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Mineralogical Aspects of Fluid Migration in the Salt Block II Experiment

Steven J. Lambert

Sandia National Laboratories

ABSTRACT

A block of evaporite rock containing the mineral assemblage halite (88%) - polyhalite (8%) - sylvite (4%) was machined into a cylinder one meter in diameter and one meter high, and was fitted with an axial heater, thermocouples and an off-gas collection system. After about 100 days of heating, identification of mineral efflorescences at the heater hole (carnallite and bischofite) showed that a significant portion of the 111 grams of water recovered (out of around 8500 grams available in the rock) migrated as a liquid, not as a vapor. A microscopic examination of rock slices from within 15 cm of the heater hole (where the temperature was 100 to 200°C, and the gradient was 3 to 15°C/cm) revealed that (1) fluid inclusions had migrated, but rarely across grain boundaries, (2) fluid inclusions had not been mobilized at distances greater than about 15 cm from the heater hole, and (3) intergranular liquid had been conspicuously mobilized within 15 cm of the heater hole.

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Introduction

In 1976, several large blocks of evaporite rock (about 1 cubic meter each) were quarried from a drift in the workings of the Mississippi Chemical Corporation potash mine which is about 18 miles east of Carlsbad, New Mexico. The blocks came from a portion of the 7th ore zone of the McNutt member of the Salado Formation (Permian) that is locally poor in potash (i.e., sylvite-KCl) content. These blocks were obtained in order to provide evaporite rock in which to conduct experiments designed to simulate some thermal aspects of heat-generating radioactive waste.

Two of the blocks have been machined to a cylindrical shape, fitted with an axial heater hole, instrumentation holes, various measuring devices, and an exterior metallic sheath, and heated according to a preplanned program. Experiments involving Salt Block I (Duffey, 1979) were designed to measure primarily the stress state of heated evaporite rock, and secondarily to determine the susceptibility of coupons of various metals to corrosion in the environment afforded by the evaporite block. Salt Block II (Figure 1), the subject of discussion here, was equipped with a hermetically-sealed sheath, a water-vapor collection system, and temperature and heat-flux guages. Thus, an opportunity was provided to observe the rate of devolatilization of the evaporite rock in response to heating by the axial element. Out of an evaporite mass of about 1700 kg, around 8.5 kg of which was water in various occurrences (estimated on the basis of data of Hohlfelder, 1979; 1980), 111 grams of water-vapor condensate was recovered during the four month experiment. The maximum temperature experienced near the heater was around 200°C, with a maximum gradient of around 15°C/cm.

Design, fabrication and history of the latest experiment are described in separate discussions (Hohlfelder, 1980). This work will describe some surficial and interior changes in mineralogy and their relevance to the understanding of the process and consequence of fluid migration in heated evaporites, particularly with respect to the Waste Isolation Pilot Plant.

One of the most readily observable changes in evaporites during heating is loss in mass resulting from escape of water from fluid inclusions, intergranular fluid, or hydrous minerals (Powers et al., 1978). Hohlfelder and Hadley (1979) have discussed the history of this devolatilization in one-kilogram samples. This report will discuss the nature of efflorescences and internal changes which appeared on the surfaces of machined evaporites after being heated, both for one-kilogram samples and for Salt Block II, a 1700-kilogram sample. The source and nature of the water that is released from heated evaporites has not been determined, nor have the mechanisms which govern fluid migration in heated evaporites been uniquely identified. Interpretations of phenomena described herein will emphasize the definition of the relative importance of various hypothesized mechanisms.

Primary Evaporite Mineralogy

Since evaporites are stratified chemical precipitates which in the northern Delaware Basin have been moderately recrystallized, significant mineralogical variations are commonly observable even in a stratigraphic thickness of a few centimeters. Consequently, a hand sample (a one-kilogram cylinder for example) of Salt Block II cannot be taken to be representative of the whole cubic meter. A visual survey of the exterior surface of the machined Salt Block II indicates about 88% halite, 4% sylvite, and 8% polyhalite. One small (kilogram) cylindrical sample, taken before machining of the large block, consisted of 93% halite and 7% sylvite, another was 90% halite, 6% polyhalite and 4% sylvite. The polyhalite in the second small cylinder was preferentially concentrated in a band about 2 cm wide parallel to the cylindrical axis. Similarly polyhalite occurs in bands (coincident with bedding) normal to the axis of the cylindrically-machined Salt Block II. Sylvite and polyhalite also occur in uniformly-dispersed irregularly-shaped blebs 1/2 to 2 cm across for sylvite and 1 to 3 cm across for polyhalite.

These mineralogies are not representative of storage horizons proposed for waste emplacement in the WIPP bedded evaporites.

Post-heating Development of Surface Efflorescence

Various kinds of machined evaporite samples, large and small, each exhibited post-heating mineralogical changes on the processed surfaces. All samples showed development of mineral encrustations containing water-soluble phases, some of which are not known to occur in the original evaporite. The morphology of the encrustations varied from powdery white patches flush with the original surface (illustrated in Plates 1 and 2), to a bulbous protrusion from the surface (Plate 3). The former type of efflorescence was observed on cylindrical exteriors of all the heated samples, but the latter type formed on the cylindrical interior of the axial heater hole in Salt Block II. All efflorescences were white in color, as opposed to the yellow-orange, red-orange and greenish-gray of the original clays and hematitic halite, polyhalite and sylvite.

Samples of the white efflorescences were hand-scraped from the machined surfaces and their mineralogy determined by x-ray diffraction. Care was taken to exclude primary minerals from the scrapings, but some primary halite was commonly unavoidably included in the scrapings, and appeared in the diffractograms.

Most notable among the efflorescences inside the heater hole (Plate 3) was the occurrence of carnallite ($KMgCl_3 \cdot 6H_2O$). This mineral is not known to occur in the portion of the McNutt potash zone occupied by the Mississippi Chemical Corporation mine. Efflorescences dominantly of carnallite were also sampled from the exterior of small (1-kilogram) cylinders of similar rocksalt heated in an oven to 260°C (Hohlfelder and Hadley, 1979). It is important to note also the occurrence of bischofite ($MgCl_2 \cdot 6H_2O$) in the mineral matter which encrusted the interior of the bellows seal above the heater hole in Salt Block II. Based on freezing stage studies of fluid inclusion studies of Salado halite, the liquid native to the evaporites as fluid inclusions is not a simple solution of NaCl, but must contain at least Mg^{++} and possibly K^+ (Roedder and Belkin, 1979). The only non-aqueous source of magnesium in Salt Block II material is the mineral polyhalite ($Ca_2K_2Mg(SO_4)_4 \cdot 2H_2O$), which dissolves incongruently to give a residue of calcium sulfate. This dissolution, however, liberates magnesium into solution as a sulfate, not as a chloride, and the source for at least the magnesium in the encrustations must be aqueous chloride, probably in the fluid native to the rock.

Efflorescences on the exterior (cooled) surface (Plates 1 and 2) occurred along grain boundaries adjacent to patches of opaque, flesh-colored polyhalite. These encrustations were composed mostly of recrystallized polyhalite. Another phase was tentatively identified as leightonite ($Ca_2K_2Cu(SO_4)_4 \cdot 4H_2O$) from a set of weak diffraction maxima, and could have arisen as a product of incipient corrosion of the outer metallic sheath, with copper partially substituting for magnesium in the recrystallized polyhalite.

The presence and absence of certain mineral phases in the efflorescences allows constraints to be placed the nature and role of the fluids which produced them. First, their mother-liquor was probably the aqueous solution native to the rock, as intragranular fluid inclusions, intergranular solution, or both. Preliminary analyses (flameless atomic absorption) gave the following approximate ratios of ionic molality in a sample of fluid inclusions: K/Na = 0.5, Mg/Na = 1.25, Ca/Na = 0.1. This solution resembles a potash mine seep in solute content (Lambert, 1978). Second, there is no evidence for large proportions of soluble calcium in the mother-liquor, contrary to the suggestion of Roedder and Belkin (1979). In addition, there would be no basis for the formation of calcium-rich liquids of extremely low vapor pressure, as proposed by Stewart, and Potter (1979). Third, at least some of the water (collected as steam condensate) released upon heating of the block appeared at the heater hole as liquid solution, not entirely as a vapor as proposed by Hohlfelder and Hadley (1979).

Post-heating Development of Morphology of Fluid Inclusions

Following the unsheathing of the large salt block it was sliced normal to the axis of the heater, and slabs were cut 5 to 10 mm thick from the central portion in the 20 cm nearest the heater and polished to provide transparency for microscopic examination. See Figure 1 for approximate location of sample slabs. The primary texture and mineralogy of the original rocksalt were largely preserved without conspicuous recystallization. The elongation of fluid inclusions in a direction radial to the heater hole, was the most noticeable change which occurred upon heating of the rocksalt. Polyhalite was unaltered since its dehydration temperature (> 300°C) was not achieved.

The fluid inclusions were observed most clearly in halite, there being but few in the less-abundant sylvite, and polyhalite being opaque. Plate 4 shows some morphologies which developed in the heated Salt Block II. Notable are the "nailheads" and "walking-stick heads" (Plates 4a and 4b, respectively) developed at the heated ends of the elongate fluid inclusion tracks. Plate 4b also illustrates the abandonment of inclusion material in the tail portion by "necking down" of the elongate track, which may give rise to "string-of-beads" form if connections persist. It is not known whether development of bulbous "hot" ends is an equilibrium feature, independent of local crystallography, or is a transient feature, preserved during the cooling phase of the experiment. Plate 5 shows fluid inclusion tracks within 6 mm of the heater hole. A boundary between halite grains occurs one-third of the way from the top of the plate. The large track in the upper left appears to have deviated upon encounter with the grain boundary, while smaller inclusions initiate or terminate at or near the boundary.

Plate 6 shows portions of a boundary containing small grains of polyhalite. The well-defined spindle-shaped inclusion (Plate 6a) terminates, while the irregular track appears to pass through the boundary. In some places, nailheads have developed very near the boundary (Plate 6b). These observations appear to reinforce the conclusion of Roedder and Belkin (1979) that only the larger inclusions tend to cross the grain boundaries during migration up the thermal gradient.

A systematic visual (microscopic) examination of polished slices of rock adjacent to the heater hole revealed a zonation of phenomena resulting from perturbation of the evaporite rock by the thermal and stress fields, hereafter called the "perturbed zone." Aside from the occurrence of recrystallized polyhalite (Plates 2 and 3), which is probably a thermal rather than a thermal gradient effect, most of the conspicuous perturbations occurred within 15 cm of the heater hole. Plates 7 through 13 are a graphic documentation thereof. Figure 2 shows approximate profiles of maximum temperatures and temperature gradients experienced by the sliced samples (see George, 1980).

At the outer periphary of the "perturbed zone," the intragranular fluid inclusions (see Roedder and Belkin, 1979, for an extensive description) are virtually intact. Just within the 15 cm radius from the heater hole, however, are a series of subannular textural elements (Plate 7) that have little relationship with original grain boundaries, fluid inclusions or bedding. As is the case with all of these post-heating microscopic observations, the time of occurrence of these features in the course of the experiment is not obvious. These features appear to be fractures with onlv a few microns of open space, and the fact that annealing of the halite has not occurred (nor has recrystallization) suggests that fracturing occurred late in the experiment, probably in the cooling phase, when mechanical contraction would be expected to place the cooler, more brittle portions of the rock in tension.

In the zone within about 11 cm of the heater hole, incipient changes in fluid inclusion morphology are evident. Plate 9 illustrates a morphology common in the periphery of the perturbed zone. This general shape, a "bullet head" pointing toward the heat source, and several "tails" pointing away, is characteristic of the larger accumulations of intragranular fluid (more than 1 mm across). Similar shapes were noted by Anthony and Cline (1971) in sylvite and by Roedder and Belkin (1980) in halite. As in the case of the latter citation, it is not known "whether this shape developed early in the run and represents a dynamic equilibrium shape or whether it was still in the process of evolving at the end of the runs." Nevertheless, the phenomenon occurs only in the halite in a zone about 7 to 11 cm from the heater, and only in larger inclusions.

Within the peripheral perturbed zone, another phenomenon conspicuously developed is the alteration of morphology of fluid accumulation along grain boundaries. Whereas Plate 8 depicts undisturbed fluid at a grain boundary, fluid at the boundary illustrated in Plate 10 has coalesced into large "droplets," which have become elongated parallel with the temperature gradient. The fact that this component of free fluid has become mobilized in a zone in which only the larger intragranular inclusions have moved (Plate 9) suggests that grain-boundary water may be a more significant contribution to mobile fluids than heretofore recognized. The model proposed by Hohlfelder and Hadley (1979) has treated the mechanism of fluid migration in evaporite blocks as porous flow. That part of the model may indeed not be far from correct, although transport entirely as vapor cannot in any way account for the observed mineralogical changes.

In the zone very near (less than 4 cm) the heater hole, elongate intragranular inclusions are common, many of which contain bubbles. Most of these inclusions are elongated parallel with the temperature gradient (Plate 11), but a significant number of them are elongated at right angles to it (Plate 12). Inclusions in this zone appear to be bounded at least in part by faces of cubic crystal forms. These inclusions have not discharged their liquid contents. "Gradient-parallel" elongate inclusions (Plate 11) appear to be composed of accumulations of fluid intermediate in volume between the large "octopus" forms (Plate 9) and those elongated perpendicular to the gradient. According to Roedder and Belkin (1980) flattened inclusions tended to move faster than elongate ones. Conversely, the same work reported a much higher rate of movement for larger inclusions. If direction of elongation is realted to size (and therefore rate of movement) is it not obvious how the two foregoing statements can be reconciled in the face of these observations.

The protusion of small inclusions within 4 cm of the heater hole could be attributed to: (1) the breakup of larger, faster inclusions, (2) the convergence of a given amount of fluid from an annular volume of rock into a smaller annular volume, or (3) a higher initial concentration of fluid near the heater hole. In any case, the larger, supposedly faster inclusions (Plate 9) have not completed their journey, but stopped at least 7 cm from the heater hole.

Evidence of escape of fluid from intragranular inclusions was found only in the 1 cm nearest the heater hole (Plate 13). Here, as illustrated before, inclusions have developed irregular tracks, with nailheads and strings-of-beads. As can be seen, many inclusion tracks terminate at the heater hole.

Conclusions

Photomicrographic observations have indicated that the 111 grams of water (out of about 8 kilograms available) released in about 100 days from the 2-metric-ton Salt Block II did not originate primarily from intragranular fluid inclusions, which are volumetrically by far the most important contribution to the total water present in the evaporite. Efflorescences encrusting the interior of the axial heater hole are composed of phases not present in the original rock. These phases, and their carrier fluid, could not have migrated in the vapor phase. The encrustations represent solutes in the aqueous phase in the rock, and consist of chlorides of sodium, potassium and magnesium, but not calcium. The most profound textural changes were observed within 15 cm of the heater hole, but even within this region ($T > 100^{\circ}C$, $\nabla T > 3^{\circ}C/cm$) intragranular inclusions have been reluctant to cross grain boundaries. The generally restricted movement of intragranular fluid during the 100-day heating phase is consistent with the low rates of individual intragranular fluid inclusion movement reported by Roedder and Belkin (1980), about 1 centimeter per year at these temperatures and temperature gradients. The impediment posed by a grain boundary would cause the net rate of intragranular fluid movement to be even lower, if the path of movement were to traverse several grains. Alternatively, some of the fluid encountering a grain boundary could become part of the intergranular fluid phase, whose movement would be governed by a different set of mechanisms. The aqueous phase at grain boundaries appears to have been mobilized, and may be the most important mobile moisture source, except within 2 cm of the heater. A precise set of mechanisms for mobilization of intergranular liquid is not well understood at this time.

Acknowledgement

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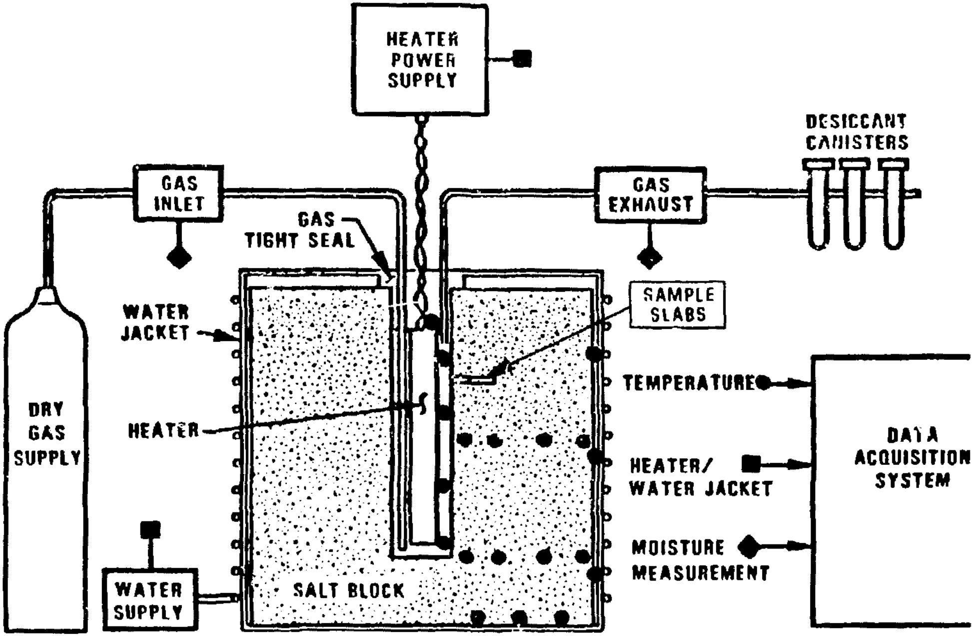

Figure 1 SCHEMATIC OF THE SALT BLOCK II EXPERIMENT

adapted from Hohlfelder [1980]

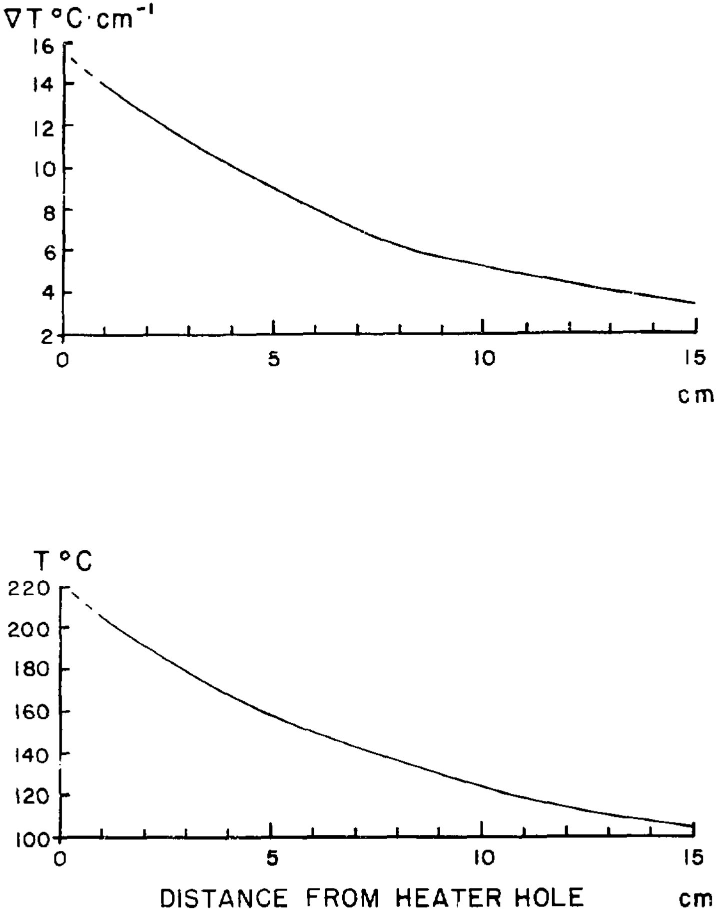

Figure 2. Approximate temperature and temperature gradient as a function of distance from heater hole in Salt Block II, steady state at maximum heater power, 1.5 kw. After George (1980).

Plate 1. Interior of axial hole (5 inches across) with sheathing in place, showing mineral efflorescences protruding from the wall (carnallite + halite). Elongate encrustations follow grain boundaries. Bellows seal (encursted with bischofite + halite), heater, instrumentation and crushed reagent-grade NaCl packing have been removed following shutdown of heating and moisture collection.

Plate 2. Outer cylindrical surface of large (1700 kg) block of evaporite rock, showing white efflorescences (recrystallized polyhalite) in the vicinity of original polyhalite, most conspicuously developed along grain boundaries.

Plate 3. Outer cylindrical surface of block of evaporite rock, showing preferred alignment of secondary (white) polyhalite efflorescence, associated with a band of original (flesh-colored) polyhalite. The alignment follows the textural (bedding?) trend of the rock, as apparently does the post-heating fracturing (near little finger).

Plate 4. Morphology of tracks of fluid inclusions in heated rocksalt. Heat source toward left. Scale bar = 500 microns.

- a. "Nailhead" track, showing flattening normal to temperature gradient..
- b. "Walking-stick head" track, showing "necking down" in tail portion.
- c. "String-of-beads" tracks, with local "nailhead" development. Shadows cast by polyhalite grains below polished surface.

Plate 5. Relationships between tracks of fluid inclusions in heated rocksalt and heat source. A small arc of the heater-hole wall has been subtended at the bottom of the photograph. Scale bar = 500 microns. Most tracks are spindle-shaped, oriented normal to the heater-hole wall, with local development of nailheads and strings-of-beads. The large inclusion (upper left) encountered and partially crossed a grain boundary. It resumed a more tortuous, bifurcated path slightly below the polished surface. Other tracks terminate or initiate (upper center) at the grain boundary.

Plate 6. Relationships between tracks of fluid inclusions and grain boundaries. Heat source toward left. Scale bar = 500 microns.

- a. Spindle-shaped and irregular tracks terminating at a grain boundary containing polyhalite. Note also the large irregular track in the center transcending the grain boundary.
- b. Nailhead development in tracks encountering a boundary between halite grains. This behavior could result in a coalescence of fluid along the boundary.

Plate 7. Subparallel curvilinear features developed in halite 13 cm from the heater hole, which is to the left in this and all remaining photomicrographs. The length of the black scale bars in this and subsequent plates represents 500 microns. Could these be tensional fractures developed upon cooling, approximately parallel to the cylindrical surface of the heater hole? Note unperturbed fluid inclusions (square outlines, center).

Plate 8. Grain boundary, approximately parallel to focal plane. Note vermiform patterns of included solution along the boundary, and unperturbed intragranular fluid inclusions (square outlines) slightly out of focus. Center is about 12.5 cm from heater hole.

Plate 9. Relatively large (>1 mm) fluid inclusion, whose shape changed during an undetermined time in the course of the heating experiment. This is but one example of many such inclusions whose leading edge has assumed a blunt point, with several 'stringers" trailing behind. These are found about 7 to 11 cm from the heater hole.

Plate 10. Another grain boundary, showing vermiform development of inclusions therein, but with a preferred orientation (radial to the heater hole, about 4 cm away), as opposed to a more random array in apparently "undisturbed" halite (Plate 8).

Plate 11. Fluid inclusions elongated radial to the heater hole, most containing bubbles, indicating that they still contain fluid. There is thus no indication of their contents' escape into the moisture-collection system, since they are completely contained in halite. These occur about 3.5 cm from the heater hole.

Plate 12. Intragranular fluid inclusions enlongated tangential to the heater hole, about 2.5 cm away. The elongation is perpendicular to any thermal gradient known to have existed during the experiment. The local crystallography appears to influence their boundaries as indicated by the square shapes.

Plate 13. Fluid inclusion tracks near the heater hole, whose curvature may be seen at the extreme left edge of the photograph. Note the development of nailheads and strings-of-beads. This is the only zone in which intragranular inclusions are actually seen to make good their "escape" into the heater hole.


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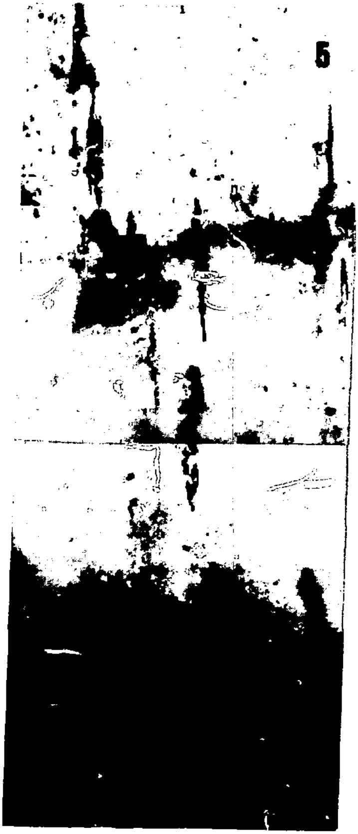
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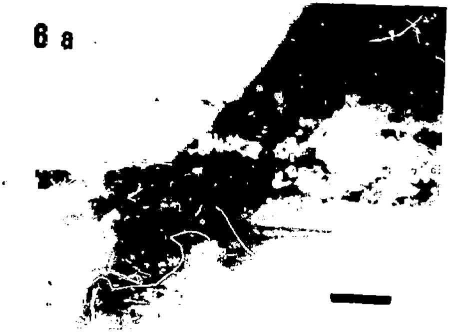
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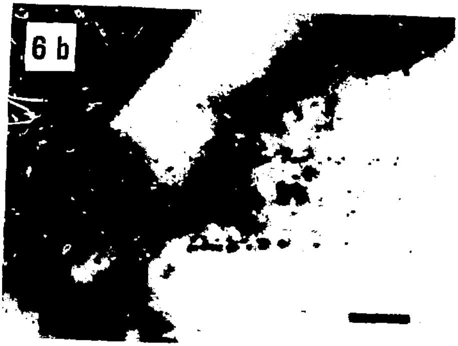
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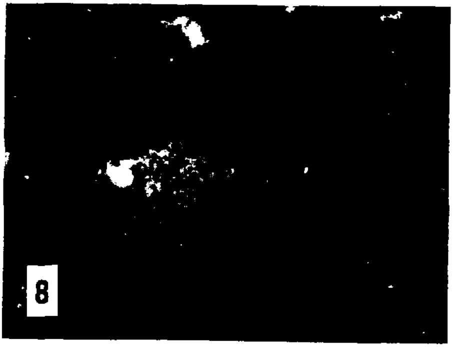
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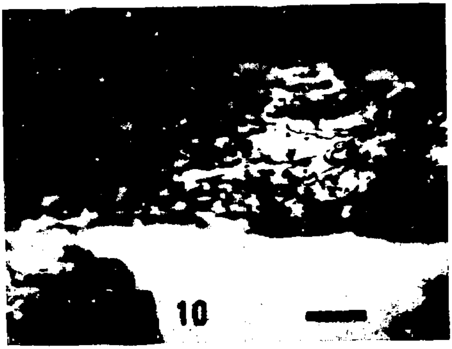
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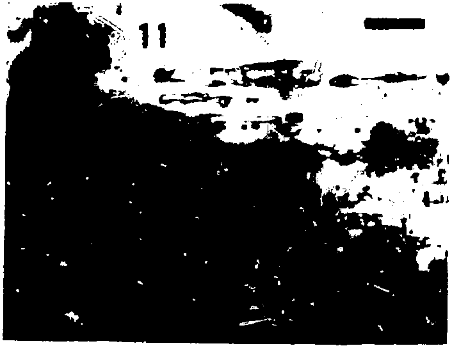
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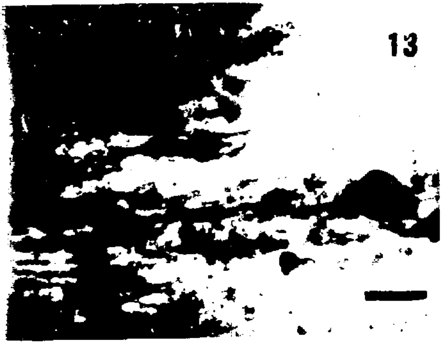
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