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SULFIDES ASSOCIATED WITH THE SALTON SEA GEOTHERMAL BRINE [1]

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ABSTRACT

Concentrated saline brine tapped by a deep well drilled for geothermal power near the Salton Sea, California, deposited metal-rich siliceous scale at the rate of 2 to 3 tons per month. The iron-rich opaline scale contains an average of 20% Cu and up to 6% Ag present in bornite, digenite, chalcopyrite, a new dense polymorph of chalcocite, stromeyerite, and native silver.

The brines are in equilibrium with an assemblage of sulfide minerals in the reservoir rocks. Sphalerite containing 16.6 mol % FeS is in equilibrium with the brine in which the activity of sulfur (a_{s_2}) is estimated at $10^{-10.2}$ at 325° C. This is in good agreement with the projected high-temperature data of Barton and Toulmin (2) for the system Fe-Zn-S. Other sulfides identified in the reservoir rocks are pyrite, pyrrhotite, chalcopyrite, and galena.

The heavy metals in solution are apparently derived from the sediments of the brine reservoir, being released from the silicate minerals in which they occur in trace amounts, as metamorphism of the sediment proceeds. Although the total of the heavy metals in solution greatly exceeds the sulfur, on a molal basis, the brine is saturated with respect to sulfide components and addition of more sulfide ion would only cause precipitation of sulfides.

INTRODUCTION

A VERY concentrated brine containing more than 25 weight percent dissolved solids was tapped by a 5,232-foot deep well, No. 1 Imperial Irrigation District (hereafter called No. 1 IID), drilled for geothermal power during the winter of 1961–1962 in the Imperial Valley, California, near the Salton Sea. In describing the unusual brine and its geologic environment, White, Anderson, and Grubbs (24) also noted some of the exciting implications to be drawn, including the "fascinating possibility that this brine is man's first sample of an 'active' ore solution of the type that probably formed many of the world's economic concentrations of ore metals in the geologic past." This possibly overoptimistic, but nevertheless intriguing suggestion was prompted in part by the accumulation of a metal-rich siliceous scale in the discharge pipes; between 5 and 8 tons of a scale containing approximately 20 percent copper and precious metal values of several hundred ounces of silver plus one-tenth ounce of gold per ton accumulated during a 3-month well test in the summer of 1962.

A temperature range from about 300° to 350° C has been reported by Helgeson (14) and bulk composition data have been reported by White (23),

[1] Publication authorized by the Director, U. S. Geological Survey.

White et al. (24) and Helgeson (12, 14). Limited isotopic data have been reported by Craig (3, 4), White (21), Doe (8), and Doe et al. (9, 10). Despite the scanty data available, conclusions can be drawn concerning the sources of heavy metals in solution. From sulfides recently identified in drill cores recovered from the brine zone, preliminary conclusions can also be drawn for the *in situ* brine.

The brine is very saline; White (22, 23) reported a salinity of 31.9 percent for a sample obtained at the end of the three-month test period of the No. 1 IID well, while Helgeson (14) reported a salinity of 25.9 percent for the brine from the No. 2 IID well. White recollected samples of erupted brine and condensed vapor from the No. 1 IID well on April 21, 1966, and the analyses of these samples are reported in Table 1 and compared with Helgeson's analysis of the No. 2 IID brine. Most of the previously existing discrepancies have either been resolved or greatly reduced. The indicated differences still evident in Table 1 may be real compositional differences, or they may be caused by differences in analytical methods. None of the indicated differences seriously affect the major conclusions of the present paper.

The high content of heavy metals in the brine is striking, and suggests a possible comparison with the even higher values of Cu and Zn reported in saline fluids from inclusions in quartz from Creede, Colo., and in fluorite from Hardin Co., Ill., by Czamanske et al. (5). Even more striking is the low sulfur content of the brine by comparison with the high content of heavy metals. For example, when Helgeson's data (14) for No. 2 IID are reported on a molal basis, the sum of the heavy metals Ag, Cu, Pb, and Zn exceeds the amount of sulfur by a factor of eight; the corresponding excess in No. 1 IID is less certain but is about fifteen.

The information to be drawn regarding the sources of the brine, heavy metals and sulfur has potentially wide consequences for economic geologists. Oxygen and hydrogen isotopic studies indicate that the waters are meteoric in origin (3, 4, 21); lead and strontium isotopic studies (8, 9, 10) indicate that little or none of the lead and strontium in the brines could have come from a magmatic source such as the associated rhyolite domes. The important question of whether *any* of the ore metals in the brine were derived from magmatic sources, or whether all the metals, together with the other brine constituents, were leached from the enclosing rocks, remains to be answered. The isotopic evidence strongly suggests, however, that most of the brine constituents have been obtained by leaching and exchange processes from the enclosing rocks, and the interesting mass balance calculations by Helgeson (13), show that this is a feasible mechanism.

PHYSICAL DESCRIPTION OF THE PIPE SCALES

During production tests on the No. 1 IID well, hard siliceous scales were deposited in the casing and discharge pipes. The scales are black, brittle materials, curved to the inside contours of the pipes and obviously layered. Because the accumulating scale tended to fill the discharge pipes, it was removed at intervals and only one sample, W-769 from the casing at the well

Table 1.--Compositions of the reservoir brines produced from the No. 1 IID and No. 2 IID wells in parts per million

Constituent	No. 1 IID [1]	No. 2 IID [2]
Sodium	50,400	53,000
Potassium	17,500	16,500
Lithium	215	210
Rubidium	137	70
Cesium	16	20
Ammonia (NH_4)	409	
Calcium	28,000	27,800
Magnesium	54	10
Barium	235	250
Strontium	609	440
Chlorine	155,000	155,000
Fluorine	15	Not reported
Bromine	120	Not reported
Iodine	18	Not reported
Sulfate (SO_4)	5.4	Total sulfur
Sulfide sulfur	16	30
Boron	390	390
Iron	2,090	2,000
Manganese	1,560	1,370
Silver	0.8	2
Copper	8	3
Lead	84	80
Zinc	790	500
Arsenic	12	Not reported
Antimony	0.4	Not reported
CO_2 as HCO_3	> 150	690
Silica	400	400
Total reported	258,360 [1]	258,765 [2]

[1] Considered best values, 1966; largely from samples of erupted brine and condensed vapor collected April 21, 1966 and analyzed by D. E. Donaldson and C. E. Roberson, U. S. Geological Survey. Contents reported for As, Pb, Zn, Sr, Cu, Cs, and I from analysis of White (22), decreased by 18.8 percent for selective loss of steam and other gases, previously suspected but now confirmed. Other constituents, in ppm: Ag 0.8, Sn 0.5, Hg 0.006, Sb 0.4, and Tl 1.5 (not previously reported). Sulfide sulfur may be greater than 16 but is less than 27 ppm.

[2] From Helgeson (14). 500 ppm CO_2 here reported as equivalent HCO_3.

head where the accumulation was thin, is claimed to represent a complete record of the deposition. An estimated 5 to 8 tons of scale was deposited during the 3-month test period.

 Three samples of siliceous pipe scale were available for study and are referred to by their field reference numbers to avoid confusion. The brine temperatures were measured directly. The samples are, in order of decreasing temperature of deposition:

1) *W-769*; deposited on the casing at the well head, at a temperature of approximately 220° C (±30° C). Sample is about 8 mm thick and was deposited through the 3-month test period.
2) *W-767*; formed in the discharge pipe about 175 feet from W-769 during the second month of the 3-month test period, at an estimated temperature of 170° C (±30° C). Sample thickness ranges from 9 to 16 mm.
3) *W-768*; formed just inside the mouth of the effluent discharge pipe about 275 feet horizontally from the well head; the estimated temperature was 130° C (±20° C). The mouth of the discharge pipe was immersed in a shallow pond of a drain canal leading to the Salton Sea. Although the brine was discharging, atmospheric oxygen was effectively excluded from the pipe and essentially no oxidation of the sulfides occurred. The sample, from 20 to 35 mm thick, formed during the second month of the 3-month test period.

Within sample W-769 only two distinct layers are evident, whereas in W-767 there are three and in W-768 six. Individual layers cannot be correlated between samples, nor is the cause of the layering clearly understood. Because the most conspicuous layering occurs in the two samples from the discharge pipe (W-767 and W-768), it is presumably related to differences in temperatures and pressures imposed by the valve settings, and hence changes in the vapor/liquid ratios in the mass flow, and does not reflect in the initial fluid composition.

Although individual layers differ macroscopically and mineralogically, they are texturally similar, containing parallel crusts with arborescent growths of exceedingly fine-grained sulfides growing inward from the inner surfaces of the pipes. The arborescent growths, in the one specimen for which the upstream and downstream directions are known (W-768), tend to curve "upstream" towards the sources of the fluid depositing them. Individual sulfide grains, some with obvious crystal faces, range in diameter from about 0.0001 mm to, in rare instances, 1.0 mm, being in general about 0.001–0.01 mm. Curving strings of individual grains appear to touch each other and retain the same general crystallographic orientation over distances of several millimeters, a conclusion indicated by the parallel orientation of exsolved lamellae from grain to grain and by a myriad of grains in a single arborescent growth having the same extinction angle under crossed nicols.

Because crystallographic continuity is so commonly maintained within individual arborescent sulfide growths, deposition of the enclosing opaline matrix must necessarily have lagged slightly behind sulfide deposition. This lag was not great however, and the sulfides were protected from further reaction with the brines once they were enclosed. Where a depositional layer ends, being replaced by another sulfide assemblage in the next layer, only the outermost fraction of a millimeter of the earlier layer is altered to be compatible with the new band. In the rare circumstance where fine fractures have developed in the scale, allowing later fluids to come into contact with earlier layers, only the sulfide grains within about 0.2 mm of the fracture

show any alteration effects. These facts clearly indicate that the opaline matrix enclosed the sulfides very soon after their formation and ensured that unaltered samples of the actual sulfides deposited were preserved for later study.

CHEMISTRY AND MINERALOGY OF THE PIPE SCALE

Bulk compositional data for the three scale samples are presented in Table 2. Although the samples are similar in containing predominantly Si, Cu, Fe, and Ag, sample W-769 deposited at 220° ± 30° C is considerably

Table 2.--Quantitative spectrographic analyses of sulfide-rich scale. Samples are composites of all the bands listed in Table 4 Semiquantitative spectrographic analysis of W-768-B, a heavy mineral fraction (S.G. >3.32) separated from W-768. Values in weight percent. Analyst: Robert E. Mays.

	W-769 (220 ± 30°C)	W-767 (170 ± 30°C)	W-768 (130 ± 20°C)	W-768-B [2]
Si	[1] M	[1] M	[1] M	M
Cu	[1] M	[1] M	[1] M	M
Fe	5.0	7.0	6.0	5.
Ag	[1] 7.0	1.3	2.8	>3.
As	.18	<.10	<.10	.3
Sb	.72	.17	.25	.7
Bi	.11	.004	.009	.03
Mn	.055	.42	.34	.07
Co	.0050	<.0004	.0006	.002
Al	[1] 3.	1.0	1.4	1.
Ga	.0016	.016	.012	.003
Yb	<.0002	.0002	.0002	.015
Be	.0036	.046	.037	.007
Mg	.014	.0085	.0080	.0015
Ca	.55	.60	.55	.2
Sr	.008	.003	:003	.002
Ba	.014	.020	.0090	.002
B	.019	.11	.080	.01
Pb	.012	.011	.007	.01
Sn	<.002	<.002	<.002	.001
Na	[1] 1.	[1] 1.	[1] 1.	.3
K	[1] 1.5	[1] 1.	[1] 1.5	0
Ti	[1] .0007	[1] .0015	[1] .0007	.0015

[1] Above or below best range for quantitative analysis; determined by 6-step semiquantitative analysis by Chris Heropoulos, U. S. Geological Survey.

[2] Results of semiquantitative analysis are reported to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, etc.; the assigned group includes the quantitative value about 30 percent of the time. Looked for but not found: P, Au, Cd, Ce, Cr, Ge, Hf, Hg, In, La, Li, Mo, Nb, Ni, Pd, Pt, Re, Sc, Ta, Te, Th, Tl, U, V, W, Y, Zn, Zr.

enriched in Ag, As, Sb, Bi, Co, Mg, and Sr, but depleted in Mn, Ga, Be, and B with respect to W-767 and W-768, deposited at $170° \pm 30°$ C and $130° \pm 20°$ C, respectively.

A heavy mineral separate with specific gravity greater than 3.32 was obtained from W-768 by our colleague Donald E. Lee. An analysis of this concentrate (W-768-B, Table 2) shows that the heavy fraction, consisting predominantly of sulfides, is enriched in Cu, S, Ag, As, Sb, Bi, Co, Sn, and Ti with respect to the bulk sample and therefore even more strongly with respect to the opaline matrix. The presence of Ti in the heavy fraction is probably due to tiny grains of brookite, observed by Lee in a grain mount of a heavy nonparamagnetic fraction.

The pipe scale was first studied by thin and polished section microscopy, but the extremely fine-grained sulfides precluded adequate and certain identifi-

Table 3 -- <u>Sulfide minerals identified in No. 1 I.I.D. well scale, and their</u>

<u>chemical compositions</u>

Name	Formula	Atomic ratios, metals/S
Digenite	Cu_9S_5 or $(Cu,Ag)_9S_5$	9/5
Bornite	Cu_5FeS_4 or $(Cu,Ag)_5FeS_4$	6/4
Chalcocite and "dense" chalcocite	Cu_2S or $(Cu,Ag)_2S$	2/1
Stromeyerite	CuAgS	2/1
Arsenopyrite	FeAsS	2/1
Tetrahedrite	$(Cu,Ag,Zn,Fe)_{12}(Sb,As)_4S_{13}$	16/13
Chalcopyrite	$CuFeS_2$	2/2
Pyrite	FeS_2	1/2

cation of all phases present. Thin section study did not reveal any crystalline silicate materials and no definite lines belonging to a silicate phase were resolved by X-ray powder diffraction techniques. The silica is in an amorphous, opaline form.

X-ray powder diffraction was used to confirm optical identification of all sulfide minerals. To improve line intensities the sulfides from individual layers were concentrated by dissolving the opaline matrix in cold HF diluted 1:1 with distilled water. The opaline matrix was completely dissolved from coarsely crushed material within a few minutes. The sulfides were essentially insoluble in the 1:1 HF, a 50 mg concentrate losing only 1 mg in weight when immersed for 6 hours. This test does not eliminate the possibility that some other phases might have been completely removed by the

initial HF treatment. That this possibility is unlikely is suggested by the fact that all crystalline phases detected in the untreated sample were found to be concentrated in the acid-insoluble residue. The sulfide minerals identified in the study are listed in Table 3.

Small portions were removed from each macroscopically distinct band in the three scale samples and analyzed by X-ray fluorescence, using a series

Table 4.--Quantitative X-ray fluorescence analyses and mineralogical contents of sulfide-rich scale from No. 1 IID well. Individual bands are indicated by number in parentheses; band (1) being the first band deposited in a given sample. asp = arsenopyrite, bn = bornite, cc II = dense Cu₂S, cp = chalcopyrite, dg = digenite, py = pyrite, strm = stromeyerite, td = tetrahedrite. Analyst: Harry J. Rose, Jr.

Sample No.		Weight Percent						Weight Ratios			Mineral Content
		Cu	Ag	Fe	As	Sb	S	Metals/S	Cu/Ag	Sb/As	
W-769 (1) 220±30°C		10.0	1.2	3.8	0.23	1.05	6.6	2.47	8.9	4.6	bn, cp, Ag
W-769 (2)	"	43.6	5.8	7.1	0.15	0.69	22.5	2.55	7.5	4.6	bn, cp, cc II, asp, Ag
W-767 (1) 170±30°C		14.0	1.2	15.7	0.20	0.52	10.2	3.10	11.7	2.6	dg, py
W-767 (2)	"	27.5	3.1	8.6	0.13	0.66	13.4	2.98	8.9	5.1	bn, cc II, Ag
W-767 (3)	"	23.6	1.0	10.6	0.13	0.57	12.8	2.80	23.6	4.4	dg, bn
W-768 (1) 130±20°C		10.1	1.0	25.4	0.30	0.55	9.9	3.78	10.1	1.8	dg, trace td
W-768 (2)	"	13.4	1.2	18.8	0.23	0.53	10.8	3.17	11.2	2.3	dg, trace td
W-768 (3)	"	19.2	1.6	11.3	0.15	0.56	12.2	2.69	12.0	3.7	dg, bn, py
W-768 (4)	"	12.4	1.6	14.0	0.15	0.53	10.9	2.63	7.8	3.5	dg, bn
W-768 (5)	"	11.5	2.1	12.0	0.14	0.45	11.6	2.26	5.5	3.2	dg, strm
W-768 (6)	"	28.2	3.4	9.8	0.11	0.55	14.2	2.96	8.3	5.0	bn, cp, cc II, strm, Ag

Table 5.--Compositions of sulfide concentrates from No. 1 IID well, compared with bulk compositions of bands from which they were concentrated. Sulfides concentrated by removing the opaline matrix with HF. Concentrate compositions adjusted by concentration factor to illustrate quantities of elements actually incorporated in the sulfide phases. Remaining major components in original bands are SiO₂ and H₂O.

Element	Band W-768(3) (130 ± 20°C)			Band W-767(2) (170 ± 30°C)		
	Weight percent			Weight percent		
	Original	Sulfide (28% of original)	Constituents of metal sulfides in original	Original	Sulfide (40% of original)	Constituents of metal sulfides in original
Cu	27.5	64.2	25.7	19.2	68.0	19.0
Ag	3.1	8.2	3.2	1.6	5.8	1.6
Fe	8.6	8.2	3.2	11.3	5.4	3.2
As	0.13	0.09	0.04	0.15	0.09	0.05
Sb	0.66	0.25	0.10	0.56	0.17	0.05
S	13.4	19.5	7.8	12.2	22.3	6.2
Total	53.39	100.44	40.04	45.01	101.76	30.10

of synthetic sulfides as analytical standards. The results of these analyses are presented in Table 4, together with the mineralogical contents of each band.

Sulfide Minerals.—As anticipated from the high copper values, the two most common minerals were the copper sulfides, bornite and digenite. Most unexpected was the identification of the dense, high pressure polymorph of Cu₂S (Skinner et al., 18), a compound with apparently identical X-ray

pattern to the metastable high-temperature tetragonal form of djurleite ($Cu_{1.96}S$), first synthesized by Djurle (7). This phase could not be separated for individual chemical analysis, however, and it slowly inverted to chalcocite; by January 1965, 30 months after deposition, it could no longer be detected in the concentrates. This instability is similar to that found in synthetic materials (18). If the unstable phase had been a djurleite polymorph, its low-temperature breakdown product should have been djurleite rather than chalcocite.

Stromeyerite or native silver were identified in five different layers (Table 4), but silver minerals were not found in the remaining six layers. In each case an appreciable quantity of silver was presumably in solid solution in the digenite and/or bornite. There is considerable evidence to support this hypothesis. Studies in the system Cu-Ag-S (18) have shown that very extensive solid solution of Ag_2S can occur in the cation-disordered high-chalcocite and high-digenite structures. Below the high-temperature inversions, at 103° C and 83° C for chalcocite and digenite, respectively, the solubility of silver in the structures is much reduced, but still appreciable. Above 500° C a continuous single-phase field, with a cation-disordered, face-centered-cubic structure, encompasses the compositions of bornite, digenite, and stromeyerite (Skinner, unpublished data). The extent of solid solution of silver in bornite at temperatures below 500° C is unknown, but appears appreciable from the data of Tables 4 and 5.

The occurrence of native silver is most interesting. It occurs only in assemblages lacking digenite, in agreement with the published phase relations (18). The assemblage silver + digenite is excluded by the assemblage chalcocite + stromeyerite. Studies in the system Cu-Ag-Fe-S (Skinner, unpublished data) have shown that bornite + silver and bornite solid solutions + silver are stable over wide temperature and composition ranges.

Anomalous mineral associations (Table 4) are readily understood from textural evidence. Many grains show minute crystal faces that clearly indicate single phase crystals at the time of formation, but have exsolved to exceedingly fine-grained intergrowths of bornite + digenite, bornite + dense Cu_2S ± stromeyerite, bornite + chalcopyrite, or digenite + stromeyerite.

The dense Cu_2S phase occurs only as exsolution lamellae in bornite; there is no evidence for its precipitation directly from the brine. Stromeyerite occurs as tiny laths intergrown with both digenite and bornite and also appears to have formed by exsolution rather than by direct precipitation from the brine.

Layers W-767(1) and W-768(2) contain traces of tetrahedrite in addition to the predominant digenite phase (Table 4). Even on the extreme assumption that all the copper atoms in the tetrahedrite structure are replaced by silver atoms, the mineral is so scare that no more than 10 percent of the total silver can reside in it; most of the silver clearly must occur in the digenite. Therefore at least 4.5 percent of the copper atoms in the digenite must be replaced by silver, although this might very well be a metastable solid solution that would exsolve with time. Unfortunately, the bornite-rich

bands are too impure to allow a similar calculation for silver solubility in bornite.

Opaline Matrix.—The opaline matrix enclosing the sulfide grains is curious in many respects. Although it is amorphous to X-rays, showing only the broad background rise around 4.2 Å, characteristic of amorphous silica, it has an index of refraction of 1.51 ± 0.02, considerably higher than that of common opals. The matrix ranges from nearly colorless to light brown; is always transparent; and shows no evidence, either optically or by X-rays, of containing finely divided inclusions of phases other than the sulfides already discussed. Unfortunately, the matrix is so intimately mixed with the fine-grained sulfides we have been unable to either separate a pure fraction for chemical analysis, or perform electron microprobe analyses free of interference from tiny sulfide grains. These limitations have forced us to use indirect means to estimate the opal composition.

Layer W-767(2) contains approximately 40 percent sulfides by weight and layer W-768(3) approximately 28 percent. Accepting the evidence previously cited, that the sulfide concentrates are essentially unaffected by the concentration process, and adjusting for their composition and amount, it is obvious from Table 4 that a major portion of both the Fe and S must reside in the matrix, thereby explaining its high index of refraction.

The quantities of As and Sb present in the matrix are minor, because their concentrations in the bulk samples are minor. However, approximately 2.2 and 5.4 wt % Fe, as well as 6.0 and 5.6 wt. % S are apparently present in the matrices of samples W-767(2) and W-768(3), respectively, and this immediately raises the question of their mode of incorporation. If they occur in submicroscopic particles, some evidence of their presence could be expected from X-ray diffraction. If they were combined to form a single compound, a relatively constant Fe:S ratio should prevail from layer to layer. In fact, however, the atomic ratio of the Fe to S trapped in the opal of layer W-768 (3) is 0.77 whereas that in layer W-767(2) is 0.56.

The only conclusion to draw is that the Fe and S are incorporated in some fashion, probably metastably, within the opaline structure, which is itself metastable. It is interesting to speculate that similar opaline materials may have been the progenitors of some of the fine-grained sulfide-bearing cherts found in epithermal deposits, the sulfides forming into distinct phases as the opal later broke down and recrystallized to chert.

SULFIDES AND OXIDES IDENTIFIED IN THE RESERVOIR ROCKS

Core samples from several drill holes within the brine reservoir contain sulfide and metallic oxide minerals.

Pyrite has been found in all wells (25) and is apparently common throughout the field; White et al. (24), for example, report pyrite in each of the five core specimens examined. The pyrite occurs as fresh, unetched crystals in pores, fractures and disseminations throughout the rock, leaving no doubt that it was in contact with the brine. Its presence with epidote in cross-cutting veinlets clearly indicates that the pyrite formed after sedimentation and dia-

genesis, and strongly suggests that the brine controls its formation and distribution.

Hematite also occurs in the core sections, having been identified from both the No. 1 and No. 2 IID wells. Hematite, like pyrite, is well crystallized, commonly specular, and is concentrated in cross-cutting veinlets. Associated minerals in these veinlets are coarse, euhedral crystals of pyrite and quartz.

Samples from the interval 6603–6612 feet in the No. 1 River Ranch well are especially interesting. A number of narrow veinlets contain sphalerite and chalcopyrite and one veinlet, at 6,612 feet, contains pyrrhotite and sphalerite. The veinlets are open and porous, containing euhedral crystals of calcite, potassium feldspar, and sulfides.

The most abundant sphalerite veinlets, from approximately 6,605 ft., have a maximum width of 3 mm, and typically contain unetched sphalerite crystals up to 2 mm in diameter, intergrown with a number of small crystals of chalcopyrite.

The sphalerites are dark colored because of a very dark outer zone, but broken surfaces reveal lighter resinous-colored cores and inner zones with well marked growth zoning. In one sphalerite sample the boundary between the outer dark zone and the lighter colored core was gradational rather than a sharp boundary as generally found for growth zoning. This same sample also had a dark-colored zone with a diffuse boundary parallel to open fractures and other surfaces of imperfection in the crystal. The irregular, diffuse nature of the boundary strongly suggests diffusional control with iron diffusing in from any surface of contact between brine and crystals, and gives us some measure of confidence that the composition of this outer iron-rich zone is that of a sphalerite in equilibrium with the present brine.

The light-colored inner portions of the sphalerite crystals are sufficiently clear to reveal small primary fluid inclusions in them. Our colleague Edwin Roedder found that the fluids in the inclusions were very saline—approximately 27 percent salinity by the depression of freezing point method—and that the filling temperatures, corrected for 6,600 feet of hydrostatic pressure, were approximately 310° C.[1] The filling temperature falls near the lower limit of the 300–350° C temperature range reported for the present brine by Helgeson (14), but the present salinity is the same as that of the fluids in the vacuoles, within the measurement error. This suggests that the temperature may have risen somewhat after deposition of the early, light-colored sphalerite, but that the brine composition has changed very little.

Electron microprobe analysis of the sphalerites showed that the lightest colored, resinous cores contain 3.0 ± 0.2 mol percent FeS, but the dark outer zones in direct contact with the brine contain 16.6 ± 0.4 mol percent FeS.

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[1] The fluid cavities are small and the total internal reflection because of the high-index sphalerite and the low-index fluid makes many of them appear to have black borders. These zones often mask the vapor bubble, particularly as it decreases in size, so the exact filling temperature is difficult to pick, and the reported temperature tends to be too low. All the pressure corrected filling temperatures, of the 33 reported by Roedder, fall in a 17° C range, with the highest at 310° C, and this is selected as the most probable temperature at which the sphalerites grew.

The only pyrrhotite found in the field to date was identified by our colleagues Mrs. Terry Keith and L. J. P. Muffler from the 6,612 foot-zone in River Ranch No. 1 well. It is directly associated with the dark-colored sphalerite, along with traces of chalcopyrite and galena. In this particular section of the River Ranch No. 1 well, pyrite is unusually scarce, but two small crystals were identified in polished sections, together with sphalerite, from the pyrrhotite zone. X-ray diffraction, using a high-angle goniometer set for its highest resolution and slowest scanning speed, reveals the pyrrhotite to be well crystallized, with the strong (102) peak sharp and uncomplicated and thus presumably hexagonal. The spacing of the (102) peak, determined by repetitive measurements against pure NaCl as a standard, is 2.0686 ± 0.0006 Å, corresponding to a composition of 47.53 mol percent Fe (16). The indicated temperature on the pyrrhotite-pyrite solvus of Arnold (1) is $267° \pm 14°$ C, though the number has a questionable significance because of the doubtful validity of the solvus at those temperatures.

DISCUSSION

Few unambiguous conclusions can be drawn from the pipe-scale deposits beyond an obvious and very important one: the Salton Sea geothermal brines not only transport ore metals, but are also capable of depositing a range of sulfide minerals in assemblages commonly cited as evidence of hydrothermal origin. The sulfur- and iron-rich opaline matrix suggests that deposition occurred under conditions far from equilibrium, and that kinetic factors might have controlled the assemblages. For these reasons it is unwise to speculate far on the basis of evidence from the pipe-scale deposits alone. However, from the information presently available a provocative picture is beginning to emerge.

For lack of further available information we have selected a temperature of 325° C, midway between the 300°–350° C limits cited by Helgeson (14), as a reasonable estimate for the brine reservoir temperature in the vicinity of the sphalerite and pyrrhotite. If the assumption is incorrect, it can only be in error by ±25° C. If we further assume that the activities of oxygen and sulfur vary with temperature, but not geographically at a given temperature throughout the brine, some interesting observations may be made. The validity of these assumptions, and hence the correctness of the observations, must necessarily await more information from the brine field.

The ubiquity of pyrite throughout the field indicates an activity of sulfur (a_{s_2}) sufficiently high to form pyrite rather than pyrrhotite. The fact that pyrrhotite does occur in the No. 1 River Ranch well suggests that a_{s_2} is close to that defined by the pyrite-pyrrhotite solvus. From the data of Toulmin and Barton (20) a_{s_2} at 325° C is $10^{-10.2}$. This estimate might be more reassuring if the composition of the pyrrhotite fell at, or close to, 325° C on the pyrite-pyrrhotite solvus, rather than the indicated 267° C. There are considerable uncertainties in the pyrrhotite phase relations at and below 325° C, however (see for instance, Hall and Yund, 11), and these, coupled with the very rapid raction rates in pyrrhotite even below 300° C at quenching

rates as rapid as 1°/min, suggests that use of the high-temperature solvus is not justified in this case. The pyrrhotite-pyrite pair could therefore only be taken to fix an upper limit of $10^{-10.2}$ for a_{s2}.

The composition of the dark sphalerite in the outer crystal zones adjacent to and presumably in equilibrium with the brine, also permits estimation of a_{s2}. The work of Barton and Toulmin (2) on the system Fe-Zn-S shows that the FeS content of sphalerite depends both on the temperature of formation and a_{s2}, with a_{s2} the more important variable. Although their experimental measurements have not been carried down to 325° C, their projection of sphalerite compositions in the assemblage sphalerite + pyrite + pyrrhotite to this temperature indicates an a_{s2} of $10^{-11 \pm 1.0}$. This agreement is support for either the Barton-Toulmin projection, or for the a_{s2} calculated from the pyrite-pyrrhotite assemblage. It is also support for the contention by Barton and Toulmin that the FeS-content of sphalerite, in equilibrium with pyrite plus pyrrhotite, reaches a maximum of approximately 19 mol % FeS at 530° C, and decreases at lower temperatures in this case passing through the composition 16.6 mol % FeS at 325° C. In this regard, it is interesting to observe that 16.6 mole % FeS in sphalerite gives an incorrectly high temperature of at least 500° C if the now discredited FeS-ZnS solvus of Kullerud (16) is used.

The *minimum* activity of oxygen, a_{o2}, is fixed by the presence of hematite. At 325° C the assemblage hematite + magnetite defines a_{o2}, as $10^{-27.1}$ (15), and this figure is at best a minimum because of the absence of magnetite.

A drill hole into a deep brine reservoir does not constitute a reasonable facsimile of an ore-depositing system. The brine is erupted at high velocity through a straight smooth-walled iron pipe; it has no chance to react with wall-rocks or to intermingle with cooler surface waters of different compositions; the flow is adiabatic so cooling occurs with great rapidity and the sulfide-opal assemblage is deposited rapidly under conditions that strongly favor disequilibrium. In addition, a gas phase separates from the brine as the pressure is released, probably also under conditions far from equilibrium. Despite qualifications concerning the conditions under which the sulfide-rich scale was deposited, several pertinent questions can be raised.

As noted earlier, the sulfur content of the brine is surprisingly low. The sulfur content of the No. 1 IID brine is 20 ppm, most of which is sulfide and Helgeson (14) reports a total sulfur content for the No. 2 IID well, irrespective of species, of 30 ppm, and indicates that the sulfate content is less than 1 ppm (Helgeson, personal communication, 1966). Both sets of data demonstrate that the total ore metals, on a molar basis, far exceed the sulfur present. Even if the data are recalculated to exclude Fe from consideration Helgeson's data indicate that ΣAg, Cu, Pb, Zn/S is approximately 8 whereas White's data indicate ΣAg, Cu, Pb, Zn/S of 15.

The abundant pyrite and other sulfides occurring as crystals with clean, unetched surfaces, strongly suggest that the brine *in situ* is in equilibrium with an extensive solid sulfide assemblage, and is therefore saturated with respect to the sulfide components. The apparent imbalance between heavy

metals and sulfur in solution does not, therefore, indicate a deficiency of sulfur, and a higher concentration of sulfide ion would only cause the precipitation of sulfides from a solution already saturated in sulfide ion, in which the metals are carried in the form of complex ions.

Using the lead and strontium in solution (8, 9, 10), as guides to the origin of the heavy metals, sediments appear to be the most likely source. The extensive metamorphic changes reported by White et al. (24) and by Muffler and White (17) indicate that many of the original silicate minerals have undergone alteration and recrystallization. In the process of these changes trace quantities of heavy metals—for example, lead from feldspars, zinc and copper from clay minerals, amphiboles, and micas—would be released to solution and concentrated there.

It is clear that this brine could not, by any simple isochemical mechanism, deposit all its heavy metals as sulfides. In fact, White et al. (24) estimate that the sulfide-rich scales discussed in this paper were formed by only a small fraction of the total Ag and Cu in solution. The more abundant heavy metals, Pb and Zn, were not precipitated at all, and less than 0.1 percent of the total heavy metals, excluding Fe, were removed from solution.

Although satisfactory answers cannot be given from the data presented in this paper, three very pertinent questions are immediately posed, and the solutions of these important problems should be sought in further work on the Salton Sea geothermal brines.

a) In what form are the heavy metals carried in solution, and how do their solubilities change with temperature? While chloride complexes probably explain the observed metal concentrations, the picture is not clear-cut and much high-temperature experimental work is required.

b) By what mechanisms do the Ag, Cu, and Fe precipitate to the virtual exclusion of the Pb, Zn, and Mn? The answer to this problem is directly related to the first question.

c) Under what circumstances might the brine deposit its heavy metals as sulfide ore deposits, and are there known ore deposits that originated from brines such as these? If the 20–30 ppm of sulfur in the brines were all combined with heavy metals and precipitated as sulfides, only a tiny portion of the heavy metal available would be removed from solution. The volume of the geothermal brine field is apparently so great, however, that even this small fraction would form a large ore deposit. The circumstance where tectonic movements would open channelways for brine movements and sulfide deposition by simple cooling or mixing with surficial waters is easily imagined.

The knowledge that a large volume of metal-rich saline fluid can be generated high in earth's crust is a very provocative thought, and one already explored to some extent by Davidson (6). The possible environments in which such brines might deposit their heavy metals are not hard to imagine, and origins for Kupferschiefer ores and Mississippi Valley type deposits by this mechanism have often been proposed. It is quite clear however, that any mechanism for the formation of sul-

fide deposits by using *all* the heavy metals requires a source of sulfur other than that now carried in solution.

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