whenever possible. As discussed below, this measurement not only has low precision, but also serious problems in terms of accuracy.

The temperature of melting of the last crystal of ice (\( T_{m(ice)} \)) was measured at heating rates of \( c. 0.7-1 \) °C min\(^{-1}\), and was verified by one or more repeat runs, which were then averaged. No phases other than ice were recognized. The very low salinity of some inclusions (e.g. Fig. 3) resulted in variable (and erroneously high) values unless heating rates at \( T_{m(ice)} \) were very slow. Most \( T_{m(ice)} \) measurements were reproducible to \( \pm 0.1 °C \), with the notable exception of those low-\( T_h \) inclusions which lost their vapor bubble on freezing. These generally yielded superheated metastable (i.e. erroneous) \( T_{m(ice)} \) values above 0 °C (up to c. +7 °C) due to high internal negative pressure (Roedder 1967).

For the crushing stage studies, small grains (<1 mm) containing suitable inclusions were mounted in matching index oil or in appropriate solvents using standard procedures (Roedder 1970).

**Results**

*Temperature of homogenization (\( T_h \))*

Our results on determination of \( T_h \) on over 400 mostly primary inclusions from all four stages ranged from 96 to 252 °C and averaged 163 °C. All thermometric data for each inclusion studied have been deposited in the British Library, Boston Spa, Wetherby, W Yorks, UK, as Supplementary
Publication No. SUP 18051 (7 pages) and are also available from the Society Library. The relatively few inclusions in sphalerite and barite that were run may not all be primary. All but the six highest values (219–252 °C) and one lowest (96 °C) are plotted on Fig. 4. From this figure it is seen that most of the data fall in the relatively narrow range 120–200 °C. Although the data for each individual stage extend over approximately the same range, the average T_{h} for Stage 0 (183 °C; n = 62) is significantly higher than those for Stage 1 (158 °C; n = 53), Stage 2 (160 °C; n = 211) and Stage 3 (156 °C; n = 64). Average T_{h} values for Stages 1 to 3 are as follows (°C): quartz, 185, 179, 168; fluorite, 147, 148, 153; sphalerite, 168, 178, 145. A number of planes of inclusions outlining healed fractures in fluorite were also run. Some of these yielded T_{h} data similar to those from nearby primary inclusions, suggesting that they may be pseudosecondary, as is sometimes very common in fluorite (e.g. Roedder et al. 1968). In other samples, such planes were lower in T_{h} than adjacent primaries and hence are thought to be truly secondary.

The T_{h} values reported here are measured values, uncorrected. To convert to formation temperatures (i.e. trapping temperatures, T_{f}), they would need to be corrected first for instrumental calibration and then for pressure. The former correction, as determined by calibration runs, amounts to −4.4 °C at 15 °C and −5.4 °C at 220 °C. The correction for pressure is positive rather than negative, and only a minimum value can be estimated. This minimum correction is only a few degrees, which cancels part of the instrumental correction. The actual pressure correction may be larger, depending upon depth of cover, CO_{2} content, etc. For example, the correction for the pressure of 1000 m of hydrostatic column of 15% NaCl would be +15 °C for an inclusion with T_{h} = 200 °C (Potter 1977).

**Temperature of eutectic melting (T_{e})**

We made 413 T_{e} determinations (Fig. 5), which ranged from c. −24 to −51 °C and averaged −40 °C. Most repeat runs agreed within ±2 °C. Many of the higher temperatures found were for inclusions having lower salinities, as might be expected from the difficulty in seeing the very small amounts of liquid that would be present at the actual eutectic. T_{e} values can only be estimated roughly, and are almost certainly higher than the true values (see Discussion). The very low T_{e} values indicate the presence of significant calcium among the solutes, as no other geologically probable ions (except Fe^{3+} and Li^{+}) yield such low values (Roedder 1984).

**Temperature of melting of last ice (T_{m(ice)})**

The temperatures of last melting of ice determined on 218 inclusions range from 0 to −10.1 °C and average −4.9 °C (Fig. 7). Using data of Potter et al. (1978) these values correspond to salinities (wt% equiv. NaCl) of 0–14.1 (av. 7.7). Thirty-two inclusions in quartz from Stage 0 show an average of −8.4 °C that is actually from a bimodal distribution, with one group of 14 at c. 9.5 °C and another 16 at c. 7.5 °C. This may be merely a result of inadequate sampling of a continuum. With one exception, all 40 values for Stage 1 range from c. −7 to −9 °C and average −8.1 °C. Stage 2 values (101) show a wide range, with most between 0 and −7 °C, and a few below −8 °C (av. −4.0 °C). Noteworthy is a group of 28 inclusions from stages 2 and 3 that are between 0 °C and −1.0 °C (Figs 3 & 7). The relatively few data (45) on Stage 3 are also spread out, from 0 to −6 °C (av. −2.1).

In both Stages 2 and 3, the lower salinity inclusions tend to have the lower values in the range of T_{m(ice)} and vice versa (Fig. 6). With the exception of a group of 22 inclusions in fluorite from Stage 2 that show low salinities (Fig. 7), the
available data are too sparse to be certain of any valid differences in \( T_{c(n)} \) between different minerals within a given stage. In some fluorite samples, planes of inclusions along healed fractures yielded salinity data that were identical to those from nearby primary inclusions, and others yielded lower salinities (just as was found for \( T_{c(n)} \)).

**Crushing stage runs**

A series of crushing runs were made to evaluate the presence and nature of noncondensible gases in the fluid inclusions. Twenty-eight inclusions in quartz and fluorite, mainly secondary (or pseudosecondary?), in samples from all four stages, were opened. Almost all inclusions crushed in matching index liquids showed major expansion of the bubble, in the range 20–30-fold by volume. If this expansion is solely of the gases in the bubble before crushing, it suggests gas pressures (at room temperature) of 20–30 atm. In half of these inclusions, the expanded bubble filled the inclusion, and additional gas may exsolve from the liquid during the expansion, so accurate pressures cannot be established (Sasada et al. 1986). Seven inclusions, from Stages 0 and 2, were crushed in alkaline BaCl\(_2\) solution; although this medium makes observation difficult, in all seven cases the bubble was seen to dissolve instantly and completely, suggesting that CO\(_2\) is the major component.

**Taolin as an example of the problems in fluid inclusion studies of ore deposition**

This brief study of the fluid inclusions in the Taolin samples has succeeded in establishing some of the parameters of the ore-forming environment, and hence some aspects of the genetic affiliation of the deposit. However, it has also provided good examples of a variety of problems that are commonly encountered in such work, and which sometimes impose serious limits on the usefulness of inclusion data. In view of the increasingly widespread application of fluid inclusion data on ore deposits, it is useful to review some of these problems and the constraints they place on the use of the data, both for Taolin and for mineral deposits in general.

**Mine sampling problems**

Appropriate and adequate sampling of a mineral deposit is one of the most important facets of any fluid inclusion study. In the present study we were fortunate in that what might be a hopelessly incomplete sampling proved to be far more representative than expected. In large part this resulted from the help of a knowledgeable mine staff, who were able to point out the four depositional stages underground in the short time available. The samples taken were thus believed to be representative of the ore stages across the vein along the particular drift that was sampled.

The degree to which any such sampling is representative must be viewed in both a larger and a smaller context. The validity of any extrapolation from this one sampling line vertically to other mine levels, and laterally along the vein, is unknown, as is any extrapolation to the other adjacent ore deposits situated along the same fault. Ding & Rees (1984) have shown that the six named deposits along the fault do differ in mineralogy; those at the ends have less of the early sphalerite and galena, and more of the late barite, but Kappelle (1980) indicates that the centre of the district, between the Shangtangchong and Yinkongshan deposits, consists of a barren barite zone. Furthermore, with increasing depth, lead and zinc values decrease and pyrite content increases. In contrast with these evidences of lateral and vertical variability, the general mineralogy and textural features of the several deposits seem to be quite uniform, as might be expected from the uniform structural setting of all the deposits along a single fault zone.

Equally important sampling problems arise in the smaller context. At any one sample location in the mine, the grain size of the ore, and the obscure textural and colour variations in the mine face that might provide evidence of paragenetic sequence, were too large to be sampled in any single hand sample. Although clear evidence of paragenetic sequence could occasionally be found (e.g. Fig. 2b), the coarse grain size generally made it impossible to relate these details to the overall paragenetic sequence.

**Inclusion sampling problems**

Superimposed on the mine sampling problems is the common problem of finding inclusions in the available material. As usual, inclusions were present in all minerals in all samples; problems only arose in finding suitable inclusions. In most ore deposit studies, 'suitable' means primary inclusions, in the ore minerals of interest, that are adequately large and clear for the measurements needed. In some Taolin quartz samples, there was an abundance of well-established primary inclusions, but most were too small for accurate low-temperature studies (e.g. Fig. 2a). Some fluorite crystals had numerous large primary inclusions (Fig. 3), but other fluorite crystals (other generations?) had only secondary inclusions, albeit in great abundance. No verified primary inclusion was found in barite, and evidence of leakage was common in barite samples.

The small amount of available sample material made it necessary to use practically all good inclusions that were found. As the abundance varied greatly between samples, a strong, statistical bias is necessarily built into the data.
obtained. Whether this bias caused significant errors is unknown, but it must be noted that such biases in favour of ‘the good samples’ are almost unavoidable in most inclusion studies.

The metallic ore minerals at Taolin present special problems. The galena is opaque, and much of the sphalerite is so dark that very thin doubly polished plates are needed for transmitted light examination. As a result, only very small volumes of sphalerite can be examined in any given preparation, and in addition, no verified primary inclusions were found in any of this sphalerite. Such problems are commonplace in ore deposit studies. The standard practice, which has been followed in literally hundreds of ore deposit inclusion studies, is to perform the fluid inclusion measurements on the associated transparent gangue minerals. These are tacitly assumed to have crystallized simultaneously with the ore minerals, from the same ore-forming fluid, usually on the basis of contact between crystals of the two phases. This common assumption is of crucial importance, but how valid is it?

Barton et al. (1963) presented a seminal paper on equilibrium in ore deposits. They discussed the terminology, concepts, and criteria involved in the recognition of equilibrium mineral assemblages, and showed that several quite different types of equilibrium between coexisting phases must be considered, and that proof of equilibrium is a far from trivial task. (Similar problems exist for sulphur isotopic equilibrium; see Ohmoto & Lasaga 1982.) In fluid inclusion work, we are normally concerned with the much simpler but still non-trivial problem of whether the two phases did in fact grow simultaneously. When examined carefully, most ore samples show clear evidence that even rather intimately associated phases have crystallized sequentially, not simultaneously (e.g. Fig. 2b). Only rather rarely can the interface between adjacent crystals of two different phases be found to indicate, unambiguously, that they grew simultaneously. The difficulty of obtaining such evidence is such that truly simultaneous growth of two phases may be more common than these few proven examples. However, the evidence for non-simultaneous growth is so common and widespread that it is safest to assume, unless proven otherwise, that the various phases have indeed formed sequentially, not simultaneously. Perhaps the most abundant evidence lies in the common crustified veins, where two, three or more ore and gangue minerals have apparently taken turns in deposition. The important corollary of this, for fluid inclusion studies, is that the mineralizing fluids must have changed in some way (P, T or X) to cause deposition of different phases. We have no way of evaluating whether the fluid was almost saturated with respect to several solid phases all the time, and miniscule changes alternately caused supersaturation with respect to one or the other phase, or whether two entirely different fluids alternated in the vein. All that can be said with certainty is that a fluid that deposits only quartz cannot be identical to an earlier or later fluid that deposits only galena.

In the present study, although fluorite is also an ‘ore mineral’ at Taolin, no evidence was found of simultaneous crystallization of fluorite and galena or sphalerite. In fact, clear evidence of sequential deposition was relatively common (e.g. Fig. 2b). The only mitigating data here are that the few (possibly pseudosecondary) inclusions in sphalerite that were usable gave microthermometric results that were in the same ranges as those from primary inclusions in associated fluorite.

Measurement problems

Except for the very small inclusions in some quartz, the poor visibility of inclusions in the dark early sphalerite, and the normal instrumental problems of calibration, etc. (Roedder 1984), measurement of the homogenization temperature (T_h) was essentially routine.

Measurements at low temperatures (the eutectic temperature (T_e) and the temperature of melting of ice (T_{mel}) did, however, present a few problems that are common in ore deposition studies. Determination of T_e is inexact, by its very nature, as it is based on the formation of the first visually apparent liquid phase on warming a previously completely frozen inclusion, usually as evidenced by an increase in the degree of translucency. The wetting of the interfaces between the tiny crystals of ice and salts in a frozen inclusion decreases the amount of reflection and hence dispersion of light at these interfaces. The presence of liquid at any given temperature is a function of the composition of the solutes in the inclusion fluid, but the recognition of it from a change in translucency on warming is a function of the amount of such liquid, which will vary with the concentration of solutes. In addition, recognition will vary with the thickness of the inclusion along the viewing direction, operator experience, grain size on freezing, and rate of warming. Three major sources of bias are present in such results, all in the same direction of yielding values that are too high (i.e. too warm). The first source is based simply on the nature of the measurement itself. The true temperature for first formation of melt must, of necessity, lie at a lower temperature than T_e, the temperature at which liquid is first visible. As natural fluid systems contain at least minor amounts of many components, the actual first melting temperature may thus be many degrees below the observed T_e, and the actual amount below is unknown. Superposed on this unavoidable bias in all T_e determinations is a second source of bias: inclusions that are too thin or thick will both give too high temperatures. Those that are too thin are rather translucent even when solidly frozen, and must have more actual liquid present to show a significant increase in translucency, or other phenomena indicating the presence of liquid, such as the recrystallization of fine grained ice. Those that are too thick have so many phase interfaces that they remain essentially opaque until considerable liquid has formed. The third source of bias is peculiar to all low-salinity inclusions, as are many of those at Taolin. Eutectic melting generally results in the loss of at least one solid phase. If an inclusion is low in salinity, only very small amounts of salts and/or salt hydrates are formed, along with ice, on freezing. If the salinity is very low, all these salts and/or salt hydrates must melt before recognizable liquid forms. Thus the very low salinity inclusions from Taolin might well have true eutectic melting 10°C or perhaps even 20°C below the visual estimate of T_e. Such bias must be weighed in any interpretation of the probable elemental composition of the salts present via comparison of T_e data with the eutectics in known salt systems.

One additional low temperature measurement problem was found that is present in almost every study of inclusions with low homogenization temperature, the occurrence of
metastable superheated ice at high negative pressures (Roedder 1967). It only occurs in those inclusions in which the expansion of ice on freezing eliminates the vapour bubble. In the Taolin samples, it was found in 23 inclusions. All inclusions showing metastable superheated ice were probably low salinity, although there is no requirement that this be true. In eleven of the 23, valid (i.e. stable) \( T_{m(\text{inc})} \) determinations could not be made, and the metastable \( T_m \) determinations are not reported here. In the other twelve, the vagaries of nucleation of the vapour phase permitted a valid determination of \( T_{m(\text{inc})} \) in one run but not in another; these showed \( T_{m(\text{inc})} \) (stable) values ranging from \(-0.2\) to \(-1.3\) °C. The difference between the stable and metastable values of \( T_{m(\text{inc})} \) for given inclusions ranged from 1.1 to 7.4 °C and averaged 3.6 °C.

Although a low value of \( T_h \) is required if an inclusion is to exhibit metastable superheated ice (because freezing will not eliminate the larger bubbles in inclusions with high \( T_h \)), not all low-\( T_h \) inclusions showed metastable equilibria. The 23 that did exhibit metastability at \( T_{m(\text{inc})} \) on one or more runs had \( T_h \) values of 100 to 142 °C. These constitute approximately half of all the inclusions that have \( T_h \) in this range. The other half nucleated a vapour bubble (and in so doing, eliminated the metastability) at temperatures below \( T_{m(\text{inc})} \), following phase sequences 2 or 3 as described by Roedder (1967), and hence gave valid \( T_{m(\text{inc})} \) values.

**Problems with changes in inclusions after trapping**

If essentially irreversible changes take place in inclusions after trapping, subsequent measurements may be invalidated. Most inclusions in barite from Taolin, as is also common in barite from other localities, showed widely divergent gas/liquid ratios. Such diversity may be a result of: (1) trapping of heterogeneous (e.g. boiling) fluids; (2) necking down after formation of vapour bubbles; and (3) leakage. Several lines of evidence seem to suggest that generally the diversity in barite is probably a result of both leakage and necking down, and the Taolin data merely confirm the conclusion that inclusion data on barite are generally unreliable.

Perhaps the most common type of irreversible change that may occur in fluid inclusions involves natural stretching or partial decrepitation. Bodnar & Bethke (1984) showed that fluid inclusions in fluorite will stretch (permanently expand) in response to high internal pressures if heated to some degree, \( \Delta T \), greater than \( T_h \). (Normally, a stretched inclusion shows no fracturing or other direct evidence of change. In some natural examples, the volume expansion of the inclusion yields fractures in the inclusion walls large enough to result in the trapping of new secondary inclusions on heating (e.g. Fig. 2d.).) The value of \( \Delta T \) varied with the size of the inclusion, large stretching at lower values of \( \Delta T \) than small ones. The value of \( \Delta T \) is also a direct function of the external pressure (Rowan et al. 1983). For inclusions in the size range encountered in the Taolin fluorite (c. 20–100 μm) at one atm external pressure, \( \Delta T \) would be c. 30–50 °C. Assuming that the relative paragenetic assignments of our samples are correct, Fig. 4 shows that some fluorite inclusions from stage 1, formed at 120–130 °C, may have been exposed to later stage 2 fluids at temperatures as high as 200 °C and perhaps as high as 250 °C, but survived. Similarly, some stage 2 fluorite which formed at 100 °C must have been exposed to stage 3 fluids at 190 °C and perhaps 225 °C. Wang et al. (1981) also report that some large secondary inclusions in fluorite from Taolin have \( T_h \) greater than \( T_h \) of smaller primary inclusions (in the same sample). The fact that the earlier inclusions still have low \( T_h \) values may be variously explained:

1. The paragenetic assignment of the sample (i.e. the inclusions) is wrong.
2. The inclusions simply did not reach a sufficiently high value of \( \Delta T \) to stretch, due to their size, salinity, external pressure, or all three factors.
3. The inclusions did decrepitate but resealed only after the surrounding fluid had become cooler (e.g. Fig. 2d).
4. Although the later fluids were hotter, the sample containing the inclusion was not actually exposed to them, as a result of changing plumbing.
5. They did stretch (but, only from \( T_h = 50 \) °C to \( T_h = 100 \) °C).

All these possible explanations may be involved, but their relative significance cannot be evaluated at this time. As each paragenetic stage has a range of \( T_h \) values for fluorite of 50–100 °C, the same problem of possible stretching exists within each stage, as well as between stages.

Numerous papers in the ore deposit literature report such temperature increases with paragenetic stage, usually without consideration of the necessary consequences in terms of probable natural decrepitation of earlier-formed, low-temperature inclusions. In some papers, the data (as reported) require that earlier inclusions, even in soft minerals such as fluorite, were subjected to 1000 bar, or more, of internal differential pressure without stretching or decrepitation. Almost certainly some of these data are erroneous, and hence it is obvious that in each such area a more detailed study is needed, with adequate sampling for inter- and intra-stage paragenetic control.

**Disagreement with previous temperature data**

Tourret (1977, p. 221) said that we should “...take inclusions for what they are: an intrinsic part of the rock, which has to be studied with all other minerals... and their results internally checked by independent methods.” Let us now compare our data on Taolin with previously published data. Wang (1978) and Wang et al. (1981) reported \( T_h \) values for 49 primary inclusions from the three ore stages at Taolin to range as follows: Sphalerite 152–216 °C, quartz 155–227 °C, fluorite 109–164 °C, and barite 100–170 °C. The samples were from the −40 to −80 m levels in the Shangtangchong mine. Although our \( T_h \) data for each of these four minerals extend over wider ranges, we agree fairly well. Wang et al. (1981) also used the decrepitation method on sphalerite for establishing the flow direction of the hydrothermal fluids. They report flow (i.e. temperature decrease) “from NW to SE”.

Wei & Ding (1984) published histograms giving \( T_h \) of inclusions in sphalerite, barite and quartz. They summarize the data as follows: dark sphalerite 350–250 and 230–160 °C; light sphalerite 300–250 °C; barite 290–230 and 200–90 °C; and quartz 360–270 and 250–110 °C. Scaling of their histograms (their figs 2 & 3) gives the following data for sphalerite and quartz, respectively: number of data plotted 90, 143; mode 170, 170 °C; arithmetic mean 185, 220 °C. The weight percent NaCl is given as 19.5–12.5% (first stage) and 15.3–7.0% (second stage).
Table 2. Inclusion data (T. Ding pers. comm. 1986)

<table>
<thead>
<tr>
<th>Stage</th>
<th>T_h (°C)</th>
<th>Salinity (wt% NaCl)</th>
<th>T_m(h2o) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>285</td>
<td>14.9</td>
<td>10.9</td>
</tr>
<tr>
<td>I</td>
<td>300</td>
<td>17.7</td>
<td>13.8</td>
</tr>
<tr>
<td>I</td>
<td>305</td>
<td>16.5</td>
<td>12.5</td>
</tr>
<tr>
<td>I</td>
<td>345</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>245</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>245</td>
<td>12.0</td>
<td>-8.2</td>
</tr>
</tbody>
</table>

1 Recalculated by us, from the reported salinity values, for ease of comparison with the present data.

Ding & Rees (1984; see also McMaster 1984), on the basis of δ²⁹S studies, propose a single-fluid, closed-system model operating at c. 220–340 °C for the ore deposition at Taolin. They also present unpublished fluid inclusion data “from Wei” (no affiliation given). These latter data include two isolated T_h values and four pairs of T_h and salinity in wt% equiv. NaCl. Three of these pairs were for samples from their Stage I (presumably equivalent to our Stages 1 and 2), and one from their Stage II (our Stage 3). These samples were from the same mine (‘Shangtancen’) as ours, but from 40 metres higher (T. Ding pers. comm., 1986). The inclusion data they report are given in Table 2. In a later paper (Ding et al. 1986) these inclusions are stated to have been in quartz.

The δ²⁹S isotope temperatures reported by Ding & Rees (1984) are based on distributions between 16 mineral pairs of galena, sphalerite, chalcopyrite and barite. (Some of these data are also given by Wei & Ding 1984.) Eight values for Stage I minerals average 299 °C and eight for Stage II average 238 °C (av. of all 16 = 268 °C).

Ding et al. (1986) report the same four inclusion data pairs as above, plus another Stage II pair (T_h = 170 °C; salinity = 9.0 wt%; T_m(h2o) calc. = -5.8 °C), but the isolated T_h value of 245° is missing. These data are credited to ‘Wei Jiaxiu, Inst. of Geology of Mineral Deposits, Beijing’. They also report 14 of the same δ²⁹S temperatures with an average of 277 °C.

The average values for T_h in sphalerite and quartz reported by Wei & Ding (1984) are higher by about 20 and 40 °C, respectively, than those we found, but the T_h data ascribed to Wei by Ding et al. (1986) are 100 °C higher, and the temperature discrepancy is even larger between the sulphur isotope data and our T_h, data, and call for an explanation. The easiest explanation would be sampling problems. The samples involved in all five studies (Wang et al. 1981; Ding & Rees 1984; Wei & Ding 1984; Ding et al. 1986; and the present study) were from the Shangtangchong deposit (except for one sulphur-isotope sample from the adjacent Yinkongshan deposit), but they came from several different levels, several tens of metres apart. Although the ore grade decreases with depth, the apparent uniformity of this mineralization in the several deposits for kilometres along the same fault zone suggests little difference is to be expected between the various sample sites. In addition, our T_h results agree with those of Wang et al. (1981), from a different level in the mine. Thus, even though only five quartz samples were reported by Ding et al. (1986) as measured by Wei for T_h and T_m, and eight total samples in our work, it is unlikely that sampling problems may explain the differences.

As pointed out above, natural stretching may have affected soft minerals such as fluorite, sphalerite, and barite. However, any stretching that may have occurred should tend to reduce the difference between our values (mainly on soft minerals) and those of Wei (on quartz, which generally does not stretch except under very severe conditions). We do not know why the six T_h estimates for quartz from Wei reported by Ding et al. (1986) (averaging 287 ºC) are 67 ºC hotter than the average of 143 T_h estimates for quartz from Wei & Ding (1984).

The only direct comparison that can be made between the inclusion data and the sulphur isotope data involves sphalerite, as true contemporaneity of deposition of the sulphides and the gangue minerals generally cannot be proved (Barton et al. 1963), and, in fact, can sometimes be disproved (e.g. Fig. 2b left). Although our data on T_h of inclusions in sphalerite are suspect, in view of the uncertain origin of most of the inclusions, the consistency of the values, and their agreement with those from obviously primary inclusions in closely associated quartz and fluorite (both earlier and later), and the agreement with earlier published data by Wang et al. (1981), suggests that they could hardly be wrong by >100 ºC. Unfortunately, neither Ding & Rees (1984) nor Ding et al. (1986) refer to the data of Wang et al. (1981) or Wei & Ding (1984).

The largest unknown in the inclusion data is the pressure correction. This is the amount that must be added to the temperature of homogenization (T_h) to obtain the temperature of trapping or formation (T_t), which is the only temperature that should be compared with the isotopic temperatures. The calculation of this correction is based on the total pressure at the time of trapping, the homogenization temperature, and the salinity. Potter (1977) provides data on the effects of salinity and T_h for various pressures, but this estimate of the total pressure must generally be based on geological reconstruction of the probable depth of cover at the time of formation. At present we have no geobarometer to indicate this former depth of cover, but we can calculate the depth that would be necessary to have our T_h data (av. 163 °C) agree with the temperatures based on the sulphur isotopic fractionation data (av. 268 °C). The differences based on salinity between 1% and 15% NaCl are relatively minor, and yield a range of calculated pressures of 1200–1350 bar. Depending upon whether the pressure is purely hydrostatic (i.e. the vein open to the surface) or lithostatic, these pressures correspond to depths of 12.0–13.5 km (hydrostatic) or 4.4–5.0 km (lithostatic). The densities assumed are 1.0 and 2.7, respectively; if the hydrostatic column were hot, it could have a density of <1, even with salts in solution, requiring an even larger depth estimate. To obtain the maximum δ²⁹S value listed (344 °C) from the high end of our T_h values (200 °C) would require 1750 bar, corresponding to 17.5 km hydrostatic depth or 6.5 km lithostatic.

The inclusion temperatures of Wei given by Ding & Rees (1984) agree with the sulphur isotope temperatures. But these inclusion data are stated to be filling temperatures (i.e. T_h), and must be corrected for pressure to obtain T_t. At these higher temperatures, fluids are more compressible, and hence the corrections for pressure are larger. Using the average T_h of the four data pairs given by Ding & Rees (284 °C), corrections for the 1200–1750 bar pressure
discussed above range from 110 to 165 °C, and hence yield formation temperature \( T_f \) of 394–449 °C, which are not in agreement with the sulphur isotope data.

We have not studied wall rock alteration at the mine, and there are some differences of opinion in the literature as to the nature and degree of alteration of the wall rocks, but visual evidence and statements by the geological staff at the mine indicate that other than introduction of silica, chlorite, and possibly sericite as void filling, wall rock effects are negligible. If verified, this lack of alteration is somewhat difficult to explain if ore fluids at temperatures as high as 340 °C (or 449 °C) were in contact with the wall rock.

**Possible application of the inclusion results to exploration**

In terms of exploration, one of the first questions raised about any ore deposit concerns its genetic affiliation. For Taolin, this question was whether it is more closely allied with the Mississippi Valley-type (MVT), or the epithermal or mesothermal types. Some of the previously published Taolin temperature data, both inclusion and isotopic, are far above the range most commonly reported for MVT. Our \( T_f \) data, and those of Wang *et al.* (1981), are much lower than the other data, and in part do overlap with MVT data, but even the average of all our \( T_f \) data (c. 160 °C) is well above most data from recognized MVT deposits \( T_f = c. 100–150 °C; Roedder 1976)\.

Perhaps the most characteristic feature of MVT inclusions, other than their temperature range, is the high salinity. With the exception of late-stage minerals (in some deposits), practically all MVT inclusion salinity values are high; 15, 20 or even 25 wt% equiv. NaCl (Roedder 1976). They rarely show daughter minerals (such as halite) and analyses show that commonly divalent ions, Mg and particularly Ca, are responsible for a significant part of the salinity found. The Taolin samples presumably also contain significant Ca, but the average salinity for all 230 determinations was only 7.7, and the highest value 14.1 wt% equiv. NaCl. Even the average of Wei’s five determinations of salinity, 14.0 wt% equiv. NaCl, is low by comparison.

Another feature of MVT inclusions is the common presence of methane as the gas phase under pressures up to some tens of atmospheres, as well as droplets of an immiscible oil phase. Neither was found at Taolin. The Taolin inclusions do contain gas at similar pressures (c. 20–30 bar), but, as shown by the crushing studies, it is \( \text{CO}_2 \).

The available inclusion data are more compatible with some version of an epithermal origin. However, most polymetallic epithermal deposits, as established by low \( T_e \) values and association with intrusive and particularly volcanic activity, have lower salinities than found here. Furthermore, although the footwall of the Taolin deposit is in granite, there is no other evidence of connection with igneous activity. Ding *et al.* (1986) suggest that their data on oxygen, hydrogen and lead isotopes indicate that the lead was probably derived from the granite, presumably by the circulation of meteoric water. This water exchanged oxygen with the granite, and may have been supplemented by some magmatic water. Ding *et al.* (1986) determined \( \Delta D \) on 10 samples of fluid inclusion water from quartz, barite, sphalerite, and calcite, and found values of −31 to −69 per mil. No significant difference was noted for samples from their Stages I and II (av. −46 and −48 per mil). On the basis of equilibrium with quartz, they calculated that \( \delta^{18}O \) of the water was +4 to 0 for Stage I, and became lighter (0 to −7) during Stage II.

It is possible that the water could be purely meteoric in origin, and gained its solutes (and its lead, zinc, fluorine and heat) solely from circulation through the granite (Nordstrom *et al.* 1985). The progressive exchange with the channel walls with time (and cooling) could thus explain the increasing lightness of the oxygen with depositional stage that Ding *et al.* (1986) report (ending with a low-temperature sample on the meteoric water line). Such meteoric-water-rock interaction was proposed by Ding *et al.* (1986) in one of their suggested models, but the high salinities were thought to present a problem. This problem is smaller than they thought, in light of our data showing lower salinities.

Our lower salinity data introduce a new problem, however. This is the question of how the ore minerals were transported by fluids that were, in some cases, almost fresh water. Large fluorite crystals are known to have formed from such waters in some hot springs deposits, but the transport and deposition of sphalerite from low-temperature, low-salinity fluid is more difficult.

The geology and mineralogy of the Taolin deposit are similar to some of the lead–zinc veins in Grenville and Ordovician rocks in St Lawrence County, New York (Brown 1983), but recent fluid inclusion studies on these deposits (Ayuso *et al.* 1987) show that although they also have low \( T_f \) values (below −50 °C), the \( T_e \) values are lower (104–152 °C) and the inclusions contain halite daughter crystals ± droplets of oil. Perhaps the most closely analogous deposits in terms of both geology and mineralogy are the lead–zinc deposits of the Phoenixville–New Galena–Ecton districts, Gettysburg basin, Pennsylvania (Smith 1977). No fluid inclusion data are available on those deposits, so we examined a series of samples from the dumps at the Wheatley mine, Phoenixville, Pennsylvania (the mines have been closed for many years). Preliminary data on both quartz and sphalerite showed primary and pseudosecondary inclusions ranging in \( T_e \) from 145 to 192 °C, and all had \( T_{\text{min}} \) c. −9 ± 0.5 °C, thus improving the analogy to Taolin. Any evidence as to the origin and nature of an ore deposit (e.g. its genetic affiliation) has possible importance in terms of exploration for extensions of the deposit, or for new deposits. At present, the Taolin fluid inclusion data provide no direct evidence as to the age of the mineralization. The age of the Moffuselian granite (136 Ma) provides a maximum age, but the mineralization could have taken place at almost any time since then. The fluid inclusion data do provide a minor constraint on the upper age; as they show no evidence of boiling, ore deposition must have occurred under a confining pressure at least equal to the vapour pressure of the ore fluids\(^1\). This vapor pressure will be highest for those inclusion fluids with highest \( T_e \) and lowest salinity. Using values of 195 °C and 1%, this vapour pressure is 14 bar (Haas 1976), equivalent to a hydrostatic column of only 140 m, or a lithostatic column of 50 m. These values would increase with increasing \( \text{CO}_2 \) content. If

\(^1\) D. O. Hayba (U.S. Geol. Survey) has suggested that the data points for Stages 1 and 2 on Fig. 6 could be interpreted as evidence for boiling, particularly if replotted in terms of enthalpy-salinity (Hayba & Bethke 1987).
similar fluid inclusions would be found to be present in ore at the surface outcrop of the veins, they would require that at least that amount of erosion has occurred since ore deposition.

Far more important for exploration purposes would be any data suggesting fluid flow directions. Unfortunately the fluid inclusion data now available are far too limited, both in quantity and paragenetic control, to recognize temperature gradients, if they exist. The very coarse texture of the ore (except some quartz), and the relatively small range of Tm values within any given crystal, suggest that deposition was slow, at relatively constant temperature, and so temperature gradients might be difficult to recognize even with detailed inclusion study. The very large range in inclusion salinities, however, indicates that the ore-forming fluids for the various stages must have had some very significant differences in origin.

It is possible that isotopic studies on specific inclusion fluids, of known Tm and salinity, may provide some constraints on the origin and history of these various fluids that could be of value for exploration.

**Conclusions**

(1) With few exceptions, temperatures of homogenization (Tm) for 400 inclusions, from all four stages, range from 120 to 200°C (av. c. 160°C). Although the data for each individual stage extend over approximately the same range, the average Tm decreases c. 30°C from stage 0 (earliest) to stage 3 (latest). In both stages 1 and 2, inclusions in quartz show average Tm c. 35°C higher than those in the closely associated fluorite from the same stage, and Tm data on sphalerite are intermediate between the equivalent quartz and fluorite.

(2) Temperatures of last melting of ice (Tm(ice)) range from 0 to −10.1°C (av. c. −5°C), corresponding to salinities (wt% equiv. NaCl) of 0 to 14.1 (av. c. 8%). Stages 0 and 1 show Tm of −7 to −10°C and average −8.4 and −8.1°C (12.2 and 11.8%), respectively; stage 2 ranges mostly between 0 and −7°C (av. −4.0°C; 6.4%); and stage 3 values are all between 0 and −4°C (av. −2.1°C; 3.5%). In both stages 2 and 3, a weak correlation of low salinity with low Tm is evident.

(3) Temperatures of apparent eutectic melting (Tm) on 413 runs on inclusions range from −24 to −52°C (av. c. −40°C). Several observational problems make these temperature estimates inaccurate at best, and the true values are almost certainly some degrees colder. The lower temperatures found require the presence of significant calcium in the fluids.

(4) No liquid CO2 was found, but CO2 is present in most inclusions at sufficient concentrations to yield tens of atmospheres pressure at room temperature.

(5) Our Tm values are in general agreement with the data of Wang et al. (1981) but are much lower than the six Tm estimates reported by Ding et al. (1986) from the same vein (170, 245, 285, 300, 305 and 345°C), and their 14 sulphur-isotope data points (221–344°C; av. 277°C).

(6) We do not know why there are major differences between our Tm data and these published data of Ding and coworkers, but the lack of visible wall rock alteration is more in keeping with our (lower) temperatures.

(7) Most of our Tm(ice) values correspond to lower salinities than the five salinity data reported by Ding et al. (1986; 9.0, 12.0, 14.9, 16.5 and 17.7 wt% equiv. NaCl).

(8) Our Tm data overlap somewhat but average appreciably higher, and our salinity data are all much lower, than are normally found in Mississippi Valley-type deposits. We believe the deposit should be classed as a low-temperature epithermal deposit, possibly formed by meteoric water circulating deeply into a granitic terrain.

(9) If the relative paragenetic assignments for our samples are correct, some of the large and enigmatic intra- and inter-stage Tm differences found raise the question of how extensive was the natural stretching or decrystallization of earlier, lower Tm inclusions by later, hotter fluids. Obviously, a more detailed sampling of the entire paragenetic sequence will be needed to clarify these problems.

(10) This study provides good examples of a variety of problems that are encountered in the application of fluid inclusion data to mineral deposit research in general.

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**References**


