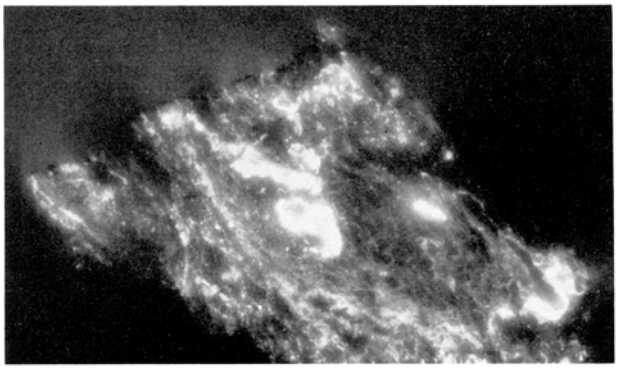

Abb. 2. Autoradiographie einer mit Uranpecherz durchsetzten Gesteinsprobe. Die unregelmässige und feine Durchdringung des Chlorit-Serizitgneises mit Uranerz (hell) ist deutlich erkennbar (Handstück Nr. 571008.5 aus Stollen Isérables. Kodak Commercial Ortho-Film, Exp. 52 h).

Der Uranträger konnte mittels chalkographischer und röntgenographischer Methoden eindeutig als Uranpecherz (Pechblende) identifiziert werden. Die Pechblende tritt meist in Form kleiner, kugeliger oder unregelmässig geformter Gebilde (Grösse meist unter 0,02 mm) auf. Sie erscheint eingeschlossen in Quarz, Chlorit (braune pleochroitische Höfe erzeugend), Serizit, selten in Karbonat und im Albit des Gesteins. Vielfach aggregieren sich die Körner zu grösseren, makroskopisch erkennbaren schwarzen Massen, die aber stets stark von Quarz oder Chlorit durchsetzt sind. Die stärker aggregierten Partien sind öfters gestreckt und verlaufen dann mehr oder weniger konkordant zu den Serizit-Chloritzügen oder Quarzlagen des Gesteins. Die Pechblende führenden Proben enthalten noch verschiedene weitere, meist schon von Auge sichtbare Erzmineralien. Nach erster Durchsicht wurden bestimmt: Pyrit, Kupferkies, Fahlerz, Bleiglanz, Covellin und als feinster Staub Hämatit. Im Dünnschliff zeigen die erzführenden Proben zur Hauptsache das Bild des normalen Gesteins: vorwiegend lagiges feinkörniges Gewebe von Quarz, unterbrochen von gewellten Serizit- und Chloritzügen. Eingelagert finden sich grössere Körner (bis über 1 mm) von Quarz und Albit, dazu in unterschiedlicher Menge Karbonat (Kalzit). Turmalin in idiomorphen dünnen Prismen tritt auffallend reichlich als Nebengemengteil auf. Das äussere Bild der Vererzung zeigt einerseits Analogien mit gewissen Cu-Bi-, Ni-Co- oder Pb-Zn-Lagergängen des umgebenden Casannaschieferkomplexes, andererseits sind doch wesentliche Unterschiede festzustellen, vor allem darin, dass die Pechblende nicht in einer Gangart, sondern verteilt im normalen Casannaschiefer selbst auftritt. Die Uranvererzung wird demnach als eine mit dem Nebengestein gleichaltrige Bildung gedeutet, während das Auftreten der genannten sulfidischen Begleiterze eher für deren jüngeres Alter spricht. Die Abbildung 2, eine Autoradiographie, vermittelt einen Eindruck von der Art der Durchsetzung des Gesteins mit Uranpecherz.

b) *Die Vererzung im Fensterstollen bei Sarreyer.* Die Feststellung von Felspartien mit stark erhöhter Radioaktivität wurde im Fensterstollen von Sarreyer (Val de Bagnes) ebenfalls mittels Szintillometer gemacht, und zwar bei *B* der Abbildung 1. Die gemessenen Aktivitäten im Stollen zeigten Werte bis 0,8 mr/h. Das aktive Gestein hat ein völlig unverdächtiges Aussehen. Es ist ein heller, karbonatführender Serizitquarzit, von vermutlich permotriadischem Alter (Serie des Mont Gond, siehe Abb. 1). Schieferungsflächen weisen einen Serizitbelag auf, der meist mit feinstem Erzpigment vermischt ist und daher dunkel erscheint. Im Schliff erkennt man in diesen metamorphen Quarziten neben rekristallisiertem Quarz, Serizit, Plagioklas und Kalzit grössere Mengen von Pyrit (grob- und feinkörnig) sowie ein feinstes, über die ganze Gesteinsmasse diffus verteiltes Erzpigment (Korngrösse um Tausendstelmillimeter). Auf einzelnen Zügen begleitet diesen Erzstaub feines Hämatiterz. In diesen Quarziten konnten Uran und Thorium quantitativ chemisch nachgewiesen werden. Auf Grund der gemachten Beobachtungen und Vergleiche[5] dürfte feinstverteilte Pechblende als Radioaktivitätsträger der Quarzite anzusehen sein.

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Résumé

Des roches radioactives ont été découvertes dans les galeries de la Grande Dixence S.A. (voir loc. *A* et *B* de la Fig. 1). Les analyses aux rayons X, les analyses chimiques et chalcographiques ont montré la présence de l'uranium sous forme de pechblende. La minéralisation se manifeste, dans les micaschistes gréseux et chloriteux, par des niveaux noirâtres. La pechblende est associée à la pyrite, la chalcopyrite, la galène, la covelline et l'hématite (loc. *A*). A Sarreyer (loc. B) la minéralisation n'est pas apparente. La roche radioactive est un quartzite sériciteux carbonaté, contenant de l'uranium.

[5] Siehe zum Beispiel CH. BIZARD, C. R. Acad. Sci. (Paris) *240*, 791 (1955).

The Genesis of the Mississippi Valley Type Deposits, USA

The three prevailing ideas on the genesis of the Lead-belt and the Tri-state deposits, or, more general, of the Mississippi Valley type deposits, are: (1) Epigenetic-hypogene origin, i.e. epigenetic hydrothermal multiple center or patchy replacement of carbonate rocks, partly controlled by bedding, composition, fractures, etc. (2) epigenetic-supergene origin, i.e. deposition by circulating groundwater, later than the formation of the sediments, and (3) syngenetic-supergene origin, i.e. weathering-derived lead formed contemporaneously with the sediments. These three interpretations, as well as a wealth of detailed observations, are contained in the publications of BÜHLER[1], BUCKLEY[2], KEYES[3], BASTIN[4], WEIDMAN[5], OHLE and BROWN[6], JAMES[7], and others.

The fourth possibility, which has not been found in the literature, appears to explain the facts best: it is the syngenetic-hypogene origin, based on the volcanic-exhalative-sedimentary interpretation.

[1] H. A. BÜHLER, 16th Int. geol. Congr., Guidebook 2, p. 45 (1933).
[2] E. R. BUCKLEY, *Geology of the disseminated lead deposits of St. Francois and Washington Counties, Missouri* (Mo. Bureau Geol. Min. IX, 1909), Part 1.
[3] C. R. KEYES, Trans. Amer. Inst. min. Engrs. *40*, 184 (1909).
[4] E. S. BASTIN, 16th Int. geol. Congr., Guidebook 2, p. 32 (1933).
[5] S. WEIDMAN, 16th Int. geol. Congr., Guidebook 2, p. 32 (1933).
[6] E. L. OHLE and J. S. BROWN, Bull. geol. Soc. Amer. *65*, 201 (1954).
[7] J. A. JAMES, Econ. Geol. *47*, 650 (1952).

The Pre-Cambrian of the Mississippi Valley region is known to consist mainly of igneous rocks: rhyolites, various porphyries, some pegmatites, many diabase and spilite dykes and sills, and granite intrusives. Tuffaceous beds with bentonites, sanidine, pumace, volcanic necks and submarine volcanic structures show that some volcanic activity has continued during the Paleozoic (see KIDWELL[8], ALLEN[9], BUCHER[10], KELLER[11], etc.).

Volcanic-exhalative activity is a common accessory process accompanying and following extrusion periods. Since the volcanic activity as a whole has decreased from early geologic times, it is reasonable to assume that the exhalation of gases, the de-gassing of the earth's crust has also decreased. BARTH[12] has related orogenic movements to the degassing of the earth. A statistical study of ore deposition in relation to geologic time suggested that ore deposition has also decreased during geologic history.

Hydrothermal vein deposition is only one product of the degassing of the earth's crust. A good portion of the volatile fraction escapes to the surface, and it is reasonable to assume that this escaping fraction has approximately as high a metal content as the portion which never reached the surface. The last assumption has been well confirmed by observations in volcanic areas, where sulfides are deposited at the present time. Numerous reports on such recent deposition are available. We can, at this time, only mention the fundamental work done by BEHREND[13], BERNAUER[14], and ZIES[15].

A detailed analysis of mega- and micro-fabrics in the field and under the microscope, combined with physicochemical considerations of syngenetic versus epigenetic, and supergene versus hypogene origin, has led to the conclusion that a volcanic-exhalative interpretation serves, at the present stage, best as a working hypothesis for the bulk of the Mississippi valley type deposits. Isotopic (BROWN *et al.*[16], FARQUHAR *et al.*[17], KULP *et al.*[18]), liquid inclusion, and other published data appear to be explained more adequately by this new approach.

It is reasonable to assume that there is a connection between the basement rock and the mineralization in the overlaying sediments. It is believed that exploration should be based on the assumption that the areas with late Pre-Cambrian and Paleozoic volcanic or fumarolic activity underlay areas of strongest mineralization. The dolomitization and the cherts are two additional products of the syngenetic volcanic-exhalative mineralization. MURATA[19] and others have shown that volcanic ashes and exhalative materials are normal and abundant sources for silica in sediments.

Criteria for syngenetic deposition are abundant. In the sandstones at the base of the Paleozoic Series the galena, marcasite, chalcopyrite, siegenite, etc. contain sand grains with no replacement features whatsoever, but with top-bottom features (see SHROCK[20]) typical for syngenetic sedimentation. The concretionary, concentric fabrics at Fredricktown and elsewhere also exhibit syngenetic features, and the abundant barite occurrences exhibit equally features which rule epigenetic replacement out.

A few additional criteria against epigenetic replacement are: the absence of corroded crystals; the presence of larger idiomorphic carbonates *inside* the sulfides; the abundance of angular breccias with only rare traces of corrosion (replacement is corrosion and any corrosion eliminates sharp angular boundaries); the absence of diffusion replacement gradients such as demonstrated by DE JONG[21]. The local zoning is best explained by exhalative deposition, whereas the causes for the broad zoning has to be explained by intracrustal migrations and differentiations in Archean times. The idea of an epigenetic diffusion-feeding and replacement deposition has thus to be abandoned. It is most interesting to note, and will be discussed in detail in a forthcoming paper (AMSTUTZ[22]), that the extreme magmatists idea, i.e. epigenetic diffusion of hydrothermal fluids, is closely comparable to the diffusionists idea of 'granitization' and ore deposition. Thus it becomes true again: 'Les extrêmes se touchent'.

With regard to principal structures related to ore deposits of the Mississippi valley type, it seems that most structures existed apparently in the basement and were, partly, rejuvenated and partly replicated in the Paleozoic sediments. The faults served, as is well known from other shield areas, as channelways for the lavas during the main Pre-Cambrian volcanic activity, and later on, as channels for the exhalative gases and fluids. Like the epigenetic replacement theory, we thus suppose the ore fluids to move up along faults. The main difference between the old epigenetic-hydrothermal idea and this syngenetic-hydrothermal theory is, therefore, basically only the time and mechanism of deposition and not the ultimate origin of the ore fluids. Stable areas have long-lasting volcanic periods which are much longer than the short lived orogenic volcanism. The best accounts on Paleozoic volcanic activity in the area of Mississippi Valley type deposits are, to the knowledge of the present author, the papers by ALLEN[9], KIDWELL[8], and BUCHER[10].

The most remarkable structural features are the numerous polygonic ring-structures which can have diameters from one to ten miles and resemble a Puiseux-net (HAVEMAN[23], p. 132–133) or a rhegmagenetic fracture system such as described from all continents by SONDER[24]. Polygonic horsts or graben are common features and are apparently inherited from the Pre-Cambrian basement and then also partly replicated in the Paleozoic sediments by rejuvenated movements[25]. The best known structures of this type are the ones in the Tri-state area, the ones controlling the ore zones at Iron Mountain (and probably also in other Missouri iron deposits), and the famous Crooked Creek structure in Central Missouri. Some of the ring type deposits in the lead belt may be due also to ring fractures and not only to ring type reefs[25]. Similar structures can be found in other parts of the Middle West (see for example BUCHER's paper on cryptovolcanic

[8] A. L. KIDWELL, Missouri geol. Survey, R. I. *4*, 83 (1947).
[9] V. T. ALLEN, J. Geol. *40*, 259 (1932).
[10] W. H. BUCHER, 16th Int. geol. Congr., Rept. *8* (1936),
[11] W. D. KELLER and A. KIERSCH, Econ. Geol. *50*, 469 (1955).
[12] T. F. W. BARTH, Verh. schweiz. naturf. Ges. *132*, 147 (1952).
[13] F. BEHREND in: H. RECK, *Santorin, der Werdegang eines Inselvulkans und sein Ausbruch, 1925–1928* (Berlin 1936), vol. 2, p. 323–327.
[14] F. BERNAUER, N. Jb. Miner. Beil. *69*, Abt. A, 60 (1934); *75*, 54 (1939).
[15] E. G. ZIES, Nat. geogr. Soc., Contr. Techn. Papers, Katmai Ser. *1*, 159 (1924); *1*, 79 (1929); Amer. J. Sci. *235*A, 385 (1938).
[16] J. S. BROWN *et al.*, Bull. geol. Soc. America *87* (abstract), 1689 (1956).
[17] R. M. FARQUHAR and G. L. CUMMING, Trans. royal Soc. Canada *48*, 9 (1954).
[18] J. L. KULP, G. C. AMSTUTZ, and F. D. ECKELMANN, Econ. Geol. *52*, 914 (1957).
[19] K. J. MURATA, Amer. J. Sci. *238*, 586 (1940).
[20] R. R. SHROCK, *Sequence in layered rocks* (McGraw Hill, New York 1948).
[21] G. DE JONG, Trans. Amer. geophys. Un. *39*, 67 (1958).
[22] G. C. AMSTUTZ, N. Jb. Min., Mh. *1*, 1 (1957) (part 1; part 2 unpublished).
[23] H. HAVEMANN, Geologie *6*, 123 (1957).
[24] R. A. SONDER, *Mechanik der Erde* (Stuttgart 1956), p. 110.
[25] G. C. AMSTUTZ, Nature (in print, 1958).

structures[10]). It is obvious that the restriction of the exploration thinking to the Paleozoic only has hampered the progress of ore finding.

Of special interest, structurally, is the brecciation and the pitches and flats. Along-side polygonal or straight graben and horst structures, the brecciation is due to faulting. Much, and possibly most, of the breccias extending over large horizontal distances, usually restricted to definite horizons, are caused by intraformational brecciation during earthquakes, which accompanied the volcanism. Brecciation is thus abundant both in the basement rocks and the Paleozoic sediments. Breccias have, locally, been cemented syngenetically by ore minerals. There is often a gradual transition from contortions of non- or partly consolidated sediments to post-diagenetic brecciation. In numerous places various generations of brecciation are visible and are associated with various generations of chert and ore mineralization. The breccias, the cherts, the dolomites, and the ore minerals are essentially syngenetic as concluded from the criteria listed above and additional information which will be presented in detail at a later date.

Pitches and flats can be explained as syn- or slightly postepigenetic structures caused by gravity differences or local tectonic disturbances. An excellent, though epigenetically interpreted, description of pitches and flats was given by Cox[26].

It is believed that this syngenetic-hypogene theory on the origin of the Mississippi Valley type deposits eliminates the difficulties encountered by the three old theories[27]. It is felt that it fits the facts better than the previous theories; yet it should be accepted as a working hypothesis and not as an authoritative dogma.

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Zusammenfassung

Die Streitfrage um die Genese der Mississippi-Valley-Pb-Zn-Lagerstätten wird zugunsten einer syngenetischen und hypogenen Entstehung aus hydrothermal-exhalativen, grossenteils kolloidal sedimentierten Erzlösungen entschieden. Diese drangen entlang uralten, immer wieder aufgebrochenen rhegmagenen Bruchsystemen auf.

[26] G. H. Cox, Illinois geol. Survey Bull. *21*, 120 (1914).

[27] After the completion of this manuscript, it came to the knowledge of the writer that a similar proposal was made with regard to many Alpine lead-zinc deposits (see Schneider[28] and Nickel[29]).

[28] H.-J. Schneider, Fortschr. Min. *32* (1953).

[29] E. Nickel, Chem. d. Erde *18*, 99 (1956).

Crystal and Molecular Structure of 3, 3′-Dibromobenzophenone

It has become increasingly clear that in benzophenone the steric hindrance between the hydrogen atoms in the 2, 2′-positions would prevent the molecule from being coplanar. It would therefore be of great interest to get a quantitative measure of this non-coplanarity by X-ray methods. With this view the determination of the crystal structures of a series of benzophenone derivatives have been undertaken in this laboratory and the present note gives the results obtained with 3,3′-dibromobenzophenone.

The crystal belongs to the orthorhombic system with cell dimensions

$$a = 3{\cdot}99,\ b = 11{\cdot}70 \text{ and } c = 24{\cdot}69 \text{ Å}.$$

The space group is Pbcn and the unit cell contains four molecules. The C=O bond in the molecule coincides with a two fold axis of symmetry in the crystal.

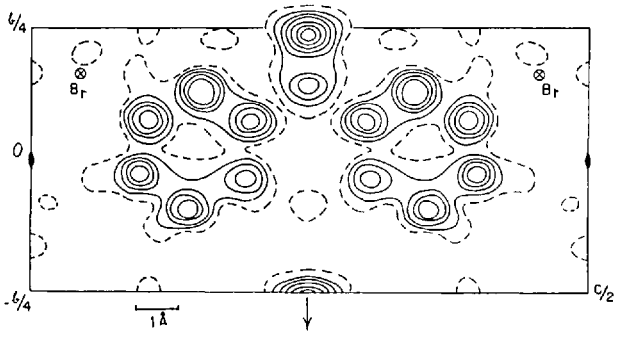

Fig. 1. — Fourier projection on the (100) plane with the Br atom removed. Contours are at arbitrary intervals. Dotted lines correspond to zero electron density.

Three dimensional Weissenberg data were obtained with CuKα radiation and the intensities were estimated visually. The structure was solved by the heavy atom method. The (y, z) coordinates of the bromine atom were determined from the Patterson projection on the (100) plane. Using the signs of a number of reflexions of the type (0kl) obtained from the contribution of the bromine atom, the first Fourier map was prepared which showed distinct peaks corresponding to the light atoms. The (y, z) co-ordinates were refined by a succession of difference syntheses. The Fourier projection on (100) plane with the bromine atom removed is shown in Figure 1. An estimate of the tilt of the benzene ring was made from the distortion it displayed on the (100) projection which gave the approximate x co-ordinate of the bromine atom. This was used for the determination of the x co-ordinate of all the atoms by the generalized Fourier projections using the (1kl) and (2kl) reflexions. The final atomic co-ordinates are given in the Table.

Atomic co-ordinates

Atom	x/a	y/b	z/c
C_1	0·025	0·075	0·196
C_2	−0·100	−0·038	0·194
C_3	−0·081	−0·092	0·142
C_4	0·055	−0·029	0·098
C_5	0·174	0·079	0·102
C_6	0·158	0·138	0·151
C_7	0·00	0·133	0·250
O	0·00	0·240	0·250
Br	0·3400	0·1573	0·0448

The R-factor for the 700 observed reflexions was 15·7%. The intramolecular distances and angles are indicated in Figure 2. The standard deviation in the bond lengths, estimated by Cruickshank's method[1] is of the order of 0·04 Å for C—C and C—O bonds.

[1] D. W. J. Cruickshank, Acta cryst. *2*, 65 (1949).