

BARITE WHICH DECREPITATES AT ROOM TEMPERATURES

BY

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The determination of temperature of mineral formation by the study of liquid inclusions and decrepitation of minerals has in recent times been paid much interest. Summaries of this subject are presented by C. V. CORRENS in his paper «Flüssigkeitseinschlüsse mit Gasblasen als geologische Thermometer», (CORRENS 1953) and by Earl Ingerson in his paper «Geologic Thermometry», (INGERSON 1955). It is commonly assumed that by heating the decrepitation takes place (presumably due to a sharp rise in pressure) nearly (?) at the same temperature at which the inclusions become filled with liquid (the gas bubbles disappear). In most of the cases described a real decrepitation first starts above 100° C.

A few years ago some white material with most extraordinary properties was given to the author for identification by cand. real. E. PHARO. When placed on the palm of the hand it decrepitates and tabular fragments 1—10 mm in cross section are thrown out to a distance of one meter or so. Each fragment will normally «detonate» again, when brought back to the hand. The decrepitation is accelerated when the material is slightly heated.

Refractive indices, cleavage, hardness, spectrographic determination etc. show that the white material is barite with insignificant amounts of strontium. Spec. grav. 4.33.

The mineral was found in 1949 at the farm Narum in Kolbu, Mjösen lake district, S. E. Norway. During the construction of a building a ditch, 1,5 meter deep, was cut through gravel down to the bedrock. It is uncertain whether the specimen (originally very much like the one shown in fig. 1) came from the bedrock or from the loose deposits of local origin. Much of the barite had already been



Fig. 1. 1/4 of a limestone lens, the central part of which is occupied by barite. A fossil (*Lituites* sp.) on the upper surface. Cephalopod Shale, probably from the Mjøsen lake district. Greatest diameter 16 cm.

spent for fun and therefore lost before Mr. Pharo got hold of it. He also tried to find more, but without success, because the house at that time was completed and everything well hidden. Small amounts of material have been used for the investigations described below and only 2—3 grams remain as reference material.

The bedrock at Narum is the black Cephalopod Shale (4aa₄) of the Middle Ordovician *Ogygiocaris* Series. The shale, which is of considerable thickness, is characterized by round limestone lenses with irregular protuberances of barite on their surfaces. White or grey barite is also sometimes found in the central part of the lenses as shown in fig. 1, (also from the Cephalopod Shale of the Mjøsen lake district). From the description given by the people living at Narum the specimen fig. 1 resembles quite closely the one they found. — It is believed that the sediment was formed in a partly land-locked sea with insufficiently aerated bottom waters (HOLTEDAHL

1909, STÖRMER 1953). From the underlying Ogygiocaris Shale (4aa₃) barite has also been described, mostly occurring as crystals on the surface of limestone lenses. As the barite seems to be limited to these and certain other shale-beds in the Cambro-Silurian sequence of Norway and Sweden it can be assumed that barium was present in the original sediment and by substitution during the consolidation of the sediment, accumulated in the limestone lenses. Holtedahl, however, maintains a secondary origin for the barite viz. that the crystals were formed by more far-travelling circulating solutions in Silurian/Devonian (pre-Caledonian folding) time.

The formation of simple crystals and concretionary nodules and lenses of barite in Swedish black shales and clayey limestone has been treated by A. Hadding (HADDING 1939), who gives the following statement: «Barytes was not formed by secondary influence. Hydrothermal, pneumatolytic and other similar processes must be entirely left out of account, as no traces whatever of such processes have been visible. The occurrence is practically simultaneous over large areas, a fact which induces us to look for regionally acting forces and conditions as barytes-forming.» «The material for the formation of barytes was confined to certain mud-beds, and no transport from one stratum to another can be shown.» «Pyroclastic material or mineral formation caused by volcanic exhalations has not been established in the barytesbearing series of strata».

The following data on barite from the Dana's System of Mineralogy Vol. II (7th ed. 1951) can be of interest for comparison with the properties of the specimen here concerned. «Barite, orthorhombic, dipyramidal» «Cleavage 001 perfect, 210 less perfect. 010 usually imperfect to indistinct but sometimes equal to 210». «Occasionally fetid when rubbed. (NH₄) has been reported in barite and liquid-filled cavities affording CO₂ or H₂S are frequently present.»

Because the material so easily breaks up on the slightest pressure or temperature-elevation ordinary thin sections could not be prepared. Naturally split thin leaves (down to 0.02 mm) have therefore been examined with and without immersion liquid and in transmitted and reflected light.

The mineral fragments are nearly always limited by the cleavage plane 001 (fig. 2), less perfect are 210 and $\bar{2}10$. No cleavage plane is developed in the 010 direction.

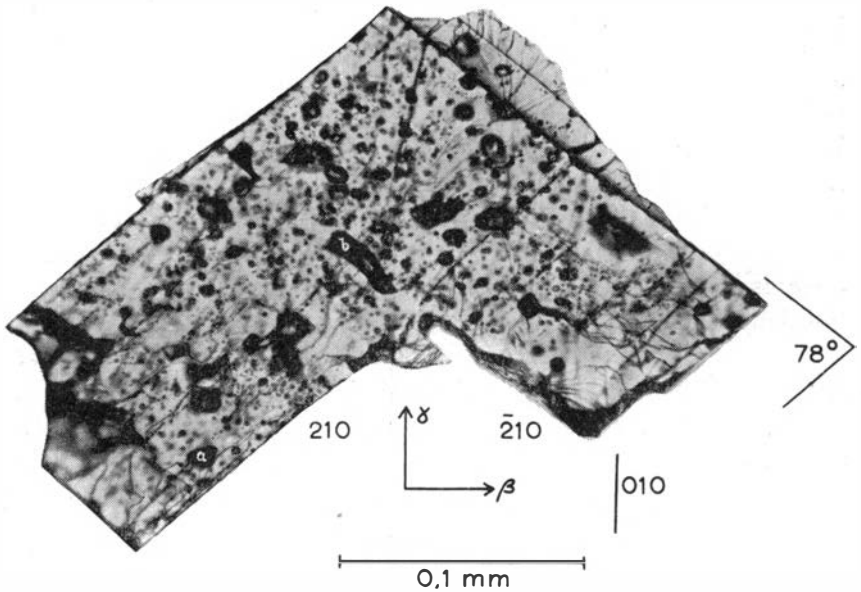


Fig. 2. Barite with inclusions, Narum, Kolbu, Mjøsen lake district. Transmitted light, no immersion liquid. Inclusions marked «a» and «b» are refound in fig. 3.

The size of the inclusions varies from 0.04 mm down to nearly nothing. They can according to their size be classified in two groups grading into each other. One group with irregularly formed and distributed inclusions 0.04—0.01 mm, and the other group with inclusions of a more regular spherical shape and of average size ~ 0.002 mm, arranged in planes corresponding to crystallographical directions. One set of planes marked by a great abundance of small inclusions is parallel to 210 and has a spacing ~ 0.03 mm, fig. 3. This distance and some greater ones are typical for most fragments. Another pronounced set of planes is parallel to 001 . The direction 010 is not developed as a cleavage plane but can be traced as shadows probably due to a plane of inclusions, fig. 2. The inclusions are believed to be primary.

When examined in transmitted light the cavities (dark patches in fig. 2—3) appear to be single-phased containing exclusively gas or liquid. However, under reflected light some gas bubbles have been observed, which suggest that the cavities are at the stage of

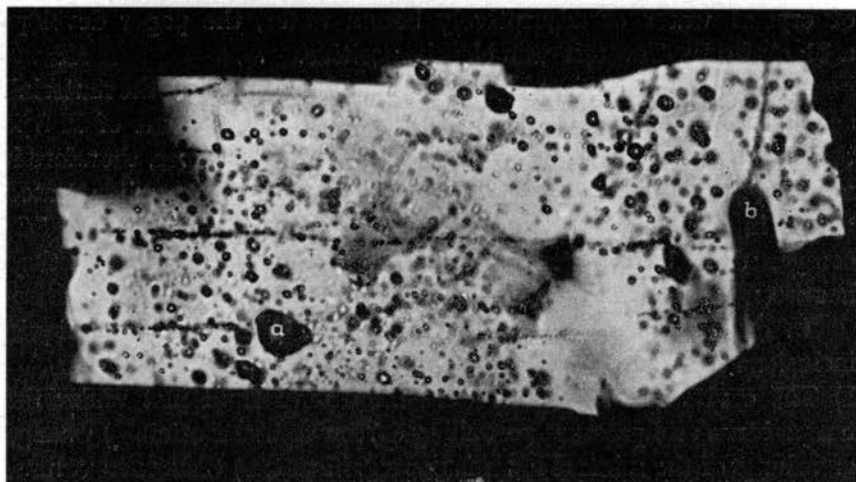


Fig. 3. The lower left part of fig. 2. Transmitted light, immersion liquid, \times nic.

complete filling or very near to it. Heating stage and apparatus for the study of decrepitation have not been available, and the amount of material was insufficient for a complete chemical analysis.

When heated to 30—40° C in distilled water, the decrepitation is vigorous and at each click a gas bubble rises rapidly. The size of each bubble is approximately 10 times as great as any single cavity. When the decrepitation takes place in BaOH-solution this becomes faintly white and cloudy which indicates that CO₂ is present. A smell resembling that of H₂S is noticed when the material is rubbed or pulverised. This is not the case when the material is heated and decrepitates. Either the smell is not that of H₂S or the amount of H₂S formed by heating is too small to register. An attempt to prove the presence of H₂S by lead acetate paper was negative both when the material was rubbed and when it was heated.

A method proposed by Feigl (FEIGL 1954) was tried for qualitative determination of water: «About 0.2—0.3 grams of well dried potassium thiocyanate is melted in a micro test tube. A small amount of the sample is added to the still colourless melt and the heating is continued until the melt turns blue. Filter paper moistened with lead acetate solution is held at the mouth of the test tube. In the presence

of crystal water or adsorptively bound water, the paper develops a black fleck». The test was clearly positive.

It can be objected that H_2S already may be present in the material, as mentioned above. In that case, however, the content of H_2S is too small to give a black spot on the lead acetate paper, therefore it most probably must be water present in the inclusions that when heated enters into the reaction $KCNS + H_2O \rightarrow KCNO + H_2S$. The SO_4 component of barite does not disturb the reaction, and this method has been used for distinguishing gypsum from anhydrite.

In determining temperatures of mineral formation from liquid inclusions it must be assumed (INGERSON 1955) that:

- 1) The cavities of inclusions were filled with fluid just under the temperature and pressure prevailing during crystallization.
- 2) Change of volume of the mineral itself is not significant.
- 3) Change in volume and concentration brought about by deposition of material during cooling are such as not to affect the results.
- 4) Primary and secondary liquid inclusions can be distinguished under the microscope.
- 5) There has been no leakage from or into the inclusions. The decrepitation method has additional difficulties, one of them is that the lag between temperature of filling of inclusions and beginning of decrepitation is highly variable from one mineral to another.

Probably the decrepitation originally started at a lower temperature when the mineral first was found than it does at present. The material has been stored in rooms where the temperature has been 25—30° C. But for the following tentative considerations the temperature of decrepitation is set at 25° C. As a first approximation it is assumed that the cavities contain only pure water and that all the assumptions mentioned above are fulfilled. In that case the PT conditions prevailing at the time of mineral formation can be read from fig. 4. The line A is drawn as in the diagram published by Kennedy, (KENNEDY 1950), and concerns a mineral in which the cavities become filled at 100° C. If for instance the mineral was formed at a pressure corresponding to 2 km rock cover, the temperature of formation was 130° C. The line B for barite here considered starting at 25° C is drawn parallel to A (and due to the nearly constant compressibility of water in the interval 100—200° C, also parallel to lines within this interval, shown in Kennedy's diagram). The line C shows

the geothermal gradient. In Permian time the line C has been steeper due to the large scale igneous activity. (The locality is situated less than 10 km from a great body of syenite). The point of intersection of line B and line C indicated in the diagram by «a» gives therefore the highest possible P and T conditions under which the Narum could barite be formed. Point «a» corresponds to 45° C and 1250 meters rock cover. From a geological point of view a rough estimate of the thickness of rock which at any time has covered the lens with barite is ~ 1000 meters.

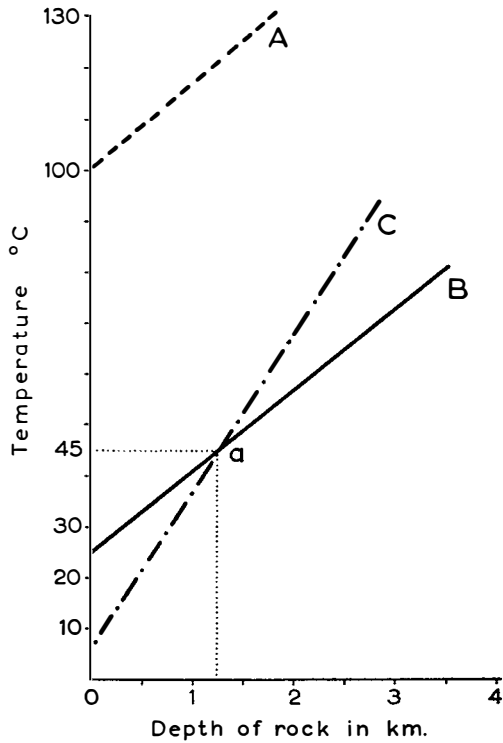


Fig. 4. Explanation in the text.

The presence of small amounts of certain gases such as CO₂ and H₂S with low critical temperatures will necessitate corrections giving a slightly higher temperature of formation (a steeper B line), whereas the presence of dissolved salts such as alkali halides will give lower temperatures.

The specimen shown in fig. 1 has a decrepitation temperature of about 80° C. This may indicate other PT conditions at the place where this barite was formed. The exact location is unknown as its label reads: «probably Mjösen lake district, probably Cephalopod shale».

Another interpretation of this difference in temperature of decrepitation of the Narum material and the lens, fig. 1, can be the following: To make the barite crack along 001, two 001 layers must be removed a certain distance δ . In order to reach this critical value of δ the temperature of a cavity must be raised a certain amount ΔT above

the filling temperature of that cavity. The bigger the cavity, the smaller is ΔT . When the Narum barite therefore contains great and small cavities and the barite of the lens contains only small cavities the latter will start its decrepitation at a higher temperature than the Narum barite even if they were formed under the same conditions.

Although so much seems uncertain about the Narum barite (the exact composition of the material filling the cavities is unknown, the history of the mineral from the time it was found could not be sufficiently controlled, etc.) it seems probable that this barite was formed at very low temperature.

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