AUTORADIOGRAPHY OF MINERALS

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ABSTRACT

Using stray slow neutrons from the cyclotron on elements having large nuclear cross-sections for neutron reactions (n, γ) and yielding radioactive isotopes of convenient half-periods, autoradiographic studies of a number of common minerals have been made. The locus and relative concentrations of the activated elements in these minerals are determined by placing polished sections of the specimens in direct contact with photographic film. The source of the effective β-radiation is determined from the decay rate and intensity of the activity. A reconnaissance study has been made of minerals containing manganese, gold, copper, tungsten, phosphorus, potassium, barium, sodium and arsenic.

INTRODUCTION

Geologists frequently see direct evidence of natural radioactivity in the pleochroic halos that spot biotite in thin sections. These microscopic discolorations result from alpha-ray bombardment of the mineral immediately surrounding tiny inclusions of radioactive elements. The small size is due to the short range of the alpha rays in the mineral. Substituting photographic plates for the sensitive mineral, Mügge[2] obtained the first autoradiographs of radioactive minerals. Numerous investigators subsequently have used this technique to determine the distribution of uranium and thorium in terrestrial materials.

Recent advances in nuclear physics make it possible to induce radioactivity in all elements. However, alpha rays are rarely emitted by these so-called artificially radioactive elements. Instead they emit beta and gamma rays. Although less effective than alphas, beta rays may be used for broader applications of autoradiography. In the present work only a few of the more obvious applications to geologic materials have been tested. It has been found that the uniform distribution of a particular element in a mineral or its localization in inclusions often can be demonstrated by the method. If the valuable element in an ore is present in minute inclusions, the position may be revealed by the radiations from the induced radioactivity. Thus, fine particles of gold in a quartz matrix or manganiferous laminae or nodules in a shale can be studied by this technique. The information obtained may be of value in the beneficiation of these materials. By means of autoradiography the irregular distribution of elements in zoned minerals can also be studied.

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[2] Mügge, O., Radioaktivität und pleocroitische Höfe: *Zentralbl. f. Mineralogie*, **71**, 144–147 (1909).

General Principles

Artificial radioactivity can be produced by bombarding stable atoms with various radiations, i.e., alpha rays, neutrons, protons, electrons, gamma rays, or deuterons. A given intensity of bombardment is capable of producing only a certain maximum induced activity, as equilibrium between the production and disintegration of active atoms is finally reached. This maximum yield is approached at a rate depending upon the half-period of the induced activity. The half-period for activation is the same as that for disintegration. For example, Mn^{56}, the isotope of manganese with atomic weight 56, has a half-period for disintegration of 2.6 hours and under bombardment reaches half its maximum intensity in 2.6 hours. Bombardments longer than about 10 half-periods produce no appreciable increase in activity.

Nuclei of different atomic forms differ in the degree to which they interact with bombarding particles. The probability of interaction can be considered as proportional to the target area presented to the bombarding particles by a given nucleus. This quantity is called the *nuclear cross-section* and is generally expressed in square centimeters. Because of the wave mechanical nature of the interaction, the cross-section may be smaller or larger than the actual nuclear area. The cross-section varies not only with different kinds of bombarding particles but also with the velocity of these particles. In this report only *nuclear cross-sections for the capture of slow neutrons* will be considered.

Neutron bombardment offers certain advantages over direct proton or deuteron bombardment of minerals. First, it is not necessary to prepare the sample in the form of a target, which, due to the energy of the beam, would require thin, water-cooled sections. Second, a flood of neutrons escapes continuously from an operating cyclotron. These by-product neutrons can be utilized at no increase in cost. Third, only one or two samples can be activated simultaneously by direct bombardment, whereas an almost unlimited number can be exposed concurrently to neutrons. Fourth, there are numerous competing reactions involved with deuterons and protons, while the reactions with neutrons, particularly slow neutrons, are quite simple. For these reasons the present research has been limited to neutron activation, and, unless otherwise stated, thermal-velocity neutrons have been used.

Suitability of Elements

Following the initial work with manganese minerals,[3] an attempt was made to list the elements in the order of their suitability for autoradiog-

[3] Goodman, C., and Picton, D. C., Autoradiography of ores: *Phys. Rev.*, **60**, 688 (1941).

raphy as determined by their half-periods and cross-sections. The more favorable elements are listed in Table 1 in the order of decreasing suitability, based on the purely arbitrary rating shown in Fig. 1. From the standpoint of cyclotron operations and also the convenience in photographing and measuring the induced activity, elements with half-periods

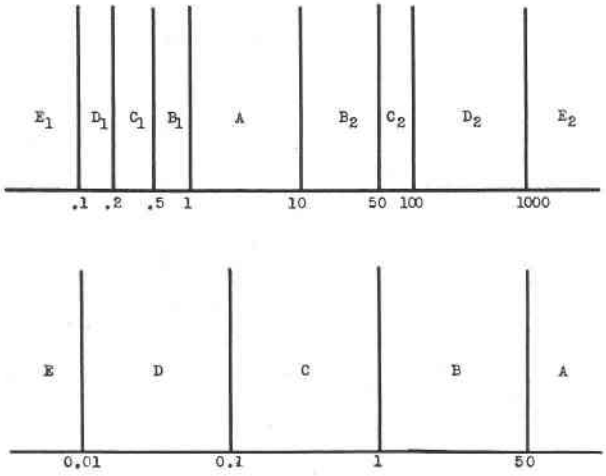

FIG. 1. Arbitrary autoradiographic rating. In the upper diagram is given the alphabetical rating of half-periods, in hours, of the induced radioactivity. The lower diagram evaluates the capture cross-sections for slow neutrons in units of 10^{-24} cm^2.

between 1 and 10 hours are preferred, hence are given an *A* rating. Those within the next, or *B*, group have either much shorter half-periods, 0.5 to 1 hour for B_1, or much longer, 10 to 50 hours for B_2. Thus, if the half-period is too long or too short, the suitability decreases accordingly. As we have seen, the larger the capture cross-section, the greater the intensity of induced activity for a given bombardment. Although in some cases difficulty results from an excessive amount of activity, in general the larger the probability of activation, the greater the sensitivity and the more suitable the element for study. Thus a second alphabetical scale is used for cross-sections. The combination of these two ratings determines the relative position of the elements in Table 1.

PROCEDURE

A hand sample (100 to 1000 grams) of the mineral to be studied is ground flat on one face. The final grinding should be with a powder of about No. 304 grade. Polishing is unnecessary, since the objective is merely to have a flat surface for direct contact with the photographic

TABLE 1. AUTORADIOGRAPHIC ELEMENTS

(The elements are arranged in the order of decreasing suitability for autoradiographic study. The dominant radioactive isotopes resulting from slow neutron bombardment are indicated together with their half-periods (d≡days, h≡hours, m≡minutes). The capture cross-sections are average values for the natural isotopic mixtures.)

Element	Radio Isotope	Half-period	Capture Cross-Section for "Average" Atom in 10^{-24} cm^2.	Rating
Dysprosium	Dy^{165}	2.5 h.	440	AA
Europium	Eu^{152}	9.2 h.	260	AA
Barium	Ba^{139}	86 m.	2	AB
Indium	In^{116}	54 m.	119	B_1A
Manganese	Mn^{56}	2.6 h.	9	AB
Arsenic	As^{76}	26 h.	3	B_2B
Copper	Cu^{64}	12.8 h.	1	B_2B
Iridium	Ir^{194}	19 h.	38	B_2B
Lanthanum	La^{140}	31 h.	5	B_2B
Tungsten	W^{187}	24 h.	10	B_2B
Gold	Au^{198}	2.7 d.	130	C_2A
Iodine	I^{128}	25 m.	6.5	C_1B
Platinum	Pt^{199}	31 m.	0.7	B_1C
Potassium	K^{42}	12.4 h.	0.1	B_2C
Sodium	Na^{24}	14.8 h.	0.4	B_2C
Calcium	Ca^{49}	2.5 h.	0.01	AD
Nickel	Ni^{63}	2.6 h.	0.03	AD
Silicon	Si^{31}	2.8 h.	0.02	AD
Yttrium	Y^{90}	60 h.	0.7	C_2C
Chlorine	Cl^{38}	37 m.	0.07	B_1D
Zinc	Zn^{69}	57 m.	0.08	B_1D
Bismuth	Bi^{210}	5 d.	0.1	D_2C
Phosphorus	P^{32}	14.3 d.	0.2	D_2C
Scandium	Sc^{46}	85 d.	2.8	E_2B
Tantalum	Ta^{182}	97 d.	4	E_2B
Vanadium	V^{52}	3.9 m.	5	E_1B
Magnesium	Mg^{27}	10.2 m.	0.03	D_1D
Aluminum	Al^{28}	2.4 m.	0.2	E_1C

film or plate. The specimens are placed in a specially constructed container located as near as possible to the cyclotron target. This container should have paraffin walls* 2 to 3 inches thick. Bombardment proceeds

* Paraffin is used because it is an inexpensive, hydrogenous solid. The high-velocity neutrons emitted by the target are more completely slowed down by collisions with particles of approximately the same mass, i.e., hydrogen nuclei. Nuclear capture cross-sections are larger for low-velocity neutrons than for the more energetic, fast neutrons.

for a few minutes to several hours, depending upon the element under study. The specimens are removed and transferred to the dark room. The flat surfaces are placed on photographic material and exposed for a few minutes to several hours. In the resulting autoradiographs dark areas directly adjoin areas of high induced radioactivity in the specimens and are caused by the interaction of the beta rays with the silver emulsion. Relatively clear areas correspond to inactive portions of the specimens. Thus, photographically, the autoradiographs are negatives. Positive prints can be made either by contact or by enlargement. The illustrations included in this report are all prints. Hence, the light areas correspond to high induced activity, and the dark areas correspond to inactive regions. To aid in the comparison of the autoradiograph with the specimen from which it was produced, a photograph of the flat surface of the mineral is obtained. The print of the direct photograph is made the same size as the print of the autoradiograph. In this manner, direct comparison can be more easily made.

As indicated in Table 1, the half-periods have a wide range of values and, with a few exceptions, are distinctly different. This characteristic can be used to identify the element whose distribution is revealed by the autoradiograph. The half-period is determined from the rate of decrease in the activity when the mineral specimen is placed in front of a beta-ray counter. For most samples the background of the counter is negligible, being only about 100 counts per minute as compared to several thousand per minute for an average induced activity. When the background is appreciable, the rate of decrease must of necessity be based on the net activity due to the sample alone. If two or three elements contribute simultaneously to the activity, these can often be resolved if the half-periods are substantially different and the decay measurements are made over an extended period of time. Occasionally two elements of nearly the same half-period are present, in which case it may not be possible to distinguish between them. However, even in these instances, activation by neutrons of selected energies may help identify individual elements if resonance levels exist in the nuclei.

Experimental Results

For reconnaissance purposes nine elements of general interest to geologists were selected for special study, namely: manganese, gold, copper, tungsten, phosphorus, potassium, barium, sodium, and arsenic. The distribution of these elements in various mineral specimens is revealed in the prints of the autoradiographs, Figs 2–11 inclusive. Experimental and expected decay curves drawn on arbitrary scales are also included, together with direct photographs of each mineral. In addition,

the pertinent nuclear properties of all the elements have been compiled to determine their suitability and characteristic reactions. Out of 41 elements for which relatively complete data are available,† at least 26 should be suitable for autoradiography, if present in high concentrations. It is, of course, desirable that common "gangue" elements have little or no activity, so that they will not interfere. Fortunately, this was found to be true of iron, sulphur and oxygen, and to a lesser degree of aluminum and silicon.

Luminescence was observed in most of the specimens known to fluoresce in ultraviolet light This effect was first observed in a scheelite specimen whose autoradiograph is not included. Tests were made on this and other specimens by separating portions of each from the photographic film with black paper and with cellophane. The paper and cellophane absorb the beta radiation to about the same degree, but visible light is completely absorbed by the black paper and is not appreciably affected by the cellophane. For the luminescent specimens, greater darkening is found below the cellophane than below the paper. After this effect had been discovered photographically, it was found that the light was visible in the dark after the eyes had become adapted.[4]

While luminescence does not interfere with the determination of the locus of the active element in a specimen, it does interfere with an estimate of the relative concentration. For example, in Fig. 10, the willemite, because of its luminescence, gives a brighter area in the print than the franklinite, although it actually contains less manganese than the franklinite.

Photography

Although all photographic materials are affected by nuclear radiations, films differ greatly in their sensitivity. This sensitivity may or may not be related to the sensitivity to ordinary light. For use with beta rays, the Eastman Kodak Company recommended medium lantern-slide plates and high-resolution 548 plates with blue sensitizing. In addition to these materials, tests were made of a number of other plates and films, including x-ray films. The sensitivity of most of these, including the 548 plates, was so low that even the highest beta activities produced little effect. On the other hand, the x-ray films are quite sensitive, as would be ex-

† These data have been arranged in a periodic table of the elements, copies of which are available without charge on request.

[4] Subsequently we learned that F. G. Wick and M. S. Vincent, *Phys. Rev.*, **58,** 578 (1940), observed luminescence in certain phosphors during exposure to neutrons. However, these investigators apparently did not have a sufficiently intense source of neutrons to induce the persistent luminescence herein reported.

pected. Although considerably less sensitive than the x-ray films, the lantern slides have moderate sensitivity to beta rays and give much finer grain and hence greater detail than the x-ray films. For this reason, medium lantern slides are recommended except when the highest sensitivity is needed.

The resolving power of the autoradiographic method is limited by (1) the grain size of the film or plate, (2) the blurring effect of rays from below the surface of the specimen, and (3) the geometrical distribution of the radiation. Grain size has been considered in the preceding paragraph. The blurring effect is not as serious as might at first be expected, since only the highest-energy beta rays can penetrate from depths as great as 1 mm. in the specimen. Because the rays are emitted equally in all directions, a cone of blackening from each active point in or near the surface of the specimen is produced in the film. This is equivalent to having the image slightly out of focus. The magnitude of these effects is indicated in the accompanying figures.

Acknowledgments

The authors are indebted to the members of the Radioactivity Center for their assistance and suggestions during this work. In particular, the cooperation of the M.I.T. cyclotron group, in providing an intense source of neutrons, and of Dr. J. W. Irvine, Jr., in permitting the use of his counter apparatus, is gratefully acknowledged. Professor L. C. Graton has been most generous in his encouragement and interest. Professors W. H. Newhouse and A. M. Gaudin provided all of the samples and offered valued criticism. Mr. E. P. Kaiser aided in the identification of willemite in one of the specimens. The more recent developments of this research have been made possible by a grant-in-aid from the American Academy of Arts and Sciences.

Figures 2–10, Autoradiographs, Photographs and Decay Curves

A print of a direct photograph is shown in the upper left corner of each figure. The corresponding autoradiographic print of the same surface, reduced to the same scale, is shown immediately below. The experimentally observed radioactivity decay curve (solid line) is shown graphically on the right, the β activity being in arbitrary units. The slope of the curve is proportional to the half-period. For comparison the expected value for the element indicated is shown as a broken line.

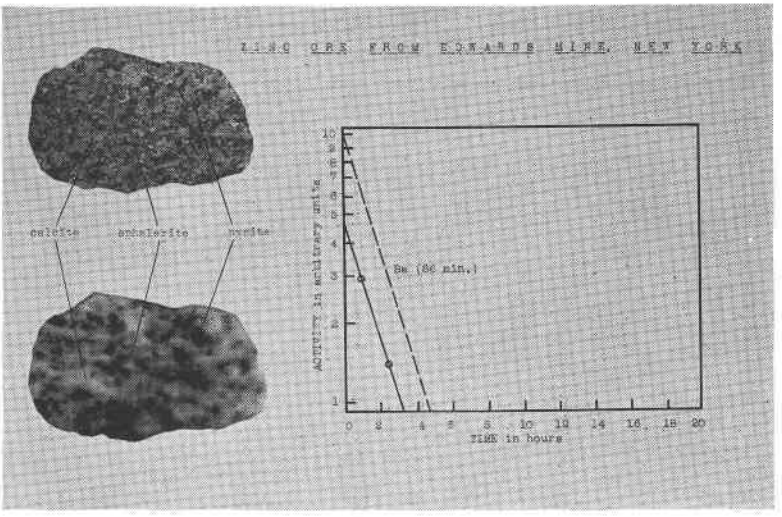

FIG. 2. Zinc ore from Edwards Mine, New York, shows high activity, possibly of barium, in calcite, intermediate activity in sphalerite and essentially no activity in pyrite.

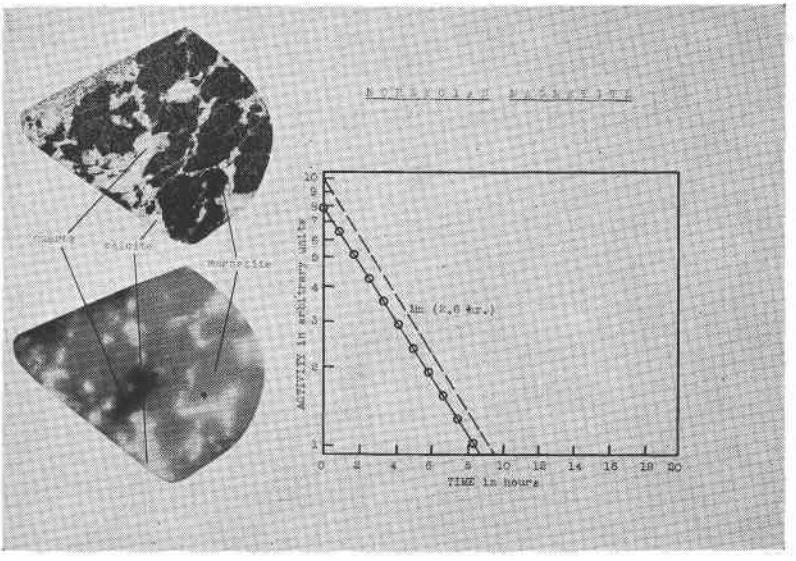

FIG. 3. Norwegian magnetite ore shows apparent high activity of manganese in calcite, moderate activity in magnetite and none in quartz.

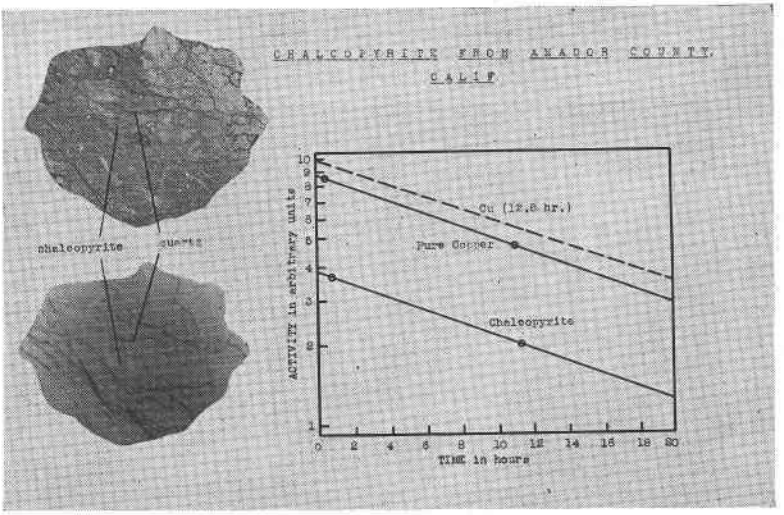

FIG. 4. Chalcopyrite from Amador County, California, shows expected uniform distribution of copper in mineral with exception of quartz stringers. Activity of pure copper was determined under similar conditions in an attempt to test quantitative application of method. Theoretical Cu content is 35 per cent, while curves indicate 43 per cent, suggesting possible greater absorption of β-rays in copper than in chalcopyrite.

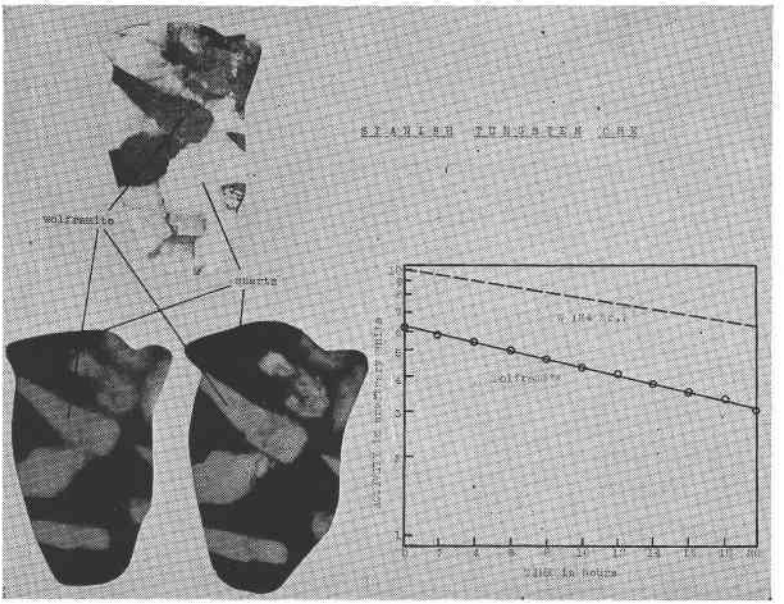

FIG. 5. Two autoradiographs of a Spanish tungsten ore were obtained. The first, lower left, made immediately after activation, reveals the distribution of manganese in the wolframite. The quartz shows no activity. After the manganese activity (half-period 2.6 h.) had practically all decayed, the second autoradiograph, showing the distribution of tungsten, was made. The decay curve observed 24 hours after bombardment has a slightly steeper slope than that of tungsten alone, presumably due to some contribution from manganese.

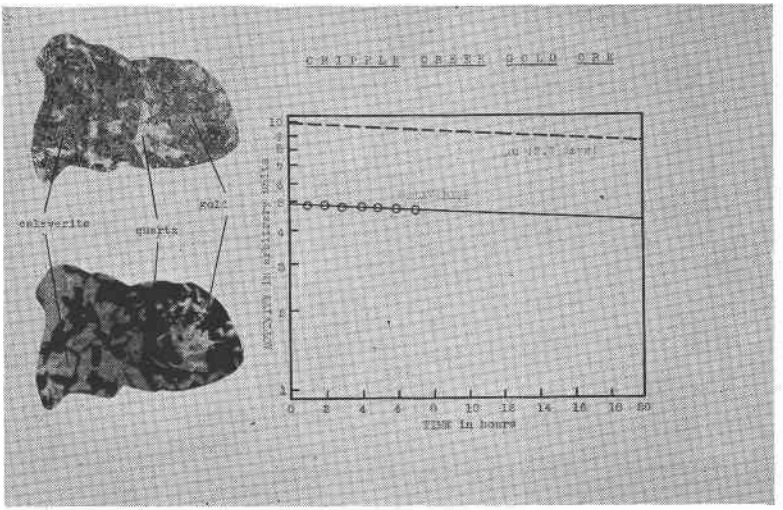

FIG. 6. The presence of native gold in the Cripple Creek gold ore is indicated by bright areas in the autoradiograph. The gray areas correspond to calaverite which has a lower gold content. Again the quartz shows no activity.

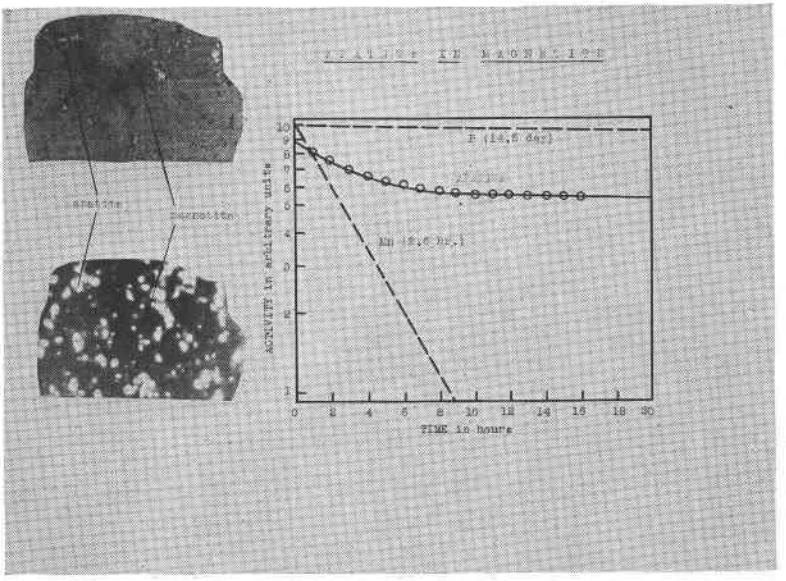

FIG. 7. A sharp contrast is shown between the apatite and the magnetite. Unlike the magnetite in the Norwegian ore of Fig. 3, this magnetite shows essentially no activity, indicating a relatively low concentration of manganese. The steeper slope in the early part of the decay curve suggests that the apatite is manganiferous. After the manganese activity has died away, the slope parallels that of phosphorus (half-period 14.5 d.).

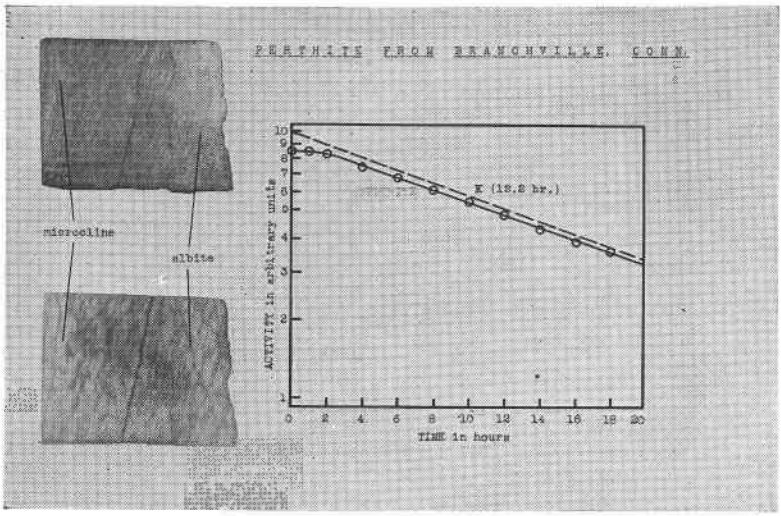

FIG. 8. After activation the microcline in a perthite from Branchville, Conn., produced a greater photographic effect than the associated albite. At first this seemed surprising, since potassium has a somewhat smaller capture cross-section than sodium (see Table 1) and both are present in approximately the same atomic concentration. Upon further study it was found that the microcline was luminescent following activation. Because of the similarity in the half-periods (Na, 14.8 h.; K, 12.2 h.), it was not possible to distinguish between these two elements in the decay curve, and sodium may have contributed as much or even slightly more to the total β activity than potassium.

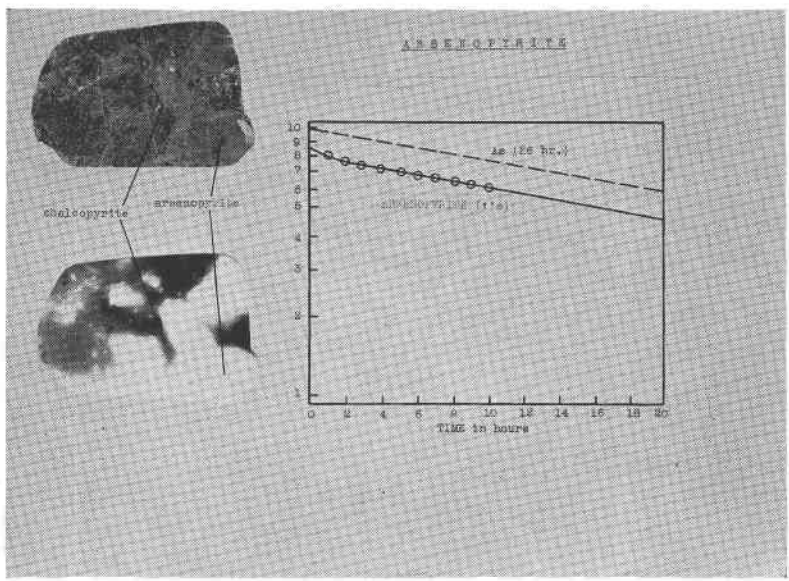

FIG. 9. In the autoradiograph the arsenopyrite crystals do not show a sharp boundary with the adjacent chalcopyrite. This effect is due to the predominance of γ over β radiation in activated arsenic. Since the γ-rays are much more penetrating and have an indefinite range, their autoradiographic effect is much more diffuse. The decay curve was obtained with 1 mm. of lead between the sample and the counter, hence it indicates the decay of the γ radiation.

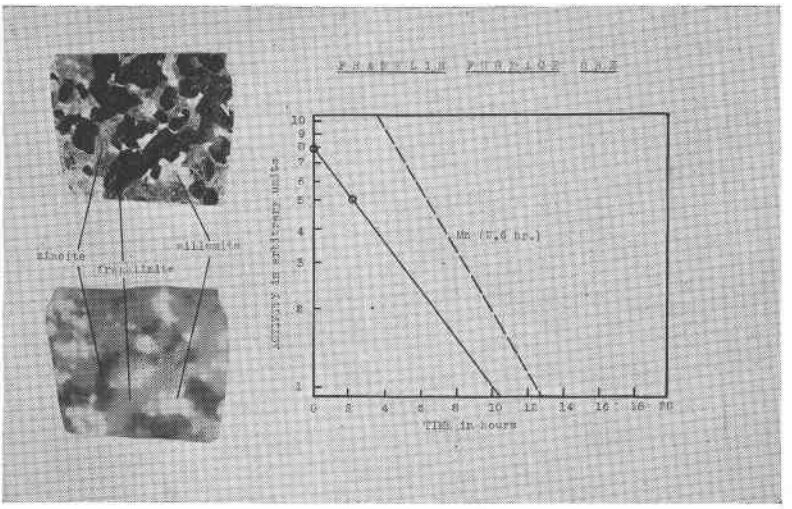

FIG. 10. Because of its luminescence, the willemite in the Franklin Furnace ore produced a distinctly darker area in the autoradiograph, hence a brighter area in the print, than the associated franklinite even though the latter is known to contain a substantially higher manganese content. The zincite showed essentially no activity. An inadequate decay curve was obtained for this sample.

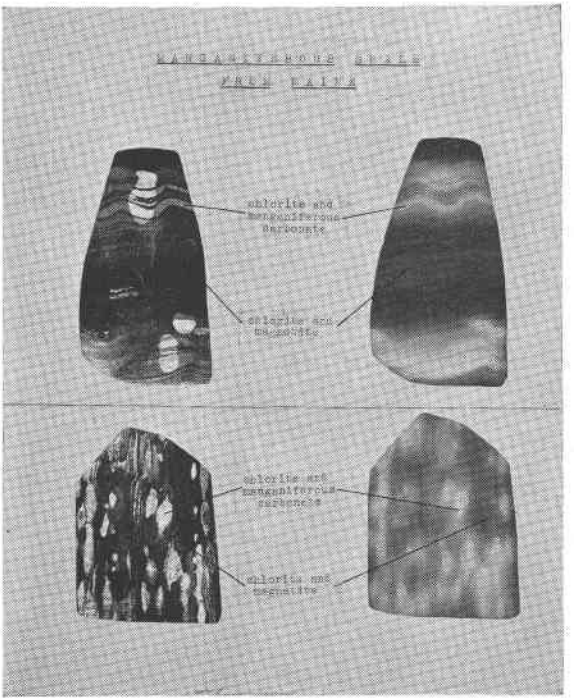

FIG. 11. The autoradiographs of two samples of manganiferous shale from Maine are shown on the right with corresponding direct photographs on the left. The light blotches in the upper left are etch marks on the polished surface. The striking localization of the more manganiferous material in certain laminae and nodules is clearly shown. These observations are of interest in the beneficiation of the ore.