FLUID INCLUSION AND RELATED STUDIES OF SPHALERITE
FROM THE LAISVALL SANDSTONE LEAD–ZINC DEPOSIT, SWEDEN

by

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(7 figures)

RESUME.— Paul BARTHOLOME nous avait conseillé d’étudier les inclusions fluides du gisement de plomb et zinc dans les grès de Laisvall. Il nous aida à installer le premier laboratoire d’étude des inclusions fluides en Suède.

En même temps que se développait l’étude des inclusions fluides par microthermométrie, notre technique d’étude microscopique s’améliorait considérablement. Utilisant des lames minces polies sur les deux faces, nous avons pu montrer que la sphalérite de Laisvall présente une coloration zonaire et que trois types au moins de ce minéral sont présents. Ces résultats suggèrent une croissance en espace libre de la sphalérite dans les grès du Précambrien tardif et de l’Eocambrien de Laisvall, ce qui est confirmé par la découverte de micro-cavités ouvertes garnies de cristaux.

Ces observations fournissent la première donnée bien établie sur l’origine paragenétique de la minéralisation de Laisvall.

La genèse du gisement comporte la séquence suivante :

a) dépôt précoce de galène, partiellement altérée,
b) les sphalérites I et II, calcite, quartz et la masse de minerai de zinc,
c) galène et sphalérite III, formant la masse de minerai de plomb.

L’étude des inclusions fluides a montré que la sphalérite III, dans le minerai de plomb des grès inférieurs, avait été déposée à la température de 165°C, soit quelque 10°C de plus que la température de dépôt de la sphalérite II dans le minerai de zinc des grès supérieurs. Des cristaux isolés de la sphalérite III des grès inférieurs montrent nettement un zonage d’origine thermale. Cependant, la salinité modale des sphalérites de chacun des trois types est de 24 %/o en équivalent poids de NaCl. La basse température de congélation des inclusions de la sphalérite donne à penser que la saumure contenait un composé de calcium et cela concorde avec les indications fournies par le point de fusion.

En conclusion, la sphalérite de Laisvall a été déposée en espace libre entre des grains de sable par une saumure contenant Na-Ca-Cl à 155–165°C.

ABSTRACT.— Paul BARTHOLOME suggested that we investigated fluid inclusions in the sandstone lead–zinc deposit at Laisvall. He encouraged the initial establishment of the first fluid inclusion laboratory in Sweden.

Concomitant with the development of fluid inclusion microthermomometry, our microscopic techniques improved considerably. Using double-sided polished thin sections we have been able to show that the Laisvall sphalerite is color-zoned and that at least three types occur. These results suggested open space growth of sphalerite in the Laisvall late Precambrian – early Cambrian sandstones, which was confirmed by the discovery of crystal-lined open microvugs. These observations provided the first well-established paragenetic data for the Laisvall mineralization. The sequence of deposition involves (1) early deposition of galena, partially leached; (2) sphalerites I and II, calcite, quartz and the bulk of the Zn ore deposited; (3) galena and sphalerite III, forming the bulk of the Pb ore.

Fluid inclusion measurements show that sphalerite III in the lower sandstone Pb ore was precipitated at 165°C, some 10°C higher than sphalerite II in the upper sandstone Zn ore. Individual crystals of lower sandstone sphalerite III display distinct thermal zoning. However, the modal salinity of all sphalerite types is 24 equivalent weight percent NaCl. The low freezing point of the sphalerite inclusions suggests a calcium component in the brine and this is consistent with the melting point data.

It is concluded that the Laisvall sphalerite was precipitated in open spaces between sandgrains from an Na-Ca-Cl brine at 155–165°C.

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INTRODUCTION

During a visit to Liège in 1972, Paul BARTHOLOME showed D.T.R. a monstrous machine in a hardboard cabinet. It turned out to be a home-made apparatus for studying the melting and homogenization temperatures of fluid inclusions. Paul was using this apparatus to examine fluid inclusions in ores from Zaire and we discussed using the technique on the Laisvall sandstone Pb–Zn deposit.

The problem in Laisvall centered around the small crystal size of the minerals filling the sandstone interstices. ROEDDER had previously examined larger crystals associated with "late veins" or joints at Laisvall (ROEDDER, 1968; LARSON et al., 1973), but it was not certain that these materials were directly related to the bulk of the mineralization. However, Paul persuaded D.T.R. to attempt the technique and forwarded us blueprints of the machine, which he himself had received from France.

It took some time to get organized in Sweden, but by 1976 we had received funding for the purchase of the new, ready-made, Chaix-Meca apparatus in conjunction with a project on fluid inclusions in the Laisvall deposit. Sten LINDBLOM was trained in the technique, a laboratory was organized and the first fluid inclusion laboratory in Sweden became a reality.

**Figure 1.** Distribution of major sandstone Pb–Zn mineralizations at the border of the Caledonides. The Nasafjäll deposit is associated with a Precambrian window in the Caledonides (from Rickard 1979).
The following paper presents a series of results from the fluid inclusion project from Laisvall. These results are concerned with the conditions of formation of one of the ore minerals, sphalerite. However, the fluid inclusion studies did not only lead to information about the inclusions themselves but also to a new approach to ore microscopy. These results are also described here.

GEOLOGY OF THE LAISVALL DEPOSIT

The geology of the Laisvall deposit has recently been described in detail by RICKARD et al., (1979). Here only a brief account will be given.

The Laisvall deposit is one of a series of deposits at the eastern border of the Caledonian mountains in Sweden (fig. 1). The ore is contained in two thin sandstone horizons (the upper and lower sandstone ores) in a late Precambrian - Cambrian autochthonous sedimentary sequence (the Laisvall group), which lies unconformably on a Proterozoic crystalline basement (fig. 2). The autochthonous sediments are overlain by nappe slices related to the Caledonian orogeny (fig. 3). The sandstones were deposited on a stable platform at the margin of the proto-Atlantic.

An illite crystallinity study revealed that the sediments of the Laisvall group have been very little

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**Figure 2.** Stratigraphy in the Laisvall area (from Rickard et al. 1979. Reproduced by permission of the Economic Geology Publishing Company).
affected by the nappe translation. The illites are characteristic of a late diagenetic environment and the effects of overthrusting are limited to about 20 m from the sole of the lowermost thrust. This is in part due to the lubricative effect of the black, carbonaceous Alum shales, which formed the thrust sole, and in part to the fact that Laisvall is situated towards the eastern limit of nappe translation in Scandinavia.

The illite crystallinity data confirm other microscopic and geologic observations which indicate that the ore minerals have not been recrystallized or remobilized during the Caledonian tectonic activity. The minerals of the ore association, which includes galena, sphalerite, calcite, barite and fluorite occur infilling the interstices between quartz grains in the sandstone. The deposit tends to be zoned macroscopically and the minerals of the ore association tend to be mutually exclusive even on a microscopic scale. The upper sandstone ore is primarily a zinc ore and the lower sandstone ore is a lead ore with little zinc.

METHODS

The methods used are broadly those described by ROEDDER (1967, 1976) and have been described in detail by LINDBLOM (1977) and LINDBLOM & RICKARD (1978a, b).

Basically, observation of fluid inclusions in relatively highly refractive minerals, such as sphalerite, requires the preparation of rather thick thin sections with precisely parallel faces. The thickness of the sections depends on the translucency of the minerals – obviously, the thicker the section the greater the chance of an
inclusion. The sphalerite sections we used were about 130 µm thick and polished on both faces.

A Chaix-Meca microthermometry apparatus was employed. The melting temperatures, \( T_f \), of the inclusions were obtained by observing the temperature at which inclusions, frozen by passing dried, CO2-free, liquid N\(_2\) coded, compressed air through the microscope stage, finished to melt. The precision is about ±0.1°C. The homogenization temperature, \( T_h \), is the temperature at which a vapor bubble in a two-phase, gas-liquid inclusion disappears or homogenizes with the aqueous phase. Heating is obtained by means of a heating element within the stage and the precision is within ±1°C.

Total reflection at the inclusion-mineral interface produces dark borders around the inclusions in collimated light. This is a severe problem in measuring homogenization temperatures in small inclusions, such as at Laisvall. This was overcome by the use of fibre-optics illumination in addition to the normal illumination of a modified Leitz Laborlux microscope.

**MICROSCOPIC RESULTS**

In hand specimens, sphalerites at Laisvall tend to be lemon-yellow to various shades of yellow-brown and wine-red. In conventional thin section, these color variations are not observed. However, the thicker, double-sided specimens used for fluid inclusion studies reveal a range of colors in sphalerite. Two main types occur: beige and various shades of yellow-orange to colorless.

**UPPER SANDSTONE SPHALERITE**

The sphalerite in the upper sandstone is commonly zoned. The zoning appears to be mainly growth zoning, but sectional color zoning has also been observed (fig. 4a, b).

The beige sphalerite shows color zoning in dark and lighter shades as well as inclusion-rich zones. The center of the beige variety may display very fine, center-symmetric zoning. Very sharp brown-orange zoning, centered on an opaque (pyrite ?) nucleus, has been observed (fig. 4b).

The yellow - colorless variety is more abundant. The zoning pattern often parallels the crystallographic contact with the beige variety (fig. 4a).

The cause of the color variation is unknown. Microprobe analyses of zoned, upper sandstone sphalerite show a relatively constant iron content of 0.32 to 0.34 wt. % across yellow-orange, colorless and beige zones. All other elements were present in concentrations below the limit for accurate microprobe analyses, although Cu, Co, Ni and Cd were detected.

**LOWER SANDSTONE SPHALERITE**

Sphalerite is relatively rare in the lower sandstone ore, where the Pb:Zn ratio is 18:1.

However, where found, the lower sandstone sphalerite shows hand specimen color variations from yellow to wine-red. No color zoning has been observed in the lower sandstone sphalerite and the polished thin section colors varied from lighter to darker yellow. Fairly homogeneous yellow-white sphalerite showed variations in iron content from 0.34 to 0.51 wt. % Fe.

**MICROVUGS**

The observation of crystallographic zoning in upper sandstone sphalerite suggested open space growth and led us to investigate if open vugs still occurred at Laisvall. The technique involved examination of cores with a stereoscopic microscope.

Large vugs were not found. However, smaller spaces were observed in coarser sandstone in the upper orebody. These “microvugs” or “macropores”, usually 1 - 5 mm in size, are commonly coated with euhedral crystals of sphalerite, galena, calcite and quartz (fig. 4c). There appears to be phases of sphalerite that both precede and supercede galena. Some of the galena seems to be etched.

Wall-growth was also observed in veins in the upper sandstone. One vein showed the following paragenesis: (1) euhedral quartz, (2) euhedral galena, (3) sphalerite growing from a crystal face of the galena. Of interest was the observation of tubular fluid inclusions growing from the galena crystal face into the sphalerite (fig. 4e).

**FLUID INCLUSION RESULTS**

**UPPER SANDSTONE**

The morphology of inclusions from the upper sandstone sphalerite is illustrated in fig. 5a. Three types of inclusions are observed:

Type 1: Approximately equidimensional inclusions, often negative crystals, 3-11 µm in size.

Type 2: Large, flat inclusions, up to 30 µm in size,
a) Yellow and colorless zones of sphalerite III, paralleling crystal faces of beige sphalerite II from the upper sandstone. The hiatus between sphalerite II and III is clearly marked as a dark line. Sphalerite II is zoned in dark and light browns.

b) Center-symmetric growth and sector zoning in sphalerite I from the upper sandstone. The crystal is nucleated on a pyrite crystal.

c) Microvug in upper sandstone with sphalerite III (sp III), galena (ga) growing on sphalerite II (sp II) and calcite. Composite drawing.

d) Typical mineralization in Laisvall sandstones; the minerals of the ore association (in this case mainly galena, black) infill interstices between sandgrains.

e) Small vein in upper sandstone showing tubular inclusions in sphalerite III (sp III) growing from a galena crystal (ga) surface with detrital (qz det) and secondary (qz sec) quartz.

f) Thermal zoning in sphalerite III from lower sandstone. No color zoning is observed here. The black patches are galena inclusions.
divided into rare inclusions with $T_H$ between 140 and 170°C (type 2:1) and those with $T_H > 200°C$, often with necking down structures (type 2:2).

**Type 3**: dark inclusions with irregular shapes, 3–50 μm in size, possibly containing hydrocarbons and occasionally with bituminous daughter minerals.

In addition, a large number of minute (<3 μm) inclusions occur following color zoning geometry or occurring as irregular strings, cross-cutting the zoning. The two-phase type 1 and type 2:1 inclusions include a gas phase which makes up between 1 and 5 o/o of the total volume.

Melting temperatures ($T_F$) show a variation between -18.6 and -27.8°C, with a modal value around

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**Figure 5**

a) Inclusion morphologies in upper sandstone sphalerite. Type 1 is identified as primary, type 2 as secondary and type 3 probably contains hydrocarbons.

b) Inclusion morphologies in lower sandstone sphalerite. Types as per (a).


-220°C (fig. 6a). A weaker mode around -270°C was noted, apparently coincident with type 2:2 inclusions. The freezing temperatures of the sphalerites are low, between -60° and -90°C. Homogenization temperatures (TH) vary between 135.3 and 170.5°C for types 1 and 2:1, with a strong modal value at 155°C (fig. 6b). Type 2:2 inclusions homogenized at more than 220°C, as expected from their form.

Intercrystalline variations in modal homogenization temperatures occurred in the upper sandstone sphalerite but were not marked. The inclusion measurements in the upper sandstone were made on the beige sphalerite variety.

LOWER SANDSTONE

The morphology of inclusions from lower sandstone sphalerite is illustrated in fig. 5b. As in the upper sandstone, three types of inclusions are observed:

Type 1: mostly regularly shaped inclusions, 3-15 μm in size, two-phase with bubbles making up 2-10 % of the total volume.

Type 2: irregular to regular, flat inclusions (sometimes more tubular), 10-50 μm in size; necking down observed.

Type 3: irregular to regular shape, 3-50 μm in diameter; one-phase, dark inclusions, possibly containing hydrocarbons.

The melting temperatures (TF) range from -27.4 to -16.5°C with a clear mode at -220°C (fig. 7a). A weaker mode at -270°C was found in one sample. However, vigorous movement of bubble and ice was observed around -270°C for inclusions with a melting temperature around -220°C. This may imply that the minor -270°C mode in the lower and upper sandstone sphalerites is artefactual. The freezing temperature of the lower sandstone sphalerite is -70 to -90°C.

The homogenization temperature (TH) varies considerably between crystals. Samples with modal TH values around 100°C and 170°C have been observed. For the bulk material the modal value is 1650°C, about 10°C higher than the upper sandstone sphalerite (fig. 7b).

Measurements in the lower sandstone were made on yellow - colorless sphalerite inclusions. Even though these crystals are not color-zoned, they commonly display marked zoning of TH values, and TH tends to increase from the center to the crystal boundaries (fig. 4f).

DISCUSSION

IMPLICATIONS OF MICROSCOPIC OBSERVATIONS

The microscopic observations demonstrate that the Laisvall sphalerite grew in open spaces. The preservation of growth zoning and the development of euhedral crystals are consistent with the discovery of pores open at the present day and lined with crystals. These crystalline pores are microscopic equivalents of the crystal vugs and cores of deposits in, for example, the Viburnum Trend, Missouri.

Sphalerite at Laisvall may be divided into three types on the basis of color:

Sphalerite I: finely banded sphalerite with center-symmetric growth zoning and, commonly, a nucleus;

Sphalerite II: beige sphalerite;

Sphalerite III: yellow-colorless sphalerite.

Sphalerite I contains abundant minute inclusions, often zonally arranged, but unfortunately too small (<3 μm) to be accurately measured by present day techniques. The center symmetric zoning is commonly fine and well-marked and often centered on a crystal of pyrite or galena.

Sphalerite II is beige in color and displays less definite zoning in darker and lighter shades of brown. It apparently followed growth of sphalerite I with very little hiatus. Sphalerite II inclusions have been measured in the upper sandstone ore. The observed temperatures and modes are TH = 135.3 - 170.5°C (155°C); TF = -18.6 - -27.8°C (-230°C).

Sphalerite III is zoned in shades ranging from colorless to yellow-orange. Inclusions are not as common here, but darker colored varieties contain more and larger inclusions than the colorless forms. Sphalerite III inclusions have been measured in the lower sandstone. They show considerable intercrystalline and intracrystalline variations in TH. The intercrystalline variations appear to constitute a form of thermal zoning from initially higher to finally lower temperatures during the growth of the crystals. The observed temperatures and modes are: TH = 125.4 - 183.2°C (165°C); TF = -16.5 - -27.4°C (-220°C).

The modal value of the sphalerite III is 10°C higher than the sphalerite II variety. There appears to be a marked hiatus between sphalerites II and III. Sphalerite III also contains abundant galena inclusions, which have not been observed in sphalerite I and II.
a) Melting temperature ($T_F$) histogram for upper sandstone sphalerite. The modal temperature is equivalent to 24 weight percent NaCl (from Lindblom and Rickard 1978. Reproduced by permission of GFF).

b) Homogenization temperature ($T_H$) histogram for upper sandstone sphalerite.

a) Melting temperature histogram for lower sandstone sphalerite. The modal temperature is the same as for the upper sandstone sphalerite. Note that the minor $-27^\circ$C mode is probably artefactual.

b) Homogenization temperature histogram for lower sandstone sphalerite. The modal value ($165^\circ$C) is $10^\circ$C higher than the upper sandstone sphalerite.
INFORMATION FROM FLUID INCLUSIONS

Many criteria have been suggested for determining the origin of fluid inclusions (ROEDDER, 1976), but these are often of dubious validity. In Laisvall, the small sphalerite crystals are usually anhedral and the origin of the fluid inclusions difficult to ascertain. However:

1) randomly distributed fluid inclusions have similar $T_H$ values in both upper and lower sandstone sphalerites;

2) parallel planes of inclusions reflect growth planes and not irregular, healed fractures.

In general, the illite crystallinity evidence, combined with the lack of annealing textures in the sphalerite, the preservation of compositional zoning, as well as the preservation of thermal zoning in fluid inclusions, suggest strongly that the inclusions represent the primary depositional environment of the Laisvall sphalerite. LINDBLOM & RICKARD (1978b) identified type 1 inclusions as primary, type 2 as secondary and pseudosecondary and type 3 as primary. The later data do not contradict this classification.

The fluid inclusion data thus show that the Laisvall ore was formed at temperatures around 155-165°C from a concentrated brine. The freezing point depression from $T_F$ measurements indicates that the solution contained about 24 equivalent weight percent NaCl, using POTTER et al.'s (1978) formulation. This is almost 1 o/o more than the eutectic point in the NaCl-H$_2$O system and suggests the presence of other components. This suggestion is supported by the very low freezing point of the Laisvall inclusions which, according to ROEDDER (pers. comm.), probably indicates the presence of calcium.

Different stages of sphalerite mineralization are characterized by different inclusion homogenization temperatures and similar melting temperatures. This implies deposition of sphalerite from the same type of solution at different temperatures. However, the range of temperature variations during the development of sphalerite III crystals (c. 50°C) equals the range observed through the whole deposit in apparently primary inclusions. This suggests a long period of growth from a cooling solution for sphalerite III. Variations between crystals suggest further that crystals were formed at various times during the cooling period. Similar variations within and between crystals have been previously observed for calcite at Laisvall (LINDBLOM & RICKARD, 1978a). It is interesting to note that, in the lower sandstone, considerable thermal variations are observed in the sphalerite which are not coincident with any color variations. Fluid inclusion measurements are probably far more sensitive to such variations than conventional microscopic techniques.

The observation of inclusions which appear to contain hydrocarbons in all sphalerite types is consistent with the analytical detection of these compounds in Laisvall sphalerite by RICKARD et al. (1975).

CONCLUSIONS

Fluid inclusion evidence indicates that the Laisvall Pb-Zn deposit was formed at around 155 - 165°C from a concentrated Na-Ca-Cl brine. Mineralization took place in several stages and the detailed paragenesis is not available from the present observations. The data from these studies suggest the following sequence of events:

1. Early deposition of galena

This galena is observed in the microvugs, apparently partially leached.

2. Deposition of sphalerites I and II, calcite and quartz

No major hiatus seems to have occurred between the precipitation of sphalerites I and II. These are galena-free and constitute the bulk of the upper sandstone zinc ore. Calcite has been observed with the sphalerites in upper sandstone microvugs. Microvug and vein observations indicate a stage of quartz mineralization coincident with and superceding the calcite.

3. Deposition of galena and sphalerite III

A combination of data from microvugs and veins together with the observations of galena inclusions within sphalerite III place the formation of the bulk of the lower sandstone lead ore at this stage.

Sphalerite formation took place in open pores between the sandgrains. Unfortunately, this does not put a time constraint on ore formation since, as pointed out by RICKARD et al. (1979), sandstones can retain considerable porosities for geological lengths of time. The multitude of small inclusions and the well-developed growth zoning in the early sphalerites suggest growth from a slowly moving solution at varying rates. The color zoning suggests occasional possible seasonal effects. However, the chemical cause of the color variation is not known at present. It is apparent that it is the result of variations in one or more trace elements (i.e. elements with concentrations less than 0.1 o/o).
The absence of marked minor element variations, such as iron, suggests a lack of direct connections between the mineralization environment and the surface.

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BIBLIOGRAPHY


