

## MINERALIZATION OF THE HANSONBURG MISSISSIPPI-VALLEY-TYPE DEPOSIT, NEW MEXICO: INSIGHT FROM COMPOSITION OF GASES IN FLUID INCLUSIONS

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### ABSTRACT

Inclusion volatiles were determined in splits of samples from the Hansonburg Mississippi-Valley-type of deposit (New Mexico) previously studied by microthermometry and fluid-inclusion microchemical analysis. The principal volatile is H<sub>2</sub>O; the principal gases are CO<sub>2</sub>, C<sub>n</sub>H<sub>n</sub> and N<sub>2</sub>, which account for about 1 mole% of inclusion volatiles, except for one sample, in which 24 mole% gases were measured. H<sub>2</sub>S was only detected in samples from early in the paragenetic sequence, when major sulfide deposition occurred. Organic compounds are C<sub>1</sub>-C<sub>6</sub> species similar to those reported in oil-field brines. Calculated gas-fugacities indicate that mineralization occurred at a pressure of about 150 to 200 bars and suggest a possible but limited unmixing of solutions; the vapor phase that developed was principally N<sub>2</sub>. Calculated pH values range from 4.3 to 5.1 and indicate little change in pH during mineralization. Calculated values  $f(\text{O}_2)$  and  $f(\text{S}_2)$  indicate that the ore solutions became less reducing during mineralization. Solutions were supersaturated with galena if lead was transported as a chloride complex. The data are not incompatible with a single ore-solution that transported both Pb and reduced sulfur. Ore fluids are postulated to have originated in a Rio Grande rift basin, migrated to the basin margin, and then into undisturbed carbonate along fractures. Mineral deposition occurred principally in response to the cooling of solutions.

**Keywords:** fluid inclusions, gaseous components, mineralization, lead, Hansonburg (New Mexico), Mississippi-Valley-type deposit.

### SOMMAIRE

On a déterminé la proportion des composants gazeux de la phase volatile de fluides incluses prélevées des échantillons étudiés antérieurement par microthermométrie et microanalyse chimique. Le composant principal de la phase volatile est l'eau, et les gaz principaux sont CO<sub>2</sub>, C<sub>n</sub>H<sub>n</sub> et N<sub>2</sub>, qui font au total environ 1% (molaire) de la phase volatile, sauf dans le cas d'un échantillon, qui en contient 24%. On a décelé le H<sub>2</sub>S seulement dans les échantillons précoces de la paragenèse, piégés lors de la déposition importante des sulfures. Les composés organiques sont des espèces C<sub>1</sub> - C<sub>6</sub> semblables à celles des saumures des bassins pétrolières. Les fugacités calculées pour ces compo-

sants gazeux indiquent que la minéralisation se serait déroulée à une pression d'environ 150 à 200 bars, possiblement accompagnée en quantité limitée d'une phase gazeuse riche en azote séparée par démixion. Le pH se situerait entre 4.3 et 5.1 et indiquerait très peu de changement pendant la minéralisation. Les valeurs calculées de  $f(\text{O}_2)$  et de  $f(\text{S}_2)$  indiqueraient que les solutions sont devenues de moins en moins réductrices au cours de la minéralisation. Les solutions sont sursaturées par rapport à la galène si le plomb est complexé comme chlorure. Les données ne sont pas compatibles avec une seule solution minéralisante qui a transporté à la fois le plomb et le soufre réduit. Les solutions auraient pris naissance dans un bassin du rift du Rio Grande, et auraient été transportées vers la bordure du bassin, et de là, dans les carbonates non dérangés le long de fractures. La déposition des minéraux dépendrait surtout du refroidissement des solutions.

(Traduit par la Rédaction)

**Mots-clés:** inclusions fluides, composants gazeux, minéralisation, plomb, Hansonburg, Nouveau-Mexique, gisement du type dit "Mississippi Valley".

### INTRODUCTION

The physicochemical conditions during metal transport and mineralization of Mississippi-Valley-Type (MVT) mineralization are not well understood. Much uncertainty exists concerning factors such as the pH of the solutions (Barnes 1979, Sverjensky 1983, Stormo & Sverjensky 1983), mechanisms of lead transport (Anderson 1975, 1983, Giordano & Barnes 1979, 1981), and processes of ore deposition (Anderson 1975, 1983, Spirakis 1983, Barnes 1983). The MVT deposits in the Hansonburg mining district, New Mexico, have previously been studied by means of fluid-inclusion microthermometry, analysis of inclusion fluids, paragenesis, and mineral equilibria in order to determine some of the physicochemical characteristics of the ore fluids (Putnam *et al.* 1983, Putnam & Norman 1983, Putnam 1980). This paper provides information on the composition of gases in fluid inclusions from the Hansonburg mining district and a discussion of the nature of the ore fluids and depositional processes indicated by all geochemical data determined to date for this deposit.

### THE HANSONBURG DISTRICT

The geology of the Hansonburg mining district is

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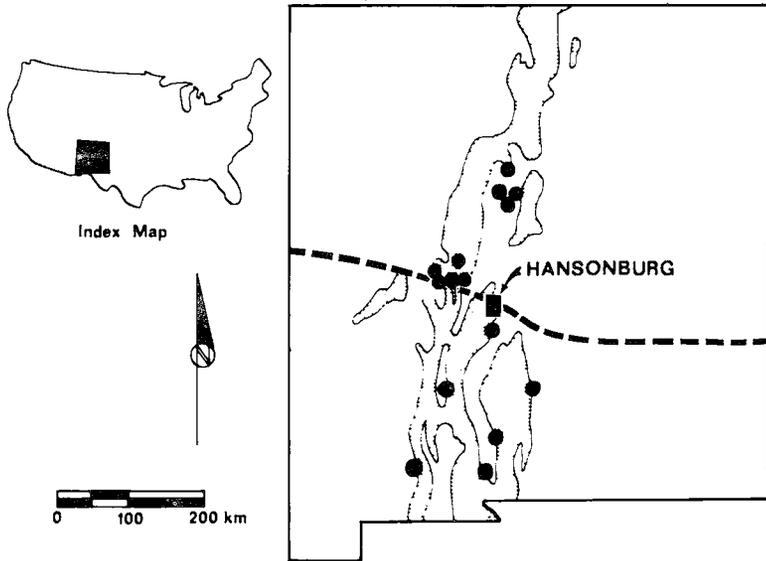


FIG. 1. Index map showing location of the Rio Grande rift (stippled pattern), Capitan lineament (dashed line), Hansonburg district, and other lead-fluorite-barite deposits (filled circles) (modified after Beane 1974).

described in detail elsewhere and will be only briefly summarized here (Putnam 1980, Allmendinger 1974, Kopicki 1962, Kottlowski 1953). The district has seen little production because of metallurgical problems in separating the mixed barite-fluorite-galena ores and lack of water for mining operations. It is located on the eastern margin of the Rio Grande rift (Fig. 1), which has been active for about the past 30 Ma (Chapin 1979). Mineralization is exposed in the Oscura uplift by major north-trending, *en échelon* normal faults along which major movement began 7 Ma ago (Chapin 1979). Basement rocks are Precambrian granite and gneisses. These are overlain by Pennsylvanian formations consisting of marine limestones, shales, and arkosic sands. Permian and Triassic red-beds and Cretaceous marine sands and shales top the succession, although in the Hansonburg district most of these have been removed by erosion.

Mineralization occurs principally in the Council Springs Member of the Pennsylvanian Madera limestone. Minor mineralization occurs as vein fillings in Pennsylvanian and Permian sediments. The Council Springs Member is massive, banded limestone that contains solution cavities up to 50 metres in width and bedding-plane anastomoses. Field evidence indicates that these karst features are the result of weathering during the Pennsylvanian. The Council Springs Member has an erosional upper contact and is unconformably overlain by 1 to 5 metres of mudstone.

Mineralization occurs sporadically over a 5-km north-south distance where Pennsylvanian rocks are exposed. Field as well as fluid-inclusion evidence indicates that deposits are localized by northwesterly-trending fractures (Fig. 2) (Putnam 1980). The deposits are associated with the east-west-trending Capitan lineament (Putnam *et al.* 1983). This paleostructure is thought to have played an indirect role in mineralization of the Hansonburg district. Uplift along this structure in the Paleozoic is postulated to have been responsible for the thinning of Paleozoic sediments in the vicinity of the Hansonburg district as well as for deposition and weathering of the Council Springs Member (Putnam *et al.* 1983).

The first mineralization consists of silicification and dolomitization, which decrease in intensity away from the barite-fluorite-galena deposits. This extends horizontally approximately 300 metres away from the deposits, and vertically encompasses all exposed Paleozoic rocks above and below mineralization. Quartz also lines many cavities. Conodont geothermometry (Cook 1985) indicates that during dolomitization and silicification, the sediments were heated to 110–140°C to 300 m horizontally from the deposits, with measurable heating of 50 to 110°C extending another 100 metres. Siderite was deposited in fractures and cavities, but it is not clear if siderite was deposited during or after silicification. This was followed by mineralization of economic interest in the Council Springs Member. First, there was minor replacement of carbonate by galena and barite, then

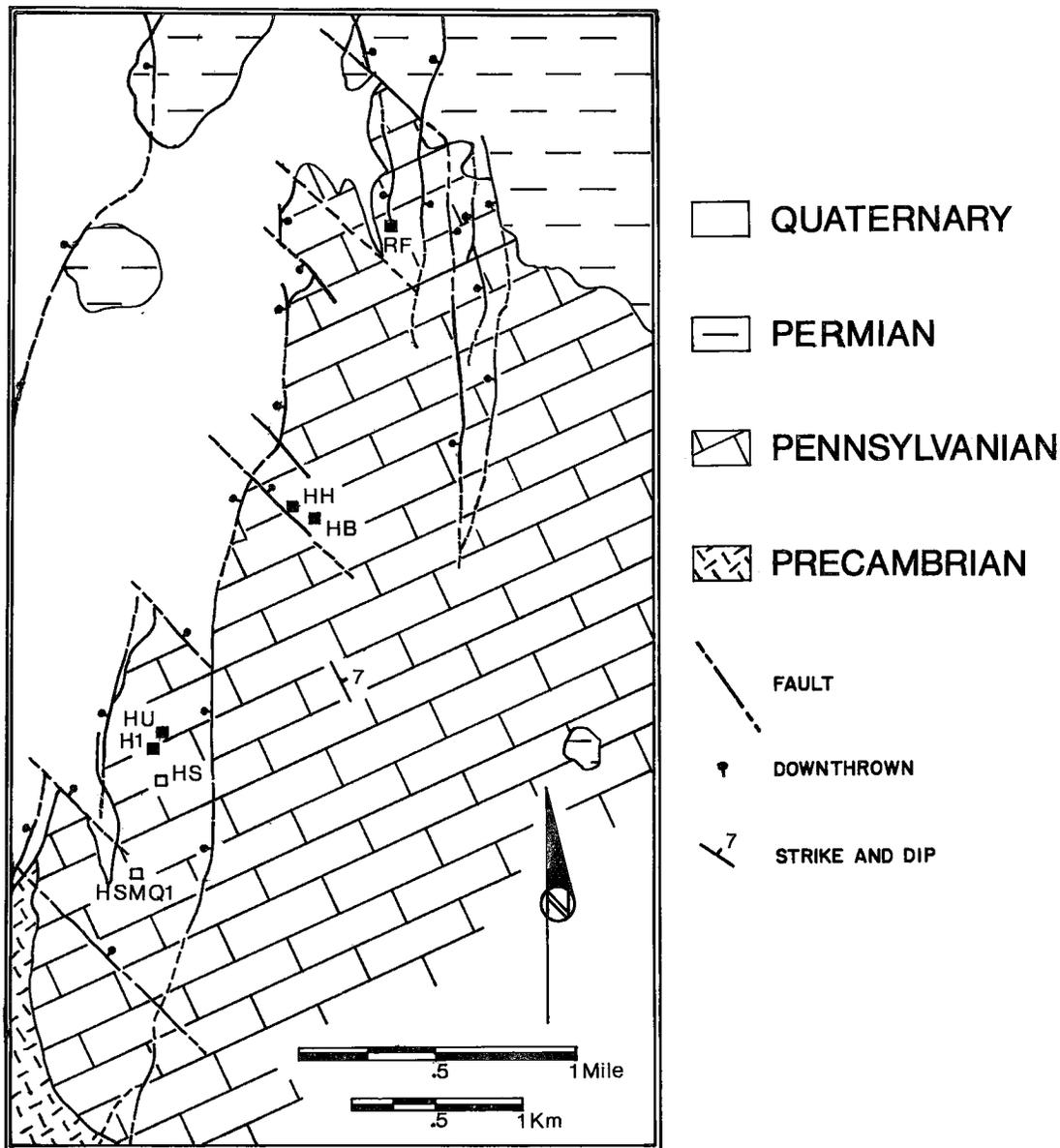


FIG. 2. Generalized geological map of the Hansonburg district, after Putnam (1980). Indicated locations of samples on Table 1 are also principal occurrences of mineralization.

open-space filling by galena, minor pyrite and sphalerite. This was followed by barite, fluorite and quartz; locally all phases coprecipitated. Fluorite is purple, green and blue in color; because of color differences, a multistage paragenesis can be determined (Roedder *et al.* 1968) for fluorite. However, the color sequence of fluorite is different at the separate occurrences of mineralization along the

Osura uplift. Chalcopyrite occurs with pyrite as solid inclusions in late fluorite. Minor siderite occurs in some cavities and was the last mineral deposited. Massive selenite fills vugs locally, but this is attributed to weathering of overlying Permian anhydrite beds. This paragenesis is somewhat different and more general than that proposed by Roedder *et al.* (1968). This is due, in part, to the greater

number of mineral occurrences studied, including workings developed by mining operations in 1980 and 1981. Because of the wide variability of fluorite coloration in the district, attempts to apply the Roedder *et al.* fluorite-coloration paragenesis to the district proved fruitless. Most mineralization was open-space filling; however, not all the open space was filled. Metre-size vugs occur in mineralized areas, and some karst-collapse features are essentially unmineralized. Mineralization is massive in major cavities and occurs as banded or "coontail" ore where bedding-plane cavities were filled. Galena is about 4% of the ore, and a galena concentrate has about 380 ppm Ag.

Previous data on fluid-inclusion microthermometry and fluid-inclusion composition (Putnam & Norman 1983, Putnam 1980, Roedder *et al.* 1968) indicate mineralization by solutions between 210 and 125°C and salinity between 18 and 10 eq. wt. % NaCl. Liquid hydrocarbons were reported in some fluid inclusions. Ore solutions were Na-dominant brines transporting between 800 and 10 ppm Pb. The  $f(\text{O}_2)$ , pH and  $f(\text{S}_2)$  of the fluids were calculated (Putnam & Norman 1983, Putnam 1980) using fluid-inclusion composition and microthermometry data for both the early stage of mineralization, when galena was deposited, and the later galena-free stage of mineralization (Figs. 3, 4).

Lead-isotope studies indicate that the lead at Hansonburg has a large component of radiogenic lead (*i.e.*, J-type lead); the data suggest a source-age compatible with basement rocks (Slawson & Austin 1960). Ewing (1979) has suggested the basement as a source of the lead at Hansonburg, whereas Beane (1974) favored Permian arkoses derived from the basement as a source. Allmendinger (1974) concluded from a sulfur isotope study of the Hansonburg district that Permian evaporites supplied sulfur to ore solutions.

#### ANALYSIS OF THE GAS PHASE

The gas phase was analyzed in splits of sixteen samples that had been previously studied by fluid-inclusion microthermometry and analysis of inclusion fluids (Putnam & Norman 1983, Putnam 1980). These samples were collected from three separate deposits in the Hansonburg district (sample locations are indicated in Fig. 2); for each deposit, mineral samples in paragenetic sequence were selected. Inclusion gases were only measured in quartz and fluorite. Samples were coarsely crushed, hand-picked to remove those that had inclusions of other minerals, then fluorite was crushed to 2 mm and quartz to 0.5 mm. They were then cleaned in organic solvents, boiling nitric acid, distilled-demineralized water and electrolytic cells.

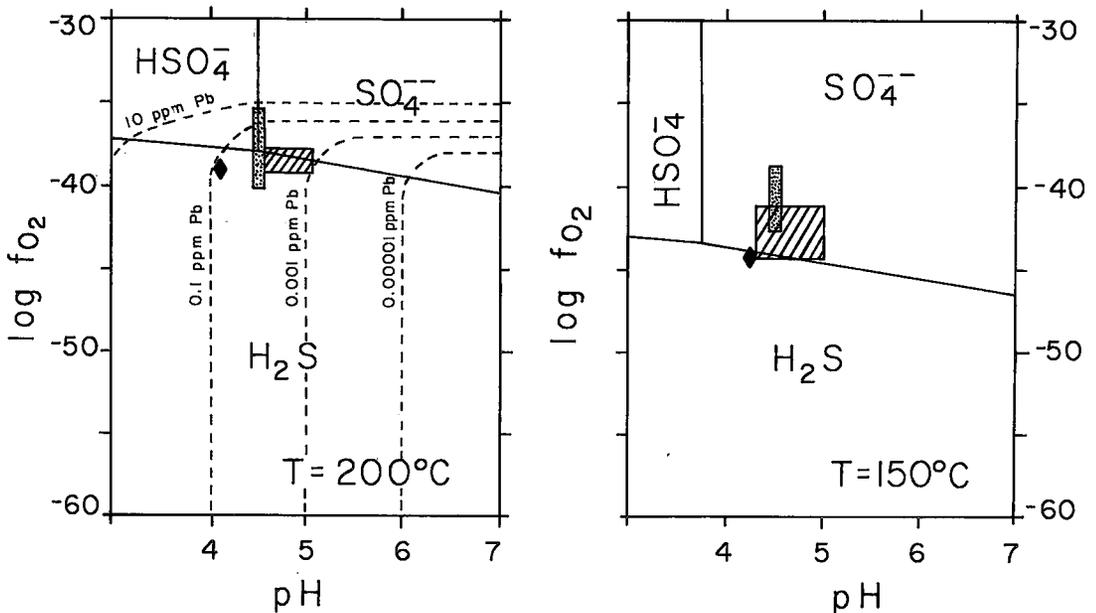


FIG. 3.  $f(\text{O}_2)$ -pH diagrams indicating the chemical conditions of the ore fluids during the galena (left) and fluorite-barite (right) stages of mineralization at 200° and 150°C, respectively. The stippled areas are calculated values from Putnam (1980), diamond is the result of PATH calculations (Putnam 1980), and hachured areas are values calculated in the present paper. Lead in the 200°C waters was calculated from the data of Seward (1984) for a solution of  $I = 2.5$ ,  $\text{Cl} = 45,000$  ppm and  $\Sigma\text{S} = 10^{-2.7}$  m.

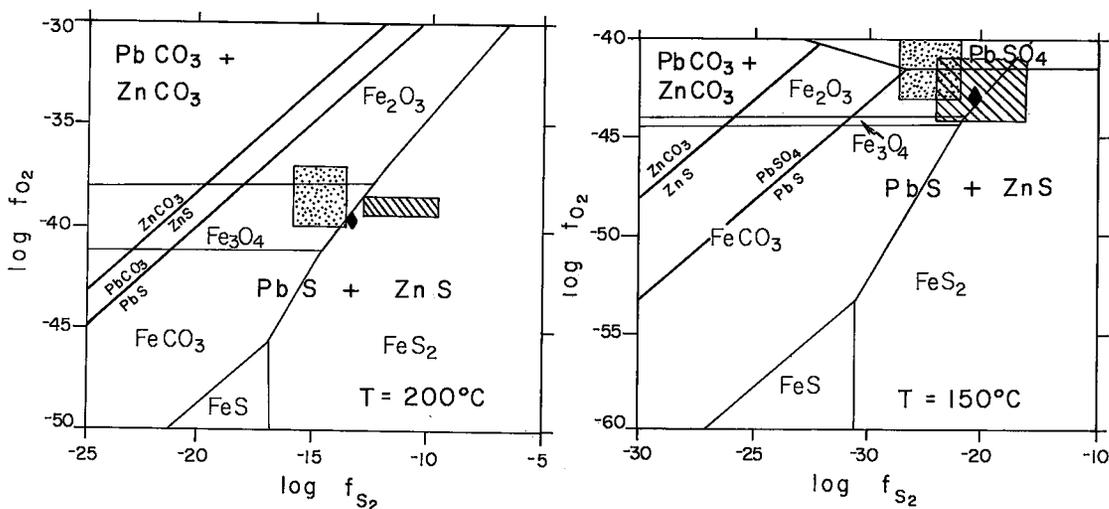


FIG. 4.  $f(\text{O}_2)$ - $f(\text{S}_2)$  diagrams for galena-stage fluids (200°C) and fluorite-barite-stage fluids (150°C). Stippled areas are from Putnam (1980), diamonds are the result of PATH calculations (Putnam 1980), and hatched areas are the values calculated here.

Volatiles were extracted in vacuum by thermal decrepitation at 400°C, separated into liquid-nitrogen-condensable and -noncondensable fractions (noncondensable gases are H<sub>2</sub>, He, CH<sub>4</sub>, CO, N<sub>2</sub> and Ar; condensable gases are NH<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub> and organic compounds with 2 or more carbon atoms) and gas ratios measured by mass spectrometry. Background gases were measured, then their peak-height values were multiplied by three and subtracted from the mass spectra of the gas analyzed. Data were reduced by a matrix-averaging technique using measured patterns of cracking and sensitivity to N<sub>2</sub> for the gases being determined. Weekly calibration of the mass spectrometer with freon-4 is performed in order to maintain the same patterns of cracking for gases; this is critical for determining ratios of CH<sub>4</sub>, CO and N<sub>2</sub> for mixtures of these gases. Water was measured by weighing or pressure measurement. These methods are described in more detail in Norman & Sawkins (1985) and Norman (1977), and are similar to those of Dyck *et al.* (1976). These techniques yield an accurate gas/water ratio; estimated errors based on analyses of gases dissolved in water are ± 5% for major species and ± 10% for minor species. However, there is no way to know how accurately volatiles in inclusion liquids are measured because there are no standards.

The principal area of uncertainty in the analyses is whether or not the volatiles measured represent those actually present in the inclusions. Some arguments will be made concerning individual species of gas; however, the best verification of the analytical results is that the data agree with physical and chem-

ical characteristics of the ore fluid determined by other means.

Sample size was approximately 5 and 10 grams, respectively, for quartz and fluorite. Each analysis yielded between 2 and 10 mg of H<sub>2</sub>O.

## RESULTS

The analyses indicate that inclusion volatiles are water containing 2.1 to 0.4 mole % gases except for one sample, in which 24 mole% gases was measured (Table 1). The principal gaseous components are CO<sub>2</sub>, N<sub>2</sub> and organic compounds.

The organic compounds are reported as CH<sub>4</sub> and C<sub>n</sub>H<sub>n</sub>, which were measured in the noncondensable and condensable gases, respectively. The C<sub>n</sub>H<sub>n</sub> volatiles are C<sub>2</sub> to C<sub>6</sub> organic compounds. Because of the multiple organic species present, positive identification of individual compounds was not possible from the mass spectra; Table 2 gives probable and inferred compounds. Because the organic species are not known with certainty, the total organic component was calculated assuming that all species are ethane and propane. This assumption introduces only a small error into the calculation of C<sub>n</sub>H<sub>n</sub> since the lighter organic species predominate, and compounds that have more than three carbon atoms generally yield an ethane or propane fragment when ionized in the mass spectrometer. The predominance of light organic compounds in the condensable fraction of gas was confirmed by an analysis by gas chromatography that indicated the principal organic gases to be ethane, propane and *n*-butane. Unfortunately,

TABLE 1. PROPORTION OF FLUID-INCLUSION GASES, CALCULATED GAS FUGACITIES, AND pH

Sample Location T <sub>h</sub> (°C)	RFF1 R-1 175- 155	RFF1 R-1 175- 155	RFF2 R-2 154- 147	HHQ1 M-1 205- 193	HHF1 M-2 198- 153	HHF1 M-3 180- 151	HBQ1 M-4 152- 146	HUF1 NH-3 158- 153	HSF4 HH-1 184- 164	HSQ2 HH-2 182- 175	HSQ3 HH-3 176- 163	HSF2 HH-4 175- 170	HSF1 HH-5 170- 168	HSQ1 HH-6 163- 151	HSF5 HH-7 155- 147	HSMQ1 SH-A 212- 140	HSMQ1 SH-B 180- 170
CO <sub>2</sub> mole%	34	18	43	40	26	3.7	37	36	35	17	22	63	25	80	16	14	8
N <sub>2</sub> × 100	27	26	5.3	6.1	4.8	2.1	8.8	5.4	96 <sup>1</sup>	6.7	7.5	8.5	7.8	7.2	4.3	9.2	7.8
CO	-	-	-	24	-	3.1	8.6	-	-	16	16	29	-	44	-	3.9	13
CH <sub>4</sub>	1.1	1.7	1.9	3.6	1.3	0.83	0.62	0.85	650	0.35	1.6	1.3	1.1	1.5	1.0	1.1	0.7
C <sub>n</sub> H <sub>n</sub>	16	18	56	5.6	33	6.5	9.0	28	1600	12	31	43	12	76	19	58	13
H <sub>2</sub>	2.8	2.1	6.1	1.2	2.9	3.1	1.4	1.6	-	5.3	2.3	2.8	2.0	2.4	5.3	1.7	33
H <sub>2</sub> S	0.53	0.92	-	0.58	0.77	0.34	-	-	57	8.7	1.1	-	-	-	-	0.83	0.02
SO <sub>2</sub>	-	-	-	-	-	6.0	-	-	-	-	-	-	-	2.2	-	-	-
He	0.02	0.02	0.02	0.005	0.03	-	-	0.04	0.30	0.003	-	0.008	0.009	-	0.01	-	-
Ar	0.41	0.06	0.04	0.005	0.06	0.03	1.3	0.03	-	0.02	0.02	0.006	0.08	0.01	0.05	0.12	0.07
H <sub>2</sub> O mole%	99.2	99.3	98.8	99.2	99.3	99.7	99.3	99.03	76.1	99.5	99.1	98.7	99.5	97.9	99.5	99.3	99.6
log f(CO <sub>2</sub> )	1.61	1.34	1.71	1.62	1.48	0.70	1.66	1.62	1.62	1.30	1.41	1.81	1.41	1.94	1.26	1.04	0.90
log f(O <sub>2</sub> )	-38.9	-39.2	-	-38.9	-39.1	-39.3	-	-	-	-39.4	-38.7	-	-	-	-	-39.3	-38.5
log f(S <sub>2</sub> )	-10.3	-10.4	-	-10.2	-10.2	-11.1	-	-	-	-10.1	-9.5	-	-	-	-	-10.3	-12.9
pH	4.6	4.8	4.6	4.6	4.7	5.1	4.7	4.6	4.6	4.7	4.3	4.5	4.7	4.6	4.8	4.9	5.0

Sample numbers are the same as in Putnam (1980); location of samples are indicated in Figure 2. Code for locations: R Royal Flush deposit, M Mex-Tex deposit, NH northern Hansonburg Hill deposit, HH Hansonburg Hill deposit, SH southern Hansonburg Hill deposit. Numbers after location refer to paragenetic sequence at sampling area; letters after location refer to zones of a single crystal. T<sub>h</sub> is the range of temperatures of fluid-inclusion homogenization, from Putnam (1980). <sup>1</sup> Combined determination of CO and N<sub>2</sub>; see text for explanation.

the gas sample was too small to measure the organic compounds present in lesser abundance. Roedder *et al.* (1968) detected high pressures of kerosene-soluble gases. They concluded that these were organic compounds in their study of the Mex-Tex deposit. They also mentioned observing little CO<sub>2</sub> when inclusions were crushed, and one of the two samples of fluorite from the Mex-Tex deposit had little CO<sub>2</sub> (sample HBF1). The amount of CH<sub>4</sub> actually present in the inclusions is problematical, since it is in minor proportion in all but one analysis and can be produced during the thermal decrepitation process from more complex compounds.

Only in sample HSF4 were liquid hydrocarbons observed, and they are very common. The analysis indicated 24 mole% gaseous components, mostly organic compounds (Table 1). The mass spectrum is similar to that obtained from other samples; however, the analytical results differ from the others in that amounts of CH<sub>4</sub>, H<sub>2</sub>S and He are considerably higher. The large amount of CH<sub>4</sub> measured in sample HSF4 is puzzling. Methane could have been

produced by thermal decomposition of the organic compounds, but if this is so, only in this sample is the ratio of methane to C<sub>n</sub>H<sub>n</sub> about 1 to 3. We suspect that the high quantities of CH<sub>4</sub>, H<sub>2</sub>S and He may be due to the greater solubility of these gases in organic liquid than brine. The large amount of CH<sub>4</sub> made it impossible to determine the amounts of CO and N<sub>2</sub>, which is done by ratios of mass peaks 12, 14 and 16. The amount of CO + N<sub>2</sub> was calculated on the basis of the mass 28 peak (Table 1). Because of the high amounts of organic material in sample HSF4, and uncertainties about the analysis, the data from this sample are not used in most subsequent calculations.

Small amounts of H<sub>2</sub> were detected. Since this can readily be produced during thermal decrepitation by reactions involving H<sub>2</sub>O, CO<sub>2</sub> and C<sub>n</sub>H<sub>n</sub>, as well as through the decrepitation of organic compounds, the amounts of H<sub>2</sub> are suspect. Carbon monoxide can similarly be produced, and we strongly suspect that all CO was produced during the thermal decrepitation process. Carbon monoxide was measured in all samples of quartz (those with Q in the sample number), but in only a few of the fluorite samples. It was noted during decrepitation that inclusions in fluorite opened soon after the furnace temperature exceeded 200°C, about the maximum measured temperature of homogenization (T<sub>h</sub>) of fluid inclusions, whereas inclusions in quartz decrepitated at about 400°C. If CO is manufactured during thermal decrepitation, it is likely that more CO would be produced by decrepitation of inclusions in quartz than in fluorite because of the higher temperatures.

Hydrogen sulfide ranges from 0.087 mole % to nondetectable amounts (*i.e.*, < 3 × 10<sup>-5</sup> mole %). The amount of H<sub>2</sub>S found in the inclusion fluids is related to T<sub>h</sub> and paragenesis; minerals that have T<sub>h</sub> lower than 170°C or were deposited late in the para-

TABLE 2. ORGANIC COMPOUNDS TENTATIVELY IDENTIFIED IN MASS SPECTRA OF HANSBURG FLUID-INCLUSION WATERS COMPARED TO THOSE REPORTED IN OIL-FIELD BRINES

Oil-field brines	Identified in Hansonburg fluid inclusions
Methane	yes
Ethane	?
Propane	?
n-Butane	yes
Isobutane	yes
Methylpentane	?
Methylcyclopentane	?
Cyclopentane	?
n-Pentane	?
Cyclohexane	yes
Benzene	yes
Toluene	yes

Organic compounds in oil-field brines from Zarrella *et al.* (1967) and McAuliffe (1969). Compounds such as ethane could not be positively identified because its mass spectrum was obscured by fragments of other organic species.

genesis have no detectable  $H_2S$  (Fig. 5). Hydrogen sulfide is not the product of sulfide decrepitation. Experiments in which finely ground sulfides were mixed with inclusion-bearing quartz, and then the inclusions were decrepitated at  $500^\circ C$ , indicate that several percent added sulfides yield only negligible  $H_2S$  (Smith 1983, Norman 1977). The odd sulfide grain that may have been missed by hand-picking the samples analyzed would not produce the  $H_2S$  in the quantities measured.

Sulfur dioxide was detected among the gases from three samples. Sulfur dioxide can be a product of thermal decomposition of some sulfates (but not barite) at  $400^\circ C$ . These sulfates could be solid inclusions or precipitates from inclusion fluids. Sulfur dioxide can also be produced by reactions between  $H_2O$  and sulfides. Since there is nothing unique about the samples in which  $SO_2$  was detected, its origin is not clear.

There are organic compounds that contain nitrogen and sulfur. We reject the idea that the majority of the  $N_2$  and  $H_2S$  measured was from thermal decomposition of such compounds for the following reasons. Most nitrogen- and sulfur-bearing compounds are not stable at the indicated temperatures of the ore fluids. No nitrogen- or sulfur-bearing organic compound was identified in the mass spectra; hence if any of these compounds are present, they are in minor amounts. In some analyses the moles of  $N_2$  exceed the moles of organic compounds; clearly  $N_2$  could not have originated solely from decomposition of organic compounds in these samples. There is no correlation between the amount of organic compounds and levels of  $N_2$  and  $H_2S$ , not considering sample HSF4. The amount of thermal decomposition during volatile extraction for many samples was probably minimal. The organic compounds present in the inclusions must be stable to temperatures of  $200^\circ C$ , and particularly for fluorite, in which inclusions decrepitated at temperatures not much greater than  $200^\circ C$ .

Nitrogen can be generated by thermal decomposition of  $NH_3$ ; however, it is highly doubtful that  $NH_3$  was present in the Hansonburg fluids. Ammonia was not observed in the mass spectra, and it can be demonstrated by calculation using the methods and data of Eugster & Skippen (1967), Eugster & Munoz (1966) and French (1966) that  $N_2$  should far exceed  $NH_3$  at  $200^\circ C$  and pressures less than 1 kbar.

#### PHYSICOCHEMICAL CONDITIONS

In the following geochemical calculations, the sources of data and methods used were the following: equilibrium and thermodynamic constants are taken from Robie *et al.* (1978) and Helgeson (1969); activity coefficients of ions were calculated from the

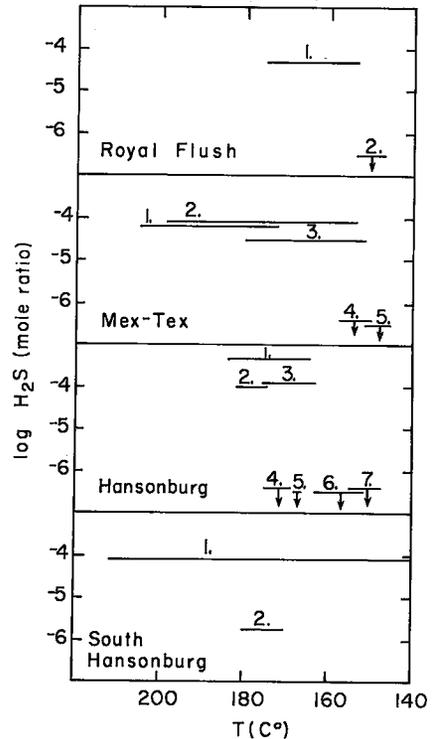


FIG. 5.  $H_2S$  content of inclusion fluids versus the range of measurements of temperature of fluid-inclusion homogenization. Numbers refer to relative paragenetic order of the sample.

modified Debye-Hückel expression from Helgeson (1969), interaction parameters ( $B^\circ$ ) from Helgeson (1969), and conventional Debye-Hückel coefficients (A and B) from Helgeson & Kirkham (1974); Henry's Law coefficients are taken from Naumov *et al.* (1974) and Cramer (1982). Gas fugacity-coefficients were assumed equal to one since they depart little from unity at the pressures and temperatures considered (Naumov *et al.* 1974).

It is assumed that the  $CO_2$ ,  $N_2$  and  $H_2S$  occurred in Hansonburg mineralizing fluids at the concentrations measured. The actual amount of  $CO_2$  in the solutions may have been slightly different than measured. Minor boiling, as discussed below, could have increased  $CO_2$  concentrations, and reduction of  $CO_2$  to CO during fluid extraction could have lowered the amount detected. Some of the  $H_2S$  could have been dissolved in an immiscible organic liquid; however, organic liquids were not observed in samples other than HSF4, and the data of Price (1981) indicate that some of the organic compounds could be dissolved in brine. Also, there is no apparent relationship between levels of  $C_nH_n$  and  $H_2S$ . It is

TABLE 3. CHEMICAL CONDITIONS OF THE HANSBURG FLUIDS

	Galena Stage	Fluorite-barite stage	Reference
T (°C)	200	150	Putnam (1980)
Ionic strength	2.5	2.0	
Ca (ppm)	3,400	3,400	
Pb (ppm)	380	460	
Cl (ppm)	45,000	26,000	
log $a(\text{SO}_4)$	-5.6	-4.7	
pH	4.85	4.6	This work
log $f(\text{O}_2)$	-39	(-41 to -44)	
log $f(\text{S}_2)$	-10.3	(-15 to -23)	
log $f(\text{CO}_2)$	1.53	1.57	
log $a(\text{H}_2\text{S})$	-2.7	(-5.5 to -11)	

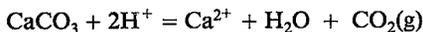
Quantities averaged from measurements and calculations from this work and Putnam (1980). Values in parentheses represent the calculated upper and lower limits in cases where direct calculation of the quantity was not possible; see text for explanation.

also assumed that Ca occurs in the ore solutions as  $\text{Ca}^{2+}$ ; this has been confirmed by experiment (Frantz & Marshall 1982).

Paragenetic and fluid-inclusion studies indicate that mineralization in the Hansburg district can be divided into an early stage, typified by deposition of galena, and a later stage, in which the principal mineralization involved fluorite and barite. Some general conditions for these stages based on prior studies, and which are used in the calculations described below, are listed in Table 3.

#### Evaluation of pH

The pH was calculated from the expression

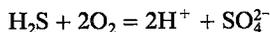


for each sample analyzed (Table 1). The calcium concentration for inclusion liquids determined by Putnam was used in the calculations. For quartz samples, the measured concentration for the particular sample was used (Putnam 1980, Table II), and for fluorite the average amount of Ca from inclusions in quartz was used (Table 2). The fugacity of carbon dioxide was calculated using the equation in Table 4, the measured amount of  $\text{CO}_2$ , mean fluid-inclusion salinity, and mean  $T_h$ .

Calculated pH for the galena stage varies from 4.5 to 5.1 (average 4.85); for the fluorite-barite stage, it varies from 4.3 to 4.8 (average 4.65).

#### $f(\text{O}_2)$

Oxygen fugacity was calculated from the expression



using the  $\text{H}_2\text{S}$  measured by gas analysis, the value of pH calculated above, and assuming that  $\text{SO}_4$  was fixed by anhydrite solubility. The reasons for assuming that  $\text{SO}_4$  is in equilibrium with anhydrite are that both Ca and  $\text{SO}_4$  were present in the mineraliz-

ing solutions; Permian formations that overlie the Hansburg district at the time of mineralization had anhydrite beds; the Tertiary rift-basins believed to be the source for fluids that mineralized the Hansburg area are characterized by fault blocks that have Permian sediments; the basins have detritus from Permian formations, and contain evaporites themselves (e.g., White Sands, NM); also, stable-isotope measurements indicate that the sulfur in the Hansburg deposit was from Permian evaporites (Allmendinger 1974). Measurements of  $\text{SO}_4$  in fluid-inclusion fluids (unpublished data of Putnam) from two samples of fluorite indicate a sulfate concentration of 1 to 2 ppm, which is in quite good agreement with the  $a(\text{SO}_4)$  used in the calculations.

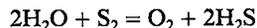
The calculated log  $f(\text{O}_2)$  during the galena stage is -38.8 to -39.3 (Figs. 3, 4). During the fluorite-barite stage, a log  $[\text{H}_2\text{S}]$  lower than -5.5 indicates a log  $f(\text{O}_2)$  greater than -44. A maximum log  $f(\text{O}_2)$  of -41 for the 150°C fluid was estimated by calculating  $a(\text{H}_2\text{S})$  from the expression



using data from Seward (1984) for galena solubility, and assuming  $\gamma_{\text{PbCl}_2} = 1$ , then using the calculated  $a[\text{H}_2\text{S}]$  to calculate  $f(\text{O}_2)$  as described above.

#### $f(\text{S}_2)$

Sulfur fugacity was calculated from the expression



using  $f(\text{O}_2)$  calculated above and the concentration of  $\text{H}_2\text{S}$  from the gas analysis. The calculated log  $f(\text{S}_2)$  during the galena stage was -9.9 to -12.9 (Fig. 4). Limits on  $f(\text{S}_2)$  during the fluorite-barite stage were calculated from the maximum and minimum  $f(\text{O}_2)$  and  $a(\text{H}_2\text{S})$  estimated above: log  $f(\text{S}_2)$  was greater than -23 but less than -15 (Fig. 4).

#### Pressure

One of the valuable applications of knowledge of the gaseous component of fluid-inclusion liquids is to estimate pressure at the time of mineralization. The assumption made is that the gases measured were homogeneously dissolved in the mineralizing fluid. Then the minimum pressure when fluids were trapped is equal to the sum of the partial pressures of the individual gases, if there was no unmixing. (The term unmixing is preferred to "boiling" as in the expression "second boiling" because it better describes the process of a gas phase forming when P,T conditions of aqueous fluid change such that its gaseous components are no longer completely miscible.)

The minimum pressure was calculated from the expression

$$P_T > P(\text{H}_2\text{O}) + P(\text{CO}_2) + P(\text{N}_2)$$

where  $P_T$  is the total pressure and  $P(\text{H}_2\text{O})$ ,  $P(\text{CO}_2)$ , and  $P(\text{N}_2)$  are the respective partial pressures of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{N}_2$ .

Calculated partial pressures of  $\text{N}_2$  and  $\text{CO}_2$  using the expressions in Table 4 range from 545 to 36 bars, and 88 to 9 bars, respectively (Table 5). The calculated partial pressure of  $\text{H}_2\text{O}$  ranges from 11 to 4 bars using data from Haas (1971). Calculated  $P_T$  varies from 591 to 57 bars, with the majority of values between 100 and 200 bars (Table 5).

Other gases measured were not used in the pressure calculation for the following reasons. Methane, hydrogen and carbon monoxide may have been produced entirely or in part during the decrepitation procedures. Besides, the amounts of these gases are such that not including them does not significantly affect the pressure calculation; the calculated partial pressures of  $\text{CH}_4$  are greater than those of  $\text{H}_2$  and  $\text{CO}$ , and they range from 2 to 23 bars, averaging 11 bars. Organic species other than methane were not included in the calculation because 1) the exact amount of each species was not determined, 2) the Henry's law coefficients of most organic species are not known at elevated temperatures, 3) some of the organic components may have occurred in the ore solutions as immiscible liquids, and 4) most importantly, the Henry's law coefficients of organic species inferred in ore solutions are quite low. Hydrogen sulfide and  $\text{SO}_2$  have such low Henry's law coefficients that their contribution to total pressure can be neglected, and He and Ar are in such low concentrations that their partial pressures are negligible.

#### Errors in calculated values

The principal source of error in the calculated values of pH,  $f(\text{O}_2)$  and  $f(\text{S}_2)$  lies, more than likely, in the thermodynamic data used in the calculations rather than in measurements of inclusion fluids. The principal source of uncertainty in the fluid-inclusion analyses is whether the measured values are representative of the average composition of fluid. The sample-to-sample variation in measured gases, together with variations in  $T_h$  (Table 1) and salinity (Putnam 1980, Roedder *et al.* 1968), indicate heterogeneity in inclusion fluids. The inclusions are large, many typically greater than 0.1 mm, which means that the analyses may have been heavily influenced by a few large inclusions. We consider, therefore, that an uncertainty of  $\pm 50\%$  for measured values to be appropriate.

The pH should be the chemical quantity calculated with the least error. An uncertainty in measured

TABLE 4. HENRY'S LAW EXPRESSIONS USED TO CALCULATE PARTIAL PRESSURES OF GASEOUS COMPONENTS

Gas	Expression
$\text{N}_2$	$K_H = (344,000 - 593 T) e^{0.0580 * S}$
$\text{CO}_2$	$K_H = (14,300 - 17.5 T) e^{0.0394 * S}$
$\text{CH}_4$	$K_H = (209,000 - 365 T) e^{0.0580 * S}$

Gas fugacity =  $K_H \times$  mole fraction of gas, T in kelvin, and salinity S in eq. wt. % NaCl.  $\text{CO}_2$  and  $\text{CH}_4$  expressions derived by curve-fitting the data of Cramer (1982);  $\text{N}_2$  expression determined by adding salting-out expression for  $\text{CH}_4$  to  $\text{N}_2$  fugacity equation in Naumov *et al.* (1974).

TABLE 5. CALCULATED MINIMUM PRESSURE OF MINERALIZATION AND PARTIAL PRESSURES OF  $\text{N}_2$ ,  $\text{CO}_2$  AND  $\text{H}_2\text{O}$

Sample	Mean $T_h$ ( $^{\circ}\text{C}$ )	Mean S eq. wt. % NaCl	$P(\text{N}_2)$ (bars)	$P(\text{CO}_2)$ (bars)	$P(\text{H}_2\text{O})$ (bars)	$P(\text{total})$ (bars)
RFF1	165	15	545	41	6	592
RFF1	165	15	525	22	6	552
RFF2	152	14	110	51	4	166
HHQ1	198	14	89	42	11	142
HHF1	160	13.5	92	30	5	127
HBF1	149	15	196	46	4	248
HBQ1	169	17	46	5	6	57
HUF1	156	14	109	42	5	157
HSF4	172	15	129	20	7	155
HSQ2	169	15	147	26	6	180
HSQ3	172	11.5	133	64	7	204
HSF2	172	11.5	86	9	7	101
HSF1	169	11.5	125	26	6	157
HSQ1	158	12.5	132	88	5	225
HSF5	151	13.0	87	18	4	109
HSMQ1-A	178	13.0	150	11	7	169
HSMQ1-B	178	13.0	127	8	7	144

See text for method of calculation.

$\text{Ca}^{2+}$  and  $\text{CO}_2$  values of  $\pm 50\%$  would imply an uncertainty in the calculated pH of 0.3 units. The calculated values of  $f(\text{CO}_2)$  may be in error by  $\pm 25\%$  because the data for  $\text{CO}_2$  solubility in NaCl liquids were used in the calculations, and the inclusion liquids are not pure NaCl brines. Considering an uncertainty in the equilibrium constant of  $\pm 0.5$  log unit and uncertainty of 0.1 log unit in the calculated activity-coefficient, the total uncertainty in the calculated pH is  $\pm 0.75$ .

The  $f(\text{O}_2)$  was calculated using calculated pH values, which introduces an uncertainty of  $\pm 0.75$  log units. Estimated  $a(\text{SO}_4)$  may be in error by as much as 2 log units. Considering the uncertainty in the equilibrium constant to be  $\pm 0.5$  log unit and possible error in the  $\text{H}_2\text{S}$  measurement, the uncertainty in the calculated  $f(\text{O}_2)$  is 2.15 log units.

The  $f(\text{S}_2)$  has an estimated uncertainty of 3.0 log unit from the combined uncertainties in  $f(\text{O}_2)$ , measured  $\text{H}_2\text{S}$  values, and equilibrium constant.

The possible errors are not so large that the calculated values are meaningless, but indicate that the hachured areas in Figures 3 and 4, which represent the chemical conditions of the mineralizing fluid, could be larger than illustrated.

Accurate individual gas/water ratios are important for calculation of partial pressures. We estimate these to be in error no greater than 10% for measurements of  $\text{N}_2$  and  $\text{CO}_2$ . There is no evidence that the amount of  $\text{CO}_2$  was greatly affected by thermal

TABLE 6. EXAMPLE OF UNMIXING OF GASEOUS COMPONENTS IN A HYDROTHERMAL FLUID AS PRESSURE DECREASES

P(total) (bars)	$f(N_2)$ (bars)	$f(CO_2)$ (bars)	cm <sup>3</sup> gas/ litre solution	weight loss (%)
194	142	45	0.0	0.0
174	123	44	1.8	0.03
154	103	44	4.1	0.05
134	83	43	6.5	0.08
114	63	43	10	0.12
94	46	42	18	0.16
74	26	40	22	0.21
54	8	38	32	0.26
34	0	27	98	0.55
14	0	7	360	1.05

Composition of gas phase formed is proportional to partial pressures of gases;  $a, g$ , at  $P = 174$  bars,  $N_2:CO_2:H_2O$  is 123:44:7. Conditions:  $T$  175°C, 0.08 mole %  $N_2$ , 0.4 mole %  $CO_2$ , salinity 14 eq. wt. % NaCl,  $P(H_2O)$  7 bars (see Table 7).

effects involving organic compounds (*i.e.*, reduction of  $CO_2$  or oxidation of organic compounds to  $CO_2$ ); the amount of  $CO_2$  measured in sample HSF4, the sample with much liquid hydrocarbons, was little different than the amount measured in other samples (Table 1). A minor amount of unmixing would have little effect on levels of  $CO_2$  in solution (Table 6). The greatest uncertainty in calculated partial pressures lies in possible errors in the constants in Table 4 and in whether or not the temperature and salinity assumed are representative of the inclusions from which the gaseous components were measured. We estimate these to contribute an uncertainty of 25% to the calculated partial pressure. Therefore an uncertainty of  $\pm 35\%$  is estimated for calculated pressure values. Since the minimum pressure was calculated, the other gaseous components will not contribute to the uncertainty of the calculated value. As discussed elsewhere, the partial pressures of the other gaseous species will probably increase the calculated minimum pressure but little.

#### Comparison with previous calculations

The pH,  $f(O_2)$  and  $f(S_2)$  here calculated for the mineralizing fluids differ somewhat from those previously calculated (Figs. 3, 4). Putnam & Norman (1983) calculated a pH assuming that the condensable gas released when samples are crushed for analysis is all  $CO_2$ . Their estimated  $f(CO_2)$  is high because not all the condensable gas consists of  $CO_2$ . Analysis of the gas phase indicates that as an average, the  $CO_2$  content of the condensable fraction is 43%. Multiplying the  $f(CO_2)$  used in the calculations of Putnam and Norman by 0.43 would change their calculated value of pH to 4.7, which is in excellent agreement with the values calculated here.

The  $f(O_2)$  and  $f(S_2)$  values here calculated for the 200°C fluids differ from those calculated by Putnam and Norman (Figs. 3, 4) because the  $a(H_2S)$  based on measurement is greater than the estimated  $a(H_2S)$  used in their calculations, and because there is a difference in the pH used in the two sets of calculations. The  $f(O_2)$  and  $f(S_2)$  values here calculated

for 150°C fluid differ from those calculated by Putnam and Norman for similar reasons; the minimum  $H_2S$  here used is based on gas measurements, and a different pH was used in the calculations.

Calculation of pH,  $f(O_2)$  and  $f(S_2)$  by the PATH program (Putnam 1980) also differs from values calculated here; these differences may be attributed to a different set of assumptions made concerning the mineralizing system for the PATH calculations. These were made by reacting a fluid of a composition determined by analysis of fluid-inclusion liquid with pyrite and calcite.

The geochemical conditions of the mineralizing fluids inferred by the three methods are similar. Considering the estimated uncertainties in values calculated in this paper, there is almost complete agreement with previous calculated values. All three methods indicate that the pH of the fluids is slightly acidic and that little change in pH occurred during the course of mineral deposition; they all indicate a decrease in  $f(O_2)$  and increase in  $f(S_2)$  relative to  $H_2S-SO_4$  equilibrium from early to late in the paragenesis. The quantities calculated in the present study are considered to be the most accurate representation of the chemical state of the Hansonburg fluid because they are based to the greatest degree on measured quantities. This is evident in the calculation of pH. The pH calculated by Putnam and Norman is 0.2 pH units low because the estimated  $CO_2$  was higher than actual  $CO_2$ . PATH calculations for which no amount of  $CO_2$  was specified indicate a pH 0.2 to 0.6 units less than that calculated here.

## DISCUSSION

### Organic compounds

The detection of organic compounds in inclusion liquids agrees with the observation of immiscible liquids in some fluid inclusions that were postulated to be organic liquids and the suggestion by Roedder *et al.* (1968) of high-pressure organic gases. Organic compounds detected are all light hydrocarbons with less than seven carbon atoms. In part, this may be the result of the method of measurement used; hydrocarbons with more than seven carbon atoms would tend to condense with water in the dry ice-alcohol trap and hence, not to be detected. However, the data suggest that the organic compounds were predominantly of the lighter types. The proportion of  $C_5$  and  $C_6$  compounds is less than that of  $C_2$ ,  $C_3$  and  $C_4$  compounds based on mass peak-heights in the mass spectra. Immiscible organic compounds were observed in most inclusions in sample HSF4. Gas analysis of that sample indicates the presence of 22.5% light organic compounds. This suggests that the observed liquid organic material contains a high percentage of light organic compounds,

because, as discussed before, it is improbable that all heavy organic compounds, if they exist, are destroyed in the extraction process.

Nitrogen is a common gas in the Hansonburg inclusion fluids. Nitrogen commonly occurs in natural gases (Tiratsov 1967); therefore, its occurrence with organic compounds in the Hansonburg fluids suggests a possible sedimentary and biological source for both the organic compounds and a proportion of the  $N_2$ . The organic species in the fluids, as best we can determine, are the same species that have been reported in basin brines (Table 2). Hence, our data are consistent with the proposal that basin brines are the fluids that mineralized Hansonburg.

#### Estimates of pressure and depth of mineralization

The majority of the calculated pressures are between 100 and 200 bars and average 150 bars (not including sample RFF1 in the average) (Table 5). Considering that minimum pressures were calculated, the data suggest that fluids were subject to a pressure of about 150-200 bars. The large variations in calculated pressures may be real, or they may in great part result from the estimated  $\pm 35\%$  error in calculated values. An estimate of the thickness of Paleozoic and Mesozoic sediments in central New Mexico from geological mapping (Wilpolt & Wanek 1951) indicates that a maximum burial of the ore horizon at 1.5 to 2 km occurred during the Early Tertiary. A pressure of 150 to 200 bars is compatible with mineralization at the time of maximum burial with ore fluid subject to hydrostatic pressure.

Sample RFF1 has a high nitrogen content and calculated minimum pressures of 592 and 552 bars, principally from nitrogen gas. A second sample of RFF1 fluorite was analyzed in order to confirm its high content of  $N_2$ . A pressure greater than 592 to 552 bars during mineralization would require 2.2 to 2.3 km overburden at lithostatic pressure (rock density = 2.6). This would not have been impossible, but measurement of pressures in sedimentary basins indicates near-hydrostatic pressures at depths of 2 km (Fig. 4.4, Hannon 1979). It is thus unlikely that Hansonburg was subject to lithostatic pressure unless mineral deposition closed most fluid channels. The vuggy, open nature of the orebodies and rocks of the Council Spring Formation suggests that this never happened. Limited unmixing of gaseous compounds from the mineralizing fluid provides a more likely explanation for the indicated high  $N_2$  pressures.

#### Possible unmixing of gaseous components

A vapor phase resulting from unmixing would contain principally  $N_2$  (Table 6, Fig. 5). If some of

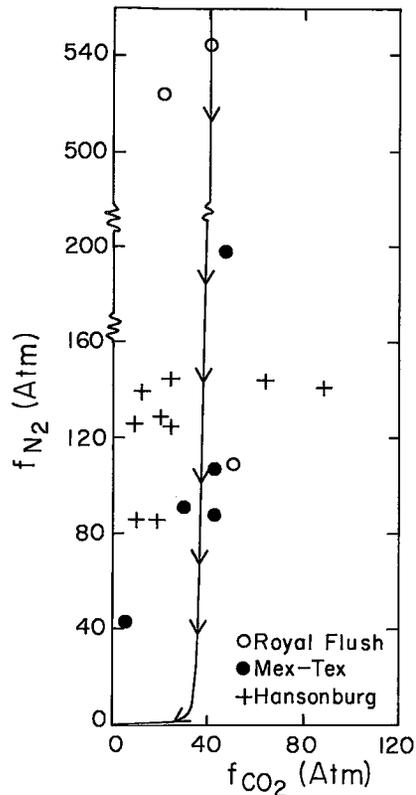


FIG. 6. Calculated  $f(N_2)$  versus  $f(CO_2)$  from Table 5. Line with arrows indicates the change in gas fugacities resulting from unmixing (see Table 6).

the vapor is trapped in inclusions, an analysis of gaseous components in inclusion fluids will yield the amount of gases in the aqueous fluid in equilibrium with the vapor phase, plus volatiles in the vapor-filled inclusions. Hence, an analysis yields a gas/water ratio higher than in the aqueous fluid. If unmixing did occur during mineralization, the excess amount of  $N_2$  in sample RFF1 and perhaps sample HBF1 could be explained by some vapor-filled inclusions among those measured. Re-examination of thick sections of sample RFF1 used for microthermometry as well as newly prepared thick sections allowed us to discover vapor-filled inclusions that we originally passed over, considering them to have opened and

TABLE 7. CALCULATED PARTIAL PRESSURES OF GAS AS A FUNCTION OF TEMPERATURE IN A LIQUID OF SIMILAR COMPOSITION TO THAT WHICH CAUSED MINERALIZATION AT HANSBURG

Temperature (°C)	$f(N_2)$ (bars)	$f(O_2)$ (bars)	$f(H_2O)$ (bars)	$P_T$ (bars)
225	88	39	19	146
200	115	42	11	168
175	142	45	7	194
150	168	48	4	220

Liquid: salinity 14 eq. wt.% NaCl;  $N_2$  0.08 mole %,  $CO_2$  0.4 mole %

filled with air. No vapor-filled inclusions in a thick section of HBF1 from the Mex-Tex deposit were noted; however, Roedder *et al.* (1968) reported small dark inclusions that they considered filled with hydrocarbons, but these possibly could be filled with nitrogen.

The possibility of unmixing is not unreasonable. Although the filling of open space by very coarse-grained minerals suggests a quiescent environment during mineralization, with no decrease in fluid pressure, deposition of quartz suggests declining temperatures during mineralization because the solubility of quartz is principally temperature-dependent (Kennedy 1950); a decrease in fluid temperature can result in unmixing of gaseous components. This is illustrated in Table 7.  $N_2$  and  $CO_2$ , like most gases, have a prograde solubility at temperatures above 100 to 150°C. Cooling a liquid saturated with  $N_2$  or  $CO_2$  will ideally result in the formation of a vapor phase. Alternatively, the mineralizing fluids could have equilibrated at about 590 bars pressure during mineralization if a condition of lithostatic pressure prevailed. The distribution in calculated gas-fugacities in Figure 6 could be the result of conditions of variable pressure because a decrease in pressure would principally result in a loss of  $N_2$ .

Although we cannot definitely conclude that limited unmixing did occur or that pressure changed from lithostatic to hydrostatic conditions, the pressure data do indicate that mineralization occurred during the time of maximum burial. This would constrain mineralization to the Tertiary prior to 7 Ma, when faulting and uplift in the Hansonburg district resulted in erosion of the Cretaceous section.

### *Chemical environment*

The chemical conditions of the Hansonburg fluids are summarized in Table 3. The data indicate that most parameters such as pH, pressure of  $CO_2$  gas, and concentration of Pb in solution remained more or less constant during the course of mineral deposition. The principal difference between early and late mineralizing fluids was a decrease in  $a(H_2S)$  and related decrease in  $f(S_2)$  and increase in  $f(O_2)$ . The data indicate that the concentration of reduced sulfur in ore fluids controlled deposition of sulfides. However, solutions remained in equilibrium with PbS and ZnS, as indicated in Figure 4, and by lack of field evidence for corrosion of early-deposited sulfides.

### *Agreement of mineralogy with chemical environment*

If the measurements reported in this study represent those in the mineralizing fluid, the chemical environment inferred from the analyses should agree with observation. The agreement between the

minerals calculated to be stable in early and late mineralizing fluids (Fig. 4) and those observed in the deposit is good. Galena, sphalerite and pyrite were all deposited early from approximately 200°C fluids. Late fluids at about 150°C deposited minor pyrite and apparently were in equilibrium with galena and sphalerite because there is no evidence of corrosion of early-deposited minerals. Late fluids also deposited siderite.

The calculated  $f(O_2)$  and pH values (Fig. 3) suggest that there were approximately equal amounts of  $SO_4$  and  $H_2S$  in the ore fluids at 200°C, which agrees with deposition of barite and galena by early fluids. Sulfate was calculated to be the dominant sulfur species in the late fluids. This agrees with barite deposition late in paragenesis accompanied by only minor amounts of sulfides.

The agreement between the calculated chemical environments and the mineralogy and paragenesis of the deposit indicates that the measurements of gaseous species are not in serious error.

### *Galena solubility*

At temperatures of 150°C to 200°C and at values of pH of 4.5 to 5.0, the principal Pb ion-paired complexes in the Hansonburg ore solutions would be those with Cl. Lead forms strong complexes with F, but the amount of F in solution here is insufficient to account for the transport of significant amounts of lead (Putnam 1980, Smith 1983). The calculated solubility of galena at the physicochemical conditions determined in this study (Fig. 3) does not agree well with the ~380 ppm Pb measured in inclusion fluids. However, this discrepancy is not of impossible dimension and could be accounted for if the  $a(H_2S)$  was lower than calculated, if Pb was complexed by an agent other than Cl, or if unknown kinetic factors are involved. The  $a(H_2S)$  was calculated assuming that the  $H_2S$  measured occurs as  $H_2S$  in the ore fluid. However, the reduced sulfur measured could have been in an intermediate state of oxidation in the ore fluids, as suggested by Spirakis (1983). If this were the case the  $f(O_2)$  and  $f(S_2)$  calculations would not be correct, but as pointed out elsewhere the good agreement between the inferred chemical environment and mineralogy of the ore deposit argue that they are not greatly in error. On the other hand, the data indicate that galena-depositing solutions were supersaturated with galena, which is to be expected if fluids were in fact depositing galena. The solubility index (S.I.) is indicated to be at least +4, but this degree of supersaturation may be governed by unknown kinetic factors and may, in fact, be normal in galena-depositing fluids.

### *Chemical controls on mineral deposition*

Field, conodont, and fluid-inclusion studies (Put-

nam 1980, Cook 1985) indicate that mineralization was controlled by northwest-trending fractures and that from these fractures, fluids flowed laterally in the Council Springs Member. Both temperatures of fluid-inclusion homogenization (Putnam 1980) and the deposition of silica, whose solubility is strongly controlled by temperature (Kennedy 1950), indicate that fluids were cooling during mineralization. It is not clear what the rate of cooling was; the thermal halo that extends 400 m from the deposit would imply a very slow rate of cooling. However, some of the thermal effects recorded by conodonts could be from the early fluids, which silicified and dolomitized the carbonate.

There is no indication of a large change in pH during mineralization; however, minor changes may have occurred. A decrease in temperature would have increased  $f(\text{CO}_2)$  and hence decreased pH. Minor replacement of carbonate accompanying deposition of quartz and galena early in the paragenesis may both have resulted from a decrease in pH resulting from a cooling of the fluid during initial stages of mineralization, when the wall-rock was cool. Although our data indicate that unmixing was minimal and the vapor phase, if it occurred, was mostly  $\text{N}_2$ , unmixing would have resulted in some  $\text{CO}_2$  loss. If there was little accompanying decrease in temperature during unmixing,  $\text{CO}_2$  loss would result in a slight increase in pH of the fluids.

The data indicate that  $f(\text{O}_2)$ ,  $f(\text{S}_2)$  and  $a(\text{H}_2\text{S})$  changed during the paragenesis. We attribute these variations to changes in the nature of the ore solutions emanating from fluid source-areas. There is no evidence that the concentration of  $\text{H}_2\text{S}$  was controlled by some process at the site of deposition.

The solubilities of galena, fluorite and barite are functions of temperature and pH of solutions in chlorine-bearing solutions at 120–210°C, with solution favored by high-temperature, acidic waters (Blount 1977, Richardson & Holland 1979a, b). We conclude that the most important factor in mineral deposition was temperature decrease.

#### Single ore-fluid

The formation of MVT deposits by mixing of metal-bearing solutions with those containing reduced sulfur has been suggested by many (*e.g.*, Richard 1983, Anderson 1983, Barnes 1983). Mixing of two fluids of differing chemistry and temperature can be determined by fluid-inclusion studies (Robinson & Norman 1984, Zimmerman & Kesler 1981), but there is no indication of mixing of two fluids either in fluid-inclusion microthermometry or fluid-inclusion analytical data. Roedder *et al.* (1968) also reported no evidence for mixing of fluids. The microchemical and gas analytical data are not inconsistent with a single fluid transporting Pb and

reduced sulfur. Our analysis of the data indicates that ore fluids were supersaturated with respect to galena, but the analyses are of inclusion fluids trapped at the site of deposition. It is to be expected that during migration of fluids, pressure and temperature were higher, and possibly pH lower, all of which would favor increased solubility of galena. Powell & Macqueen (1984) have suggested inorganic reduction of sulfur by organic compounds at the site of deposition for the Pine Point deposit. As there is little organic material in the Pennsylvania carbonates in the Hansonburg district, this hypothesis does not seem applicable.

#### Refined model

The data presented here allow refinement of the genetic model for the Hansonburg district previously presented (Putnam *et al.* 1983). The source of the fluids is postulated to be the Jornada de Muerto Basin to the west of the Hansonburg district. This basin has been developing since Rio Grande rifting began about 30 Ma ago. The high heat-flow in the Rio Grande rift (Reiter *et al.* 1975) and the depths 5 to 6 km in the rift basins (Cape *et al.* 1983, Mitchell & Jiracek 1983) indicate that there is no problem in obtaining 200°C waters from these basins. Dissolved constituents in the fluids could be derived from basin-fill sediments, that consist of detritus from Precambrian to Tertiary rocks as well as from unweathered rock in large fault-blocks. Organic compounds could have been leached from Paleozoic or Mesozoic sediments or have been derived from Tertiary biological material in the basin fill.

We contend that formation waters were expelled from the rift basin by a combination of overburden pressure and increasing temperature. Solutions moved laterally to the margins of the rift basin and moved upward along rift-bounding faults, then migrated into the little-disturbed Paleozoic sediments on the margins of the rift along northwesterly trending fractures, thence into the karst unit of the Council Springs Member. Indication that mineralization occurred before 7 Ma ago allows 23 Ma for basin formation and mineralization.

Mineralization occurred over a considerable length of time. Pre-ore hydrothermal fluids dolomitized and silicified the carbonate adjacent to northwest-trending fractures and the Council Springs member. This was the major and most widespread mineralization event. This was followed by sulfide-barite-fluorite mineralization, which was confined to open spaces in the Council Springs Member and minor fracture-fillings in Permian and Pennsylvanian sediments. The initial mineralization occurred in response to 210–150°C fluids transporting both Pb and reduced sulfur, which deposited galena, quartz, fluorite and barite, as the fluids cooled in contact

with wall rock. Later fluids at 180 to 125°C deposited fluorite and barite while cooling but only minor quantities of sulfides because they were nearly devoid of reduced sulfur.

Uplift along the Osura fault has recently exposed the mineralization. Lead-fluorite-barite mineralization similar to that in the Hansonburg district occurs on uplifted fault-blocks along the Rio Grande rift (Fig. 1); we conclude that this mineralization has a similar genesis as that in the Hansonburg district. The Hansonburg district is the most important occurrence of Pb-fluorite-barite mineralization associated with the Rio Grande rift; this is believed to be principally the result of pre-existing open space for mineralization.

### CONCLUSIONS

On the basis of the analysis of gaseous components of fluid inclusions from mineralization in the Hansonburg district, the following conclusions have been reached:

- 1) Ore fluids were basin brines characterized by roughly equal amounts of organic compounds (C<sub>1</sub>-C<sub>6</sub>), N<sub>2</sub> and CO<sub>2</sub>. Gases constituted ~1% of the fluids.
- 2) Early mineralizing fluids that deposited sulfides contained ~10<sup>-2.7</sup> moles H<sub>2</sub>S.
- 3) Sulfide deposition was controlled principally by the amount of H<sub>2</sub>S in the ore fluid.
- 4) A single hydrothermal fluid transporting both Pb and H<sub>2</sub>S was responsible for mineralization at Hansonburg.
- 5) The pH of the ore fluids was 4.3 to 5.1, and no major fluctuation of pH occurred during mineralization.
- 6) Pressure during mineralization was at least about 150 to 200 bars, and mineralization occurred at depths of about 1.5 to 2 km.
- 7) Mineralization was principally in response to cooling of the fluids.
- 8) Data on gas composition permit a reasonable estimation of the chemical conditions during mineral deposition and can be used to place constraints on pressure conditions.

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