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Origin of marcasite and its implications  
regarding the genesis of roll-front  
uranium deposits

by  
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Origin of marcasite and its implications regarding the  
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Abstract

Study of five roll-type uranium deposits (three in Texas and two in Wyoming) has resulted in the recognition of ore-stage marcasite in each deposit. Ore-stage marcasite is identified by its close association with uranium- and vanadium-bearing phases in the ore zones; by its close association with ferroselite at and near the redox boundary in some deposits; by its abundance and distribution across deposits; and by its textural relationships with identifiable pre-ore iron disulfide minerals (primarily pyrite). In deposits that are essentially devoid of fossil vegetal debris, marcasite is the dominant ore-stage sulfide and occurs in a large volume of rock beyond the ore zones. In deposits that contain organic matter, ore-stage pyrite is at least as abundant as ore-stage marcasite. Many factors and processes may lead to the formation of either marcasite or pyrite as an ore-stage mineral in roll-type deposits. One of the dominant factors is the complex interrelationship of pH and sulfur species that are precursors of iron-disulfide minerals. Experimental work and study of geochemical environments analogous to those governing the formation of roll-type deposits indicate that relatively low pH (less than about six) and the presence of elemental sulfur favor marcasite, whereas higher pH and the presence of polysulfide ions favor pyrite. Conditions that favor marcasite as the dominant ore-stage iron disulfide are likely to arise during uranium deposition in host rock without fossil vegetal matter. In host rock containing carbonaceous debris, the presence of polysulfide ions and pH buffering any anaerobic bacterial metabolic processes apparently lead to the formation of ore-stage pyrite.

## Introduction

Iron-disulfide minerals are an extremely important constituent of roll-front uranium deposits. In these deposits an ore-stage sulfide is produced as part of the ore-forming process (Rackley, 1972; Granger and Warren, 1969, 1974; Adler, 1974). Insight into conditions of iron-disulfide formation is thus central to understanding the mechanisms of ore formation. For this reason we have undertaken petrographic and geochemical studies on iron-disulfide phases in several ore bodies. In this paper we report on one facet of these studies, the presence of ore-stage marcasite. The distribution and abundance of ore-stage marcasite in a series of deposits is documented, followed by a general review of the geochemical conditions which favor the formation of marcasite over pyrite, and then by a discussion of these conditions as they relate to ore forming processes. Finally, we attempt to integrate this material in an explanation of observed marcasite distributions.

### Marcasite Distribution in Roll-front Uranium Deposits

Anomalously high concentrations of iron-disulfide minerals in roll-type uranium deposits result from an ore-stage generation of sulfide being superimposed on a pre-ore generation (Harshman, 1966, 1972, 1974; Granger and Warren, 1969; Warren and Granger, 1973; Melin, 1969; Bailey, 1969; Dahl and Hagmeier, 1974). In fact, ore-stage marcasite has been recognized in the ore zones of roll-type deposits in Wyoming by Harshman, 1972; Bailey, 1969; Davis, 1969; and Melin, 1969. Detailed descriptions of the distribution of ore-stage marcasite are sparse, however, and petrographic distinction between ore-stage and pre-ore sulfide is generally lacking.

Identification of ore-stage marcasite is based on its close association with uranium- and vanadium-bearing phases in ore zones, its association with

ferroselite (itself an ore-stage mineral) at and near the redox boundary in some deposits, and by observed textural relationships with pre-ore sulfides. Using these criteria, we have observed ore-stage marcasite in each of the five deposits studied in detail (Reynolds and Goldhaber, 1979). Three of these deposits are located on the south Texas Coastal Plain and two in the intermontane basins of Wyoming (fig. 1). Those in Texas are the Benavides deposit in the Oligocene-Miocene Catahoula Tuff, Webb County, Texas, the Lamprecht deposit in the Miocene Oakville Sandstone Live Oak County, Texas, and the Panna Maria deposit in the Eocene Tordillo Formation Karnes County, Texas. One of the Wyoming deposits occurs in the Eocene Wind River Formation of the Shirley Basin, the other, in the Eocene Wasatch Formation of the Powder River Basin.

We have discussed in other papers (Reynolds and Goldhaber, 1978; Goldhaber and others, 1978), the geology, sample suite, iron-disulfide minerals, and sulfur isotopes of the Benavides deposit (fig. 2). The host rock for this deposit is devoid of fossil vegetal matter. Before mineralization, sulfide minerals were formed in the host rock by reaction of iron-bearing phases with  $H_2S$  introduced through a fault about 1.5 km downdip from the present roll front. These pre-ore sulfides (dominantly pyrite) are present as texturally simple forms and as replacements of detrital iron-titanium (Fe-Ti) oxide minerals. In reduced rock of core 2, (not profoundly affected by mineralization processes) pyrite composes about 90 percent or more of the iron-disulfide population and occurs most commonly as subhedral and euhedral crystals. In most samples of reduced rock in and beyond ore in cores 3 through 8, however, marcasite is more abundant than pyrite and occurs commonly as overgrowths on subhedral and euhedral pyrite crystals and as overgrowths on pyritized Fe-Ti oxide minerals. In ore, marcasite is

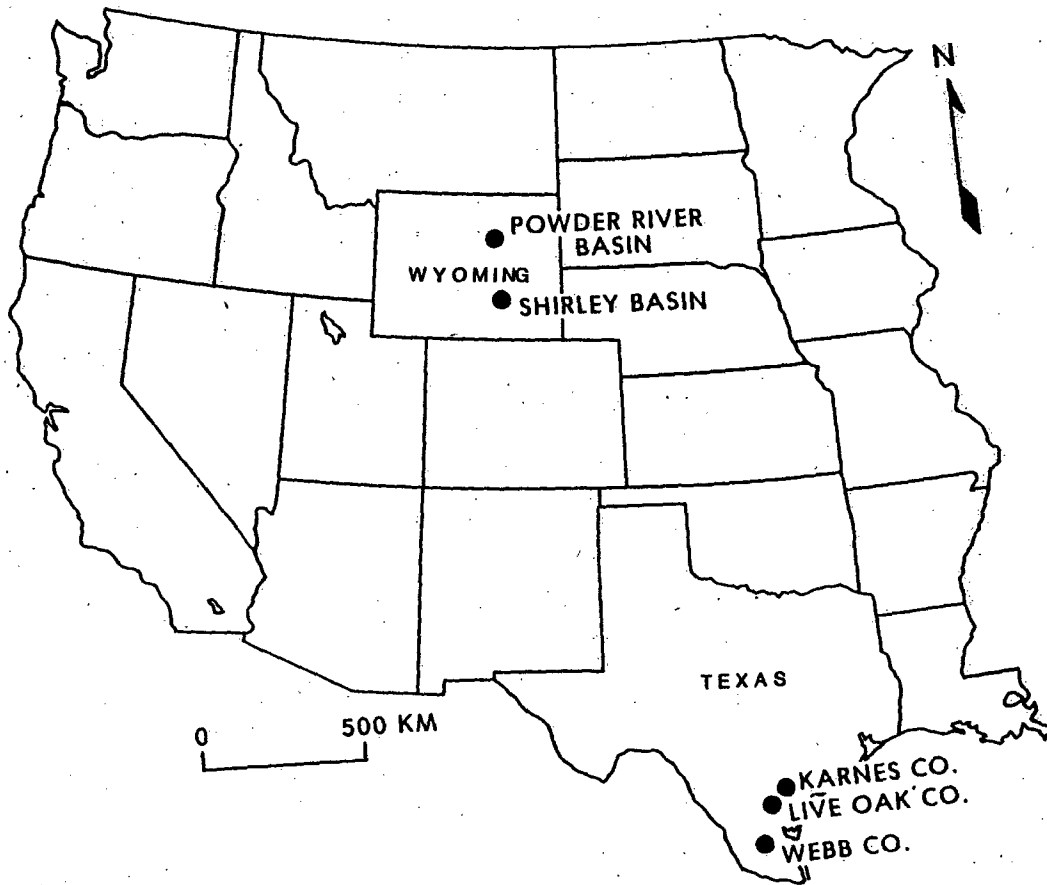


Figure 1.-- Map showing locations of the five roll-type uranium deposits studied.

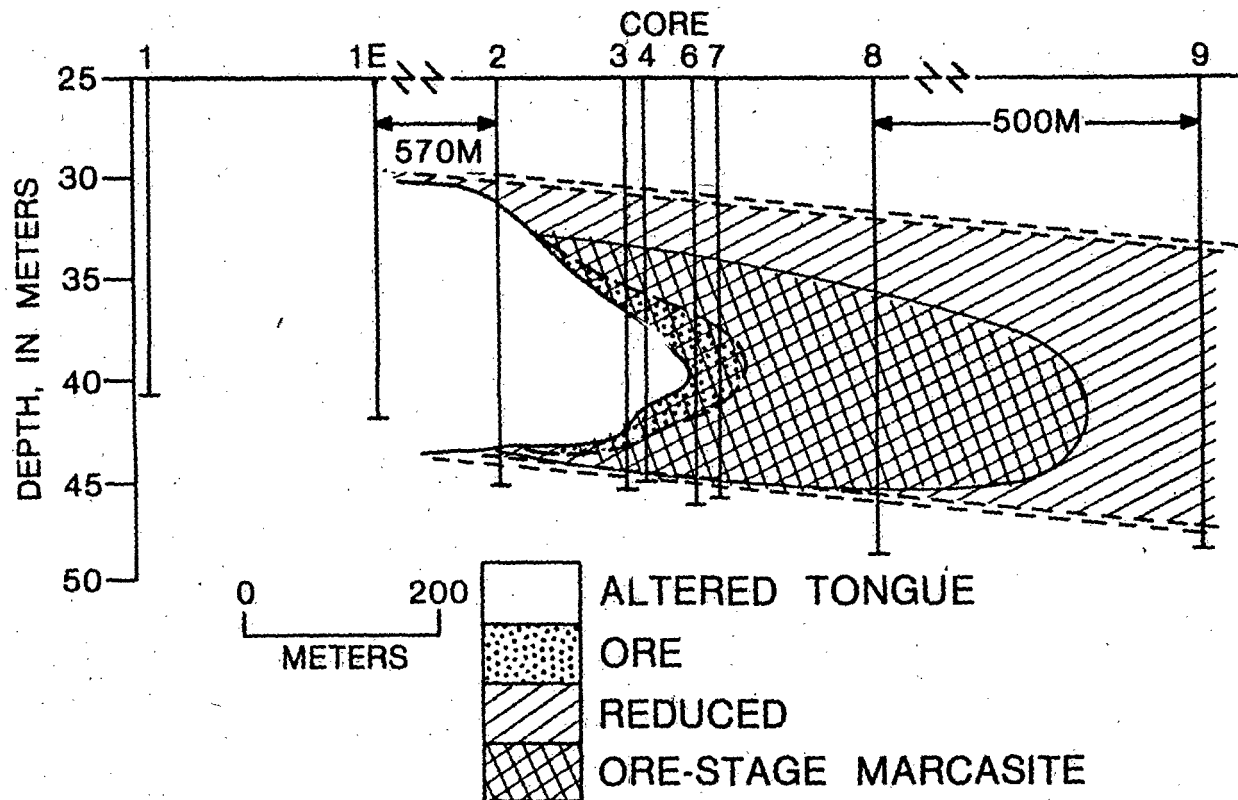


Figure 2.--Cross section of the Benavides deposit showing the distribution the core holes, major geochemical zones, and ore-stage marcasite (cross-hatched pattern).

intimately associated with uranium-bearing phases (Reynolds and others, 1977). These textural relationships point to marcasite as the dominant ore-stage iron-disulfide mineral. Ore-stage marcasite occurs as much as about 3 m vertically from limb ore and at least as far as about 200 m downdip from the redox interface (fig. 2).

Similar to the Benavides deposit, host rock of the Lamprecht deposit (also a fluvial sandstone devoid of organic matter) underwent an initial (pre-ore) stage of sulfidization related to fault-introduced  $H_2S$ . Akin to those of the Benavides, pre-ore iron-disulfide minerals are dominantly pyrite and occur in texturally simple forms (Goldhaber and others, 1978). Above and below the altered tongue, marcasite is more abundant than pyrite and increases in abundance (relative to pyrite) with increasing proximity to the limb ore where it composes as much as 90 percent of the total  $FeS_2$  population. In this part of the roll deposit, textural relationships among the iron-disulfide minerals are similar to those seen in rock enveloping the oxidized tongue of the Benavides deposit, in that marcasite occurs commonly as overgrowths on pyrite. The pyrite nuclei, constituting the earliest recognizable sulfide generation, consist of subhedral and euhedral crystals and of relict Fe-Ti oxide minerals replaced completely or in part by pyrite. Such textural relationships are observed as far as about 400 m downdip from the roll front in core 10 (fig. 3).

Unlike host rocks of the Benavides and Lamprecht deposits, the host rock of the Panna Maria is a coastal barrier sandstone body that is associated with lagoonal-facies sediment. Both facies contain locally abundant fossil vegetal matter. The host sand is bounded on its upper surface by a bed of mineralized lignite. Evidence for an extrinsic source of sulfide such as fault-introduced  $H_2S$  is lacking, and the earliest recognizable forms of iron-disulfide minerals



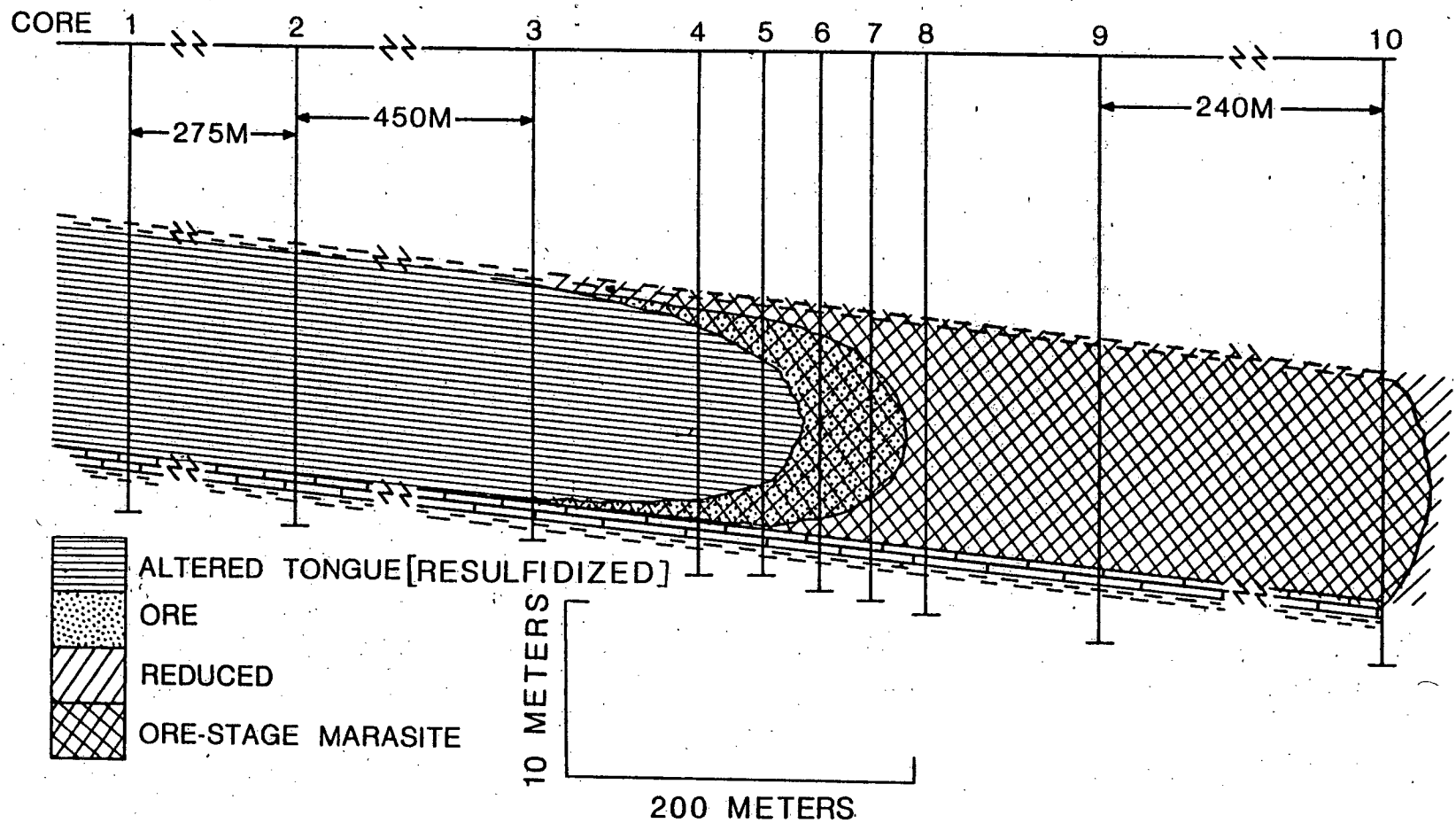


Figure 3--Cross section of the Lamprecht deposit showing the distribution of the core holes, major geochemical zones, and ore-stage marcasite (cross-hatched pattern).

deposit are diagenetic (probably biogenic) framboidal pyrite and aggregates of tiny pyrite crystals (about 10  $\mu$ m across).

One core penetrating the upper and lower limb ore and the altered tongue has been studied (fig. 4). Marcasite is abundant in the upper limb ore (60 percent of the  $\text{FeS}_2$  population), and marcasite increases in abundance with increasing proximity to the upper and lower redox boundaries (fig 4).

Marcasite is commonly present as overgrowths surrounding framboids and aggregates of pyrite crystals. In this core, however, marcasite is confined to the ore zones and does not even occur within the full extent of mineralized rock of the lower limb. In addition, pyrite overgrowths on pyrite and marcasite grains, and on aggregates of pyrite crystals have been observed throughout much of the reduced portion of the core and may represent ore-stage pyrite.

The Irigaray deposit comprises at least two superimposed rolls in different stratigraphic positions within arkosic sandstone host rock that locally contains abundant fossil organic matter. The stacked roll-front geometrics are best defined chemically and petrographically in core 7, in which the two altered tongues, each bounded by limb ore and separated by reduced barren ground, are present (fig. 5).

From slightly above the uppermost ore zone in core 7 and in stratigraphically equivalent beds in cores 8 and 9, pyrite constitutes the entire population of iron-disulfide minerals. This pyrite is the pre-ore sulfide generation and occurs as framboids, as subhedral to euhedral crystals, as interstitial cement, and as replacements of detrital Fe-Ti oxide minerals and plant fragments.

Marcasite, however, is typically confined to the ore zones, to rock adjacent to ore, and to beds downdip from and stratigraphically equivalent to the ore rolls. In ore, marcasite together with pyrite is intermixed with

# KARNES COUNTY TEXAS

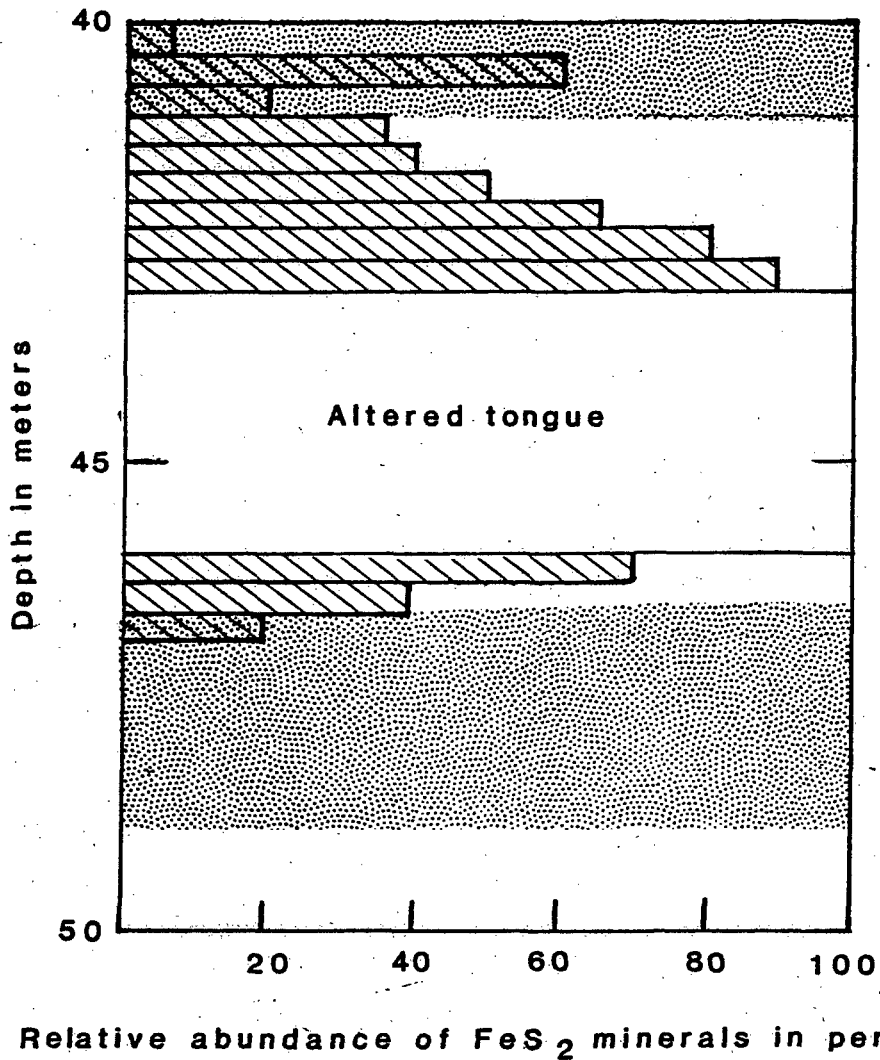


Figure 4.--Plot showing relative amounts of marcasite to the total FeS<sub>2</sub> population as a function of depth in one core of the Karnes County deposit. Mineralized rock is indicated by a stippled pattern.

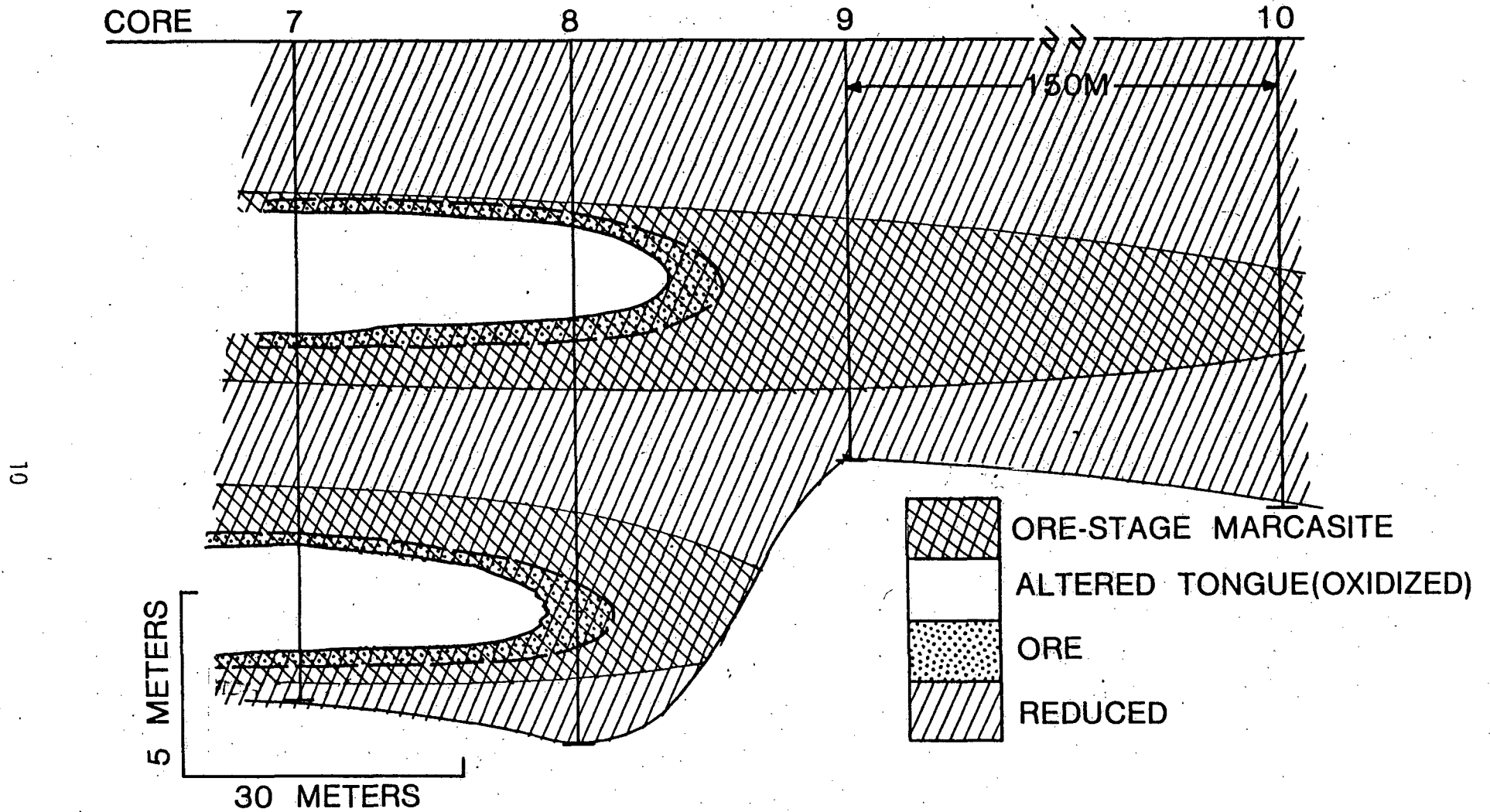


Figure 5.--Cross section of the eastern part of the Irigaray deposit (cores 7 through 10) showing the distribution of the core holes, major geochemical zones, and ore-stage marcasite (cross-hatched pattern).

uranium- and vanadium-bearing grains; and at the lower redox boundary of the deeper ore roll in core 7, marcasite is intergrown with ferroselite.

Marcasite is present but confined to within about 1.5 m of limb ore in reduced barren ground between the two ore rolls in core 7 where it occurs as overgrowth rims on pre-ore pyrite. Volumetrically minor amounts of marcasite as thin rims on framboids of pyrite are found downdip in front of the ore rolls in cores 9 and 10 (fig. 5). Samples that contain marcasite also contain pyrite as distinct overgrowth rims on framboids and on plant fragments previously replaced by pyrite, and as intergrowths within marcasite rims. The paragenetically late pyrite appears to be contemporaneous with ore-stage marcasite.

Akin to the Irigarary, the host rock of the Shirley Basin deposit (Petrotonics section 9 pit) locally contains fossil vegetal matter. The distribution of nineteen samples collected by E. N. Harshman across the reduced barren, ore, and oxidized zones of the uranium roll is shown in figure 6. Harshman (1972) described textures and occurrences of the iron-disulfide minerals in these samples and he recognized pre-ore pyrite and ore-stage marcasite and pyrite. He also noted that, in ore, the abundance of marcasite decreased with increasing distance downdip from the redox boundary (samples 19 to 12).

Our supplemental study of the same 19 samples supports Harshman's interpretations and has also resulted in the recognition of ore-stage sulfides in reduced barren ground. Ore-stage marcasite is present as overgrowth rims on pre-ore framboidal pyrite as far as 2 m in front of the ore roll. Marcasite, of indeterminate origin, occurs, but is rare 8 m from ore and is absent 10 m from ore (sample 4). In addition, pyrite forms distinct rims around framboids throughout reduced barren ground and may represent ore-stage pyrite.

# SHIRLEY BASIN, WYOMING

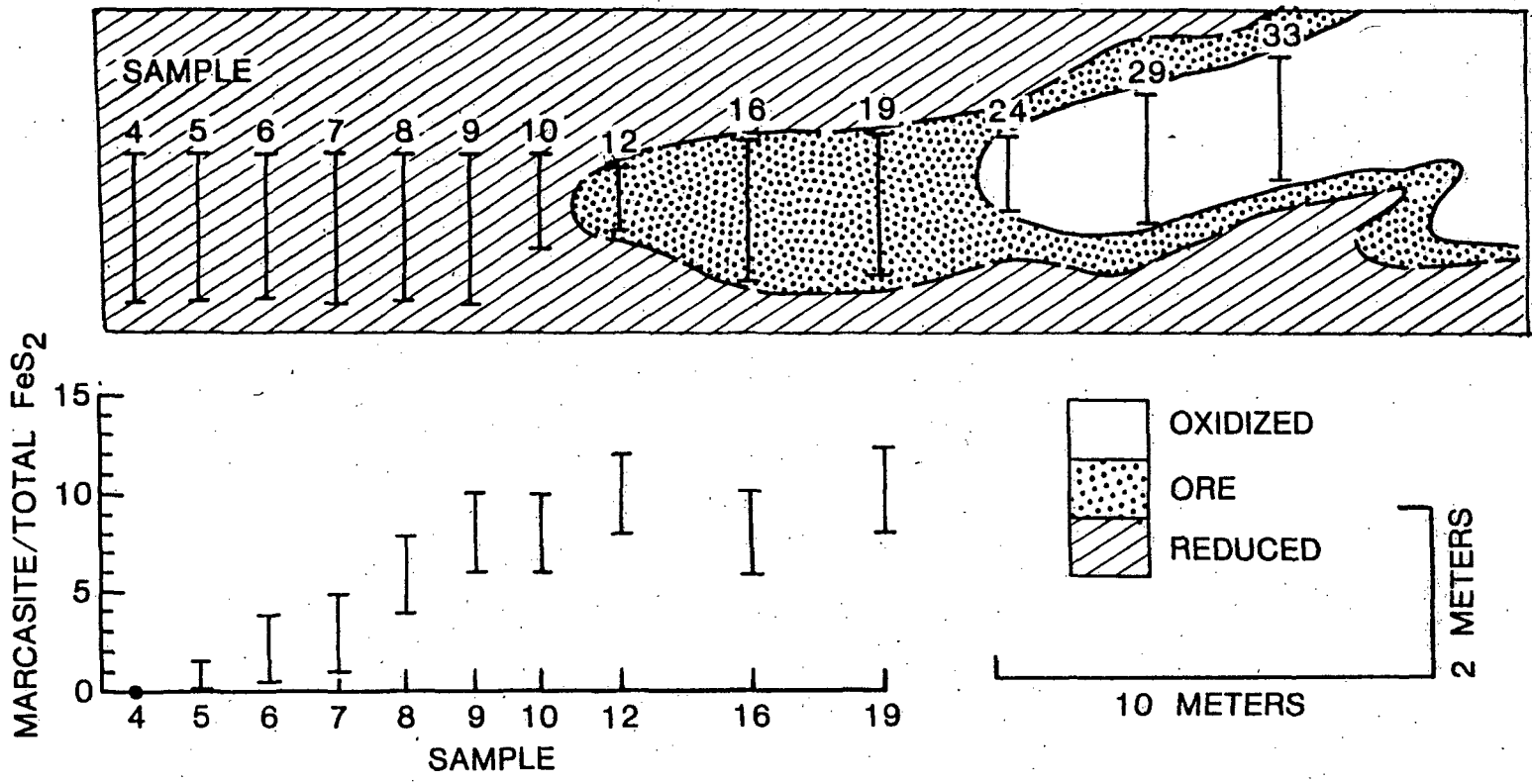


Figure 6.--Cross section of the Petrotomics section 9 pit, Shirley Basin, showing the distribution of samples and geochemical zones discussed in text (modified from Harshman, 1972).

## Discussion of Marcasite Genesis

In order to evaluate the significance of the observed marcasite distribution with regard to the genesis of the uranium deposits, it is necessary to have an understanding of the origin of the marcasite itself. In this section we review the available experimental and observational data on the origin of marcasite. Although the roll-type deposits presumably form at near-surface temperatures (T) and pressures (P), marcasite forms over a relatively large T range, and data for the entire T range is valuable and will be discussed.

For some time it has been argued that pyrite and marcasite are not strictly dimorphs, but rather, that marcasite is slightly sulfur deficient (Buerger, 1934, Rising 1974). This hypothesis was originally formulated (Buerger 1934) on the basis of chemical analyses of the two phases. Reconsideration of the analytical data (Kullerud and Yoder, 1959) demonstrated that conclusions based upon these data are at best equivocal. However, additional lines of evidence tend to support the conclusion that marcasite is a sulfur-deficient phase. Kelly and Turneaure (1970) documented the alteration sequence in Bolivian tin deposits: hexagonal pyrrhotite ( $\text{Fe}_9\text{S}_{10}$ ) monoclinic pyrrhotite  $\text{Fe}_7\text{S}_8$  marcasite ( $\text{FeS}_{2-x}$ ) pyrite ( $\text{FeS}_2$ ). Although some overlap was observed between marcasite and pyrite deposition, the sequence nevertheless suggests progressive enrichment in sulfur.

Kullerud (1966) heated marcasite with elemental sulfur in a dry system at 2Kb pressure and  $T > 150^\circ\text{C}$  and observed that pyrite initially formed on the surface of marcasite. With time, the conversion to pyrite moved inward towards the center of the marcasite grains. These results were interpreted as indicating that sulfur addition to marcasite forms pyrite. Rising (1974) documented the inversion of marcasite to pyrite at temperatures between 157 and  $331^\circ\text{C}$  at sulfur fugacities buffered by the assemblage pyrite-pyrrhotite.

He noted a marked dependence of the rate of this reaction on marcasite grain size and concluded that the results were best explained by a process of sulfur diffusion into marcasite leading to pyrite.

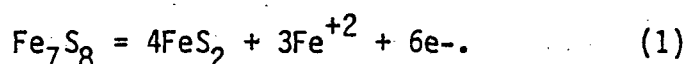
If marcasite is in fact sulfur deficient, it could have a stability field intermediate between the pyrite and pyrrhotite fields (Rising, 1974). In a series of experiments designed to test this hypothesis, Rising was able to demonstrate that marcasite was not deposited from a solution equilibrated with pyrite and pyrrhotite. Marcasite, therefore, is metastable with respect to pyrite at  $T > 157^{\circ}\text{C}$ . This conclusion was extended over a wider temperature range (5 to  $700^{\circ}\text{K}$ ) by Gronvold and Westrum (1976) from calculations based on heat-capacity measurements of the two phases. It follows (Gronvold and Westrum, 1976) that marcasite is thermodynamically metastable with respect to pyrite over the entire temperature region of its geologic occurrence and must therefore owe its formation to kinetic factors.

The major identifiable hypothesis for the kinetic favorability of marcasite over pyrite is that of Rickard (1969), who argued that marcasite forms from the reaction of mackinawite ( $\text{FeS}_{0.9}$ , tetragonal) and solid elemental sulfur, whereas pyrite formation occurs via reaction of polysulfide ions  $\text{S}_x^{-2}$ , where  $x$  is typically 3 to 6) and ferrous iron. Polysulfide ions and ferrous ions are produced during the dissolution of mackinawite and thus it was argued that it could be a precursor to both marcasite and pyrite. In support of the proposed mechanism for marcasite formation, Rickard cites an experiment in which mackinawite was heated in a dry system with elemental sulfur. Marcasite and minor amounts of elemental sulfur were observed as products when the mixture was heated to  $70^{\circ}\text{C}$  for two months. When heated to higher temperatures, the same initial reaction mixture produced marcasite and pyrrhotite ( $100^{\circ}\text{C}$ , 24 hours), or pyrite ( $150^{\circ}\text{C}$ , 48 hours). Furthermore, in

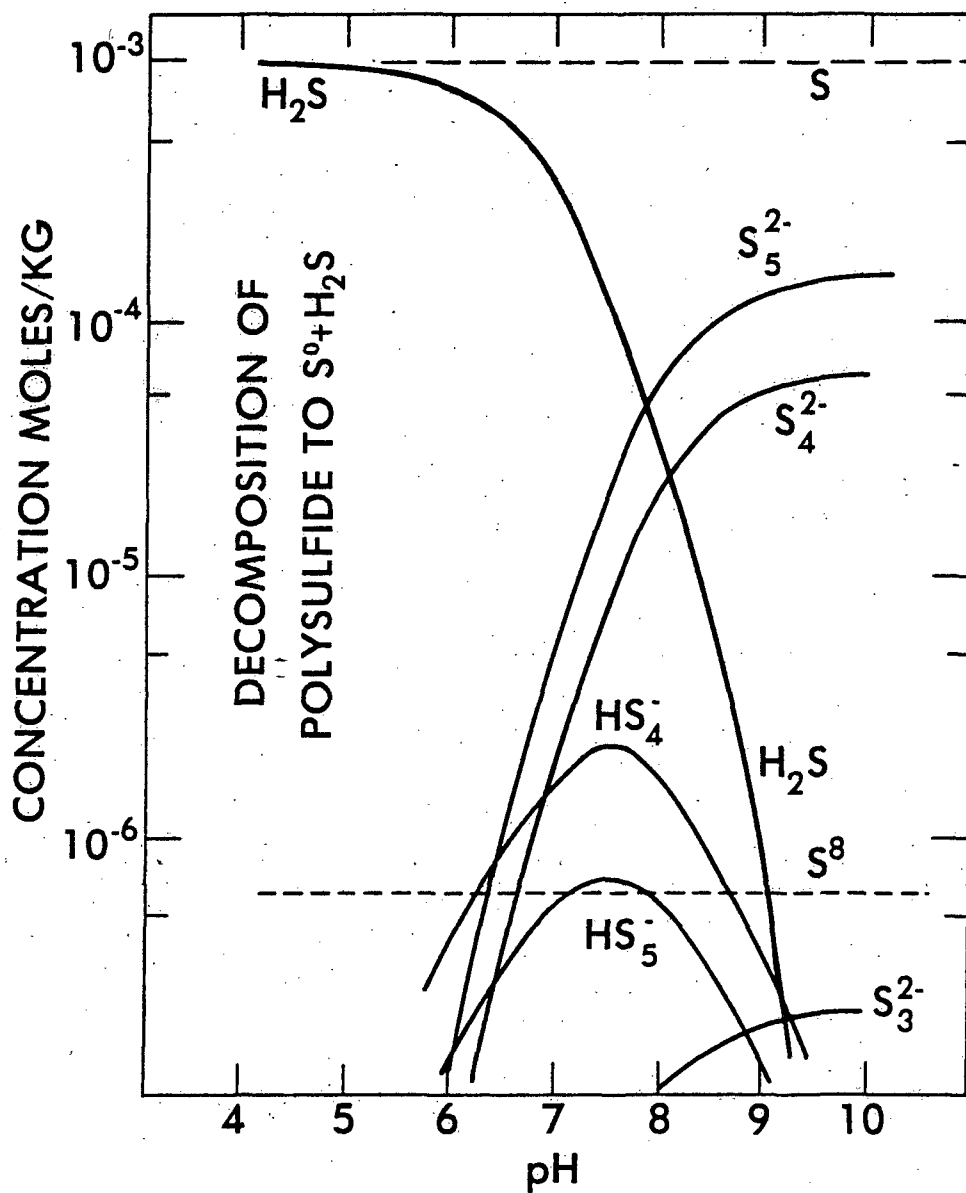


studies of the reaction between ferrous iron and sodium polysulfide in aqueous solution, Rickard found that the proportion of marcasite to pyrite increased with decreasing pH. This effect was attributed to the decomposition of polysulfide ions at moderate to low pH values. Polysulfide ion decomposition is illustrated in figure 7, modified from Boulegue (1974), in which the equilibrium distribution of sulfur species is shown as a function of pH for fixed total dissolved sulfur at 25°C. Polysulfide ion concentration decreases abruptly below pH 8. Invariably, however, the polysulfide decomposition reaction occurs under nonequilibrium conditions and leads to a mixture of colloidal sulfur and H<sub>2</sub>S rather than H<sub>2</sub>S and HS<sup>-</sup> as shown on figure 7.

In addition to its postulated formation from mackinawite, marcasite is known to be produced as an alteration product of pyrrhotite. Kelly and Turneaure (1970) carefully documented the textural relationships between pyrrhotite and marcasite. They noted that the marcasite forming from pyrrhotite is highly porous and pointed out that if pyrrhotite alters via loss of iron (a constant sulfur process), a 26% volume increase would occur; this is consistent with the observed textures. This reaction may be written as:



Iron loss is further suggested by the association of marcasite with siderite (Kelly and Turneaure, 1970) which apparently consumed a portion of the iron produced by equation (1). A similar mechanism of iron loss from pyrrhotite to produce marcasite (and pyrite) was confirmed by Fleet (1978). Ramdohr (1975) reviewed the low temperature weathering of pyrrhotite which yields FeS<sub>2</sub> (pyrite and marcasite) with a characteristic range of textures, and concluded that the major product of this reaction may be pyrite rather than marcasite.



DISTRIBUTION OF SULFUR SPECIES IN  
THE SYSTEM  $\text{H}_2\text{S} - \text{S}_8 - \text{H}_2\text{O}$  AS A  
FUNCTION OF pH at  $25^\circ\text{C}$

Figure 7.--Equilibrium distribution of dissolved sulfur species in the system  $\text{H}_2\text{S} - \text{S}_8 - \text{H}_2\text{O}$  as a function of pH at  $25^\circ\text{C}$ . Presence of solid elemental sulfur produced under disequilibrium conditions by polysulfide ion disequilibrium is indicated schematically.

Although it is clear from the above that marcasite may form from alteration of a "monosulfide"-type phase (mackinawite or pyrrhotite), we believe that the major pathway for marcasite formation in sedimentary uranium deposits does not involve these mechanisms. An important consideration in reaching this conclusion is the complete lack of textures in polished section of the type observed from authentic cases of monosulfide alteration. There are, however, additional lines of evidence and these are discussed below.

Of the experimental studies on marcasite synthesis, the most extensive and well documented work to date was done by Allen and his coworkers (Allen and others, 1912; Allen and others, 1914). They succeeded in synthesizing marcasite over a wide range of temperature (25-300°C). Their experiments conducted at 25°C produced 96% marcasite and 4% pyrite and involved the following initial reactants:  $\text{FeSO}_4$ , 0.18 molar;  $\text{H}_2\text{SO}_4$ , 0.0015 molar; elemental sulfur; and  $\text{H}_2\text{S}$  at 1 atmosphere pressure. We have calculated the saturation state of the pertinent iron-sulfide phases for these starting conditions (for details of the calculation see below). When compared to the solubility product for mackinawite (Berner 1967) it may be shown that the initial solution was undersaturated with respect to mackinawite. As precipitation of marcasite proceeded, the degree of undersaturation with mackinawite increased. It may be concluded therefore, that mackinawite could not have been an intermediate in marcasite formation in this experiment.

On the other hand, where mackinawite and an iron-disulfide phase are observed forming together, the iron disulfide is almost invariably pyrite rather than marcasite. This is true of experimentally produced sulfides (Berner 1964) and of natural occurrences of sedimentary sulfides. Recent nearshore marine sediments commonly contain abundant pyrite as well as "monosulfide"-type iron sulfide phases. The pathway for pyrite formation is known

to involve both mackinawite and zero-valent sulfur species as intermediates (Berner, 1970; Sweeney, 1972; Rickard, 1969; Goldhaber and Kaplan 1974), and to proceed both by sulfidization of a monosulfide phase and direct precipitation from solution (Goldhaber and Kaplan, 1974; Howarth, 1979). Yet despite the complexity and variety of geochemical transformations involving iron and sulfur in recent marine sediments, no marcasite has been reported.

Of particular interest with regard to the conversion of iron monosulfide to iron disulfide is the common occurrence of the framboidal texture in marine (Love and Amstutz, 1966; Sweeney and Kaplan, 1973) and nonmarine (Valentyne, 1963) sediments. Experimental evidence on the mechanism of framboid formation (Sweeney and Kaplan, 1973) has demonstrated that precursor spherical iron monosulfides are converted to pyrite by addition of elemental sulfur. Because marcasite framboids have not been recognized from marine sediments, this constitutes a further line of evidence that sulfidization of the monosulfide mackinawite to disulfide favors pyrite.

We conclude from the preceding analysis that environments which favor mackinawite precipitation are not conducive to marcasite formation, and that pyrite is the end product of sulfur-iron transformations in such systems. Because mackinawite is many orders of magnitude more soluble than either pyrite (Berner, 1967) or marcasite (Gronvold and Westrum, 1976) it follows that high degree of supersaturation with respect to the  $\text{FeS}_2$  phase favors pyrite formation over marcasite.

As was the case with mackinawite, the strongest evidence that pyrrhotite need not be involved in marcasite formation comes from the work of Allen and others, (1914). Their most extensive data were obtained at 200°C and 300°C in runs which lasted 1-4 days. The results from 200°C are reproduced in figure 8A. Fixed amounts of ferrous sulfate, elemental sulfur, hydrogen sulfide, and

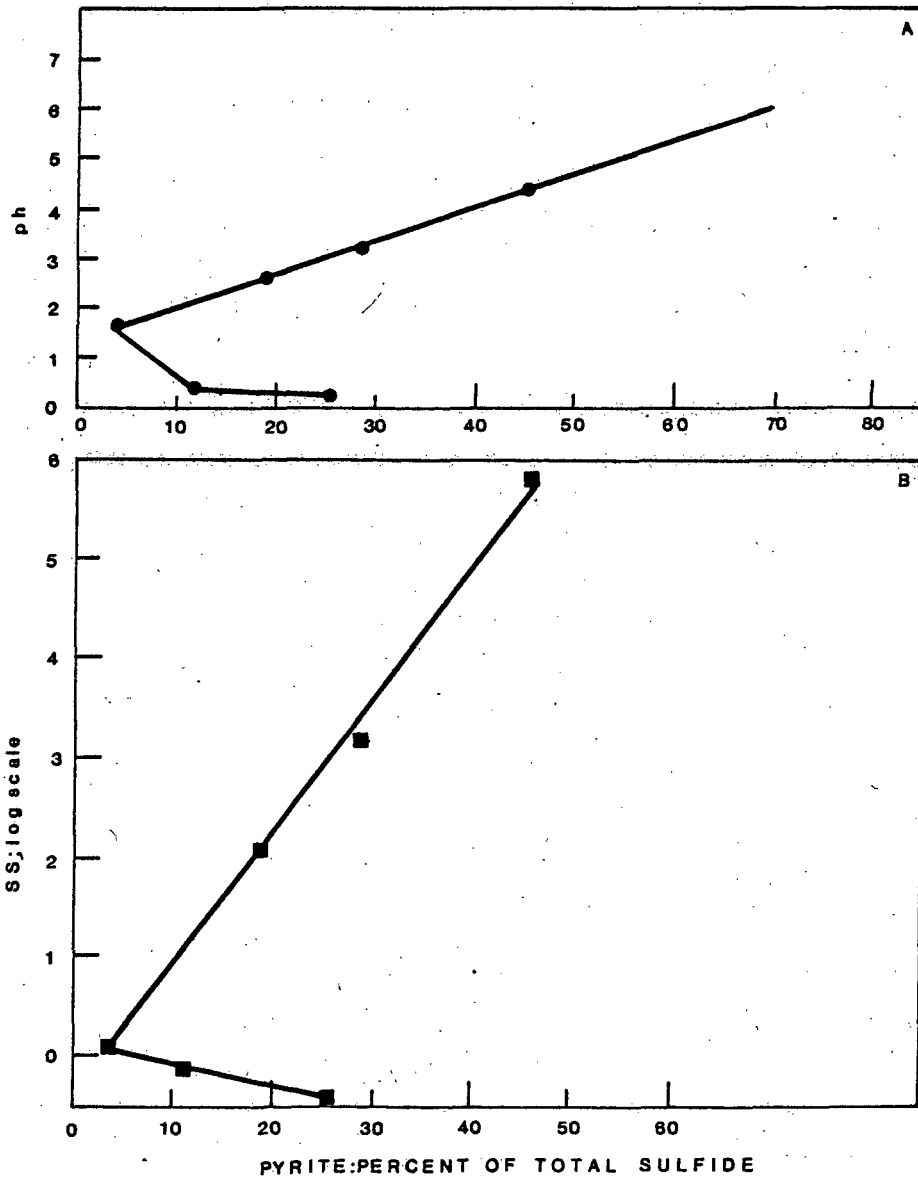


Figure 8.--A, Plot of percentage yield of pyrite of total iron disulfide as reported by Allen and others (1914) for experiments at 200°C against the initial pH of their starting mixture calculated in this paper for 200°C. B, Plot of the percentage of pyrite of total iron disulfide for the same experiments as A), against the saturation state of the initial solutions with respect to pyrrhotite at 200°C (see equation 2).

water were heated with various amounts of sulfuric acid. They found that the proportion of marcasite to pyrite increased with increasing initial acid concentration in the range 0.01 to 0.20 molar (pH 4.4 to 1.6), whereas pyrite content increased at acid concentrations greater than 0.20 molar (pH 1.6). We have reanalyzed the data of Allen and others, (1914) in order to determine the initial saturation state of the solution with respect to pyrrhotite at 200°C, by solving a simultaneous set of equations for all protolytic equilibria in the system in terms of the hydrogen-ion activity. Activity coefficients were calculated using an extended form of the Debye-Huckel equation (Helgeson, 1967) and an initial estimate of the ionic strength. The self-consistent set of thermodynamic data from Helgeson (1969) was used for the required ionization equilibria, stability of phases, and solubility of H<sub>2</sub>S. In some cases a second iteration of the calculation was required to correct the initial ionic strength estimate. Ferrous ion complexing with sulfate and bisulfide ions is minor and was neglected (Rising, 1974; Crerar and Barnes, 1976). Hydrolysis of elemental sulfur to H<sub>2</sub>S plus H<sub>2</sub>SO<sub>4</sub> is quantitatively insignificant under the conditions of the experiments (Ellis and Giggenbach, 1971). Figure 8B is a plot of the results of this calculation. The saturation state (S.S.) of pyrrhotite, expressed as the log of the initial ratio of activity of ferrous iron times activity of sulfide ion in the experimental solution to the same product for pyrrhotite saturation (equation 2), is plotted against the percentage of pyrite observed in

$$\text{S.S.} = \log \frac{(\text{Fe}^{+2}) (\text{S}^{-2})}{K_{\text{sp}}(\text{T})} \quad (2)$$

the final products. Values of the S.S. >0 indicate supersaturation with respect to pyrrhotite; 0 indicates saturation, and values <0 indicate under-

saturation. Clearly the percentage of marcasite is inversely related to the degree of oversaturation over most of the pH range of the experiments. The maximum experimental percentage of marcasite (96%) occurs when the initial solution is only slightly over saturated with respect to pyrrhotite at 200°C. As acid is added to the starting mixture, undersaturation with respect to pyrrhotite occurs and the pyrite content increases, although marcasite is still by far the dominant phase. The implications of the results at pH 1.67, which yielded 96 percent marcasite are of particular interest. As this solution was approximately just saturated with pyrrhotite, the precipitation of any iron-sulfide phase decreased iron and sulfide activity such that undersaturation with pyrrhotite occurred (the pH also decreases during the course of the precipitation; see Allen and others 1914). Furthermore, calculations (not illustrated) using the same starting reactant concentrations demonstrate that, for a given set of conditions, the system becomes progressively less saturated with pyrrhotite as the temperature decreases. The mixture which produced 96 percent marcasite was never supersaturated with pyrrhotite, and pyrrhotite thus cannot be an intermediate in marcasite formation at pH 1.67 or any lower pH. On the other hand, the data are consistent with pyrrhotite serving as a reactive and transient intermediate in pyrite formation at pH >1.67 in a manner analogous to the behavior of mackinawite at lower temperature. Reaction of pyrrhotite with elemental sulfur has independently been shown to rapidly produce pyrite at temperatures greater than 80°C (Rickard, 1969; Sweeney and Kaplan, 1973; Allen and others, 1912). This process must be very rapid at 200°C as pyrrhotite was not observed among the products in runs lasting only a few days. The increase in pyrite below pH 1.67 may represent the inversion of the earliest marcasite to pyrite. This inversion is relatively rapid at 200°C (Rising, 1974). An additional observation concerning

the results of Allen and co-workers is that iron species in solution was not affecting the results as iron was present as  $\text{Fe}^{2+}$  only.

Unfortunately, the demonstration that marcasite can form without a mono-sulfide precursor (mackinawite or pyrrhotite) still leaves undefined the mechanism by which marcasite does form. One probable pathway may be identified, in which marcasite is precipitated by a direct reaction of aqueous sulfide and ferrous iron with zero valent (elemental) sulfur. Rising (1974) pointed out that elemental sulfur as a separate phase was a reactant in essentially all successful marcasite synthesis. Our own experimental work bears directly on this question. We saturated a mixture of 0.18M acidified ferrous chloride and excess USP flowers of sulfur with  $\text{H}_2\text{S}$  (pH<4) in a ground-glass stoppered bottle. No precipitate formed initially, but when the mixture was heated to  $80\pm 5^\circ\text{C}$  a black precipitate started to form at the interface between the solution and the sulfur floating on the surface of the liquid. This black material gradually detached itself from the sulfur layer and accumulated at the bottom of the bottle to be replaced by additional precipitate formed at the sulfur-solution interface. When examined by X-ray diffraction and visually in polished sections, the precipitate was found to consist dominantly of marcasite (>90 percent) in thin sheets which still retained the irregular morphology of the sulfur substrate.

Control of iron-disulfide morphology, if related to the presence of a separate elemental sulfur phase, is not likely to be influenced by the crystal structure of this sulfur because marcasite has been produced experimentally at temperatures above the transition from orthorhombic to monoclinic sulfur ( $95^\circ\text{C}$ ), above the melting point of monoclinic sulfur ( $114^\circ\text{C}$ ), and even above the temperature at which liquid sulfur undergoes a polymerization reaction ( $160^\circ\text{C}$ ).



Further corroborative evidence for the proposed significance of solid elemental sulfur in marcasite formation is provided by the temperature dependence of the pH at which one hundred percent marcasite is produced under laboratory conditions. At 200°C, this pH is approximately 1.67 (fig. 8). At room temperature this pH rises to about 4.4 (Rickard 1969). It has been shown (Barnes and Kullerud 1961) that, with all other conditions held constant, the stability field of elemental sulfur itself shrinks to progressively lower pH values with increasing temperature, thus necessitating the lower pH values to stabilize marcasite.

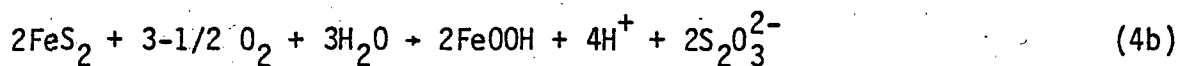
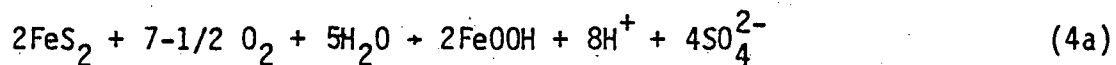
Although the mechanism of marcasite formation in the presence of elemental sulfur (and the absence of polysulfides) seems well founded on the basis of laboratory studies, certain occurrences of marcasite in nature raise a note of caution that other mechanisms or pathways may be possible.

Marcasite commonly forms as replacements of woody material in which the original cell structure is pseudomorphically retained (Edwards and Baker, 1951). It is difficult to envision a process by which elemental sulfur could be transported to and localized within these cell walls, although perhaps sulfur formation via acidification of a polysulfide solution by a process occurring within or near the cell wall might be invoked.

In summary, marcasite formation is favored by low pH. This pH effect operates via pH control on sulfur geochemistry. Reaction between polysulfide and ferrous ions favors pyrite or iron monosulfide and further sulfidization of monosulfide likewise leads to pyrite. Interaction of ferrous iron, aqueous sulfide, and solid elemental sulfur produces marcasite.

## Conditions of Marcasite Formation Related to Uranium Mineralization

At the redox interface of roll-type uranium deposit, oxygen dissolved in ground water reacts with oxidizable substances in the solid phases. These reactions remove oxygen from solution and produce soluble products that are then carried down dip into reduced rock as well as insoluble products which remain in the solid phase. The major reduced phases reacting with and consuming this oxygen are iron disulfide (Granger and Warren, 1978) and organic matter. Hydrogen ions are produced by both these reactions (equations 3 and 4a and b)



The hydrogen ions produced by these reactions will reduce the pH in the vicinity of the redox interface (Harshman 1972). The magnitude of this pH decrease depends upon a number of complex and interrelated factors. The rate of hydrogen-ion generation is related to the rate of delivery of dissolved oxygen to the redox boundary. Since the oxidizable substances in a given volume of uranium host rock are typically present far in excess of the concentration of dissolved oxygen present (Granger and Warren 1978), oxygen supply becomes the limiting factor in the oxidative process (equations 3 and 4a and b). This factor is more important in determining hydrogen-ion production than the ratio of organic matter to  $\text{FeS}_2$  undergoing oxidation, as both reactions

lead to approximately 1 mole of  $H^+$  produced per mole  $O_2$  consumed (actually 1 to 1.07). The controls on the rate of delivery of  $O_2$  to the redox boundary are discussed by Granger and Warren (1978), and are in general the same factors that govern bulk transport of the ground water itself, but also include the initial concentration of  $O_2$  in recharge waters and partial removal of  $O_2$  in the soil zone. Deposits forming in similar host rock settings with a high hydrostatic head or high permeability will have a proportionally higher rate of hydrogen-ion generation than deposits forming from ground waters with identical concentration of  $O_2$  but lower head and permeability. Unfortunately, we do not have sufficient information on the paleo hydrostatic head or permeability of the deposits studied to make a valid comparison between them. We can point out that the length of the altered (oxidized) tongue varies widely between deposits. In the Shirley Basin, for example, oxygenated ground water would have had to travel approximately 8.1 km after entering the recharge area before intersecting the present position of the roll-front. In the Lamprecht deposit the corresponding distance is only 2 km, and the Irigary is probably intermediate between these two extremes (E. S. Santos, oral commun., 1979). During transport of oxygenated ground water toward the redox interface slow chemical or biochemical reactions might remove appreciable amounts of  $O_2$  and lead to less intense hydrogen-ion production at the redox interface. Included among these possible reactions are: oxidation of resistant ferrous-iron-bearing phases and oxidation of residual unreacted organic matter in the host bed or in the adjacent confining beds at the upper and lower margins of the host unit.

Hydrogen ions generated by oxidative processes at the redox boundary will be subjected to a variety of removal mechanisms as the low-pH ground water flows into reduced rock. These include interaction with indigenous host-rock

constituents; destruction of feldspars, exchange reactions on clays and destruction of detrital and (or) authigenic carbonate. Immature arkosic host sands, as well as sands with an appreciable clay matrix, will presumably be a more effective sink for hydrogen ion than more mature quartzite sands.

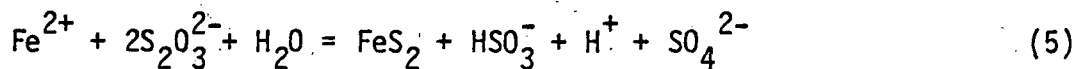
An additional and potentially major influence on pH of ground water in reduced rock is governed by the presence or absence of anaerobic bacterial metabolism. A number of studies, reviewed by Goldhaber and Kaplan (1974), have shown that bacterial sulfate reduction is a dominant influence on the pH of pore fluids of recent marine and non-marine sediments. Because sulfate is a charged ion, its removal from solution by reduction requires that the products of this metabolic activity ( $\text{HS}^-$ ,  $\text{HCO}_3^-$ ) must likewise be charged to maintain electrical neutrality. Aqueous sulfide is highly reactive and will be rapidly removed to form  $\text{FeS}$  and  $\text{FeS}_2$ , thus leaving the charge in solution residing on aqueous carbonate species such as  $\text{HCO}_3^-$  plus  $\text{CO}_3^{2-}$ . These reactions serve to maintain the pH at relatively high values within the range 7 to 8.4 (Goldhaber and Kaplan, 1974). This behavior contrasts sharply with what will occur via aerobic destruction of organic matter which produces an acidic species,  $\text{CO}_2$  (equation 3), or destruction of organic matter by anaerobic process in the absence of sulfate reduction (Martens and Goldhaber, 1978).

The higher pH values which are established in the presence of sulfate-reducing bacteria produce polysulfide ions in much greater concentration than solid elemental sulfur and thus favor pyrite over marcasite precipitation. In addition, these higher pH values cause a shift in sulfide equilibria away from  $\text{H}_2\text{S}$  and towards  $\text{HS}^-$  (and  $\text{S}^{2-}$ ) ions (fig. 7). This has the effect of increasing the degree of saturation of these solutions with iron-monosulfide phases (such as mackinawite) which will then precipitate in preference to either pyrite or marcasite (Goldhaber and Kaplan 1974, Howarth 1979). Further sulfi-

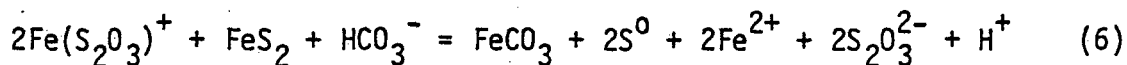
dization of this mackinawite will, as has been discussed previously, lead to pyrite preferentially.

Polysulfide ions are apparently a common constituent of sulfidic ground waters in organic-rich aquifers (Boulegue, 1977) as well as the pore fluids of organic rich recent marine sediments (Berner, 1963). These environments bear a strong geochemical resemblance to the reducing side of a roll front (or unaltered rock) within an organic-matter-bearing uranium-host sandstone, and the ground water participating in the ore-forming process should, therefore, contain polysulfides except perhaps locally near the redox boundary where the pH may decrease to 6 or less (fig. 7).

In ore forming environments without organic matter or in which heterotrophic bacterial metabolism is otherwise inhibited, geochemical sulfur transformations may be expected to proceed via different pathways than in organic-rich hosts. Granger and Warren (1969, 1974) have postulated a range of possible mechanisms. They hypothesize that pyrite oxidation does not lead exclusively to sulfate (equation 4a) but rather, that it produces metastable and chemically reactive oxidation products (such as thiosulfate,  $S_2O_3^{2-}$  equation 4b; and sulfite  $SO_3^{2-}$ ) whose oxidation state is intermediate between sulfate and sulfide. These ions would be carried by oxygen-depleted ground water. Once in the reducing environment, thiosulfate or related metastable species could represent the sulfur source for ore-stage pyrite by reacting with ferrous iron according to a disproportionation reaction of the type:



They further propose (Granger and Warren, 1974) a link between metastable sulfur species and production of elemental sulfur (equation 6);



Elemental sulfur production is postulated to occur during oxidation of iron disulfide by ferric iron contained in a ferric-thiosulfate complex. In order to test for production of metastable sulfur species during pyrite oxidation, we have carried out a series of inorganic pyrite-oxidation experiments. The studies indeed confirm that metastable sulfur oxy-anions are produced by this process (Goldhaber and Reynolds, 1977). Some results of these experiments, which were carried out under conditions of constant pH (using a pH stat), temperature, and oxygen concentration are summarized in figure 9. This figure illustrates the distribution of soluble sulfur species as a percentage of the total sulfur in solution arising from short-term (less than 2-day) oxidation experiments. Clearly, species such as thiosulfate and sulfite are dominant at the higher pH values, whereas tetrathionate ( $\text{S}_4\text{O}_6^{2-}$ ) and sulfate become dominant as the pH at which oxidation occurs is decreased. Because pyrite oxidation at the roll front is likely to occur at pH values less than 7, it is necessary to consider the possible geochemical role of the tetrathionate ion. Whereas thiosulfate can be shown to react with ferrous iron to produce an iron-sulfide phase (equation 5) the same is apparently not so for tetrathionate. Ferrous-tetrathionate solutions were prepared in our laboratory and they produced a yellow nonsulfide precipitate. However, tetrathionate reacts rapidly with dissolved sulfide to produce thiosulfate and colloidal elemental sulfur (equation 7).

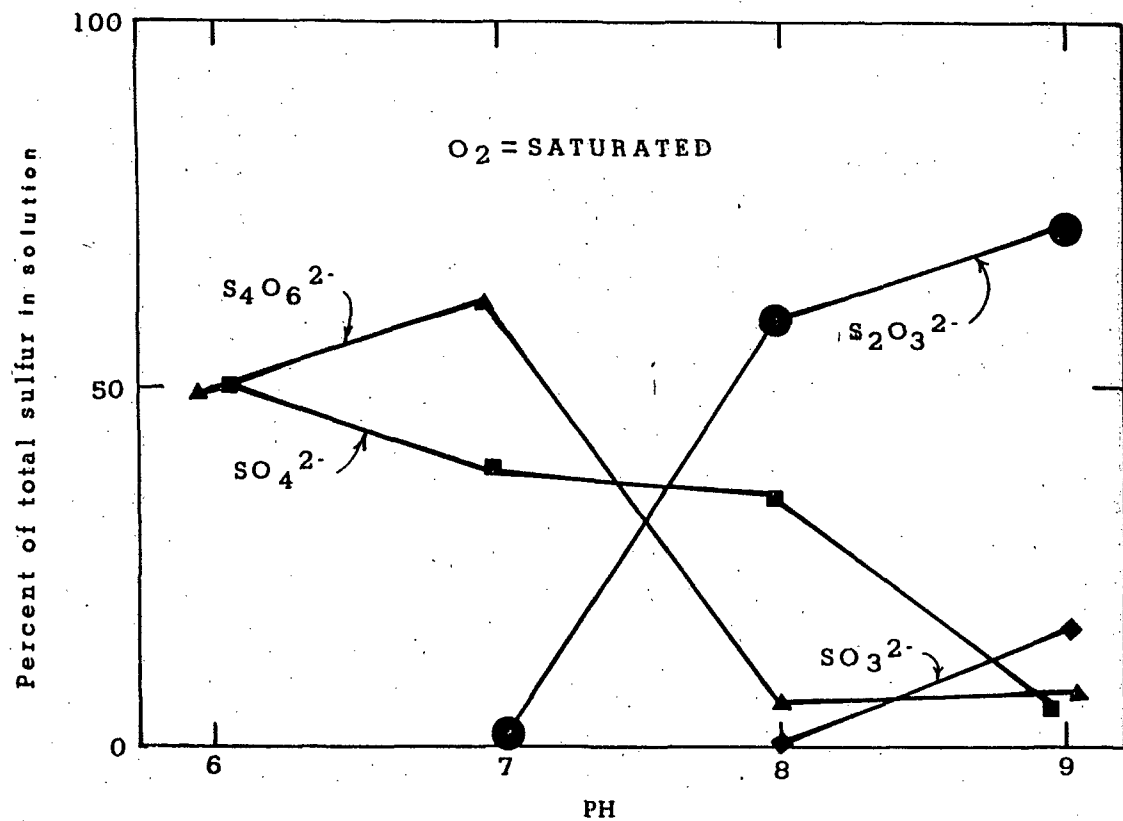
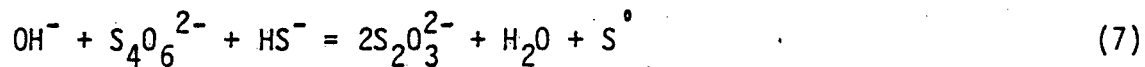


Figure 9.--Results of pyrite oxidation experiments conducted at 30°C at constant pH (in a pH stat) and with  $O_2$  at saturation. Data are expressed as percentage of the total sulfur in solution represented by a given species during the course of a run against pH of the run. The variation of this percentage during an experiment is shown as a vertical bar.



This reaction is favored by increasing pH (Kilroy, 1979) and thus tetrathionate conversion to thiosulfate may be more complete as solutions move away from the redox boundary and are progressively neutralized by hydrogen-ion interactions with the host rock.

Thiosulfate itself, whether produced directly by pyrite oxidation (equation 4b, fig. 9) or by chemical transformation of tetrathionate (equation 7), is also a source of elemental sulfur. This is so because thiosulfate decomposes to a mixture of colloidal elemental sulfur and sulfite (although minor reactions involving polythionates and sulfide also may occur). The rate equation describing the lag time prior to initial appearance of sulfur in dilute solutions has the approximate form (Zaiser and LaMer, 1948; Dinigar and others, 1951; Davis, 1958).

$$\frac{1}{t} = k(\text{H}_0^+)^{1/2} (\text{S}_2\text{O}_3^{2-})_0^{3/2} \quad (8)$$

where  $t$  is the time after mixing of reagents at which elemental sulfur ( $\text{S}_8$ ) appears and  $(\text{H}^+)_0$  and  $(\text{S}_2\text{O}_3^{2-})_0$  are the initial concentrations of hydrogen ion and thiosulfate respectively. Equation 8 predicts that the initial time of elemental sulfur appearance is one order of magnitude later at pH 7 than at pH 5, with all other variables being held constant. The longer times for sulfur appearance at higher pH values may still allow significant formation of elemental sulfur in ground-water flow systems because relatively long times are available for reaction. Taking a reasonable flow velocity for ground water of perhaps several meters per year, then several tens of years to perhaps a hundred years would be available for reaction, which is the time a



given parcel of water is traversing the distance interval (as much as 400 m) represented by core samples down dip from an ore roll. Considering that the initial appearance of elemental sulfur from millimolar thiosulfate solutions at pH 5 requires hours or less, the time available for reaction at pH 7-8 appears more than adequate to form elemental sulfur down dip from the roll front on the time scale of ground-water movement.

The possible central role of thiosulfate in marcasite formation is emphasized by the recent experimental work of El-Dahhar and Barnes (1979). These authors report that whereas mixtures of ferrous iron and  $H_2S$  produce pyrite at  $25^{\circ}C$ , when thiosulfate is added to this mixture at pH values less than 4.4, marcasite is the dominant product. Mixtures of marcasite and pyrite were formed by  $Fe^{2+}$ ,  $H_2S$  and  $S_2O_3^{2-}$  at pH's between 4.4 and 5 but only pyrite formed above pH 5. Because thiosulfate decomposes to elemental sulfur under acidic conditions as discussed above, there is at least the possibility that marcasite observed forming at low pH's (<5) in these experiments is related to the presence of a separate elemental sulfur phase rather than a direct reaction involving undecomposed thiosulfate. It is not known whether thiosulfate itself participates directly in marcasite formation or whether it serves indirectly as a source of elemental sulfur; nevertheless the results of El-Dahhar and Barnes clearly document the important role of metastable sulfur species in affecting iron-disulfide crystal structure.

In summary, the geochemistry of sulfur in ground-water systems with active redox boundaries may be profoundly different depending on whether or not the reduced portion of the aquifer contains viable heterotrophic sulfate reducing bacteria. In the presence of these organisms the ground water pH will be relatively high and solubilization of elemental sulfur as aqueous polysulfide ions will occur. In nonbiogenic systems polysulfide ion formation may be subordinate to generation of solid elemental sulfur.

## Discussion of Deposits

As noted above, marcasite is present as an ore-stage sulfide in each deposit studied. The ultimate control on its presence in these ore bodies is the depressed pH which is generated by oxidative processes at the redox boundary (Goldhaber and others, 1978; equations 3, 4 a and b). This pH is presumably sufficiently low ( $<6$ ) to destabilize polysulfide ions (fig. 7) and favor development of marcasite by the presence of elemental sulfur in the solid phase.

In contrast to this qualitative similarity in the development of ore-stage marcasite in each of the deposits, there are marked quantitative differences between deposits in its abundance and relative distribution. The deposits may be divided into two groups; those in which the abundance of ore-stage marcasite is at most equal to but generally much less than ore-stage pyrite (Shirley Basin, Irigaray, and Panna Maria), and those deposits in which the marcasite is clearly the dominant ore-stage sulfide (Benavides and Lamprecht deposits). Marcasite tends to be localized nearer the roll-front in the first group than in the second. The same division of ore bodies can be made on the basis of the presence or absence of abundant organic matter. Thus, on the basis of the discussion of the previous section, the two types of marcasite distributions may be rationalized if it is assumed that ore-stage iron disulfide in host rock with organic matter was generated via the metabolic activities of sulfate-reducing bacteria whereas non-biogenic processes led to ore-stage iron-disulfide generation in host rock without organic matter. Ground water in reduced rock of deposits formed under the influence of anaerobic bacterial metabolism will have higher pH's and may have higher polysulfide content in the reduced zone than ground waters in reduced zones of host rock without organic matter. These factors will favor formation

of pyrite. Inorganic mechanisms, on the other hand, may lead to higher concentrations of elemental sulfur and lower pH's that favor formation of marcasite. The development of marcasite in reduced barren ground down dip from the roll in the Lamprecht and Benavides deposits may be related to slow decomposition of thiosulfate or tetrathionate in ground water to elemental sulfur.

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