GL03771

F ORE FLUIDS

O-NaCl at elevated tem-

ation method of study of

ystem $H_2O-CO_2$ at high

ioxide in NaCl solutions
5–454.

d inclusions: *J. Geology*,

1962: *U.S. Geol. Survey*

ems: *L'vov Gosudarst.*
., 135–169 (in Russian).
Flüssigkeiten und Gase;

pegmatites of the Black

ts physical and chemical

cal properties of water:

ull. *Geol. Soc. Am.*, 68,

vaters: *Bull. Geol. Soc.*

ute (Missouri-Kansas-
ol. *Soc. Am.*, 69, 1660.
s *in subsurface Environ-*
etroleum Geologists.
l composition of sub-

Rocky Mountains of

quartz: Final Report
. *Sta., Georgia Inst. of*

mplified by the Belle-
English).
nd A. A. Moskalyuk
ses. *Nauch.-Issledov.*
ssian).
clusions in synthetic

eralien und Gesteine:

f the Engineer Dept.
f the Fortieth Paral-

# Mercury and Base-Metal Deposits With Associated Thermal and Mineral Waters*

DONALD E. WHITE

*U. S. Geological Survey*

A review of the kinds of natural thermal and mineral waters that are physically most closely associated with Hg and base-metal-Ag deposits may clarify the geochemistry of transport and deposition of these metals. Factors affecting composition, concentration, pH, and Eh in the upper parts of spring systems must also be considered for all epithermal ore deposits and can even increase our understanding of some other types of ore deposits.

Previous investigators generally have favored transport of mercury as the sulfide complex $HgS_2^{2-}$ in alkaline sulfur-rich solutions; transport of elemental Hg in a vapor phase, at least locally, has also been favored. The present paper demonstrates that thermal and mineral fluids now associated with Hg deposits are characterized by relatively high contents of Na,[1] $HCO_3$, B, and $NH_4$; by modest contents of sulfide and total dissolved constituents; and by neutral pH's.[2] The alkaline sulfide theory is not excluded completely by

*Publication authorized by the Director, U.S. Geological Survey

[1]The ionization state of species is ordinarily not indicated in this report except where a very specific species is intended, such as $HgS_2^{2-}$. Na, for example, includes $Na^+$ as well as all other Na species.

[2]Unless otherwise noted, all pH's of this paper were determined in a laboratory at room temperature in samples collected carefully to preserve $CO_2$ and other sensitive species. In situ pH's at natural temperatures are discussed in the section on Steamboat Springs but very few measurements have been made.

present evidence, but on the other hand, no strong support is found for alkaline solutions high in sulfide and in close association with Hg. Moreover, kaolinite, dickite, illite, and montmorillonite are hydrothermal minerals of many commercial Hg deposits. These minerals suggest, in the light of experimental work, that Hg-bearing ore solutions have low cation/$H^+$ ratios and are not far from neutral in pH. In contrast, minerals such as hydrothermal albite, K-feldspar, and zeolites, which are indicative of alkaline environments, are rare or absent from commercial mercury deposits. Several possible transport mechanisms compatible with the mineralogy are suggested by the nature of the presently associated fluids.

Fluids convincingly related to base-metal deposits are very scarce near the earth's surface. Recent evidence from the Salton Sea geothermal area of California and a few hot springs indicates that very saline brines high in Na, Ca, and Cl are very potent solvents for base metals and Ag as well as some sulfide, but the brines are on the whole sulfur deficient. This evidence, in combination with Roedder's data from fluid inclusions (Chapter 12) and Helgeson's thermodynamic calculations (1964) suggests that sulfur-deficient thermal saline brines may be the dominant type of base-metal ore fluid. If this hypothesis is valid, either some mechanism is necessary to provide enough local S to deposit the base metals as sulfides, or the ore-forming process is commonly a very inefficient one.

Strongly saline brines seldom, if ever, reach the surface in undiluted form because their density is so much higher than that of normal surface waters. Thermal waters now found at the surface near some epithermal base metal deposits are relatively dilute and are high in $HCO_3$ and $SO_4$; they cannot be simple dilutions of the hypothesized saline brines. These dilute spring waters also commonly deposit Mn oxides that are high in W, Cu, Pb, Zn, and As (Hewett and others, 1960, 1963; Hewett, 1964); contents of each of these metals in the bicarbonate waters are low (<1 ppm range), but the Mn oxides are highly effective scavengers of the small amounts that are present. The time and space relationships between these near-surface dilute bicarbonate waters and the deep brines are not known with certainty, but the hypothesis is advanced here that $CO_2$ and $H_2S$ are more mobile than Cl and migrate upward, either by means of a vapor phase or by selective effects of semipermeable membranes.

Most thermal and mineral waters near the earth's surface are low in ore-metal content and are not obviously related to ore deposits, even when closely associated with volcanism. Deep drilling in Yellowstone Park, Wyoming (reviewed by White, 1955a), Steamboat Springs, Nevada (White and others, 1964), Wairakei, New Zealand (Steiner, 1953), and Reykjavik and Hveragerdi, Iceland (Sigvaldason, 1963; White and Sigvaldason, 1963) has revealed many types of hydrothermal alteration that occur with ore deposits. No Hg or base-metal ore deposits have been found in any of these

WATERS

strong support is found for
association with Hg. More-
ite are hydrothermal miner-
erals suggest, in the light of
tions have low cation/H⁺
ontrast, minerals such as
which are indicative of alka-
mmercial mercury deposits.
ible with the mineralogy are
ated fluids.

posits are very scarce near
on Sea geothermal area of
ery saline brines high in Na,
tals and Ag as well as some
deficient. This evidence, in
nclusions (Chapter 12) and
uggests that sulfur-deficient
of base-metal ore fluid. If
sm is necessary to provide
ulfides, or the ore-forming

e surface in undiluted form
t of normal surface waters.
me epithermal base metal
$O_3$ and $SO_4$; they cannot be
. These dilute spring waters
in W, Cu, Pb, Zn, and As
; contents of each of these
ppm range), but the Mn
amounts that are present.
near-surface dilute bicar-
wn with certainty, but the
e more mobile than Cl and
ase or by selective effects

arth's surface are low in
to ore deposits, even when
ng in Yellowstone Park,
t Springs, Nevada (White
ner, 1953), and Reykjavik
ite and Sigvaldason, 1963)
tion that occur with ore
been found in any of these

areas, although siliceous muds deposited at Steamboat Springs, Nevada, and Ohaki and Waiotapu, New Zealand, contain Au, Ag, and Sb of normal ore grade; the total quantity is small.

## PROPOSED MECHANISMS FOR MERCURY TRANSPORT AND DEPOSITION

Krauskopf (1951) reviewed the recognized possibilities for mercury transport, within the limitations of data available at that time. He concluded that $HgS_2^{2-}$ in alkaline sulfide solutions and elemental Hg in a vapor phase are the most likely possibilities. Transport of volatile $HgCl_2$ along with $H_2S$ is also possible where liquid $H_2O$ is absent, but in the presence of water HgS is precipitated. Other possibilities considered by Krauskopf and concluded to be inadequate are that Hg is transported: as HgS in simple solution in pure water, and in pure water saturated with atmospheric $CO_2$; as sulfomercuric acid, $H_2HgS_2$ (or the bisulfide complex, $HHgS_2^-$ or $HgS_2H^-$); as a mercury chloride complex, $HgCl_4^{2-}$; in solution in water with $H_2S$ but dependent upon low ionization or solubility of $H_2S$ at high temperature; in gases containing sulfur but depending on a decrease in $H_2S$ in equilibrium with $SO_2$ and other gases at high temperature; and thermal instability of HgS in the presence of a moving vapor phase at high temperature, with HgS dissociating into elemental Hg and S. Supersaturation and colloidal transport were also recognized by Krauskopf as possible mechanisms, but were not discussed in detail because thermodynamic data are inapplicable. Other possible mercury complexes were not considered because the complex-forming constituents ". . . are scarce in vein solutions [and] it seems safe to conclude that no complex ion except $HgS_2^{2-}$ is likely to play a role in the formation of quicksilver ores" (Krauskopf, 1951, p. 509). Recent experimental work has largely concerned the sulfide complex, $HgS_2^{2-}$ (Dickson and Tunell, 1954; Tunell, 1964; Dickson, 1964) and the several bisulfide complexes, (Schwarzenbach and Widmer, 1963; Barnes and Czamanske, Chapter 8). Dickson and Tunell have demonstrated that solutions sufficiently high in pH and total sulfide are very potent solvents for HgS as well as for $Sb_2S_3$ and $As_2S_3$. Precipitation of these metal sulfides can result from decrease in temperature (for HgS, down to its solubility minimum near 100°C), a decrease in pH, dilution, or any combination of these factors. Decrease in pressure does not tend to precipitate these sulfides.

Minimum concentration of $Na_2S$ in Dickson's experiments (1964, p. 627) was 0.66 weight percent (3650 ppm of sulfide); at 149°C and 750 bars, 690 ppm of Hg was in solution; pH was not stated but presumably was 11 or higher.

Schwarzenbach and Widmer (1963) found that solubility of black HgS

(metacinnabar) at 20°C in the presence of excess sulfur decreased rapidly with decreasing pH from 14 down to about 9; the decrease in Hg solubility was marked but much less rapid from 9 down to about 5; and was constant below pH 5 (where total Hg concentration was about 0.003 ppm). These investigators concluded that the dominant Hg species in solution were, respectively, $HgS_2^{2-}$, $HgS_2H^-$ (one bisulfide complex), and $Hg(SH)_2$. The bisulfide complex is evidently present and dominant near neutrality, where Hg solubility ranges from about 0.003 ppm (pH 5) to 0.1 ppm (pH 9) at 20°C. The effect of higher temperature on these solubilities had not been determined (see Chapter 8).

## MERCURY DEPOSITS WITH ANALYZED MINERAL WATERS

Probably more than 10 percent of all mercury deposits are associated with thermal or mineral waters, with abnormally high subsurface temperatures, or with notable amounts of $CO_2$, $H_2S$, or hydrocarbon gases. This is in spite of the fact that most Hg deposits are mined only to shallow depths where abnormal thermal gradients and gases easily escape detection. In contrast, abnormal geothermal gradients, mineral waters, and gases are seldom noted in deep mines of other metals (except, as will be seen, in epi-thermal base metal and Ag-Au deposits). This anomaly is explainable if Hg is deposited at or near the surface in hot-spring systems and if many Hg deposits are recent enough in age to have genetically related thermal fluids still circulating in their structural systems.

The evidence for active or very recent transport of mercury by presently associated fluids is convincing for only a few mercury deposits. The structural and stratigraphic controls of some deposits conceivably guide the migration of later unrelated fluids.

Table 13.1 contains nearly all available chemical analyses of thermal and mineral waters associated with mercury deposits. Some samples were analyzed in the laboratory for Hg, but results were largely negative (<0.02 ppm). A systematic search should now be made for Hg at the collection site, using one of the sensitive methods developed recently (Hosohara and others, 1961; U.S. Geological Survey, unpublished data).

The waters of Table 13.1 that are associated with Hg deposits range from 6.1 to 9.2 in pH, and total sulfide species (reported as equivalent $H_2S$) are from less than 1 to about 180 ppm. Are some or all of these waters related genetically to their associated mercury deposits and if so, what can we learn about processes of mercury transport and deposition?

In the search for an answer to these questions, the most pertinent characteristics of geologic setting, mineralogy, and presently associated fluids are

WATERS

s sulfur decreased rapidly
decrease in Hg solubility
about 5; and was constant
about 0.003 ppm). These
species in solution were,
plex), and $Hg(SH)_2$. The
nt near neutrality, where
5) to 0.1 ppm (pH 9) at
solubilities had not been


posits are associated with
subsurface temperatures,
carbon gases. This is in
only to shallow depths
ily escape detection. In
l waters, and gases are
t, as will be seen, in epi-
maly is explainable if Hg
ystems and if many Hg
ly related thermal fluids

of mercury by presently
ury deposits. The struc-
conceivably guide the

analyses of thermal and
s. Some samples were
largely negative ( <0.02
Hg at the collection site,
(Hosohara and others,

Hg deposits range from
as equivalent $H_2S$) are
of these waters related
f so, what can we learn
n?

most pertinent charac-
ly associated fluids are

summarized below, with special attention being given to the few areas that have provided the greatest understanding, including Sulphur Bank, the Wilbur Springs district, Steamboat Springs, and Amedee Springs.

## Sulphur Bank, California

Sulphur Bank (Fig. 13.1) is the most productive mineral deposit in the world that is clearly related genetically to hot springs (White and Roberson, 1962, p. 398). Many other large mineral deposits are hypothesized to be related to former hot springs, but at Sulphur Bank the relationship is unusually clear and other possibilities are highly improbable. The total production of 4.7 million Kg of Hg (130,000 flasks, 76 lb per flask) is exceeded by only three other mines in the United States. The ore is late Quaternary in age and was localized to a major extent immediately below the water table that existed prior to mining. Much ore is in a basaltic andesite lava flow and older lake deposits of probably Pleistocene age, as well as in underlying graywacke and shale of the Mesozoic Franciscan Formation. Mercury minerals seem to be restricted to depths of less than about 300 ft.

The present thermal waters are exceptionally high in total $CO_2$, B, and $NH_4$ (Table 13.1, analysis 1), as compared to other kinds of thermal and mineral waters (White, Hem, and Waring, 1963 tables 12 to 27). The $NH_4$ content of 460 ppm is near the maximum that has been recorded in natural waters; the B content of 620 ppm is nearly equal to Cl and is exceeded by that of only a very few waters, including Ngawha Springs in New Zealand (Table 13.1, analysis 13). Total natural rate of discharge of deep water, calculated to a Cl content of 640 ppm, is about 200 liters per minute.

At the water table a vapor phase relatively rich in $H_2S$ separates from liquid water, and near the surface the $H_2S$ oxidizes to native sulfur and sulfuric acid. Leaching by sulfuric acid above and near the water table produces a characteristic suite of minerals that includes amorphous opal, $\beta$-cristobalite,[3] anatase, kaolinite, alunite, and a variety of soluble sulfates; sparse fine-grained cinnabar may also occur with these minerals. Below the original water table that existed prior to mining, the characteristic minerals (Table 13.2) include cinnabar, marcasite, pyrite, metacinnabar, stibnite, calcite, dolomite, quartz, and buddingtonite, the recently described ammonium feldspar that is abundant and widely dispersed (Erd, White, Fahey, and Lee, 1964). Hydrocarbons were originally abundant in near-surface parts of the mine but are now scarce in the walls of the present large open pit; methane is an important constituent of the gases.

[3] In this report, $\beta$-cristobalite designates a silica species with broad x-ray peaks generally near 4.10 and 2.51 Å; optically, this mineral is similar to opal that is amorphous by x-ray.

### TABLE 13.1. Chemical analyses of waters associated with mercury and base-metal deposits, in parts per million

(Ionization state or species of complex not distinguished)

| | | Temp. collected (°C) | pH | Na | K | NH4 | Ca | Mg | Fe | Mn | HCO3[a] | Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Waters associated with mercury deposits** | | | | | | | | | | | |
| 1. | Sulphur Bank, Lake Co., Calif. | 69½ | 6.8 | 1,190 | 23 | 464 | 20 | 55 | [d]0.1 | [d]0.2 | 3,290 | 64 |
| 2. | Wilbur Springs district, Colusa Co., Calif. | | | | | | | | | | 2,710 | 1,90 |
| | a. Abbott mine | ~35 | 7.1 | 1,500 | 39 | 22 | 64 | 443 | [d]0.04 | 0.0 | 7,390 | 11,00 |
| | b. Wilbur Springs (Sulphur Creek group) | 57 | 7.2 | 9,140 | 460 | 303 | 1.4 | 58 | 0.1 | 0.3 | 7,240 | 11,00 |
| | c. Elgin mine[e,f] | 68½ | 7.4 | 9,110 | 506 | 243 | 5.9 | 29 | 0.04 | 0.0 | 1,490 | 22 |
| 3. | Mayacmas district, Calif. | | | | | | | | | | | |
| | a. Valley mine, Napa Co. | 32 | 6.5 | 476 | 8.2 | 2.5 | 19 | 90 | 0.6 | 0.1 | 708 | |
| | b. Big Injun mine, Lake Co.[e] | ~21 | 6.8 | 26 | 0.9 | — | 34 | 142 | — | — | — | 0 |
| | c. The Geysers, Sonoma Co. | ~100 | ~1.8 | 12 | 5 | 1,400 | 47 | 281 | 63 | 1.4 | 2,480 | |
| 4. | Skaggs Springs, Sonoma Co., Calif. | 54 | 7.2 | 912 | 33 | — | 14 | 5.4 | — | — | 8,060 | 1,5 |
| 5. | Altoona mine, Trinity Co., Calif.[e,g] | 12½ | 7.0 | 3,710 | 220 | 18 | 28 | 39 | 0.07 | 0.01 | | |
| 6. | Beaver Creek district, Siskiyou Co., Calif. | | | | | | | | | | 4,280 | 1,5 |
| | a. West Cinnabar Spring[e] near HG prospect | 14 | 6.5 | 2,070 | 53 | Present | 124 | 92 | — | — | 203 | 5,7 |
| 7. | Mt. Diablo mine, Contra Costa Co., Calif. | 21 | 7.7 | 3,100 | 53 | 57 | 431 | 12 | 0.3 | 0.1 | 314 | 8 |
| 8. | Steamboat Springs, Washoe Co., Nevada[e,h] | 60 | 6.1 | 637 | 61 | <1 | 16 | 1.0 | — | — | 199 | |
| 9. | Cordero mine, Humboldt Co., Nevada[e,i] | 56 | 8.1 | 115 | 2.4 | 0.3 | 3.2 | 0.2 | 0.06 | 0.01 | 37 | |
| 10. | Amedee Springs, Lassen Co., Calif.[j] | 92 | 8.5 | 227 | 6.8 | 0.5 | 16 | 0.0 | 0.01 | 0.00 | [k]106 | |
| 11. | Boiling Springs, Valley Co., Idaho | 88 | 9.2 | 74 | 1.9 | — | 2.2 | 0.0 | 0.4 | 0.004 | 174 | |
| 12. | Apapel'sk Springs, Kamchatka, U.S.S.R. | 96 | 8.1 | 372 | 22 | 0 | 16 | 5.2 | 0.7 | 0 | 340 | 1, |
| 13. | Ngawha Springs, New Zealand | 48 | 6.4 | 830 | 63 | 148 | 7.8 | 2.5 | — | — | 204 | 2, |
| 14. | Toya Springs, Hokkaido, Japan | 47 | 7.3 | — | — | — | 267 | — | — | — | 535 | 9. |
| 15. | Cymric Oilfield, Kern Co., Calif. | ~81 | 7.5 | 5,820 | 132 | 51 | 373 | 115 | 1.2 | 0.08 | | |

Left portion of table:

(ot distinguished)

| Ca | Mg | Fe | Mn |
|---|---|---|---|
| ts | | | |
| 20 | 55 | [d]0.1 | [d]0.2 |
| 64 | 443 | [d]0.04 | 0.0 |
| 1.4 | 58 | 0.1 | 0.3 |
| 5.9 | 29 | 0.04 | 0.0 |
| 19 | 90 | 0.6 | 0.1 |
| 4 | 142 | — | — |
| 47 | 281 | 63 | 1.4 |
| 14 | 5.4 | — | — |
| 28 | 39 | 0.07 | 0.01 |
| 124 | 92 | — | — |
| 431 | 12 | 0.3 | 0.1 |
| 16 | 1.0 | — | — |
| 3.2 | 0.2 | 0.06 | 0.01 |
| 16 | 0.0 | 0.01 | 0.00 |
| 2.2 | 0.0 | 0.4 | 0.004 |
| 16 | 5.2 | 0.7 | 0 |
| 7.8 | 2.5 | — | — |
| 67 | — | — | — |
| 73 | 115 | 1.2 | 0.08 |

Right portion of table:

| HCO₃[a] | Cl | SO₄ | H₂S[b] | B | SiO₂ | Others | Analyst, Reference |
|---|---|---|---|---|---|---|---|
| | | | | | | Waters associated with mercury deposits | |
| 3,290 | 644 | 598 | 12 | 620 | 42 | [d]As, 0.00; [d]Cu, 0.01; [e]As, Sb, Hg <0.02 | C. E. Roberson (White and Roberson, 1962, table 1)[c] |
| 2,710 | 1,900 | 467 | <1 | 56 | 16 | [d]As, 0.00; [d]Cu, 0.006 | C. E. Roberson (White and others, 1963, table 23)[c] |
| 7,390 | 11,000 | 23 | 178 | 292 | 190 | As, Sb 0.0; [d] W 9; [d]Pb 1; [e]Hg 0.22 (BL)W | W. W. Brannock (White and others, 1963, table 15)[c] |
| 7,240 | 11,000 | 6.8 | 170 | 240 | 244 | [d]W, 7; [d]Cu, 0.03; [e]Hg 0.04 (BL) | C. E. Roberson, U. S. Geological Survey[e,f]. |
| 1,490 | 229 | 16 | <1 | 67 | 95 | As, 0.00; [d]Cu 0.2 | J. P. Schuch (White and others, 1963, table 23)[c] |
| 708 | 2 | 154 | — | 0.7 | 74 | Sr, 0.1; Li, 0.0 | C. E. Roberson, U.S. Geological Survey[e] |
| — | 0.5 | 5,710 | — | 3.1 | 225 | Cr, 2; [e]Hg 0.07 (BL) | E. T. Allen (White and others, 1963, table 20) |
| 2,480 | 58 | 6.5 | <1 | 92 | 74 | [e]Sb, 0.01; [e]As, Hg < 0.02; [e]Hg 0.06 (BL) | R. N. Martin (White, 1957b, p. 1676) |
| 8,060 | 1,560 | 352 | 18 | 121 | 60 | As, 0.05 | H. C. Whitehead, U.S. Geological Survey[e,g]. |
| 4,280 | 1,540 | 8 | — | 89 | — | Li, 4.9 | C. E. Roberson, U.S. Geological Survey[e] |
| 203 | 5,770 | 1.6 | 0.4 | 191 | 16 | As, 0.00; [d]Cu, 0.1 | C. E. Roberson (Pampeyan, 1963, table 4)[c] |
| 314 | 824 | 107 | 8 | 48 | 220 | As, 1.7; Sb, 0.3; [e]Hg 0.00; 0.10(BL) | W. W. Brannock, U.S. Geological Survey[e,h] |
| 199 | 26 | 59 | 0.2 | 0.7 | 60 | As, 0.07; [d]Mo, 0.02 | H. C. Whitehead, U.S. Geological Survey[e,i]. |
| 37 | 160 | 288 | <1 | 4.1 | 96 | [e]As, 0.15, [e]Sb, 0.01 | J. P. Schuch (White and others, 1963, table 23)[c,j] |
| [k]106 | 14 | 12 | <1 | 0.1 | 81 | As, Sb < 0.1 | Henry Kramer (White and others, 1963, table 23) |
| 174 | 168 | 499 | — | 16 | 182 | As, 1.6 | (Ivanov, 1958, p. 204) |
| 340 | 1,250 | 347 | 6 | 912 | 178 | As, 0.2; Hg, 0.1 | A. J. Ellis (written communication, 1964)[l] |
| 204 | 2,142 | 588 | 0 | 28 | | Evap. res. 5,000 | M. Nishimura (written communication, 1965) |
| 535 | 9,840 | 1.6 | 0 | 140 | 47 | As, 0.0; [d]Cu, 0.04; Hg, 0.1 to 0.4 (BL) | C. E. Roberson (Bailey and others, 1961)[c] |

**TABLE 13.1.** (*Cont.*)

| | Temp. collected (°C) | pH | Na | K | NH₄ | Ca | Mg | Fe | Mn | HCO₃ᵃ | Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Waters associated with base-metal deposits | | | | | | |
| 16. Tamagawa Springs, Japan | 98 | 1.2 | 114 | 65 | — | 210 | 83 | 105 | 4.2 | — | 3,240 |
| 17. Arima Springs, Hyogo Pref., Japan | 90½ | 6.4 | 16,200 | 3,160 | ᵉ44 | 3,530 | 24 | 187 | 61 | 146 | 33,260 |
| 18. Salton Sea geothermal area, Imperial Co., Calif. | ~220 | ~5.5 | 51,000 | 25,000 | 482 | 40,000 | ᵈ35 | 3,200 | 2,000 | — | 185,000 |
| 19. East Tintic district, Utah Co., Utah | 60 | 6.1 | 2,270 | 228 | 2.4 | 375 | 53 | 1.0 | 0.6 | 749 | 3,670 |
| 20. San Juan Mountains, Colo. a. Ouray Springs, Ouray Co., Colo. | 62 | 6.8 | 111 | 8.0 | — | 376 | 6.1 | 0.4 | 0.9 | 128 | 4 |
| 21. Centennial mine, Houghton Co., Mich. | Cold | 6.5 | 11,900 | 38 | <10 | 62,900 | 179 | 1.0 | 2.5 | 24 | 128,000 |

ᵃIncludes $HCO_3^-$ and $CO_3^{2-}$ but not free $CO_2$ or $H_2CO_3$.
ᵇAlso includes $HS^-$ and $S^{2-}$ computed as $H_2S$.
ᶜSee original reference for additional analyzed constituents.
ᵈQuantitative spectrographic analysis of evaporated residues, converted to ppm of original water.
ᵉNot previously published. As, Sb, and Hg by Fred Ward and C. A. Horr, U.S. Geological Survey; Hg analyses by Buckman Laboratories, Memphis, Tenn., indicated as: Hg 0.2 (BL).
ᶠAlso includes, in ppm: Al, 0.4; Li, 10; Sr, 3.7; F, 3; Br, 30; I, 25; NO₃, 5; As, CO₃, NO₂, 0.0.
ᵍAlso includes, in ppm: Al, 1.4; Li, 8.5; F, 10; Br, 32; I, 13; Cu, Pb, Zn, Hg, NO₂, NO₃, PO₄ 0.0.
ʰSpring 50, Low Terrace, also includes, in ppm: Li, 7.1; F, 1.9; Br, 0.1; I, 0.1. This spring is viewed as most representative of deep waters with all $CO_2$ in solution; see Table 13.3 and text.
ⁱAlso includes, in ppm: F, 13; Br, 0.1; I, 0.1; PO₄, 0.14; Sr, Li, NO₃, NO₂, Ba, Al, 0.0.


The waters and gases are still transporting and depositing some mercury and antimony. Pebbles in one spring pool were coated by cinnabar on their undersides, and black metacinnabar on other sides. Sooty metacinnabar was also found surrounding a gas vent. Stibnite and aragonite were deposited from hot springs on a quarry floor, but crystals of cinnabar attached to the stibnite could have been deposited either chemically or mechanically. Tiny crystals of late stibnite are widely dispersed throughout the mine.

| I4 | Ca | Mg | Fe | Mn |
|---|---|---|---|---|
| eposits | | | | |
| 210 | 83 | 105 | | 4.2 |
| 3,530 | 24 | 187 | | 61 |
| 40,000 | d35 | 3,200 | | 2,000 |
| .4 | 375 | 53 | 1.0 | 0.6 |
| 376 | 6.1 | 0.4 | | 0.9 |
| 62,900 | 179 | 1.0 | | 2.5 |

| CO3[a] | Cl | SO4 | H2S[b] | B | SiO2 | Others | Analyst, Reference |
|---|---|---|---|---|---|---|---|
| | | | | | | Waters associated with base-metal deposits | |
| ~ | 3,240 | 1,330 | — | 23 | 324 | Cu, 0.01; Pb, 1.0; Zn, 2.8; Hg, 0.01 | Iwasaki and others, 1963[m], Minami and others, 1958 |
| 146 | 33,260 | 1.0 | <1 | 106 | 69 | Cu, 0.1; Pb, 0.4; ⁿZn 0.2 | Nakamura and Maeda, 1961[e] |
| ~ | 185,000 | 56 | ~1 | 300 | >110 | ⁿZn, 970; ᵒPb, 104; ᵈCu, 10; ᵈAg.1 | J. D. Hem and others (D. E. White, in press)[o] |
| 149 | 3,670 | 391 | 0.3 | 5.6 | 48 | As, 0.6 | H. C. Whitehead (Lovering and Morris, in press)[e] |
| 128 | 45 | 1,030 | 0.0 | .2 | 49 | As, 0.00; ᵈCu, 0.02, ᵈAg, 0.002 | H. C. Whitehead (Burbank and Luedke, 1961)[e] |
| 24 | 128,000 | 88 | — | 2.5 | <10 | ᶜCu, 0.7; Sr, 320 | C. E. Roberson (White and others, 1963, table 24)[e] |

[j]Also contains in ppm: Cu, 0.01; Pb, 0.009; Mo, 0.06; W, 0.2 (White and others, 1963, table 23), evaporated residue, 180°C, 827, and, by Fred Ward, As, 0.15; Sb, 0.01; Hg less than 0.02. The total $CO_2$ species include $CO_3$, 10 and $HCO_3$, 27. Other nearby springs of nearly identical compositions discharge at temperatures as high as 99°C and with pH's up to 8.9.

[k]Consists of 79 ppm $HCO_3$ and 27 ppm $CO_3$.

[l]Jubilee Bath; also contains in ppm: Li, 8.0; Rb, 0.3; Cs, 0.55; F, 0.3; free $CO_2$, 245; As and Hg from earlier samples from same spring.

[m]Also reported, in ppm: Al, 158; As, 2.3; Ag, 0.003; F, 120, and traces of other metals.

[n]Reported by Ikeda (1955, and earlier papers): As, 0; Sr, 2.0; Ba, 59; Li, 53; Rb, 3.3; Cs, 2.4; $SO_4$, 0; $H_2S$, 0.9; $CO_2$, 370, and other constituents, summarized by White and others (1963, Table 16).

[o]Also determined, in ppm: Al, 450; Sr, 410; Ba, 200; Li, 300; F, 18; Br, 146; I, 22; $NO_3$, 35 (J. D. Hem, U.S.G.S.); Cs, 22 (H. C. Whitehead, U.S.G.S.), Sr, 740; Rb, 168 (Carl Hedge, U.S.G.S., isotope dilution); Pb, 104; U, 0.0053 ±0.0008 (Bruce Doe, U.S.G.S., isotope dilution); Li, 305; Rb, 150; Cs, 20; $NH_4$, 500; B, 520; F, 12 (A. J. Ellis, New Zealand); Zn, 970; Cu, 3.7; As, 15; Sb, 0.5; Sn, 0.65; Hg, 0.008 (Fred Ward, U.S.G.S.).

Present temperatures at Sulphur Bank are in the order of 80°C at the surface (with ebullition and an abundant $CO_2$-rich vapor phase), 130°C at 500 ft (White and Roberson, 1962, p. 425), and 185°C near 1400 ft (McNitt, 1963, p. 11). Corresponding temperatures for boiling of pure water under hydrostatic pressure at these depths are approximately 100°C, 190°C, and

---

RS

es, converted to ppm of

d and C. A. Horr, U.S.
emphis, Tenn., indicated

I, 25; $NO_3$, 5; As, $CO_3$,

Cu, Pb, Zn, Hg, $NO_2$,

1.9; Br, 0.1; I, 0.1. This
all $CO_2$ in solution; see

$NO_3$, $NO_2$, Ba, Al, 0.0.

siting some mercury
by cinnabar on their
Sooty metacinnabar
agonite were depos-
cinnabar attached to
ly or mechanically.
roughout the mine.

TABLE 13.2. Minerals from mercury-containing deposits of Table 13.1

| | Production in Flasks of Hg | pH of Water | Cinnabar | Meta-cinnabar | Pyrite | Marcasite | Stibnite |
|---|---|---|---|---|---|---|---|
| 1. Sulphur Bank, Calif. | 130,000 | 6.8 | X-D | r-D | x | X | c-D |
| 2. Wilbur Springs district, Calif. | | | | | | | |
|   a. Abott mine | 45,000 | 7.1 | X | x | r(?) | X | r |
|   b. Sulphur Creek group | 5,000 | 7.2 | x-D(?) | | x | | |
|   c. Elgin mine, Calif. | >40 | 7.4 | c-D(?) | | | | |
| 3. Mayacmas district, Calif. | | | | | | | |
|   a. Aetna and Valley mines | 66,000 | 6.5 | X | r(?)D(?) | x | | |
|   b. Big Injun mine | 400 | 6.8 | x | r(?) | | | r |
|   c. The Geysers | None | Acid | r-D(?) | | x | r | |
| 4. Skaggs Springs mine, Calif. | 300 | 7.2 | r | x-D(?) | | | |
| 5. Altoona mine, Calif. | 35,000 | 7.0 | X | | X | | |
| 6. Beaver Creek district, Calif. | | | | | | | |
|   a. HG mine | Small | 6.5 | x | | x | | |
| 7. Mt. Diablo mine, Calif. | 12,000 | 7.7 | x | X | x | x | r |
| 8. Steamboat Springs, Nevada | Small | 6.1 | c-D | | x | r | x-D |
| 9. Cordero mine, Nevada | 60,000 | 8.1 | X | | X | x | |
| 10. Amedee Springs, Calif. | None | 8.5 | c-D | c-D | r | | |
| 11. Boiling Springs, Idaho | None | 9.2 | c-D | r-D | r | | |
| 12. Apapel'sk Springs, U.S.S.R. | None | 8.1 | r-D | | | | (?) |
| 13. Ngawha Springs, New Zealand | >600 | 6.2 | x-D | | | x | r |
| 14. Cymric Oilfield, Calif. | Several thousand | 7.5 | | | | | |

Key: X — abundant    x — present, moderate amounts    c — common, but quantity not large
   r — rare    D — good evidence for active or very recent deposition    D (?) — active deposition claimed by at least one observer but perhaps questionable

240°C. Even if a $CO_2$-rich vapor phase does not now exist in the present system at depths below a few hundred feet because temperatures are too low for the prevailing pressures, a vapor phase could have existed formerly with no change in the system other than a higher rate of upflow of the thermal water. With the same high temperatures at great depth and a higher rate of upflow, less heat per unit of water is lost by conduction, and higher temperatures are retained to shallower depths. This would result in deeper formation of a vapor phase than at the present time.

ATERS

ble 13.1

| | Meta-cinnabar | Pyrite | Marcasite | Stibnite |
|---|---|---|---|---|
| r-D | x | X | c-D |
| x | r(?) x | X | r |
| r(?)D(?) | x | | |
| r(?) | | | r |
| | x | r | |
| x-D(?) | | | |
| | X | | |
| | x | | |
| X | x | x | r |
| | x | r | x-D |
| | X | x | |
| c-D | r | | |
| r-D | r | | |
| | | | (?) |
| | x | r | |

on, but quantity not large
D (?) — active deposition claimed

| Quartz-chalcedony | Opal or β-cristoballite [a] | Kaolinite | Montmorillonite [b] | Illite [c] | Carbonates | Zeolites | Hydrocarbons | Other Hydrothermal Minerals; Comments |
|---|---|---|---|---|---|---|---|---|
| x | [d]r | [d] | X | X | x | | c | NH4-feldspar (see text) |
| c | [a]X | | | | x | | X | Chalcopyrite, bornite, Au rare |
| x | [d] | [d] | | | x | | x | Native Au |
| r | [ad]X | [d] | | | x | | x | Aragonite(?) |
| X | [a]X | | | | x | | x | NiS reported; "clays" |
| X | [a]X | | x | | x | | x | Native Hg, chlorite, gypsum |
| x | [d] | [d] | | x | x | x | | Zeolites, K-feldspar, carbonates at depth in steam zone |
| x | [a]X | x(?) | x | x | | | x | Realgar, orpiment depositing (?) |
| X | ? | | | c | X | | | Native Hg, barite |
| x | | | | | x | | | Native Hg (?) |
| X | [a]X | x(?) | | x | x | | x | |
| X | [ad]X | [d]x | x | X | x | r | | K-feldspar, albite, Au, Ag, metastibnite |
| X | [ad]X | [d]x(?) | X | | | | | Hematite, NH4 feldspar, barite, Hg oxychlorides |
| | | | X | x | (?) | X | | Native Hg |
| | | | X | c | c | c | | Mn oxide, chlorite |
| X | [d](?) | (?) | | | | | | See text |
| x | [d](?) | (?) | | | | | x | Native Hg |
| | | | | | | | X | Native Hg and Hg-organic compounds (?) in fluids |

[a] β-cristoballite by x-ray. (D.E.W.)
[b] Montmorillonite as a separate phase.
[c] 1Md mica, normally including randomly interlayered montmorillonite.
[d] Deposit also characterized above and near water table by abundant amorphous opal and kaolinite, commonly with alunite and native S.

ow exist in the present
e temperatures are too
have existed formerly
e of upflow of the ther-
eat depth and a higher
conduction, and higher
would result in deeper

## Wilbur Springs District, California

The Wilbur Springs district includes the important Abbott mine and four or five smaller mercury deposits. The district is especially notable for its association of Hg with petroleum, hydrocarbon gases, and saline waters having chemical characteristics of oilfield brines (White, 1957b). The most recent volcanic rock in the region is the extrusive dacite dome of Chalk

**Fig. 13.1.** Index map of California and Nevada, showing localities referred to in text.

Mountain about 8 miles to the west (and an equal distance northeast of Sulphur Bank).

The Abbot mine in the southwestern part of the district is near the northwest end of a tabular mass of brecciated and partly opalized serpentine. The serpentine breccia that localizes the ores has been interpreted as intrusive sills or as extruded debris interlayered with Mesozoic sedimentary rocks. Cinnabar occurs with metacinnabar, opal ($\beta$-cristobalite), marcasite, carbonates, quartz, and abundant hydrocarbons (Table 13.2). The ore deposits occur along a strike length of 5500 ft, but exploration at depth has failed to find commercial ore at more than 600 ft below the outcrop. Unusual vein matter called froth veins (Bailey, 1959) are abundant in the upper parts of ore bodies. These veins consist of closely packed spherical shells of opal ($\beta$-cristobalite); each shell is filled with light brown petroleum that generally contains a gas bubble. Bailey concluded that the shells were deposited at interfaces between a hydrous liquid and immiscible droplets of oil. Cinnabar was locally deposited within the silica shells, indicating that at least one of the immiscible fluids was transporting and depositing mercury. Methane and other hydrocarbons are so abundant in the mine that fire and explosion

are constant hazards; solid and liquid hydrocarbons are abundant enough to affect the roasting of some ore.

Bailey reports that attempts to determine homogenization temperatures on the light petroleum inclusions in a froth vein were unsuccessful, probably because the enclosing shells of opal are porous. Oil from the inclusions was then heated gradually to determine the lowest temperature of distillation, which was found to be about 145°C. This may indicate the approximate temperature of deposition, assuming that a vapor phase was present at the time, but pressure effects cannot be evaluated.

A somewhat heavier and darker sample of petroleum that had flowed from a new underground opening in ore was investigated by S. R. Silverman, California Research Corporation. The oil contains no porphyrins (Silverman, written communication, 1961); carbonyl (C=O) groups are in relatively high concentration; and compounds of high molecular weight are relatively abundant. Chemically, the oil is highly aromatic in type; its $C^{13}/C^{12}$ ratio is +3.3 permil, which according to Silverman is similar to that of petroleum and oil seeps from Cretaceous rocks a few miles to the east in the Sacramento Valley; its API gravity is 18.2.

Thermal saline water discharges from the lowest adit of the mine at a rate of about 75 to 100 liters per minute. The water (Table 13.1, analysis 2$a$) is notably high in $HCO_3$, Cl, and B; the high Mg/Ca ratio indicates reaction with serpentine. The rising thermal saline water presumably mixes with some drainage water of surface origin that contains $SO_4$ from oxidizing marcasite in the mine workings.

The Manzanita, Wide Awake, and Central-Empire mercury mines are adjacent to Sulphur Creek, about 1 mile northeast of the Abbott mine and half a mile southwest of Wilbur Springs. These small mines, here called the Sulphur Creek group, are in sandstone, shale, minor conglomerate, and serpentine, all of Mesozoic age, near the southeast end of a major mass of serpentine that is about 30 miles long and as much as 6 miles wide, and forms the core of the Wilbur Springs anticline. Hot-spring water similar to that of Wilbur Springs (Table 13.1, analysis 2$b$; White, 1957$b$, p. 1675) discharges from numerous individual vents adjacent to Sulphur Creek, and from seeps near mine workings as much as 100 ft above the creek. Total discharge of high-chloride water into Sulphur Creek is 400 to 500 liters per minute.

As at Sulphur Bank, the near-surface rocks are bleached by sulfuric acid formed by oxidation of $H_2S$. Native sulfur is also a common intermediate product of oxidation. The bleached rocks consist largely of an opaline residue from silicate minerals, along with quartz from the original sediments. Some opalized serpentine now consists of $\beta$-cristobalite, quartz, magnesite, pyrite, and relict chromite.

Cinnabar of the Sulphur Creek deposits was closely associated with

native sulfur and bituminous substances (Fairbanks, 1894). Native gold was also reported from the Manzanita mine. Fairbanks and others were convinced that cinnabar was still forming in these deposits, which were worked deep enough to encounter thermal water.

The waters of Wilbur Springs (Table 13.1, analysis 2b) are very high in Cl, HCO₃, B, NH₄, and H₂S; chemically, they are very similar to oilfield waters of the NaCl type (White and others, 1963, tables 12, 15) except for unusually high $HCO_3$ and B. The high Mg/Ca ratio reflects an influence by serpentine. On-site measurements were made by Ivan Barnes and G. G. Ehrlich of the U.S. Geological Survey. The pH at discharge temperature of 53°C was 7.06 ± 0.02; Eh was −0.194 ± 0.003 volts.

Sediment in the vent of the Wilbur Main Spring is partly detrital grains from nearby rocks and partly native S from oxidation of $H_2S$; Hg content of a sediment sample is 8 ppm (H. McCarthy, U.S. Geological Survey; 1967). Petroleum has been noted in the Wide Awake mine and is evidently similar to that of the Abbott mine.

The Elgin mine is 3 miles northwest of the Abbott and Manzanita mines and is near the crest of a precipitous ridge adjacent to and about 400 ft above Sulphur Creek. The mercury deposit and its associated hot springs are localized on a contact of serpentine intruded into shale, sandstone, and conglomerate. The thermal water (Table 13.1, analysis 2c) is remarkably similar to that of Wilbur Springs and other saline springs of the district. Discharge from the mine area is 100 to 150 liters per minute, and its temperature of 68°C is the highest recorded for the district.

Serpentine and sedimentary rocks of the Elgin area are locally leached to a porous opaline residue, much of which is amorphous and commonly associated with native S. Some silicified serpentine consists of dense glassy opal (β-cristobalite) that probably formed at or near the local water table. Cinnabar is sparsely distributed in altered serpentine and shale. Fairbanks (1894) stated that deposition of cinnabar was still continuing, but confirming evidence has not been found.

## Mayacmas District, California

The Mayacmas district is a northwest-trending belt of Hg deposits and thermal springs that lies south and west of Sulphur Bank and the Wilbur Springs district (Fig. 13.1). The mineralized belt is about 25 miles long and 7 miles wide, but the most productive deposits are within half a mile of a straight line through the length of the district (Bailey, 1946, 1962; Yates and Hilpert, 1946). The bedrocks are Franciscan graywacke and shale, serpentine, and rhyolitic flows and tuffs of Pliocene and Pleistocene age. Younger basalt flows occur in the eastern part of the district.

MER

The Ae
serpentin
Quicks
immediat
soon aba
3a) and (
in the Ae
The Vi
balite). N
not foun
The Bi
eastern N
by a stro
well as at
water fro
discharge
minute.
and nati
mite, mo
cinnabar
is slightl
HCO₃ of
abnorma
evidence
Repla
other mi
Great W
nearly ai
other de
guide to
In the
nounced
The Gey
Superhe
a few hu
generate
3c) are s
water. T
of H₂S i
per mini
totally a
presuma

The Aetna and Valley mine area in the eastern Mayacmas is underlain by serpentine and Franciscan rocks cut by olivine basalt dikes.

Quicksilver was first discovered in the Valley mine, but the Aetna mine immediately to the northwest was the most productive. The Valley mine was soon abandoned because of abundant flow of hot water (Table 13.1, analysis 3a) and $CO_2$; its old shaft now supplies much of the thermal water utilized in the Aetna resort. The rate of flow has not been determined.

The Valley mine is largely in serpentine replaced by dense opal ($\beta$-cristobalite). Metacinnabar and hydrocarbons occur in the Aetna mine but were not found in the Valley mine.

The Big Injun, Anderson, and Big Chief mines in a nearby part of the eastern Mayacmas are warm to hot, and many workings are characterized by a strong odor of $H_2S$. Thermal water discharges from all three mines as well as at Anderson Springs (Yates and Hilpert, 1946, p. 283); an analysis of water from the Big Injun Mine is shown in Table 13.1, analysis 3b. Rate of discharge from each of the mines probably does not exceed a few liters per minute. The Big Injun deposit contains some ore with abundant cinnabar and native Hg. The host rock is serpentine replaced by chalcedony, dolomite, montmorillonite, and chlorite; hydrocarbons, gypsum, pyrite, metacinnabar, and stibnite have also been identified. Water from the lowest adit is slightly thermal and is evidently largely of surface origin, but the high $HCO_3$ of the analysis is much above normal surface and ground waters. The abnormal temperature of the mine and high $CO_2$ content of the water are evidence for upflow of some deep thermal water.

Replacement of serpentine by opal and carbonates is characteristic of other mines in the eastern Mayacmas district, including the Corona, Helen, Great Western, and Mirabel mines. Opal from the Mirabel ranges from nearly amorphous to $\beta$-cristobalite with strong x-ray peaks, but opals of the other deposits have not been studied. Hydrocarbons are considered a useful guide to ore.

In the western part of the Mayacmas district, thermal activity is pronounced at The Geysers, the Little Geysers, and the Sulphur Bank area of The Geysers (unrelated to the Sulphur Bank mine; Bailey, 1946, p. 213). Superheated steam at temperatures of 200°C and higher occurs at depths of a few hundred to several thousand feet and is being utilized commercially to generate electricity (McNitt, 1963). The hot springs (Table 13.1, analysis 3c) are surficial condensates of steam, probably with some shallow meteoric water. The pH's of such springs are typically very low, $SO_4$ from oxidation of $H_2S$ is high, and total discharge of water is generally a few liters or less per minute (White, 1957a, 1961; Allen and Day, 1927). Chloride is almost totally absent in the spring waters and condensates from the steam wells, presumably because volatilities of all metal chlorides are very low at the

prevailing temperatures and pressures. A sample of condensed steam from one geothermal well (No. 4 of Allen and Day) was reported (Buckman Laboratories, 1957) to contain 0.13 ppm Hg and 3.2 ppm B; sediment in the sample contained 149 ppm Hg, much more than in normal sediments. A sample of native S formed in the condensing system of the power plant contained 50 ppm of Hg (H. McCarthy, U. S. Geological Survey, 1967).

Cinnabar in noncommercial amounts occurs in all of the thermally active areas, especially at Sulphur Bank. Cinnabar at the surface is associated with kaolinite, opal (amorphous), and native sulfur; in several deep roadcuts, cinnabar occurs with pyrite, marcasite, and kaolinite. Drill cuttings and ejecta from 500 to 2800 feet below identified mercury minerals contain the zeolites wairakite and analcite, in addition to K-feldspar, pyrite, chlorite, and quartz. Northwest of Sulphur Bank beyond the intense thermal activity, the Cloverdale mercury mine contains $H_2S$-bearing waters and the nearby Buckeye mine encountered much $CO_2$.

## Skaggs Springs, California

The Skaggs Springs mine (Everhart, 1950) is in massive arkose of the Franciscan Formation. The arkose is veined and cemented by dark opal, chalcedony, and quartz. Metacinnabar and a little cinnabar occur with realgar, orpiment, curtisite (crystalline $C_{24}H_{18}$?) and black amorphous hydrocarbons. Methane was encountered in some of the underground workings. Original silicate minerals of the arkose are partly altered to kaolinite, illite, and montmorillonite. Opal ($\beta$-cristobalite) occurs in veinlets and interstices, at least in part later than metacinnabar and realgar. The deposits were mined to a depth of only 135 ft.

Hot springs occur immediately downstream from the mine (Table 13.1, analysis 4) and are exceptionally high in $HCO_3$ and B relative to Cl; $SO_4$ and $H_2S$ are both notably low. Total visible discharge from the three principal springs is about 100 liters per minute. Realgar and metacinnabar, according to Everhart, were being deposited as irregular masses in the vents of these springs. Confirming evidence has not been recognized in recent years but conditions may have changed.

## Altoona Mine, California

The Altoona mine is 25 miles southwest of Mt. Shasta, a large late Quaternary volcano, and is in hydrothermally altered diorite and serpentine of Mesozoic age (Swinney, 1950). Cinnabar and native Hg occur with pyrite, an iron-bearing dolomite, barite, and quartz.

Carbonated water was encountered in 1959 in a diamond drill hole below the 600-ft level of the mine. The water (Table 13.1, analysis 5) was cold, but its exceedingly high content of $HCO_3$, Cl, and B is clear evidence that it is,

at least in part, of deep origin and must have had a much higher temperature. Its present temperature indicates either a very slow present rate of upflow or that the water was trapped, perhaps during an end stage of ore formation.

## Beaver Creek District, California

The northernmost Hg deposit of the California Coast Range that is known to be associated with mineral waters is the HG prospect in north-central Siskiyou County. Mineral springs and the Hg deposit are localized on and near a contact between quartz-mica-chlorite schist and younger (?) amphibolite, marble, and quartzite (P. E. Hotz, U.S. Geological Survey, written communication, 1961). These rocks are intruded by serpentine.

As in the Altoona mine, the water temperatures are low, partly because rates of discharge are very low (a few liters per minute). The spring waters (Table 13.1, analysis 6a) are high in $HCO_3$, B, and Cl, but low in $SO_4$.

## Mount Diablo District, California

A large roughly circular mass of Franciscan rocks, serpentine, and diabase was forced upward in the core of a major anticline flanked by late Mesozoic and younger rocks (Pampeyan, 1963). Small plugs of late Tertiary rhyodacite intrude the older rocks. Serpentine occurs in the fault zone that bounds the upthrust mass and is even more abundant in parts of the interior.

Metacinnabar and cinnabar occur in silica-carbonate alteration of serpentine in the bounding fault zone of the upthrust plug; cinnabar also occurs in calcite veinlets in one of the rhyodacite intrusions. Gangue minerals consist of quartz, opal ($\beta$-cristobalite), dolomite, calcite, marcasite, pyrite, hydrocarbons, and minor late stibnite (Pampeyan, 1963). Sheared Franciscan graywacke is interlayered with serpentine in parts of the fault zone, and is locally altered to kaolinite, illite, and chlorite. Methane, $H_2S$, and $SO_2$ are prominent in some underground workings of the Mount Diablo mine.

Saline springs discharge from several places in and near the bounding fault. Such a spring existed near the portal of the drainage adit of the Mount Diablo mine in an area now covered by waste dumps. The most highly mineralized spring found by Pampeyan (Table 13.1, analysis 7) discharges from fractures in an Hg prospect in rhyodacite in the boundary fault half a mile southeast of Mount Diablo mine. The spring waters are characterized by a dominance of Na, Ca, and Cl; $NH_4$, B, and I (15 ppm) are relatively high; $SO_4$ and $H_2S$ are very low. These characteristics and the associated hydrocarbons suggest that the waters are connate and are of the Na-Ca-Cl subtype (White, 1957b; White, Hem, and Waring, 1963 Tables 13, and 16); this subtype has not been noted elsewhere in close association with mercury deposits.

## Steamboat Springs, Nevada

The Steamboat Springs area is treated extensively here because Hg, Sb, Au, and Ag are being deposited at the present time; detailed study of this area by the author and his associates has led to an understanding of many physical and geochemical principals that are applicable to other areas; and the geochemical data on Sb in its waters and minerals may provide some clues to a better understanding of Hg.

The metal precipitates from thermal waters of this area have been of interest to mining geologists and geochemists for many years (White and others, 1964). The different types of hydrothermal alteration are also being studied in detail (Sigvaldason and White, 1962; Schoen and White, 1965). The bedrocks of the area are metamorphic rocks and granodiorite of Meso-zoic age overlain by Tertiary and Quaternary volcanic rocks and alluvial sediments. The record of hot-spring activity is long and involved, extending through all or most of the last million years of Quaternary time. The area of most intense thermal activity is about 5 sq km.

Thermal springs now discharge only from the eastern part of the area in and near Steamboat Creek, where the water table is generally within a few feet of the ground surface. In the western part, springs were formerly active, but water levels are now 40 to 100 ft and more below the surface. Thermal water still circulates at depth in faults and fractures of this western area but discharge occurs below the surface through the more permeable wall rocks, eventually flowing directly into Steamboat Creek. Total discharge of saline water from the system (computed to Cl content of analysis 8, Table 13.1) is about 4000 liters per minute, of which less than 10 percent emerges at the surface from visible hot springs. The thermal water of the system is over-whelmingly meteoric in origin; there is no positive isotopic evidence for any magmatic water or other water of deep origin (Craig, Boato, and White, 1956; White, Craig, and Begemann, in press). Perhaps as much as 5 percent of magmatic water could escape detection by isotopic methods. The chemi-cal evidence from elements such as Li, As, B, and $CO_2$ favors a small mag-matic contribution (White, 1957a, p. 1646).

At depths of many hundreds of feet in the system, thermal water without a vapor phase rises at a nearly constant temperature of about 175°C. When this water rises within 350 ft of the surface in the hot core of the system, a $CO_2$-rich vapor phase is first formed. Boiling becomes extensive as the water rises and as hydrostatic pressure continues to decrease with decreasing depth. Temperatures are commonly close to but slightly lower than the theoretical boiling-point curve for pure water because of the $CO_2$ and $H_2S$ dissolved in the water.

The high-temperature springs and erupting geothermal wells are relatively

**TABLE 13.3.** Partial chemical analyses of springs and erupting wells, Steamboat Springs, Nevada, in parts per million, arranged in order of increasing temperature

| Spring or Well[a] | Temp. (°C) | pH[b] | Cl[b] | B | SO₄ | S[c] | CO₂[d] | Na | K | As | Sb | K/Na | SO₄/Cl | As/Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

TABLE 13.3.  *Partial chemical analyses of springs and erupting wells, Steamboat Springs, Nevada, in parts per million, arranged in order of increasing temperature*

| Spring or Well[a] | Temp. (°C) | pH[b] | Cl[b] | B | SO4 | S[c] | CO2[d] | Na | K | As | Sb | K/Na | SO4/Cl | As/Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 33 | 43 | 6.33 | 596 | 35.4 | 91 | 1.0 | | 519 | 43 | 1.7 | 0.1 | 0.083 | 0.153 | 0.0029 |
| 50 | 60 | 6.1 | 824 | 47.8 | 107 | 7.1 | 618 | 637 | 61 | 1.7 | .3 | .096 | .130 | .0021 |
| 4 | 66 | 6.49 | 894 | 45.2 | 152 | 2.7 | | 691 | 57 | 2.5 | .0 | .083 | .170 | .0028 |
| 3 | 71 | 6.11 | 878 | 44.7 | 125 | 4.8 | | 671 | 75 | 2.5 | .0 | .112 | .143 | .0028 |
| 21 | 71 | 6.28 | 904 | 49.9 | 143 | 3.3 | | 673 | 77 | 2.8 | .0 | .114 | .158 | .0031 |
| 9 | 73 | 6.31 | 846 | 46.5 | 131 | [e]6.8 | | 635 | 71 | 2.6 | .0 | .112 | .155 | .0031 |
| 10 | 74 | 6.36 | 856 | 47.7 | 128 | [e]7.0 | | 643 | 72 | 2.7 | .0 | .112 | .150 | .0032 |
| 2 | 77 | 6.37 | 864 | 44.0 | 129 | 8.1 | | 659 | 73 | 2.4 | .0 | .111 | .150 | .0028 |
| 20 | 81 | 6.57 | 866 | 47.7 | 134 | 4.1 | | 649 | 73 | 2.6 | .0 | .113 | .155 | .0030 |
| 25 | 86 | 7.40 | 876 | 48.7 | 106 | 3.9 | | 671 | 68 | 2.5 | .3 | .101 | .121 | .0029 |
| 53 | 87 | 7.34 | 888 | 49.0 | 115 | 1.9 | | 646 | 59 | 3.1 | .2 | .091 | .169 | .0035 |
| 8 | 89 | 7.9 | 865 | 49.4 | 100 | 4.4 | | 653 | 71 | 2.7 | .4 | .109 | .116 | .0031 |
| 18 | 93 | 7.08 | 896 | 49.0 | 123 | 2.9 | | 674 | 79 | 2.7 | .2 | .117 | .137 | .0030 |
| 16 | 94 | 7.28 | 888 | 50.2 | 125 | 3.4 | 217 | 668 | 77 | 3.0 | .1 | .115 | .141 | .0034 |
| 32 geyser well | 95 | 7.63 | 892 | 48.7 | 106 | 1.4 | | 672 | 68 | 2.7 | .5 | .101 | .119 | .0030 |
| 7 | 96 | 7.16 | 898 | 50.2 | 121 | 3.3 | | 681 | 64 | 2.8 | .2 | .094 | .135 | .0031 |
| 23-n geyser | 96 | 8.38 | 914 | 50.2 | 119 | 3.8 | | 692 | 77 | 2.7 | .2 | .111 | .130 | .0030 |
| 5 | 96 | 7.61 | 920 | 45.6 | 113 | 3.7 | | 699 | 81 | 2.9 | .1 | .116 | .123 | .0032 |
| 12 | 96 | 7.77 | 944 | 51.8 | 121 | 3.0 | | 716 | 82 | 3.1 | .4 | .115 | .128 | .0033 |
| Steamboat well No. 4 | 96 | 8.75 | 672 | 36.6 | 90 | 2.2 | 219 | 558 | 51 | 1.9 | .3 | .091 | .134 | .0028 |

Analyst: W. W. Brannock, U.S. Geol. Survey.

[a]All samples collected April 26, 1950 except for Springs 8 and 50, collected Aug. 9, 1949.

[b]Determined at room temperature by D. E. White in pyrex bottles with same degree of filling ($\sim$99%), carefully stoppered and pH meter standardized. Reported values ordinarily reproducible to 0.05 pH units or less. Determined day after collection.

[c]Total sulfide sulfur, fixed when collected by adding $CdCl_2$.

[d]Total $CO_2$ by Harmon Craig on separate samples collected 1952 to 1954 for isotope analyses; figure for Spring 50 is average of 6. GS-5 drill hole, not included in this table, contained 616 ppm total $CO_2$ at pH 6.20 (20°C) in a nonerupted water sample, but only 165 ppm total $CO_2$ in water at pH 8.79 during steady state eruption, with remaining $CO_2$ in vapor phase.

[e]Probably includes some native sulfur.

low in dissolved $CO_2$ (Table 13.3). Loss of $CO_2$ to the vapor phase commonly shifts the pH upward from 1 to 2 pH units; the greatest observed shift is about 2.6 units. About 14 percent of the water vaporizes to steam when the pressure on water at 175°C is suddenly decreased to atmospheric pressure. This assumes no loss of heat by conduction; in the natural system the percent of steam that is evolved ranges from near 0 to about 15 percent. In this process, the dissolved constituents are concentrated in the remaining water. On the cooler margins of the thermal system, where much heat is lost by conduction and pressures at these lower temperatures prevent boiling, all or most of the $CO_2$ is retained in solution in the water. Primarily for this reason, pH's of the low-temperature springs of Table 13.3 are relatively low. Spring 50 in many respects is representative of water hundreds of feet deep in the thermal system where all $CO_2$ is still in solution, and for this reason is listed in Table 13.1.

All identified cinnabar in the Steamboat thermal area occurs within 50 ft of the present topographic surface, and none has been identified in core and cuttings from any drill holes at greater depths. Some cinnabar occurs above present water table in leached rocks where sulfuric acid forms by oxidation of evolving $H_2S$; much of this cinnabar lines solution cavities and was clearly deposited after the cavities were formed. Such cinnabar is viewed as good, and in places conclusive, evidence for deposition of mercury from a vapor phase. Fine-grained cinnabar deposition from thermal waters below the water table is also prominent in some old chalcedonic sinter. As much as 0.02 percent Hg was also found in opaline muds, (amorphous to poorly crystallized $\beta$-cristobalite) precipitated in fissures below the surface and transported upward in suspension at times of unusually vigorous discharge (Brannock and others, 1948, pp. 222–225). Hg was also identified in steam from one well and two natural vents, and tiny crystals of cinnabar were selectively precipitated on galena suspended for several months in two different thermal wells.

The distribution of Sb is significant because of some similarity in the ores and geochemistry of Hg and Sb. Stibnite occurs in veinlets and cavities to a maximum depth of 150 ft below the surface. In six drill holes in the Low and Main Terraces, the deepest observed stibnite occurs at temperatures that range from 100°C to 146°C, that in four of the six being between 125°C and 132°C. The deepest stibnite was found at 147 ft in the Rodeo well of the Main Terrace, where the temperature is 146°C. Analyses of drill core without regard to visible stibnite show that sinter and hydrothermally altered rocks near the surface commonly contain 100 to 1000 ppm Sb. Altered rocks below 300 ft in depth, in contrast, nearly always contain from 2 to 10 ppm Sb, or only a little more than the normal content of fresh igneous rocks of the area. The siliceous muds previously mentioned contain as much as 4 percent Sb, as well as about 10 ppm Au, 400 ppm Ag, and 45 ppm Hg

the vapor phase common-
greatest observed shift is
porizes to steam when the
to atmospheric pressure.
natural system the per-
about 15 percent. In this
d in the remaining water.
here much heat is lost by
res prevent boiling, all or
water. Primarily for this
13.3 are relatively low.
ter hundreds of feet deep
ion, and for this reason is

l area occurs within 50 ft
een identified in core and
cinnabar occurs above
acid forms by oxidation
on cavities and was clear-
nabar is viewed as good,
f mercury from a vapor
ermal waters below the
nic sinter. As much as
, (amorphous to poorly
below the surface and
ually vigorous discharge
also identified in steam
rystals of cinnabar were
everal months in two

me similarity in the ores
veinlets and cavities to a
rill holes in the Low and
rs at temperatures that
ing between 125°C and
the Rodeo well of the
alyses of drill core with-
hydrothermally altered
1000 ppm Sb. Altered
ways contain from 2 to
ntent of fresh igneous
itioned contain as much
m Ag, and 45 ppm Hg

(H. McCarthy, U.S. Geological Survey, 1967). Stibnite also occurs as needles, radiating-clusters, and rarely as dense layers on the borders of a few spring pools. Of the springs included in Table 13.3, stibnite was deposited from Spring 8 and to a lesser extent Springs 2 and 3 during the years of systematic observation (1945 to 1952); active deposition was probable in several other springs but the evidence was less conclusive. A sample of stibnite needles and calcite crystals deposited in Spring 8 in 1949 contained 12 ppm Hg (H. McCarthy, U.S. Geological Survey, 1967). Metastibnite, the amorphous orange-red antimony sulfide, was deposited on rocks and vegetation from the discharge streams of several newly drilled erupting wells, and is also the dominant antimony mineral in some siliceous muds.

The data of Table 13.3 and the rate of discharge of the whole spring system indicate a significant transport of Sb and As in the thermal waters, equivalent to about 5 metric tons of As and 1 ton of Sb per year. Sb is generally present in higher concentrations in the high-temperature waters, which are also very likely to have a high pH at the surface, as discussed previously. Springs that emerge at temperatures below 85°C evidently precipitate all or most of their initial Sb content (probably about 0.5 ppm), but almost no As. Decreasing temperature, as will be seen, is evidently the dominant factor in precipitating Sb, with changes in pH of less importance.

First, let us review the principal factors that influence pH of the waters. The important upward shift in pH with loss of $CO_2$ to the vapor phase has been discussed. This shift, as much as two and a half pH units, is localized within the upper 350 ft in the hotter parts of the system.

The high $SO_4/Cl$ ratios of some of the analyses of Table 13.3 suggest that at least a part of the $SO_4$ originates from near-surface oxidation of $H_2S$, and is then incorporated in water circulating in the upper part of the spring system. $H^+$ ions are released in the reaction $H_2S + 2O_2 \rightarrow 2H^+ + SO_4^{2-}$. In an unbuffered water, the pH will shift drastically downward from oxidation of only a little $H_2S$, but waters that are strongly buffered by $CO_2$ species are much less subject to change. The general magnitude of the effect is evident from the following examples, calculated by Ivan Barnes, U.S. Geological Survey: A water initially at pH 7.2 and buffered by 300 ppm of total $HCO_3^-$ and $CO_3^{2-}$ contains 4 ppm of $H_2S$ that is oxidized by direct addition of $O_2$; the computed final pH is 7.0. If 16 ppm of $H_2S$ oxidizes but other conditions are otherwise unchanged, the final pH is 6.7.

The maximum difference in $SO_4$ contents in Table 13.3, converted to constant chlorinity of 800 ppm, is shown by Springs 4 and 8. The difference in content of $SO_4$ (44 ppm at chlorinity of 800 ppm) is equivalent to 15 ppm S; this could be accompanied by a downward shift in pH of about a half pH unit in Spring 4. Is this hypothesized downward shift in pH limited in its effects to the upper part of the system where all recognized stibnite and cinnabar are localized? Evidence on this point has been obtained from $SO_4/Cl$

ratios of water samples from the geothermal drill holes. The ratios in the three analyzed samples from drill holes cased to depths of at least 220 ft, thereby eliminating shallower water perhaps higher in $SO_4$, range from 0.143 to 0.148. These are all well within the range of $SO_4/Cl$ ratios of Table 13.3. Drilled depths of the three holes range from 400 to 575 ft, but depths of origin of inflow within the uncased intervals are not known. From this we conclude that effects from differences in $SO_4$ are not localized in the uppermost stibnite-bearing part of the system.

Another change in pH is caused by hydrolysis of silicate minerals, also called hydrogen metasomatism (Hemley and Jones, 1964, pp. 541–547; Chapter 6, this volume). The cumulative effect of hydrolysis throughout the whole system is no doubt very important, tending to raise the pH, but $CO_2$ and $HCO_3^-$ are present as buffers. The rate of alteration in the upper few hundred feet of the system is difficult to determine but is probably so low that the effect on pH in this shallow zone is small relative to other factors.

Pure water and natural waters change in pH with temperature alone. The pH of the neutral point is about 6.1 at 100°C and 5.7 at 200°C. The dissociation of each dissolved constituent differs with temperature. The behavior of some substances in water has been determined experimentally (Khitarov and Ryzhenko, 1963) but very little is known about changes in pH of natural waters in response to temperature alone. Ellis and Wilson (1961) suggested that waters high in $SO_4/Cl$ may be neutral at high temperature but acid at low temperature because of changes in the second dissociation constant of sulfuric acid. Natural waters may shift across the neutral point in either direction, depending on the relative abundance of various dissolved substances.

At Steamboat Springs, in situ determination of pH at high temperature showed the following:

Spring 18 at 88°C had a pH of 6.7 as compared to 6.95 determined in the laboratory at 19°C. Spring 21 at 82°C had an in situ pH of 6.4 as compared to 6.65 at 19°C. The neutral point, for comparison, is 6.2 at 85°C. Precision of the determined values is not known, but the data suggest that waters of both springs are slightly acid at low temperature, but slightly alkaline at their vent temperatures.

The pH's mentioned here, and those obtained by Ivan Barnes and G. G. Ehrlich at Wilbur Springs are the only in situ data included in this report. Detailed investigations of this type are needed to evaluate the differences reported here.

From all of these relationships, however, we conclude that antimony and mercury are transported upward from deep in the system in nearly neutral liquid water of low total sulfide content (25 ppm or less) without a vapor phase. In the upper 350 ft of the system where temperatures are high enough, a $CO_2$-enriched vapor phase forms, increasing the pH of the water and probably the solubility of $Sb_2S_3$. In the upper 150 ft, stibnite is precipitated,

WATERS

ll holes. The ratios in the
depths of at least 220 ft,
gher in $SO_4$, range from
of $SO_4/Cl$ ratios of Table
90 to 575 ft, but depths
re not known. From this
are not localized in the

of silicate minerals, also
nes, 1964, pp. 541–547;
r drolysis throughout the
to raise the pH, but $CO_2$
eration in the upper few
e but is probably so low
relative to other factors.
h temperature alone. The
5.7 at 200°C. The dis-
th temperature. The be-
termined experimentally
known about changes in
alone. Ellis and Wilson
e neutral at high temper-
ges in the second dis-
nay shift across the neu-
ve abundance of various

pH at high temperature

6.95 determined in the
pH of 6.4 as compared
is 6.2 at 85°C. Precision
a suggest that waters of
but slightly alkaline at

van Barnes and G. G.
included in this report.
evaluate the differences

lude that antimony and
ystem in nearly neutral
less) without a vapor
atures are high enough,
pH of the water and
stibnite is precipitated,

primarily because of decrease in temperature but perhaps augmented locally by decreasing pH from oxidizing $H_2S$. In the hottest near-surface part of the system, the pH increase from loss of $CO_2$ is probably dominant over changes related to decreasing temperature and other factors and much Sb is retained in solution.

HgS is precipitated at even shallower depths and lower temperatures than $Sb_2S_3$. Near the surface, some Hg is transported in a vapor phase.

## Cordero Mine, Nevada

The Cordero Mine is in volcanic tuffs, flows, and breccias of Tertiary age (Bailey, 1962, p. 5; Tunell, 1964, p. 1022). Near the surface some of these rocks are silicified opalite, locally with kaolinite and alunite. Cinnabar, native Hg and mercury oxychlorides occur in veinlets and disseminations in the opalite. Most of the mercury production has come from a large ore body 300 to 800 ft below the surface. The volcanic rocks at these depths are altered largely to montmorillonite with some quartz, kaolinite, and opal ($\beta$-cristobalite). Buddingtonite, the recently discovered ammonium feldspar (Erd and others, 1964), occurs in some high-grade ore. Cinnabar was preceded by abundant marcasite and a little pyrite. Alunite, disordered kaolinite, and iron oxides are locally abundant below the premining water table, but may be related to recent downward-percolating meteoric water acidified by oxidation of marcasite.

The water supply for the mine camp is pumped from two thermal wells in alluvium about a third of a mile downslope from and north of the main shaft. The upper of the two wells is 580 ft deep and discharges water at a temperature of 56°C (Table 13.1, analysis 9); the lower well is 550 ft deep, its water is slightly lower in temperature (53°C) but is nearly identical chemically except for a somewhat lower pH (7.3). In prospect holes between the thermal wells and the mine workings, temperatures were as high as 43°C at depths of 200 ft.

Temperatures in the mine workings are considerably above normal. Large flows of hot water (40°C) were encountered at depths of about 600 and 800 ft below the surface. Discharge from the deeper zone resulted in a decrease in yield from the thermal wells, proving interconnection (V. P. Haas, Cordero Mining Co., 1964). The mine drainage water is complex in origin, consisting in part of cold near-surface downflow acidified by oxidizing marcasite and pyrite and in part of thermal water that probably is similar chemically to analysis 9, Table 13.1.

## Amedee Springs, California

Amedee Springs is of interest because metacinnabar, cinnabar, and native Hg are precipitating in spring vents and discharge channels (Tunell, 1964, p. 1019).

The thermal waters rise through alluvium of the large basin of Honey Lake; total discharge is about 4000 liters per minute, and the highest discharge from any single spring or closely associated spring group is approximately 1200 liters per minute. The pH of the water is 8.5 (analysis 10), which is near the maximum of Table 13.1; the dominant constituents are Na, $SO_4$, Cl, and $SiO_2$. The present Honey Lake is saline and its basin is undrained; it is therefore likely to contain some evaporites, perhaps accounting for some of the dissolved constituents of the thermal waters.

Cinnabar in layers up to 2 mm thick line the orifices of many spring vents. In the surrounding pools and channels black metacinnabar generally overlies cinnabar and has been identified as far as 25 ft downstream from the vents. Tunell estimated (1964) the total mass of HgS in the spring aprons to be 100 to 200 kg, but this may be somewhat high.

According to Tunell, the Hg sulfides are deposited on calcareous tufa and lake sediments. Recent x-ray study by the author has shown that the sediments are arkosic, with abundant montmorillonite, some illite, and surprisingly little carbonate. The most abundant mineral is heulandite, a calcium zeolite (distinguished from clinoptilolite by disappearance of the prominent 8.9Å x-ray peak upon heating at 450°C). Some specimens are almost pure heulandite with veinlets and disseminations of cinnabar, but others have an outer porous layer 2 mm thick consisting of euhedral crystals of chabazite, another calcium zeolite. This layer also contains narrow alternating bands of cinnabar and metacinnabar, each of which is intimately associated and probably coprecipitated with chabazite. Metacinnabar is the latest sulfide of these specimens, but near the spring vents a few projections just above water level have an outermost layer of amorphous opal deposited from evaporating splash.

The euhedral chabazite was deposited directly from the hot-spring waters. The earlier heulandite, according to local evidence, could have formed by devitrification of volcanic glass in alkaline lake water or by hydrothermal alteration caused by the slightly alkaline hot-spring waters; direct precipitation is a third and probably less likely alternative.

Amedee No. 1 geothermal well was drilled in February 1962 to a depth of 885 ft; it is near the middle of the principal north-trending groups of springs and about 100 ft north of a prominent fenced group of springs (NW¼NW¼NE¼ sec. 8, T. 28 N., R. 16 E.). Drill cuttings from the surface to 770 ft consist largely of greenish-gray clay, silt, and sand containing zeolites, quartz, volcanic debris, and clay minerals. Pyrite is rare and no other sulfides were recognized. Illite interlayered with montmorillonite is the dominant clay mineral in the upper 200 ft; montmorillonite as a separate phase occurs in the upper part and is the dominant clay mineral below 400 ft. Heulandite is the major zeolite but some samples also contain clinoptilolite (judging from heating behavior, 450°C); stilbite is sporadically

'VATERS

f the large basin of Honey
minute, and the highest dis-
ted spring group is approxi-
er is 8.5 (analysis 10), which
n' constituents are Na, SO₄,
nd its basin is undrained; it
erhaps accounting for some
ers.
rifices of many spring vents.
etacinnabar generally over-
?⁵ ft downstream from the
HgS in the spring aprons to
gh.
ited on calcareous tufa and
or has shown that the sedi-
nite, some illite, and sur-
ˈˈeral is heulandite, a cal-
by disappearance of the
0°C). Some specimens are
ninations of cinnabar, but
nsisting of euhedral crystals
r also contains narrow al-
ˈˈch of which is intimately
azite. Metacinnabar is the
ing vents a few projections
amorphous opal deposited

rom the hot-spring waters.
ˈˈe, could have formed by
water or by hydrothermal
ing waters; direct precipi-
ive.
ebruary 1962 to a depth of
north-trending groups of
ˈˈenced group of springs
cuttings from the surface
silt, and sand containing
als. Pyrite is rare and no
with montmorillonite is
ft; montmorillonite as a
ˈˈ dominant clay mineral
ome samples also contain
C); stilbite is sporadically

abundant. Below 770 ft, where bedrock was penetrated (Edward Zajac, Magma Power Company, written communication, 1964), the well cuttings consist dominantly of volcanic fragments with prominent x-ray peaks similar to feldspars of outcropping volcanic rocks three-quarters of a mile to the northeast near the base of the Amedee Mountains. Secondary minerals in the cuttings include montmorillonite, heulandite, and traces of stilbite and pyrite.

After the drilling and preliminary testing of this well, the casing was pulled; the well now discharges as a vigorously flowing spring with almost no local evidence of its man-made origin. Measured discharge was 330 liters per minute (Zajac, February 19, 1962), and its temperature was 98.0°C (White, October, 1964). Subsurface temperatures measured in the flowing well by Edward Zajac were 107°C from 885 ft up to 400 ft in depth, and 104°C from 300 to 100 ft. These relationships indicate that water at 107°C is flowing up from the bottom of the well and between 300 and 400 ft in depth mixes with somewhat cooler water; this mixture then rises as a single liquid phase at 104°C. At a depth of only 10 to 20 ft, pressure on the water column has decreased sufficiently for boiling to occur; a vapor phase then forms and the temperature decreases gradually to 98°C at the surface.

The colors of rocks and sediment in this man-made spring are dark gray deep in the vent, dark purple-gray around the vent and for 10 ft down the center of its discharge channel, and green-gray in adjacent more oxidized bordering parts. The dark purple-gray color may be caused by recently precipitated cinnabar but the film is so thin that its nature was not evident under the microscope. This spring should be monitored in future years because useful data on rate of deposition can be obtained from it.

A water sample from this spring included the following, in ppm: Ca, 16; Mg, 0.1; Na, 228; K, 5.1; Li, 0.3; HCO₃, 12; CO₃, 18; SO₄, 274; H₂S, 0.5; Cl, 160; B, 3.7; evaporated residue (180°C), 830; pH is 8.9 (analyst, Robert Schoen, U.S. Geological Survey). From these data, we conclude that water of the new spring is remarkably similar to the previously analyzed spring. The only certain differences are about 0.5 ppm of H₂S and 0.4 units in pH; the indicated differences in SO₄ are largely if not entirely analytical, judging from the near identity of cations and evaporated residue, and an excess of anions (11.50 equivalents per million) in analysis 10, Table 13.1, versus cations (10.87 epm). The rapid rate of upflow of water in the new spring probably results in slightly greater loss of CO₂ to the vapor phase, thereby accounting for most of the difference in pH; the 0.5 ppm of H₂S in the new spring water may oxidize to SO₄ in the natural system, thereby accounting for a slight difference in pH. The conclusions to be drawn from the described relationships are that the general character of the water is already determined when it has risen within 870 ft of the surface. The upflow is in a single liquid phase except in the uppermost

several tens of feet, where boiling occurs. The small and as yet unmeasured content of Hg is therefore transported in a slightly alkaline water of very low sulfide content, at least in the upper thousand feet or so of the system.

Amedee No. 2 well was drilled about 900 ft south of No. 1 in the south part of the principal flowing groups of springs. Water level stands at about 3½ ft below the surface, where the temperature is 85°C; the well has never discharged. A reconnaissance study of cuttings provides tentative conclusions on structure and the alteration minerals at depth. The basin sediments in this well are only 250 ft thick; from here to 1080 ft, the bottom of the hole, the cuttings consist of fragments of altered volcanic rocks with the same dominance of feldspars noted near the bottom of Amedee No. 1. Heulandite is the dominant zeolite, stilbite is sporadic, and laumontite was noted in abundance near 200 ft and in lower concentrations in several other samples. Montmorillonite as a separate phase is everywhere the dominant clay mineral, suggesting that the prominent illite of the upper part of Amedee No. 1 has formed by fixation of K from the thermal water with decreasing temperature (see White, 1965, fig. 6 and related discussion). Amedee No. 2 was drilled largely in the footwall of a major NNE fault that dips to the west and has a bedrock displacement of at least 500 ft. This fault provides the structural control for the spring system.

Amedee No. 3 well, 1½ km NE of the springs at the base of the Amedee Mountains, was drilled to a depth of only 198 ft. Evidence for hydrothermal activity is completely absent. Cuttings consist entirely of fragments of volcanic rock with some montmorillonite; zeolites and illite are absent. These facts help to confirm a hydrothermal origin for the zeolites and illite of the hot spring area.

## Boiling Springs, Idaho

Boiling Springs is geochemically similar to Amedee Springs in some respects but the geologic setting differs greatly (White, 1955a, pp. 124–125; Tunell, 1964, p. 1020). The springs discharge from a northeast-trending fault in granodiorite of the Idaho batholith. Temperatures range from 81°C to 88°C, or approximately the boiling point for pure water at this altitude. Total discharge from the group was about 750 liters per minute (1953), and the largest discharge from any single spring was about 100 liters per minute. Discharge of gas bubbles was relatively low; it was estimated to be less than 10 liters per minute from the largest spring. The relatively low discharge of steam and other gases is evidence that temperatures do not rise rapidly with depth, and boiling is restricted to the uppermost part of this spring system as previously described for Amedee.

A little cinnabar coats the throats of some springs; 3 ft and more downstream from the vents, metacinnabar overlies cinnabar. From 10 to 15 ft

downstream, the thin dark coating is largely manganese oxide associated with minor metacinnabar.

The largest spring is near the north end of the group and has a concrete framework with a pipe leading to a nearby Forest Service cabin. Within the framework, the vent is visible below the water level to a depth of about 3 ft, where an open fissure extends at least a short distance to the north and south along the controlling shear zone. When observed in 1953, the granodiorite was somewhat bleached in appearance and completely lacked any visible coating of cinnabar or metacinnabar. The concrete structure, although at least two years old, showed no visible HgS. Possible explanations for these facts are: The mercury sulfides are not being deposited now; they are being deposited very slowly; or they are deposited only after the water emerges at the surface. None of these possibilities is supported by strong evidence, but the second is viewed as the most probable and is similar again to conclusions drawn for Amedee. The rate of deposition is probably very slow because the total quantity of visible mercury on the spring vents and aprons was estimated to be only a kilogram or so.

Granodiorite of the shear zone a few inches below the ground surface contains quartz, plagioclase, and orthoclase of the original rock; the identified alteration minerals are dominantly montmorillonite with some chlorite and minor illite. A sample of granodiorite from the surface of the discharge apron of one of the springs contained the same minerals, but a thin outer layer consisted of metacinnabar, stilbite, pyrite, and a little clinoptilolite and calcite.

The water of Boiling Springs has the lowest total dissolved constituents of Table 13.1; these constituents (analysis 11) are dominated by Na, carbonates, and $SiO_2$. Its relatively high pH of 9.2 is consistent with findings elsewhere (White, Hem, and Waring, 1963, table 26, and unpublished data) that dilute meteoric waters heated in contact with unstable silicate minerals and without auxiliary $CO_2$ are consistently high in pH, and are commonly within the range of 9 to 10. A high pH is to be expected as a result of hydrolysis of silicates, and is consistent with the experimental results of Hemley (1959; Hemley and Jones, 1964). At Boiling Springs, the chemical constituents provide no evidence for a nonmeteoric contribution, other than perhaps the mercury itself and traces of antimony and sulfide. The low content of $SO_4$ (12 ppm) severely limits the amount of $H_2S$ that can be hypothesized to oxidize deeper in the system. The quantity of atmospheric $O_2$ soluble in meteoric water at 10°C can oxidize only 6 ppm of $H_2S$, producing a total of 17 ppm of $SO_4$. The determined quantity of 12 ppm of $SO_4$, however, is about the content to be expected in the surface water that is recharging the system. Even if this surface water is assumed to have no initial $SO_4$, an upper limit of only 4 ppm of $H_2S$ can be oxidized. Removal of sulfate as anhydrite at depth is very unlikely, because the Ca

content is so low and other sulfates of low solubility are viewed as improbable.

## Apapel'sk Springs, Kamchatka, U.S.S.R.

The Apapel'sk hot springs are in a tributary valley of the Anavgai River in the central range of Kamchatka (Shcheglov, 1962). For many years cinnabar had been known in the spring sediments, but this was presumed to come from Tertiary rocks of the surrounding region. The chemical similarity between Apapel'sk (Table 13.1, analysis 12) and springs such as Amedee and Boiling Springs in the United States led Shcheglov to search for evidence of active deposition of Hg.

The thermal area is underlain by Pliocene volcanic rocks cut by a major fault. In the spring area and elsewhere near the fault, the volcanic rocks are silicified and kaolinized; deposits of As, Sb, Hg, and base metals also occur along the fault zone, but evidently not in the immediate vicinity of the thermal area.

There are about fourteen springs which emerge in a swampy area of about 1 sq km. Six springs on the borders of the valley are characterized by vigorous boiling but rates of discharge are not stated. The water analysis (Table 13.1, analysis 12) is remarkably similar to that of Amedee (analysis 10). The gases, according to Ivanov (1958), consist dominantly of nitrogen with only minor amounts of other constituents.

Shcheglov recovered a piece of silicified tuff from the throat of one of the springs. The exposed surface was covered with brown iron oxides; bright red cinnabar was recognized in isolated filmy spots up to 0.5 sq cm in area. These films developed shrinkage cracks upon drying. Cinnabar was identified by its optical properties and by chemical analysis. The total amount was small, and none was found in internal parts of the specimen. The evidence for active or very recent deposition of cinnabar is similar to that of Amedee and Boiling Springs.

## Ngawha Springs, New Zealand

Mercury deposits are closely associated with the Ngawha springs of North Auckland, North Island (Fleming, 1945; White, 1955a). Chemically and in geologic environment, Ngawha is very similar to Sulphur Bank, California (White and Roberson, 1962; James Healy and A. J. Ellis, written communication, 1964; Ellis and Mahon, 1966).

The Ngawha Springs discharge through shales and sandstones of Cretaceous or early Tertiary age overlain by late Cenozoic volcanic rocks, alluvium, and lacustrine sediments. Basalt and rhyolite of Quaternary age

also occur nearby. According to Healy, geological and geophysical evidence suggests that these rocks are underlain by graywacke at a depth of about 2000 ft. Graywacke dominates the basement rocks of the North Island and is of interest because of its similarity to rocks of the Franciscan formation associated with many Hg deposits of California.

Cinnabar impregnates the upper 10 ft of acid-leached lake beds, peat, and hot-spring sinter, which are localized in circular depressions regarded as explosion craters. Associated minerals are native Hg, S, marcasite, hydrocarbons, chalcedony, opal, and a little stibnite. According to some observers, cinnabar is probably still being deposited.

Early attempts at mining through shafts were abandoned because temperatures were too high. In 1930 the deposit was successfully mined with a drag-like excavator. The ore was largely swamp mud and was low in grade and difficult to roast.

The Ngawha thermal waters (Table 13.1, analysis 13) are dominated by Na, Cl, B, $HCO_3$, and $SO_4$; the proportion of B to total dissolved matter is one of the highest yet recorded, even exceeding that of Sulphur Bank (Table 13.1, analysis 1). The $NH_4$ content of Ngawha waters is also very high. The springs range from strongly acid to nearly neutral; the highest pH's are from the hottest waters, at least in part because these springs have somewhat higher rates of upflow and lose more $CO_2$ in a vapor phase. The $SO_4$ contents are highly variable and are to a major extent inversely related to pH. Here, as in other spring systems where $H_2S$ is oxidizing near the surface, the rate of discharge of a spring exerts a very important control on pH near the surface. A spring of low discharge and extensive nearby oxidation of $H_2S$ will be acid, but a spring of high discharge in an otherwise similar environment will be only slightly acid to alkaline because the $H_2SO_4$ that forms is diluted and flushed from the system.

A gas sample from Velvet Bath, near and similar to Jubilee Bath (analysis 13), contained, in volume percent: $CO_2$, 90.6; $CH_4$, 6.7; $N_2$, 1.8; $H_2$, 1.0; $H_2S$, 0.02.

## Toya Springs, Hokkaido, Japan

Native Hg was observed by Dr. J. Harada and others in the orifice of Toya-Ko Onsen spring, Abuta-cho, Hokkaido (Prof. Masakichi Nishimura, written communication, 1965). The native Hg evidently was not from an accidental breaking of a thermometer; after the orifice was completely cleaned of sand and Hg, more Hg reportedly reappeared.

The water is high in Cl and moderately high in $SO_4$, $HCO_3$, and B (Table 13.1, analysis 14); its pH is 7.3, and sulfide was searched for but not found.

According to Nishimura, a noneconomic impregnation of cinnabar occurs at Toyoura 10 km from the spring, and in an iron sulfide deposit 4 km from the spring.

## Cymric Oilfield, California

Native Hg and possibly other forms of Hg occurs in petroleum, natural gas, and brine of the Cymric oil field, Kern County, California (Bailey and others, 1961). Although this occurrence differs greatly from other deposits considered here, this oil field is of special interest because hydrocarbons and methane are frequently associated with Hg deposits, and because the waters of the Wilbur Springs and Mt. Diablo districts are chemically similar to oil-field waters, as previously mentioned.

The Cymric oil field is near the west side of the San Joaquin Valley 40 miles west of Bakersfield and on the southeastern extension of a remarkably aligned group of Hg deposits that include, at approximate 25-mile intervals from northwest to southeast (Bailey, 1962), the New Almaden, Stayton, Central San Benito, New Idria, and Parkfield districts. The Cymric oil field is 45 miles southeast of the Parkfield district.

The oil field yields petroleum from 11 separate zones that range in age from Eocene to Pleistocene with a composite thickness of more than 8500 ft. Shale and siltstone are dominant but the petroleum occurs in interbedded sandstone and silty sandstone. Temperatures of producing zones range from 49°C at 3000 ft to 81°C at 5320 ft; these temperatures are slightly higher than normal in California for the depths and lithologies.

Analyzed Cymric crude oils contain remarkably large quantities of Hg, with reported concentrations from 1.9 to 21 ppm; the later is one of the highest reported for any natural fluid. The natural gas that separates from petroleum and brine upon release in pressure is saturated with Hg vapor at the oil field, but the Hg evidently combines with $H_2S$ from "sour" natural gases from other oil fields and is precipitated in the pipe lines. Some native Hg separates from crude oil at the local pumping stations.

Brines associated with producing oil wells (analysis 15, Table 13.1, and Bailey and others, 1961) contain Hg in amounts reported from less than 0.02 to 0.2 ppm. The Hg content of dark sediment recovered from water sample bottles ranged from 470 to 3600 ppm, which is far in excess of normal sedimentary rocks ($< 1$ ppm). If the Hg of this sediment is assumed to have been in solution at the time of collection, the total Hg content ranges from 0.17 ppm in the Eocene brine to 0.45 ppm in the Miocene brine. $H_2S$ was not detected in any brine sample, and total sulfate and thiosulfate are no more than a few ppm. The total quantity of Hg discharged from all fluids during the life of the field has not been determined, but is probably equivalent to many thousands of flasks.

WATERS

mpregnation of cinnabar
in an iron sulfide deposit

curs in petroleum, natural
ty, California (Bailey and
eatly from other deposits
est because hydrocarbons
deposits, and because the
stricts are chemically sim-

he San Joaquin Valley 40
extension of a remarkably
roximate 25-mile intervals
New Almaden, Stayton,
districts. The Cymric oil

e zones that range in age
kness of more than 8500
troleum occurs in inter-
res of producing zones
these temperatures are
e depths and lithologies.
y large quantities of Hg,
; the later is one of the
gas that separates from
turated with Hg vapor
with H2S from "sour"
itated in the pipe lines.
local pumping station.
ysis 15, Table 13.1, and
reported from less than
recovered from water
hich is far in excess of
his sediment is assumed
, the total Hg content
5 ppm in the Miocene
, and total sulfate and
al quantity of Hg dis-
s not been determined,
asks.

Except for the Hg content, the petroleum and brines of the Cymric oil field are chemically similar to the fluids of other California oil fields. Hg is also reported to occur in smaller concentrations in other San Joaquin Valley oil fields, but no detailed data are available.

## OTHER DEPOSITS AND SPRING SYSTEMS PERTINENT TO MERCURY TRANSPORT

Abnormal temperatures, unusual gases, and mineral waters have been detected in some epithermal ore deposits but in relatively few metal mines of other types. Of the total number of such occurrences now known, roughly two-thirds are associated with Hg deposits. Some of these are described in the previous section but other data of a more fragmentary or qualitative nature are summarized in Table 13.4.

Because most Hg mines are shallow, only the highest rates of temperature increase are normally noted. Many other deposits characterized by gradients one and a half times or more of normal probably exist undetected because absolute temperatures are not uncomfortably high.

Of the gases that suggest a genetic relationship to hot springs, $H_2S$ is the easiest to detect in small quantities. $CH_4$ is looked for wherever suspected because of the explosion hazard. $CO_2$ is likely to be the most abundant of gases but is likely not to be noticed except where $O_2$ is diluted below life-sustaining levels.

Table 13.4 also includes some pertinent mineralogical data not mentioned elsewhere. Dickite, for example, is a characteristic clay mineral in the Terlingua and Monte Amiata districts. Dickite has been looked for but not yet found in the near-surface acid environments of hot-spring systems where kaolinite is common. Dickite may indicate a hypogene origin at temperatures and pressures above those of explored parts of geothermal systems.

Also significant to Hg deposits are those thermal waters notably high in As. The high-As waters tend to be similar chemically to the high $HCO_3$ waters of Table 13.1.

At Crabtree Springs, Lake County, California (White, Hem, and Waring, 1963, table 22, fig. 1) thermal water similar to that of Sulphur Bank issues from altered serpentine. The hydrothermal minerals include opal (amorphous and $\beta$-cristobalite), magnesite, dolomite, and veinlets of realgar, pyrite, and marcasite. Mercury has also been reported, but I have not detected any Hg minerals. The water contains 1 ppm As, 3900 ppm $HCO_3$, and 290 ppm B; its pH is 6.7.

Aver'ev (1960) has summarized data from some remarkable As-bearing waters of Sinegorsk in southern Sakhalin Island. The waters are strikingly

TABLE 13.4. Other deposits and spring systems pertinent to mercury transport

| | | Temperature | Gases[a] | |
|---|---|---|---|---|
| 1. | Coso Hot Springs, Inyo Co., Calif. | Near boiling; vapor | Hg, $H_2S$, probably $CO_2$ | Hg in vapor |
| 2. | New Idria mine, San Benito Co., Calif. | ? | $CH_4$, $H_2S$ | Methane for |
| 3. | New Almaden mine, Santa Clara Co., Calif. | ? | $Co_2$ in mine, cold springs | $CO_2$ once p stibnite ar (Clarke, 191 |
| 4. | Phoenix mine, Stanislaus Co., Calif. | ? | Gas with 61% $CH_4$ | Some native |
| 5. | Oceanic mine, San Luis Obispo Co., Calif. | ? | Explosion hazard—$CH_4$? | Hydrocarbo |
| 6. | Great Eastern mine, Sonoma Co., Calif. | ? | Explosion hazard—$CH_4$? | Native S an adits of tt |
| 7. | Sulphur district, Humboldt Co., Nev. | Warm vapor | $H_2S$ | Springs simi |
| 8. | Brady's Hot Springs, Churchill Co., Nev. | Boiling water | $CO_2$, $H_2S$ | (Yates and tion inclu |
| 9. | Terlingua district, Brewster Co., Tex. | Warm | $CH_4$, $H_2S$ | Livingstonit |
| 10. | Huitzuco, Mexico | ? | $H_2S$ and ? | 1964) Water too h |
| 11. | Nuevo Mercurio, Zacatecas, Mexico | Hot water | ? | Cinnabar w |
| 12. | Chaguarama Valley, Venezuela | Springs, geyser, to 100°C | | |
| 13. | Monte Amiata district, Tuscany, Italy | | | (Falini, 196 |
| | Abbadia San Salvatore mine | Up to 48°C at 407 m; 63°C at 440 m | $CO_2$, $H_2S$ | illite-mon |
| | Siele group | ~40°C | $H_2S$ and ? | Native S dt |
| 14. | Tagburos Hot Springs, Palawan, Philippine Is. | 95°C | ? | Cinnabar a Metallic H rounding |
| 15. | Dobra Voda Spring, Yugoslavia | Cold ? | | All rich ci through (Berce, 1 |
| 16. | Idrija mine, Yugoslavia | Cold ? | | Hg mineral |
| 17. | Irkutsk region, U.S.S.R. | Thermal | | 1963) |

[a]$CO_2$ presumably also present in all or most deposits but not specifically identified.

[b]Data

| Gases[a] |
| --- |
| Hg, H$_2$S, probably CO$_2$ |
| CH$_4$, H$_2$S |
| Co$_2$ in mine, cold springs |
| Gas with 61% CH$_4$ |
| Explosion hazard—CH$_4$? |
| Explosion hazard—CH$_4$? |
| H$_2$S |
| CO$_2$, H$_2$S |
| CH$_4$, H$_2$S |
| H$_2$S and ? |
| ? |
| CO$_2$, H$_2$S |
| H$_2$S and ? |
| ? |

ut not specifically identified.

## Comments, Reference[b]

Hg in vapor of drill hole; HgCl occurs with cinnabar

Methane formerly a serious hazard; metacinnabar and native Hg with dominant cinnabar

CO$_2$ once produced commercially (Bailey and Everhart, 1964, p. 188); native Hg and stibnite are minor constituents
(Clarke, 1916, p. 667)

Some native Hg

Hydrocarbons, opaline silica-carbonate rock abundant

Native S and HgS may still be depositing from vapor; odor of H$_2$S especially prominent in adits of the Devils Corral area
Springs similar to Steamboat Springs, nearly neutral pH; minor cinnabar

(Yates and Thompson, 1959) Clay minerals identified by D.E.W. from Thompson's collection include kaolinite, illite-montmorillonite, and dickite (Fresno and Contrabando mines)
Livingstonite, stibnite, anhydrite, S, dolomite, gypsum (McAllister and Ortiz, 1945; Tunell, 1964)
Water too hot and high in discharge to control (David Gallagher, oral communication, 1960)

Cinnabar with native S; water contains B, NH$_4$ (Cortese, 1904)

(Falini, 1960; S. Gherardi, written communication, 1961.) Clays include kaolinite, dickite, illite-montmorillonite (D.E.W.)
Native S depositing; dickite common (D.E.W.)

Cinnabar around spring orifices (Irving, 1954)
Metallic Hg (50 grams/m$^3$) in sand and gravel around spring; cinnabar deposits in surrounding area (Mandic', 1957)
All rich cinnabar ore below thrust plate without surface outcrop; discovery reportedly through native Hg in springs, and native Hg in channels through upper plate of thrust (Berce, 1958; oral communication)
Hg mineralization commonly accompanied by thermal springs; no details (Znamirovskii, 1963)

[b]Data reviewed by White, (1955a), unless noted

similar to Sulphur Bank (Table 13.1, analysis 1) except in concentration; one analysis includes, in ppm: Na, 6566; K, 125; Ca, 260; Mg, 208; $NH_4$, 56; $HCO_3$, 8944; free $CO_2$, 3000; Cl, 6195; $SO_4$, 36; Br, 32; I, 13; B, 566; As, 61; and pH is 6.1. The water is cold, with a temperature of only 7°C; discharge is not stated. North of this analyzed spring the contents of $CO_2$ and As decrease to zero but NaCl and B are stated to remain unchanged.

Nalachevskii hot springs, Kamchatka (75°C) and Dzhul'fin warm springs, Transcaucasus (26.5°C) are both NaCl waters high in $HCO_3$ and free $CO_2$ with respective pH's of 6.4 and 6.1 and As contents of 7.7 and 20 ppm. Aver'ev concludes that As and $CO_2$ are closely related.

## SUMMARY OF CHARACTERISTICS OF MERCURY DEPOSITS AND ASSOCIATED FLUIDS

Conclusions that can be drawn from the natural fluids associated with Hg deposits include the following:

1. Total sulfide contents range from less than 1 ppm to about 180 ppm. Other rare natural waters of higher sulfide content (White, Hem, and Waring, 1963, tables 15, 16, 19, 27) have no obvious relationship to Hg deposits.

2. Waters presently associated with commercial quantities of Hg (Tables 13.1 and 13.2) range in pH from 6.1 to 8.1 and the average is close to neutrality. HgS is definitely being deposited at Sulphur Bank and Steamboat Springs, and is probably being deposited at Ngawha Springs in New Zealand.

3. Amedee, Boiling Springs, and Apapel'sk (Table 13.1, analyses 10–12) prove that some HgS is transported in and deposited from slightly alkaline waters (pH 8.5–9.2). Recent deposition of new HgS, it should be mentioned, is easier to prove in subcommercial spring vents than in mines. The spring vents are relatively undisturbed; in mines, previously deposited Hg minerals are available for mechanical transport and perhaps for solution and re-deposition.

4. The high $CO_2$ content of these waters exerts a major and probably dominant control in determining their neutral to slightly acid pH's, and all theories for Hg transport must consider the probability that $CO_2$ is high in the ore solutions.

Thirteen of the analyses of Table 13.1 are considerably higher in $HCO_3$ than normal ground waters and of these, ten exceed 500 ppm. An $HCO_3$ content of more than 300 ppm usually points to some source for $CO_2$ other than the atmosphere and soil zone. Volcanic emanations and meta-morphic reactions involving carbonates are reasonable explanations for the excess $CO_2$. The total $CO_2$ is even higher than indicated by Table 13.1

because these analyses do not include $CO_2$ already in a vapor phase when the samples were collected, or free $CO_2$ and $H_2CO_3$ not determined by standard water analysis. The proportion of free $CO_2$ increases greatly as pH decreases.

Most of the waters of Table 13.1 rise along the same structures that localized the Hg deposits. Regardless of whether the excess $CO_2$ is magmatic or metamorphic, or whether some other fluid high in Hg content was formerly involved but is now minor or absent, the present supply of $CO_2$ presumably was available to the permeable structures at earlier times. Fedorchuk and others (1963) and Maslova (1963) have supplied additional evidence for an influence by $CO_2$. They have analyzed fluid inclusions in HgS-bearing quartz from Russian deposits. The average analysis is remarkably similar to that of Sulphur Bank and is, in ppm: Na, 1300; K, 380; Cl, 660; $HCO_3$, 1510; total concentration, 3850; pH is 6.0 to 6.5. Roedder (1962, p. 44) found liquid $CO_2$ in fluid inclusions in cinnabar-bearing quartz from the Red Devil mercury mines of Alaska.

5. The $SO_4$ of analyses of Table 13.1 is evidently derived from a variety of sources. The meteoric ground water involved to some extent in all of these systems must contain some $SO_4$. Dilute ground waters typically contain a few tens of ppm; ground waters related to evaporites and oxidizing sulfides can contain much more than 100 ppm (see, for example, White and others, 1963, tables 11, 14, and 24).

Some $SO_4$ can also form by reaction of $H_2S$ with atmospheric $O_2$ in solution in meteoric water of the spring systems. The solubility of atmospheric $O_2$ in water at 10°C, for example, is 11 ppm, which is sufficient to form 17 ppm of $SO_4$ from 6 ppm of $H_2S$.

$H_2S$ and atmospheric $O_2$ react at and above the water table of many hot-spring systems to form sulfuric acid. Downward percolation of $SO_4$ can then occur, perhaps followed by convection and recirculation of the acidified water. These effects are especially prominent where the net rate of discharge and flushing from a system is low but upflow of $H_2S$ is high; high temperature at the water table is effective in separating $H_2S$ in a vapor phase to insure access of $O_2$ and high reaction rates.

Sulfide-bearing waters may also react with Fe oxides and silicates to form Fe sulfides. Oxygen is released and is then available to form $SO_4$ from S still in the water. The rates of these reactions are dependent in part upon diffusion of sulfur species through wall rocks. The effects are probably gradual for great distances along a channel of fluid flow. Some theories of ore transport assume that the ore fluids are initially high in sulfide and that sulfate is low or absent. The limited evidence available from fluid inclusions (Roedder, Chapter 12) suggests that $SO_4$ concentrations may greatly exceed total sulfide; this is also my conclusion for many hot-spring systems.

All mechanisms that involve oxidation of S to $SO_4$ in the water are accompanied by release of hydrogen ions formerly undissociated in $H_2S$ or $HS^-$. The effect in lowering pH would be large in slightly buffered waters, such as analyses 9–12, Table 13.1, but must be slight in strongly buffered waters where only a small part of the total $SO_4$ is from oxidation of S within the system. The critical factor on pH is the ratio of newly formed $SO_4$ to the total buffering capacity of the water, which is dominated by the $CO_2$ species.

6. Most waters associated with Hg deposits (Table 13.1) are notably high in $NH_4$ and B. The possible effect of high concentration of these constituents on Hg solubilities has not been tested. $NH_4$ is of special interest because of its strong complexing tendencies. Krauskopf's statement (1951, p. 509) that complex-forming constituents other than sulfide are scarce in vein solutions is questionable in the light of recent findings.

7. The frequent association of gaseous, liquid, and solid hydrocarbons with Hg deposits suggest that organic complexes of Hg should also be considered. The possibility is strengthened by evidence from the Cymric oil field, California. On the other hand, hydrocarbons are notably scarce in Hg deposits of the Great Basin. Organic complexing seems unlikely to explain all mercury transport.

8. Vapor transport of Hg above the water table, probably as elemental Hg with S vapor, is indicated locally at Sulphur Bank, Elgin, Steamboat Springs, Ngawha, and Coso where powdery cinnabar lines cavities formed by acid-leaching. Ore deposits of such nature are typically small and low in grade and indicate a strong acid environment uncharacteristic of the highly productive deposits. The volatility of elemental Hg might be mentioned here. Representative values, in mm of Hg pressure, are: 0°C, 0.00019; 100°C, 0.27; 200°C, 17; 300°C, 247.

9. Thermal instability of HgS in the presence of a moving vapor phase (Krauskopf, 1951, pp. 515–520; 1964, p. 43) can account for the transport of HgS noted above. Transport of Hg and S in vapor is also possible below the water table in near-surface parts of spring systems where temperatures are high enough. Waters that are high in $CO_2$ or other dissolved gases may be accompanied by a vapor phase at temperatures below boiling of pure water. Such a vapor phase could transport significant amounts of Hg.

Most spring systems explored for geothermal energy, however, are not high enough in temperature or $CO_2$ content for vapor to exist at depths of more than a few hundred feet. Whether a system such as that of Sulphur Bank has a $CO_2$-rich vapor phase at depths of 1000 ft and greater has not been proved, but this seems possible.

10. HgS may be thermally unstable even in the absence of a vapor phase. Dickson (1964, p. 633) found experimental evidence at 250°C that cinnabar in $Na_2S$ solutions without a vapor phase dissociates to elemental

\TERS

SO$_4$ in the water are ac-
undissociated in H$_2$S or
slightly buffered waters,
light in strongly buffered
s from oxidation of S
e ratio of newly formed
, which is dominated by

(Table 13.1) are notably
concentration of these
H$_4$ is of special interest
skopf's statement (1951,
han sulfide are scarce in
t findings.

and solid hydrocarbons
s of Hg should also be
ence from the Cymric
bons are notably scarce
lexing seems unlikely to

e, probably as elemental
Bank, Elgin, Steamboat
r lines cavities formed
typically small and low
uncharacteristic of the
ntal Hg might be men-
ssure, are: 0°C, 0.00019;

a moving vapor phase
count for the transport
or is also possible below
ms where temperatures
other dissolved gases
atures below boiling of
ficant amounts of Hg.
ergy, however, are not
apor to exist at depths
such as that of Sulphur
ft and greater has not

absence of a vapor
vidence at 250°C that
issociates to elemental

Hg and S. The reaction was detectable after four weeks but was negligible in shorter runs. This finding suggests that HgS may consistently be thermally unstable at high temperatures, not only in the presence of vapor, as reviewed above, but also in a sulfide-bearing hydrous phase. The minor effects found by Dickson in runs of a few weeks may be of major significance in an open system active for thousands to hundreds of thousands of years.

Minerals of Hg deposits that are particularly significant in problems of Hg transport include:

1. The hypogene-alteration clay minerals, montmorillonite, illite, kaolinite, and dickite (Tables 13.2 and 13.4). These minerals suggest low to moderate cation/H$^+$ ratios in the ore solutions (Hemley and Jones, 1964, and Chapter 6) and weakly acid to slightly alkaline pH's. In contrast, hydrothermal albite, K-feldspar, and zeolites indicate relatively high cation/H$^+$ ratios and high pH's, but are notably absent from commercial mercury deposits. Albite is abundant in unaltered graywacke at Sulphur Bank, but is largely replaced by buddingtonite and illite-montmorillonite in and near ore (White and Roberson, 1962; Erd and others, 1964). K-feldspar and albite are abundant hydrothermal minerals of epithermal Ag-Au deposits and in many active hot-spring systems with waters of pH 7 to 9.5 (White, 1955a). The absence of K-feldspar and albite, and the abundance of kaolinite, dickite, illite, and montmorillonite in Hg deposits are not easily reconciled with any theory that requires pH's much on the alkaline side of the neutral point.

2. The Hg minerals of Amedee and Boiling Springs (Tables 13.1 and 13.2) are closely associated with zeolites (heulandite, clinoptilolite, stilbite, chabazite, and laumontite). Here, as in other thermal springs associated with zeolites, pH's are clearly on the alkaline side of neutrality. But the total quantity of Hg is low in these deposits, and zeolites are rare or absent from commercial Hg deposits. Amedee and Boiling Springs may not provide critical clues in understanding all Hg deposits.

3. Many minerals of Hg deposits probably are not thermodynamically the most stable phases for their environments; disequilibrium evidently has played an important role.

Opal probably is never a stable phase. The initially deposited substance is generally amorphous to x-rays but with time and sufficient temperature, amorphous opal is reconstituted to $\beta$-cristobalite or chalcedony; the latter is considered as distinct from, and slightly less stable than, well-ordered quartz. Opal forms from waters strongly supersaturated in SiO$_2$ with respect to quartz, and this supersaturation most commonly occurs in water that is decreasing rapidly in temperature. Most opal has formed at temperatures below 140°C (White and others, 1956, p. 54).

Metacinnabar is probably not stable at Amedee, Boiling Springs, and Sulphur Bank, and is unlikely to be stable in close association with opal

or cristobalite. Dickson and Tunell (1959) have shown that pure meta-cinnabar is stable above 344°C at one atmosphere of pressure. In the presence of Fe and Zn in solid solution, the inversion temperature may be at least as low as 240°C. Equilibrium inversion temperatures may be depressed even more by larger amounts of Fe and Zn in solid solution in HgS. Metacinnabar may never be a stable phase in nature but may form where deposition is too rapid or is for other reasons unfavorable for the stable phase, cinnabar.

The field of stability of marcasite has not been defined, if such a field exists. Marcasite may generally form metastably in neutral to acid environments at low temperatures.

The common hypogene kaolinite-group mineral of Hg deposits is well-ordered kaolinite. Disordered kaolinite occurs frequently above the water table in Hg deposits and hot-spring systems, and was identified locally below the premining water table at Sulphur Bank and the Cordero mine. Dickite has been reported in recent years from numerous Hg deposits in the U.S.S.R. (for example, Kekeliya and Saliya, 1963), from Alaska (MacKevett and Berg, 1963), Texas (Table 13.4), and the Monte Amiata district of Italy (Table 13.4). Dickite is evidently a common kaolinite-group mineral in many large and relatively deep Hg mines, but it is notably absent in the shallow deposits of Table 13.2 and the explored parts of hot-spring systems. The significance of these facts is not clear, and stability relationships between dickite and kaolinite are not known, but dickite may be the most stable phase and kaolinite, both ordered and disordered, may normally be metastable.

All illite of Hg deposits that has been identified by type is 1M disordered, and is presumably metastable, with one or more of the ordered micas as the stable phases.

The stability relationships of many hydrocarbon and metal-organic compounds are not well known; some that occur in Hg deposits may be metastable.

Sanidine, orthoclase, and albite of the original host rocks commonly resist hydrothermal alteration, and may be preserved metastably in some deposits. In addition, the hydrothermal K-feldspar found at Steamboat Springs (not closely associated with Hg) and in epithermal Ag-Au and Mn deposits is consistently monoclinic and not triclinic, the probable stable form at low temperatures.

4. The metastable (?) minerals of Hg deposits discussed above seem to be more common in the deposits of Table 13.2 than in Hg deposits as a whole. Amorphous opal and $\beta$-cristobalite are especially suggestive of near-surface deposition at temperatures of 140°C or less (White, Brannock, and Murata, 1956, pp. 53–54). These relationships greatly strengthen the

nown that pure meta-
re of pressure. In the
on temperature may be
temperatures may be
Zn in solid solution in
nature but may form
ns unfavorable for the

defined, if such a field
neutral to acid environ-

of Hg deposits is well-
iently above the water
was identified locally
nd the Cordero mine.
merous Hg deposits in
, 1963), from Alaska
nd the Monte Amiata
a common kaolinite-
mines, but it is notably
explored parts of hot-
nt clear, and stability
nown, but dickite may
d and disordered, may

type is 1M disordered,
the ordered micas as

nd metal-organic com-
deposits may be meta-

nost rocks commonly
d metastably in some
found at Steamboat
bithermal Ag-Au and
riclinic, the probable

cussed above seem to
in Hg deposits as a
becially suggestive of
ss (White, Brannock,
greatly strengthen the

probability that most if not all the deposits of Table 13.2 were deposited
recently near the present surface, and are indeed related genetically to their
associated waters. The alternative explanation requires a coincidence in
structural control, with wide separation in time between Hg deposition
and present activity. This is unlikely as a general explanation but is, of
course, possible for some individual deposits. The dilute waters of the Big
Injun and Cordero deposits, for example, may be unlike the original ore
fluids. The frequent occurrence of late stibnite in the deposits of Table 13.2
is a puzzling fact because the stibnite of many Hg deposits is earlier than
cinnabar. The significance of this is not known, but it helps to establish
the present waters as ore-bearing fluids and increases the probability that
the waters are related genetically to the Hg deposits.

5. The stability relationships of native Hg associated with six deposits
of Table 13.2 and at least five of Table 13.4 to other minerals are not
known. Native Hg is commonly considered hypogene in origin (see, for
example, Fedorchuk, 1958); some means of transport other than as HgS
in a high-sulfur system seems necessary.

## CONCLUSIONS ABOUT MERCURY DEPOSITS

Mercury may be relatively mobile in many thermal environments. Sig-
nificant transfer in a vapor phase is indicated in some deposits at tem-
peratures below 100°C. HgS is unstable at higher temperatures in the
presence of a vapor phase that can include some excess sulfur. Recent
evidence suggests that HgS may also be unstable in sulfide-bearing water
lacking a vapor phase at temperatures at least as low as 250°C. With long
geologic times, HgS may not persist in the presence of moving fluids at
temperatures as low as 150°C.

HgS is highly soluble in strongly alkaline solutions of high sulfide content,
but the involvement of such solutions in depositing Hg in nature has not
been demonstrated. The evidence reviewed in this report favors slightly
alkaline to slightly acid ore solutions of modest sulfide content; the bisulfide
complex is a distinct possibility. Mechanisms that involve thermal insta-
bility of HgS, with or without a vapor phase, should also be considered.
Other likely mechanisms include complexing with $NH_3$ and organic con-
stituents. An influence by constituents such as $CO_2$, $SiO_2$, and boron com-
plexes can be eliminated with confidence only after adequate testing.

The solubility of HgS in natural waters of different kinds has received
very little attention. Aidin'yan (1962) found that dilute natural waters can
dissolve more native Hg and cinnabar than distilled waters; actual Hg
contents of surface waters are much lower than their solubility limits. The

total Hg content of sea water near Japan is a few parts per billion, and most of this is evidently tied up in organic constituents such as plankton (3.5 to 19 ppm Hg; Hosohara and others, 1961).

The possible sources of mercury that become incorporated in ore fluids have received little attention in this review. As mentioned, Hg may be mobile in many high-temperature environments. Abundant evidence indicates that it becomes concentrated in shallow epithermal deposits but is rare in mesothermal and hypothermal deposits except as broad geochemical halos that argue for its high mobility. Limited data suggest that recent marine clays contain many times the Hg content of average igneous rocks (Aidin'yan and others, 1963). Certain regions may be high in Hg in most or all rocks and thus may have primary enrichment favorable for later concentration into ore deposits by one process or another. The Hg content of all rocks of the Crimea, for example, is reported to range from $n \times 10^{-6}$ to $n \times 10^{-3}$ percent with a mean content of $n \times 10^{-4}$ percent (Bulkin, 1960). For comparison, average shales have $4 \times 10^{-5}$ and average igneous rocks $8 \times 10^{-6}$ percent of Hg, according to Vinogradov (1962).

Igneous rocks may have lost most original Hg, but on the other hand shales may be enriched, especially if plankton and other organisms are Hg concentrators. No reliable data are available on the Hg content of sedimentary rocks as compared to their metamorphosed equivalents. Ellis (Ellis and Mahon, 1964; Chapter 11) has demonstrated that the hydrothermal constituents Cl, B, F, As, and $NH_3$ are largely leachable from a wide variety of rocks. The concentration of any element in the fluid phase can be explained by contact of each mass unit of water with enough new mass units of rock.

Extensive geothermal drilling during recent years has revealed a little Hg near the surface at The Geysers and Steamboat Springs. Exploration in Iceland, Yellowstone Park, New Zealand, Italy, and Japan in other areas of high temperature and close physical association with volcanism has not yet provided evidence that all or even most Hg of commercial deposits is derived from volcanic sources.

White (1957b; White and Roberson, 1962) has suggested that Hg may be driven out of sedimentary rocks subjected to high temperatures. The transporting fluid could be interstitial connate water driven out by compaction, or metamorphic water released by reconstitution of hydrous minerals. High contents of $NH_3$ and I in the associated spring waters are evidence for an organic history, and point to a connate or metamorphic origin.

Of the deposits considered here, those of Sulphur Bank, Steamboat Springs, The Geysers, Ngawha, Coso, and Monte Amiata most clearly owe their high temperatures to Quaternary volcanism. A direct volcanic contribution of water and Hg seems possible, although the proportion of volcanic water is evidently too small to detect by isotopic methods (Craig

VATERS

ew parts per billion, and
ituents such as plankton

n-orporated in ore fluids
mentioned, Hg may be
Abundant evidence indi-
pithermal deposits but is
ept as broad geochemical
data suggest that recent
of average igneous rocks
y be high in Hg in most
ment favorable for later
another. The Hg content
l to range from $n \times 10^{-6}$
$\times 10^{-4}$ percent (Bulkin,
$0^{-5}$ and average igneous
radov (1962).

, but on the other hand
other organisms are Hg
the Hg content of sedi-
hosed equivalents. Ellis
rtrated that the hydro-
argely leachable from a
ement in the fluid phase
water with enough new

rs has revealed a little
t Springs. Exploration
nd Japan in other areas
with volcanism has not
commercial deposits is

suggested that Hg may
high temperatures. The
driven out by compac-
on of hydrous minerals.
ng waters are evidence
r metamorphic origin.
hur Bank, Steamboat
miata most clearly owe
A direct volcanic con-
gh the proportion of
otopic methods (Craig

and others, 1956). A present dominance by metamorphic and connate waters is favored isotopically at Sulphur Bank and the Wilbur Springs district (White and Roberson, 1962, pp. 415–418).

Magma and thermally affected sedimentary and metamorphic rocks may all contribute Hg, with proportions differing from place to place and possibly with time. The commonly held preference for a volcanic source alone is not supported by the available evidence.

## FLUIDS ASSOCIATED WITH BASE METALS

As recently as twelve years ago surprisingly few data relating base-metal ore deposits to hot springs were available (White, 1955a, p. 144). The most common kinds of hot-spring waters closely associated with volcanism generally contain base metals and Ag only in the parts-per-billion range (White, Hem, and Waring, 1963, tables 17 and 18). This may be consistent with the geologic evidence that base-metal deposits are formed far below rather than near the surface. Recent studies of natural thermal waters, in spite of these facts, have revealed much evidence that bears on the origin and geochemistry of these deposits.[4]

Increasingly strong evidence is accumulating to indicate that very saline Na-Ca-Cl brines at high temperature are potent solvents for base metals and silver in the presence of some sulfide. The geochemistry of natural thermal and mineral waters is reviewed in this chapter; strong additional support is from fluid-inclusion studies (Roedder, Chapter 12) and from theoretical considerations (Helgeson, 1964). The evidence from thermal and mineral waters is fragmentary, at least in part, because saline brines of this type seldom appear at the surface except in cooled and greatly diluted form; their densities are relatively high, even at high temperature, and they are not ordinarily displaced by circulating dilute meteoric waters.

In contrast, relatively dilute fluids high in $CO_2$ are associated with some epithermal base-metal deposits now existing near the surface because of erosion, but evidently formed originally at much greater than present depths. Also, some dilute hot spring waters of the $HCO_3$ type deposit Mn oxides high in base metals and Ag as well as As, W, and other elements, suggesting a relationship to base-metal deposits at depth (Hewett, 1964; Hewett and others, 1960, 1963). If the dominant base-metal ore solutions are brines of the Na-Ca-Cl type, as here hypothesized, some three-dimensional mechanism is necessary to provide for selective upward enrichment of $CO_2$ in order to reconcile the previous statements. Two possible mechanisms involve separation and selective upward migration of a $CO_2$-enriched

[4]See summaries of Salton Sea and Red Sea geothermal systems and three base-metal ore districts reviewed by White (1967).

vapor phase relative to a saline liquid phase; and selective high mobility of $CO_2$ relative to Cl through semipermeable membranes (White, 1965). The latter does not involve a separate vapor phase.

Some hot-spring waters of the puzzling acid $SO_4$-Cl type have as much as several ppm of Cu, Pb, and Zn in solution. Tamagawa Hot Spring, Japan, is a well-studied example of this type with a remarkably high discharge of 9300 liters per minute (Iwasaki and others, 1963; analysis 16, Table 13.1). The relationship, if any, of such waters to base metal deposits is not clear.

## Arima, Japan

The hot springs of Arima, Japan, are remarkable for their high salinity (Table 13.1, analysis 17) and the presence of base-metal sulfides in the system. The springs discharge from a Miocene rhyolitic intrusion, 40 miles from the nearest Quaternary volcano (Nakamura and Maeda, 1961; H. Kuno, written communication, 1960). Other nearby rocks are Mesozoic granite and Tertiary sedimentary rocks. Hydrothermal alteration near the surface in parts of the hot-spring area is characterized by alunite and quartz, suggesting that a vapor phase high in $H_2S$ and probably $CO_2$ has separated from the system containing the water of analysis 17, Table 13.1.

Wells drilled at Arima to increase the supply of hot water penetrated hydrothermally altered rhyolite at depth that contains galena, sphalerite, siderite, pyrite, and calcite, according to Nakamura and Maeda (1961). One core sample contained 0.014 percent Ag, 2.85 percent Pb, 2.08 percent Zn, and considerable Fe, S, and $CO_2$. Ikeda (1955) reported Cu, Pb, and Zn, each from 0.1 to 0.4 ppm, in water from a thermal well. Prior to the drilling of wells, the highest temperature of natural springs was about 40°C, but 133°C was recorded at a depth of 168 m.

The spring waters are very high in Na, Ca, and Cl (Table 13.1, analysis 17) and are also notable for their high contents of Fe (up to 200 ppm), Mn (up to 67 ppm), alkali metals, and B. The very high salinity and $CaCl_2$ content led White and others (1963, table 16), probably incorrectly, to include Arima with springs similar to oilfield brines of the Na-Ca-Cl type, because this is the dominant type of water in sedimentary basins of pre-Tertiary age (White, 1965).

The hot-spring gases consist largely of $CO_2$ and $H_2$, with less than 2 percent $N_2$, $O_2$, and Ar. $H_2S$ was not detected in the gases and was found only in traces in the spring waters. $SO_4$ is also remarkably low. These springs, in respect to Fe, Mn, base metals, and total S are clearly sulfur-deficient. They are not known to be depositing the base-metal sulfides found in the drill core, but active deposition is a reasonable hypothesis in view of their diluted equivalence to the Salton Sea geothermal brine referred to below.

l selective high mobility
embranes (White, 1965).

4-Cl type have as much
T magawa Hot Spring,
a remarkably high dis-
hers, 1963; analysis 16,
s to base metal deposits

le for their high salinity
se-metal sulfides in the
olitic intrusion, 40 miles
and Maeda, 1961; H.
y rocks are Mesozoic
mal alteration near the
terized by alunite and
and probably $CO_2$ has
analysis 17, Table 13.1.
f hot water penetrated
ns galena, sphalerite,
ra and Maeda (1961).
percent Pb, 2.08 percent
reported Cu, Pb, and
rmal well. Prior to the
springs was about 40°C,

Cl (Table 13.1, analysis
f Fe (up to 200 ppm),
high salinity and $CaCl_2$
robably incorrectly, to
of the Na-Ca-Cl type,
entary basins of pre-

H$_2$, with less than 2
e gases and was found
emarkably low. These
al S are clearly sulfur-
e base-metal sulfides
asonable hypothesis in
othermal brine referred

## Salton Sea geothermal area, California

Recent drilling for geothermal energy near Salton Sea, California (Fig. 13.1) has revealed an area of many square miles that is underlain by very saline thermal brine of extraordinarily high metal content (Table 13.1, analysis 18; White, Anderson, and Grubbs, 1963; Muffler and White, 1965; Doe and others, 1966; White, 1967; Skinner and others, 1967). Temperatures in the order of 300°C or higher occur at depths of about 5000 ft.

The geothermal area is centered near a northeast-striking line of pumiceous obsidian domes of late Quaternary age (<50,000 yr by K/Ar, R. W. Kistler and J. D. Obradovich, U.S. Geological Survey) and is within the major structural trench that includes the Gulf of California, Imperial Valley, and Salton Sea. The rocks penetrated by the drill holes are upper Cenozoic clastic sediments, dominantly from the Colorado River drainage basin. The rocks now range from unconsolidated sediments near the surface to low grade metamorphic and hydrothermally altered equivalents at depth. Dominant constituents of the brine (Table 13.1, analysis 18) are Cl, Na, Ca, and K. A wide variety of other elements are present in extraordinarily high concentration, including Fe, Mn, Zn, Pb, Cu, and Ag. Also of special significance is the low total sulfur content, with about 56 ppm $SO_4$ and very low sulfide. With respect to the high content of sulfophile metals, this brine is clearly sulfur-deficient (Lovering, 1961). In the reservoir environment of the brine, the original sulfide content of the total fluid must have been somewhat higher than the brine sampled at the surface after separation of a vapor phase. In addition, about 10 percent of the original copper and silver of the brine was deposited as sulfides in the discharge pipes. Scale deposited in these pipes is primarily bornite and amorphous opal that is high in Fe; other identified minerals include chalcocite (high form, originally identified as high djurleite), digenite, pyrite, chalcopyrite, stromyerite, native silver, tetrahedrite, and arsenopyrite (Skinner and others, 1967).

Except for the late Quaternary obsidian and pumice domes, the only surface expressions of the large geothermal anomaly are several groups of small mud volcanoes (White, 1955b, pp. 1121–1122) that lie on and near the southeastern extension of a major branch of the San Andreas fault. Springs and mud pots that are still above the rising level of Salton Sea (1964) have chloride contents in the order of 5000 ppm. Prior to 1950 a large group of mud volcanoes was accessible 0.6 miles southeast of Mullet Island, the northernmost of the rhyolite domes. This group of springs is now submerged below the surface of Salton Sea. One vigorously spouting spring near the vent of a small active geyser of this group was sampled in 1948 (White, 1955b, p. 1114). It had a Cl content of 69,500 ppm, a pH of 6.97 (after loss of some $CO_2$), and a temperature of 100.2°C. Its Cl content

is about 40 percent of that of analysis 18, Table 13.1. All of the mud volcano waters are best explained by upward leakage of deep saline brine that is diluted moderately to extensively near the surface by meteoric water.

Supporting chemical evidence for upward leakage of deep brine is provided by dark gray travertine a few inches thick that was deposited by the spouting spring and geyser previously mentioned. A semiquantitative spectrographic analysis of this travertine includes the following, in percent: Si, 2; Al, 0.3; Fe, 0.1; Mg, 0.07; Ca, major; Na, 0.2; Ti, 0.015; Mn, 10; As, 0.7; B, 0.05; Ba, 0.1; Cu, 0.0015; La, 0.01; Sr, 0.3; Zn, 0.07. The very high content of Mn and moderately high As, Sr, Zn, Ba, and B are unusual for hot-spring carbonates. Most of the sample is translucent gray in color, with a few thin black bands of Mn oxides. By x-ray, the only identifiable mineral other than calcite is a little quartz. The calcite is unique among hot-spring travertines that I have examined: the 104 x-ray peak has a spacing of 3.019 Å, distinctly less than the 3.035 Å of pure calcite. This difference can be caused by substitution of ions smaller than Ca in the calcite crystal lattice; these include Mg, Mn, Fe, and Zn. Mn is the only element abundant enough in the spectrographic analysis to account for the required stuffing; the principal mineral is manganiferous calcite with 9 percent $MnCO_3$ (Prinz, 1964; $N_0$ index of refraction 1.675). In all other hot springs known to be depositing calcite and Mn (Hewett and Fleischer, 1960; 1963; White, 1955a) the Mn occurs as oxides with no evidence for significant $MnCO_3$ in the calcite.

Pyrite is the dominant sulfide found in the well cuttings, but sphalerite is locally common and chalcopyrite also occurs. Spectrographic and wet analyses confirm local high concentrations of Zn, Ag, Cu, and Pb as well as other ore metals but no ore bodies of commercial size have yet been recognized. The Salton Sea geothermal brine has about 6 times the salinity and more than 1000 times the base-metal content of the Arima spring waters previously described, but these waters are otherwise geochemically similar in dominance of Cl, Na, Ca, and K; their notable contents of Fe, Mn, alkali, and ore metals; and their deficiency in sulfur.

The origin of the Salton Sea geothermal brine is not considered in detail here. The author formerly favored a magmatic origin (White, Anderson, and Grubbs, 1963) but recent isotope evidence of D/H and $O^{18}/O^{16}$ in the brines, thermal springs, and cold meteoric waters of the area (Harmon Craig, written communications, 1963, 1964) strongly favors a meteoric origin for the water of the brines. In addition, the Pb and Sr isotopes require a strong influence by the sediments (Doe and others, 1963; written communications, 1964), although a magmatic origin for some Pb and Sr of the brine is permitted by the data.

If the water is overwhelmingly meteoric, as now seems probable, it has circulated to great depths. The very high chloride content is best explained

ATERS

ble 13.1. All of the mud
kage of deep saline brine
surface by meteoric water.
xage of deep brine is pro-
at was deposited by the
. A semiquantitative spec-
following, in percent: Si,
2; Ti, 0.015; Mn, 10; As,
3; Zn, 0.07. The very high
Ba, and B are unusual for
nslucent gray in color,
-ray, the only identifiable
calcite is unique among
ne 104 x-ray peak has a
5 Å of pure calcite. This
s smaller than Ca in the
and Zn. Mn is the only
nalysis to account for the
ganiferous calcite with 9
ction 1.675). In all other
In (Hewett and Fleischer,
des with no evidence for

ll cuttings, but sphalerite
Spectrographic and wet
, Ag, Cu, and Pb as well
ercial size have yet been
about 6 times the salinity
it of the Arima spring
otherwise geochemically
r notable contents of Fe,
sulfur.

s not considered in detail
origin (White, Anderson,
/H and $O^{18}/O^{16}$ in the
rs of the area (Harmon
ongly favors a meteoric
the Pb and Sr isotopes
nd others, 1963; written
gin for some Pb and Sr

w seems probable, it has
content is best explained

by solution of salt deposits; the high content of many different elements, relative to crustal abundances of these elements, must then result from water-rock reactions at high temperature, as proposed by Ellis (Chapter 11; Ellis and Mahon, 1964). The elements Pb, Zn, Ag, B, Li, and Cs are much more abundant by weight in the brine than in ordinary sedimentary rocks (compare data of Table 13.1, analysis 18 with Vinogradov, 1962 and unpublished data). A leaching hypothesis requires contact of each mass unit of brine with many mass units of previously unleached rock. This problem can be eased at least in part if magmatic water high in these elements is also involved in the system.

Regardless of origin, the Salton Sea geothermal brine is impressive for its metal-transporting capacity, but its full potential for depositing base metals as sulfides depends upon the availability of more sulfur than the brine now contains. Possible mechanisms for supplying this sulfur are mentioned in a later section.

One final item of interest of the Salton Sea geothermal system is evidence for upward escape of $CO_2$ relative to Cl, as indicated in general terms on p. 608. The mechanism of escape is not yet clearly established. It may involve a $CO_2$-rich vapor phase, and/or differences in mobility of $CO_2$ and Cl in escaping through fine-grained sediments serving as semipermeable membranes, perhaps as proposed by White (1965).

The $CO_2/Cl$ ratio of the very saline Na-Ca-Cl brine in the deep reservoir is not yet well defined but is probably less than 0.005 by weight. In contrast, the shallow saline waters of the area that represent dilute leakage from the system are enriched in $CO_2$, with $CO_2/Cl$ ratios generally from 0.1 to 0.5 or more. A published analysis of water from the formerly productive $CO_2$ gas field of the area (White, Hem, and Waring, 1963, p. F42) has a $CO_2/Cl$ ratio of 0.09, not considering abundant $CO_2$ escaping in the vapor phase and other free $CO_2$ in solution and not included in the water analysis. Much or all of the $CO_2$ is produced by metamorphic and hydrothermal reactions between calcite, dolomite, and silicates in the system (Muffler and White, 1965). Relatively shallow reactions involving dolomite account for some, but not all of the indicated upward increase in the $CO_2/Cl$ ratio.

### East Tintic District, Utah

Large reserves of Pb-Zn-Ag ore were discovered recently in the East Tintic district, Utah (Lovering and Morris, 1965). The deposits are closely associated with thermal water high in Na, Ca, and Cl (Table 13.1, analysis 19) and higher in salinity than most thermal spring water associated with Quaternary volcanism (White, Hem, and Waring, 1963; Tables 17–21).

The Tintic area contains folded and faulted Paleozoic rocks overlain by an extensive cover of Eocene volcanic rocks. The hypogene minerals are galena, sphalerite, chalcopyrite, pyrite, Zn-bearing rhodochrosite, manganosiderite, chalcedony, barite, sericite, kaolinite, dickite, and quartz. In permeable rocks above the water table the sulfides and Mn-bearing carbonates are oxidized. Prior to discovery of thermal saline water below the water table, the ore mineralization was considered early Tertiary in age; the origin of the present thermal activity and its relationship to the ore deposits is not yet clear.

The thermal water contains some Pb and other heavy metals in solution in low concentrations. A pump used to dewater ore below the 1220 ft level of the new workings was dismantled after a few months of use. The cast-iron pump head and propellor blades were pitted extensively. An outer irregular replacement(?) layer as much as 1 mm thick consists largely of Pb and yields x-ray patterns of lead oxides (litharge and massicot), metallic Pb, and one or more unidentified minerals. Other metals of interest are, by semiquantitative spectrographic analysis, in percent: Ag, 0.007; Cd, 0.1; Cu, 0.07; Ni, 0.001; Sb, 0.15; and Zn, 0.1.

## San Juan Mountains, Colorado

Epithermal base-metal deposits high in Ag occur in Colorado in and near the Creede and Silverton calderas of late Tertiary age. The Creede ore deposits in the eastern San Juans (Roedder, Chapter 12) are considered to have formed only a few hundred feet below the then-existing surface. The relatively recent age, slight amount of erosion, and hot-spring travertine mounds nearby with preserved topographic form attest to a close relationship of these deposits to hot springs. No present thermal anomaly has been recognized but the mines are shallow and a geothermal anomaly could easily escape detection. Fluid inclusions in sphalerite and gangue minerals consist of Na-Ca-Cl brine exceedingly high in ore metals (reviewed by Roedder, Chapter 12) with reported concentrations of at least 60 ppm Cu, 620 ppm Mn, and 410 ppm Zn. Reliable analyses for $SO_4$ and sulfide are not yet available from these tiny inclusions, but the high contents of Mn, Zn, and Cu and the absence of detectable odor of $H_2S$ with crushing suggest that the brines are sulfide deficient, even if all $SO_4$ is considered potentially as sulfide. The Quaternary hot springs that deposited the nearby travertine mounds are very likely to have been dilute $Na-Ca-HCO_3$ waters with high $CO_2/Cl$ and $SO_4/Cl$ ratios (see White, Hem, and Waring, 1963, table 25), contrasting strongly with the Na-Ca-Cl brines of the inclusions. An interpretation of these relationships is offered in a later section.

The ore deposits of the Silverton caldera in the western San Juans are also relatively young and were deposited at only moderate depths below

/ATERS

Paleozoic rocks overlain by
he hypogene minerals are
ring rhodochrosite, man-
ite, dickite, and quartz. In
les and Mn-bearing car-
nal saline water below the
red early Tertiary in age;
its relationship to the ore

r heavy metals in solution
e below the 1220 ft level
months of use. The cast-
ted extensively. An outer
thick consists largely of
ge and massicot), metallic
her metals of interest are,
cent: Ag, 0.007; Cd, 0.1;

ccur in Colorado in and
ertiary age. The Creede
Chapter 12) are considered
the then-existing surface.
, and hot-spring travertine
m attest to a close rela-
sent thermal anomaly has
a geothermal anomaly
in sphalerite and gangue
gh in ore metals (reviewed
ations of at least 60 ppm
lyses for SO₄ and sulfide
but the high contents of
or of H₂S with crushing
if all SO₄ is considered
that deposited the nearby
lute Na-Ca-HCO₃ waters
Hem, and Waring, 1963,
brines of the inclusions.
n a later section.
e western San Juans are
moderate depths below

the present surface. Thermal anomalies have not been recognized in the mines. Ouray hot springs in the north part of the caldera probably constitute a late stage of caldera activity (Burbank and Luedke, 1961; Table 13.1, analysis 20). These spring waters are high in Ca and $SO_4$ and in $CO_2/Cl$ ratio, and they deposit travertine and Mn oxides highly enriched in Ba, Cu, Pb, Zn, Sb, and W (Hewett and others, 1963, p. 29).

The Rico and Dunton districts on the west flank of the Silverton caldera are characterized in some places by abnormally high temperatures, $HCO_3$ waters low in Cl, and $CO_2$ and $H_2S$ gases (Bastin, 1923); E. T. McKnight, U.S. Geological Survey, oral communication, 1965). The high $CO_2/Cl$ ratios of present fluids contrast strongly with the single reported analysis of fluid inclusions from the Rico district (Roedder, Chapter 12), which is dominated by Cl, Ca, Na, and K. $HCO_3$ was not determined by Roedder but is unlikely to be very high in view of the exceptionally high Ca content (10,400 ppm).

## Other base-metal–Ag deposits associated with thermal and mineral waters

In the Silver Cliff district, Custer County, Colorado, deep exploration in the Geyser mine encountered a base-metal–Ag vein associated with mildly thermal (27°C) bicarbonate water (Emmons, 1896). The vein contained galena, sphalerite, chalcopyrite, argentite, tetrahedrite, ruby silver minerals, bornite, calcite, quartz, and chalcedony. The associated water was dominated by Na and $HCO_3$, with a total of nearly 4000 ppm $CO_2$ species and only 186 ppm Cl. The discharging water evidently deposited travertine with Fe, Mn, Zn, Pb, and Cu similar to that of Ouray Springs.

Thermal waters of low mineralization occur in the deep workings of the Comstock and Tonopah districts, Nevada. The mines are known principally for their bonanza Ag ores but base-metal sulfides also occur. The thermal waters differ from normal dilute surface waters in their high contents of $SO_4$; presumably the present thermal waters differ greatly from earlier fluids that deposited the ores.

The Blue Bell mine on the east shore of Kootenay Lake, British Columbia, Canada, encountered high flows of thermal water in workings deeper than 300 ft (W. T. Irvine, written communication, 1957). The ore consists of galena, sphalerite, chalcopyrite, and pyrrhotite replacements of limestone. On the 525 ft level the temperature was 27°C; the water included, in ppm: Ca, 430; Mg, 280; Na, 440; $HCO_3$, 1700; $SO_4$, 280; Cl, 80; F, 2.0; B < 0.1; and $SiO_2$, 110; the abundant free $CO_2$ was not determined; pH was 6.5. In composition this water is much like the bicarbonate waters described from Colorado. The latter, however, are in a region of late Cenozoic volcanism and epithermal ores. In contrast, the ore deposits of Kootenay Lake are

presumably early Tertiary or older and lack the characteristics of epithermal deposits.

Thermal waters also occur in several base-metal deposits of Mexico (W. T. Irvine, written communication, 1958). In the San Antonio mine, Santa Eulalia district, Chihuahua, water at 35°C occurs at depths of 1280 to 1700 ft in galena-sphalerite ore that replaces limestone. The ores may be related to Miocene intrusive rocks. The water is dominated by sulfate (1100 ppm $SO_4$) and has a reported content of 400 ppm free $CO_2$; Cl was not reported. The Naica mine, also in Chihuahua, encountered 50°C water at depths below 430 ft; $SO_4$ is by far the dominant anion. Ores here also are galena and sphalerite replacements of limestone and may be related to Miocene intrusive rocks.

The Yakumo mine, Hokkaido, is a rhodochrosite-sphalerite-galena deposit in propylitized volcanic rocks (Kayama and Iriye, 1957). Temperatures up to 61°C were measured in water flowing into the mine workings about 600 ft below the surface. Partial analyses indicate the Na-Ca-Cl type of water with considerable $SO_4$ and Mg. $Fe^{2+}$ was found in most samples; pH's ranged from 5.7 to 6.6; and total dissolved constituents were 3.5 to 7 grams per liter.

At Casapalca, Peru, base-metal–Ag deposits of late Tertiary age are similar mineralogically to the epithermal base-metal deposits of Colorado. Cretaceous limestone is overlain by Tertiary volcanic rocks and red beds and are intruded by porphyries. Thermal water occurs in the deeper workings and in hot springs of the nearby area. Compositions of these waters (Ulrich Peterson, oral communication, 1964) are very similar to those of Ouray (Table 13.1, analysis 20) and are high in $HCO_3$ and $SO_4$ relative to Cl.

The Cauquenes Hot Springs are 2 km from El Teninente (Braden), one of the large porphyry copper mines of central Chile (Ann de Grys, written communication, 1964). The springs discharge from continental sedimentary and volcanic rocks; they are near the highest in Cl (2200 ppm) of central Chile and are of the Ca-Na-K-Cl type; the evaporated residue contains detectable Pb by spectrographic analysis, with some V, Mn, and Cu. Because El Teninente is a porphry copper deposit, a direct relation to Cauquenes hot springs may be unlikely, but the ore deposits and the springs could be different manifestations in time of Cenozoic volcanic activity, according to de Grys.

The Michigan Cu mines have long been known for saline brines in the deeper workings (Table 13.1, analysis 21). The brines were supposed by Lane and Alter (1941) to have been incorporated in basaltic lava flows at the time of extrusion, and were assumed to remain unchanged chemically and physically with time; they constitute Lane's example of connate water (see White, 1965). The brines are of the Na-Ca-Cl type and are notable

'WATERS

naracteristics of epithermal

netal deposits of Mexico
n the San Antonio mine,
occurs at depths of 1280
mestone. The ores may be
is dominated by sulfate
l00 ppm free $CO_2$; Cl was
a, encountered 50°C water
anion. Ores here also are
and may be related to

ochrosite-sphalerite-galena
and Iriye, 1957). Tempera-
ng into the mine workings
indicate the Na-Ca-Cl type
ns found in most samples;
constituents were 3.5 to 7

s of late Tertiary age are
netal deposits of Colorado.
lcanic rocks and red beds
ccurs in the deeper work-
mpositions of these waters
e very similar to those of
$CO_3$ and $SO_4$ relative to Cl.
Teninente (Braden), one of
le (Ann de Grys, written
n continental sedimentary
Cl (2200 ppm) of central
porated residue contains
me V, Mn, and Cu. Be-
a direct relation to Cau-
deposits and the springs
nozoic volcanic activity,

for saline brines in the
rines were supposed by
in basaltic lava flows at
n unchanged chemically
xample of connate water
Cl type and are notable

for extremely high Ca/Na ratios. The sample of Table 13.1, analysis 21, was from a slow seep from the Kearsarge amygdaloid; some constituents may have been oxidized at the time of collection. The brines are likely to be trapped samples of the ore-transporting fluid.

## GEOCHEMICAL CONSIDERATIONS FOR BASE-METAL TRANSPORT

The scanty evidence from waters closely associated with base-metal deposits (Table 13.1; Roedder, Chapter 12; Hall and Friedman, 1963) suggests that the dominant ore fluids for base metals and Ag are very saline brines high in Na, Ca, and Cl, and weakly alkaline to slightly acid in pH. The data suggest that base-metal content is directly related to temperature and Cl content, and also tends to increase with Ca content. The brines highest in Fe and Mn may also be highest in Zn, Pb, Cu, and Ag.

The analyzed natural brines highest in base metals are also so low in total S that they are strongly deficient in S; Roedder (Chaper 12) has found similar indications in fluid inclusions. The Salton Sea geothermal brines and the extraordinary metal-bearing scales deposited from erupting brines provide evidence that the fluids contain some sulfide in their natural high-temperature environment, but the total S in any given volume of fluids is stoichiometrically far too small to precipitate all dissolved sulfophile metals as sulfides. If deficiency in S is found to be a common phenomenon in base-metal ore fluids, some means for providing a local supply of S is essential if these fluids are to fulfill much of their potential in forming mineral deposits.

At least six different mechanisms may supply enough local S to form ore bodies. In the first model, a deep zone is assumed to contain very saline Na-Ca-Cl brine with base metals and Ag in concentrations ranging from a few ppm to thousands of ppm, and largely as Cl complexes. In an upper zone, dilute meteoric waters are circulating actively. In an intermediate zone, mixing occurs by convection or diffusion, and may be either sharp or gradational.

Temperatures in the main brine reservoir are assumed to be high enough and pressures low enough to form a vapor phase enriched in $CO_2$ and $H_2S$, which rise through the brine into the overlying zone. Thus, these gases escape upward faster than Cl and the base metals. Most of the liquid brine recirculates by convection within the reservoir but some escapes into the intermediate zone enriched in $CO_2$ and $H_2S$. Metal sulfides precipitate in and near this zone of mixture because temperatures are lower, the water is less saline, and the available S, now enriched, competes successfully with Cl

complexes for the sulfophile metals. In this model, the main reservoir of saline metal-rich brine continues to be deficient in S; base-metal sulfides are precipitated only locally where the deficiency is overcome.

Perhaps as open-space deposition continues, permeability decreases along the routes of escape of the fluids. However, some $H_2S$ and $CO_2$-rich vapor can continue to escape after all metal-bearing brine is excluded. Repeated fracturing or faulting may then occur, resulting in increased permeability along the channels. Metal-enriched brine again escapes upward, perhaps thereby accounting for the pulses commonly observed in ore mineral parageneses.

The commonly held theory that $CO_2$ and sulfur gases are somehow retained at depth through periods of peak intensity of magmatism and metamorphism, and are then released during late waning stages is not reasonable. Instead, $H_2O$, $CO_2$, and sulfur gases probably escape continuously, but with differing absolute rates and ratios relative to the base metals. If the S in these gases is insufficient to precipitate all sulfophile metals escaping from the brine reservoir into the intermediate zone, some Mn, Fe and other heavy metals may be retained in solutions now enriched in $CO_2$. Mn and Fe may precipitate largely as carbonates, as proposed by Hewett and others (1960, 1963, 1964). Near the surface, in an increasingly oxidizing environment, any $Mn^{2+}$ still in solution eventually precipitates as Mn oxides that selectively scavenge any Cu, Pb, Zn, Ag, As, W, and other heavy metals not precipitated in the deeper zones.

Other models for supplying S are largely variants of the first. In a second model, a vapor phase is not required. Rates of mobility of water and other constituents are assumed to differ greatly in escaping through shales or other semipermeable membranes (White, in press). $H_2O$, $H_2S$, $CO_2$, and other uncharged species, according to this hypothesis, are more mobile than the electrically charged species. In addition, systematic differences in the charged species may depend upon magnitude and nature of charge, ionic radius of each species, including differing degrees of hydration, and other factors. (For problems of maintaining electrical charge balance, see White, in press.) Base-metal sulfides are precipitated in those parts of a complex and imperfect membrane system where temperatures and concentrations permit S to compete successfully with the Cl complexes for the available base metals.

In a third model, metal-rich brine migrates from the reservoir up into an intermediate zone where pyrite has previously formed by any of several mechanisms; perhaps with decreasing temperature and dilution of the brine, the available S, largely stored in pyrite, now recombines successfully with the base metals and Ag, introduced as chloride complexes (Lovering, 1961).

In a fourth model, the base metals are concentrated in the brine of the reservoir at an early stage, but $H_2S$ continues to stream up into the reser-

T  R S

the main reservoir of
base-metal sulfides are
ome.

ermeability decreases
H₂S and CO₂-rich
brine is excluded. Re-
in increased permea-
escapes upward, per-
served in ore mineral

s are somehow re-
magmatism and meta-
ges is not reasonable.
pe continuously, but
base metals. If the S
metals escaping from
Fe and other heavy
CO₂. Mn and Fe may
ett and others (1960,
ing environment, any
xides that selectively
avy metals not pre-

the first. In a second
y of water and other
g through shales or
H₂O, H₂S, CO₂, and
s, are more mobile
natic differences in
d nature of charge,
es of hydration, and
charge balance, see
in those parts of a
ratures and concen-
complexes for the

reservoir up into an
l by any of several
ilution of the brine,
es successfully with
(Lovering, 1961).
in the brine of the
n up into the reser-

voir. With time and decreasing temperature, first the Fe in solution is largely precipitated as pyrite, and then the base-metal sulfide ores are deposited in this reservoir, rather than above it. According to this hypothesis, ore deposits in the Salton Sea system will form at some time in the future.

In a fifth model, much pyrite has already formed in the reservoir. With decreasing temperature, the S of pyrite successfully recombines with base metals that are no longer stable as chloride complexes.

In a sixth and final model considered here, base-metal sulfides are deposited where two different and presumably unrelated solutions happen to mix; one is high in base metals but deficient in S, and the second supplies the necessary S.

Several of these models can account successfully for the very saline metal-rich brines that are the indicated dominant transporting agents of transport of base metals and Ag; they can also account for localization of sulfide ore deposits, and for the depth zones of Mn oxides, carbonates, and metal sulfides as proposed by Hewett and others (1960, 1963, 1964); and finally they can account for the CO₂-rich waters and gases of many late Cenozoic ore deposits formed at depth but now located near the surface because of erosion.

If future experimentation in metal-sulfide systems, and study of fluid inclusions demonstrate that ore fluids can transport enough S to satisfy their contents of sulfophile metals, the models discussed above may be of little or no significance. But if S-deficiency is found to be a common phenomenon, is as hypothesized here, one or more of these models may prove useful in understanding the localization of hypogene ore deposits.

One problem not yet considered is the relationship, if any, between the bicarbonate waters associated with the upper parts of base-metal systems and the bicarbonate waters of Hg deposits. The latter, as we have seen, tend to be exceptionally high in B, NH₄, and I/Cl; S is generally appreciable; and Fe and Mn are low. In contrast, the spring waters that deposit Mn oxides with adsorbed heavy metals have only modest contents of B, NH₄, and I, no detected S, but significant Fe and Mn; nearly all occurrences are east of a line through central Nevada, as are most of our base-metal deposits. Ore fluids that deposit base metals evidently contain some Hg, as proved by the Hg geochemical anomalies found in many base-metal districts, but no evidence points convincingly to a genetic relation between commercial base metal and Hg ores in the same district.

Geologic and geochemical relationships suggest that Na-Ca-Cl brines competent to dissolve base metals can form in at least three different ways.

1. *Late-stage magmatic brine.* During magmatic differentiation, Ca is largely precipitated in the early formed minerals, especially plagioclase. After the magma has largely crystallized and perhaps after most H₂O, CO₂,

and $H_2S$ have escaped, deuteric reaction such as albitization of plagioclase enriches the residual fluid in Ca. Base metals concentrated in early formed Fe-Mg minerals may go back into solution at this time by a deuteric-release mechanism (Mackin and Ingerson, 1960). A workable mechanism for separating this dispersed brine from a largely crystallized and somewhat cooled magma chamber is not evident. The Creede deposits of Colorado with their Ca-rich fluid inclusions constitute very convincing evidence that some mechanism must exist. At Creede, volcanic rocks lie on a Precambrian crystalline basement with no known sedimentary or low-grade metamorphic rocks within 50 miles that could provide other sources of saline water.

2. *Connate waters of sedimentary rocks, heated sufficiently after deep burial or in close proximity to a local thermal anomaly.* Hall and Friedman (1963) have shown that fluid inclusions from ore deposits of Wisconsin and Illinois are strikingly similar chemically and in deuterium content to oil-field waters of the Na-Ca-Cl type (White, Hem, and Waring, 1963, table 13). The outstanding difference between these waters is the higher K/Na ratio of the inclusions. A high content of K was formerly considered to favor a magmatic origin (White, 1957a,b) but much recent evidence (Ellis, Chapter 11; Orville, 1963; White, 1965) has demonstrated a strong temperature dependence for the K/Na ratio.

3. *Meteoric water that has dissolved evaporites and then reacts with rocks in a geothermal environment, as favored here as the dominant mechanism in the Salton Sea geothermal system.* All three waters may be geochemically similar in most respects. If physical conditions are also similar and the supply of metals from the rocks is adequate, each should be a satisfactory solvent for base metals and Ag.

Saline Na-Ca-Cl brine formed by any of these mechanisms could provide heavy metals for syngenetic concentrations in sedimentary rocks. In a marine environment, dense brines forced upward by compaction of sediments or magmatic pressure would eventually approach the sediment surface with much less dilution than in a continental environment, for topographic inequalities under the ocean do not provide a pressure drive for circulation of water, as on the continents. Dense brine that is being forced upward would displace ordinary ocean water of lower density. Especially in permeable sands, the brine could spread out over a large area, even though the deeper channels of escape are restricted. If such a brine is metal-rich and S-deficient, diagenetic reactions could occur, especially in and near organic-rich muds where S is being actively produced by reduction of $SO_4$. The brines could also be discharged directly on the sea floor, where topographic lows would be favored by the high density of the brine. Such an environment would also be especially favorable for trapping of organic matter and production of S from $SO_4$. Strictly syngenetic concentrations of heavy metals could then be deposited.

The left column shows fragmentary text from the facing page:

ITERS

ition of plagioclase
ntrated in early formed
ne by a deuteric-release
rkable mechanism for
tallized and somewhat
deposits of Colorado
vincing evidence that
ks lie on a Precambrian
ow-grade metamorphic
ources of saline water.
*d sufficiently after deep*
*y.* Hall and Friedman
sits of Wisconsin and
terium content to oil-
Waring, 1963, table 13).
he higher K/Na ratio of
considered to favor a
vidence (Ellis, Chapter
a strong temperature

*d then reacts with rocks*
*dominant mechanism in*
may be geochemically
so similar and the sup-
a satisfactory solvent

hanisms could provide
imentary rocks. In a
y compaction of sedi-
ach the sediment sur-
al environment, for
ovide a pressure drive
se brine that is being
ter of lower density.
out over a large area,
ted. If such a brine is
d occur, especially in
oduced by reduction
n the sea floor, where
of the brine. Such an
trapping of organic
etic concentrations of

# References

Aidin'yan, N. Kh. (1962) Content of mercury in some natural waters: *Akad. Nauk SSSR, Inst. Geol. Rudn. Mestorozhd., Petrog. Mineralog. i Geokhim. Tr.,* no. 70, 9–14 (in Russian).

———, N. A. Ozerova, and S. K. Gipp (1963) Distribution of mercury in contemporary sediments: *Akad. Nauk SSSR, Inst. Geol. Rudn. Mestorozhd, Petrog. Mineralog. i Geokhim. Tr.,* no. 99, 5–11 (in Russian),

Allen, E. T. and A. L. Day (1927) Steam wells and other thermal activity at "The Geysers," California: *Carnegie Inst. Washington Pub. 378.*

Aver'ev, V. V. (1960) Nature of carbon dioxide arsenous waters and their ore-forming activity: *Vopr. Formirovaniya i Rasprostr. Mineral'n. Vod SSSR,* Moscow, Sb., 87–103 (in Russian).

Bailey, E. H. (1946) Quicksilver deposits of the western Mayacmas district, Sonoma County, California: *California J. Mines and Geol., 42,* 199–240.

——— (1959) Froth veins, formed by immiscible hydrothermal fluids, in mercury deposits, California: *Bull. Geol. Soc. Am. 70,* 661–663.

——— (1962) Mercury in the United States, exclusive of Alaska and Hawaii: *U.S. Geol. Surv. Mineral Inv. Resource Map MR-30,* scale 1:3, 168,000.

——— and D. L. Everhart (1964) Geology and quicksilver deposits of the New Almaden district, Santa Clara County, California: *U.S. Geol. Surv. Prof. Paper 360.*

———, P. D. Snavely, Jr., and D. E. White (1961) Chemical analyses of brines and crude oil, Cymric field, Kern County, California: *U.S. Geol. Surv. Prof. Paper 424-D,* D306–D309.

Bastin, E. S. (1923) Silver enrichment in the San Juan Mountains, Colorado: *U.S. Geol. Survey Bull. 735-D,* 65–130.

Berce, Boris (1958) Geology of the Idrija mercury deposit: *Geol. Razprave in porocila, 4,* 5–62.

Brannock, W. W., P. F. Fix, V. P. Gianella, and D. E. White (1948) Preliminary geochemical results at Steamboat Springs, Nevada: *Am. Geophys. Union Trans., 29,* 211–226.

Bulkin, G. A. (1960) Certain genetic features of mercuric ore manifestations in the Crimea: *Akad. Nauk SSSR Dokl. 131,* 1143–1146 (in Russian),

Burbank, W. S. and R. G. Luedke (1961) Origin and evolution of ore and gangue-forming solutions, Silvera caldera, San Juan Mountains, Colorado: *U.S. Geol. Surv. Prof. Paper 424-C,* C7–C11.

Clarke, F. W. (1916) The data of geochemistry, 3d ed.: *U.S. Geol. Surv. Bull.* 616.

Cortese, Emilio (1904) A quicksilver deposit: *Eng. Mining J. 78,* 741–742.

Craig, Harmon, Giovanni Boato, and D. E. White (1956) Isotopic geochemistry of thermal waters: *Natl. Research Council, Comm. Nuclear Sci., Nuclear Sci. Ser. Rept. 19,* 29–38.

Dickson, F. W. (1964) Solubility of cinnabar in $Na_2S$ solutions at 50–250° and 1–1,800 bars with geologic applications: *Econ. Geol. 59,* 625–635.

——— and George Tunell (1954) The saturation curves of cinnabar and metacinnabar in the system $HgS$-$Na_2S$-$H_2O$ at 25°C: *Science, 119,* 467–468.

——— and ——— (1959) The stability relations of cinnabar and metacinnabar: *Am. Mineral., 44,* 471–487.

Doe, B. R., C. E. Hedge, and D. E. White (1966) Preliminary investigation of the

source of lead and strontium in deep geothermal brines underlying the Salton Sea geothermal area: *Econ. Geol. 61*, 462–483.

Ellis, A. J. and W. A. J. Mahon (1964) Natural hydrothermal systems and experimental hot-water/rock interactions: *Geochim. Cosmochim. Acta, 28*, 1323–1357.

———— and ———— (1966) Geochemistry of the Ngawha hydrothermal area: *New Zealand J. Sci., 9*, 440–456.

———— and S. H. Wilson (1961) Hot spring areas with acid-sulfate-chloride waters: *Nature, 191*, 696–698.

Emmons, S. F. (1896) The mines of Custer County, Colorado: *U.S. Geol. Survey, 17th Ann. Report, pt. 2*, 405–472.

Erd, R. C., D. E. White, J. J. Fahey, and D. E. Lee (1964) Buddingtonite, an ammonium feldspar with zeolitic water: *Am. Mineral., 49*, 831–850.

Everhart, D. L. (1950) Skaggs Springs quicksilver mine, Sonoma County, California: *California J. Mines and Geol., 46*, 385–394.

Fairbanks, H. W. (1894) Some remarkable hot springs and associated mineral deposits in Colusa County, California: *Science, 23*, 129–121.

Falini, Filippo (1960) Notizie preliminari su una campagna di indagini e ricerche per minerali di mercurio nella regione del M. Amiata (province de Siena e Grosseto): *Periodico di Mineral. 29*, 1–27.

Fedorchuk, V. P. (1958) Origin of native mercury: *Geochemistry, no. 3*, 345–352.

————, E. E. Kostyleva-Labuntseva, and I. N. Maslova (1963) Problem of the genesis of mercury-antimony deposits: *Geologiia Rudn. Mestorozh. 5*, 91–99 (in Russian); reviewed in 1964, *Econ. Geol., 59*, 184.

Fleming, C. A. (1945) Hydrothermal activity at Ngawha, North Auckland, with a section on underground water by J. Healy: *New Zealand J. Sci. and Tech., 26*, 255–276.

Goldsmith, J. R. and D. L. Graf (1960) Sub-solidus relations in the system $CaCO_3$-$MgCO_3$-$MnCO_3$: *J. Geology, 68*, 324–335.

Hall, W. E. and Irving Friedman (1963) Composition of fluid inclusions Cave-in-Rock fluorite district, Illinois, and upper Mississippi Valley zinc-lead district: *Econ. Geol., 58*, 886–911.

Helgeson, H. C. (1964) *Complexing and Hydrothermal Ore Deposition:* New York: Pergamon.

Hemley, J. J. (1959) Some mineralogical equilibria in the system $K_2O$-$Al_2O_3$-$SiO_2$-$H_2O$: *Am. J. Sci., 257*, 241–270.

———— and W. R. Jones (1964) Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism: *Econ. Geol., 59*, 538–569.

Hewett, D. F. (1964) Veins of hypogene manganese oxide minerals in the southwestern United States: *Econ. Geol., 59*, 1429–1472.

———— and Michael Fleischer (1960) Deposits of the manganese oxides: *Econ. Geol., 55*, 1–55.

————, ————, and N. M. Conklin (1963) Deposits of the manganese oxides—supplement: *Econ. Geol., 58*, 1–51.

Hosohara, K., H. Kozuma, K. Kawasaki, and T. Tsuruta (1961) Total mercury content in sea water: *Nippon Kagaku Zasshi, 82*, 1479–1480.

Ikeda, Nagao (1955) Chemical composition of the water of Tenmangu-no-yu: *Chem. Soc. Japan J., 76*, 1079–1082 (in Japanese).

Irving, E. M. (1954) Note on the first discovery of commercial mercury in the Philippines: *Philippine Geol. 9*, 1–7.

Ivanov, V. V. (1958) Fundamental laws governing the formation and distribution of thermal waters of Kamchatka: *Akad. Nauk SSSR, Lab. Vulkanologii Tr., 13*, 186–211 (in Russian).

Iwasaki, I.,
  hot sprin
  Technolo
Kayama, Is
  mine, Ho
Kekeliya, S
  *Kavkazsk*
  195–201.
Khitarov, N
  solutions:
Krauskopf,
  fluids: *Ec*
———— (1
  *Econ. Geo*
Lane, A. C
  circulatio
Lovering, T
  *Geol., 56*,
———— an
  in the Ea
McAllister,
  Guerrero
Mackin, J. I
  fluid: *U.S*
Mackevett,
  mine, Ala
McNitt, J.
  fornia: *C*
Mandic', V
  valley [Se
Maslova, I.
  solutions
  *Mineral.*
Minami, E.
  hot sprin
  860–865.
Muffler, L.
  Quaterna
  (abst.): *A*
  1965, 119
Nakamura,
  in Arima
  *n.s., 12*, 4
Orville, P. N
  *J. Sci., 26*
Pampeyan,
  Costa Co
Prinz, W. C
  $MnCO_3$-C
Roedder, Ed
Schoen, Rol

WATERS

nes underlying the Salton Sea

othermal systems and experi-
nochim. Acta, 28, 1323–1357.
' awha hydrothermal area:

is with acid-sulfate-chloride

Colorado: U.S. Geol. Survey,

1964) Buddingtonite, an am-
49, 831–850.
Sonoma County, California:

ings and associated mineral
129–121.
pagna di indagini e ricerche
a (province de Siena e Gros-

Jchemistry, no. 3, 345–352.
slova (1963) Problem of the
dn. Mestorozh. 5, 91–99 (in

wha, North Auckland, with
Zealand J. Sci. and Tech., 26,

:ions in the system CaCO₃-

of fluid inclusions Cave-in-
pi Valley zinc-lead district:

Ore Deposition: New York:

e system K₂O-Al₂O₃-SiO₂-

of hydrothermal alteration
eol., 59, 538–569.
oxide minerals in the south-

he manganese oxides: Econ.

ts of the manganese oxides—

suruta (1961) Total mercury
9–1480.
water of Tenmangu-no-yu:

commercial mercury in the

e formation and distribution
R, Lab. Vulkanologii Tr., 13,

Iwasaki, I., T. Katsura, and others (6) (1963) Geochemical studies on Tamagawa hot spring: in *Geochemistry of the Tamagawa hot springs*, Tokyo: Tokyo Inst. Technology, 22–23.

Kayama, Isao and T. Iriye (1957) Geochemical studies on the hot springs at Yakumo mine, Hokkaido: *Nippon Kagaku Zasshi, 78*, 989–993 (in Japanese).

Kekeliya, S. A. and D. G. Saliya (1963) Dickite from Abkhaz mercury deposits: *Kavkazsk. Inst. Mineral'n. Syr'ya, Min. Geol. i Okhrany Nedr SSSR Tr., no. 4*, 195–201.

Khitarov, N. I. and B. N. Ryzhenko (1963) On estimating the pH of hydrothermal solutions: *Geochemistry, no. 12*, 1208–1210.

Krauskopf, K. B. (1951) Physical chemistry of quicksilver transportation in vein fluids: *Econ. Geol., 46*, 498–523.

——— (1964) The possible role of volatile metal compounds in ore genesis: *Econ. Geol., 59*, 22–45.

Lane, A. C. and C. M. Alter (1941) Connate waters recognized in underground circulation [abst.]: *Bull. Geol. Soc. Am., 52*, 1919–1920.

Lovering, T. S. (1961) Sulfide ores formed from sulfide-deficient solutions: *Econ. Geol., 56*, 68–99.

——— and H. T. Morris (1965), Underground temperatures and heat flow in the East Tintic district, Utah: *U.S. Geol. Surv. Prof. Paper. 504-F*.

McAllister, J. F. and D. H. Ortiz (1945) Quicksilver-antimony deposits of Huitzuco, Guerrero, Mexico: *U.S. Geol. Survey Bull. 946-B*, 49–71.

Mackin, J. H. and Earl Ingerson (1960) An hypothesis for the origin of ore-forming fluid: *U.S. Geol. Surv. Prof. Paper 400-B*, B1–B2.

Mackevett, E. M., Jr. and H. C. Berg (1963) Geology of the Red Devil quicksilver mine, Alaska: *U.S. Geol. Surv. Bull. 1142-G*, G1–G16.

McNitt, J. R. (1963) Exploration and development of geothermal power in California: *California Div. Mines and Geol. Spec. Rept. 75*.

Mandic', Vidosava (1957) Metallic mercury in the spring Dobra Voda in the Ibar valley [Serbia]: *Vesnik Zavoda geol. i geofiz. istrazivanja N.R. Srbije 14*, 135–136.

Maslova, I. N. (1963) Ultramicrochemical investigations of the composition of solutions in inclusions in quartz from antimony-mercury ore deposits: *Vses. Mineral. Obshch. Zap., 92*, 706–707.

Minami, E., G. Sato, and K. Watanuki (1958) Arsenic and lead contents of the hot springs of Tamagawa, Akita Prefecture—II: *Nippon Kagaku Zasshi, 79*, 860–865.

Muffler, L. J. P. and D. E. White (1965) Recent metamorphism of Pliocene and Quarternary sediments of the Salton Sea geothermal field, California, U.S.A. (abst.): *Abstracts of the International Symposium on Volcanology, New Zealand, 1965*, 119–120.

Nakamura, H. and K. Maeda (1961) Thermal waters and hydrothermal activities in Arima hotspring area, Hyogo Prefecture (Japan): *Japan Geol. Surv. Bull., n.s., 12*, 489–497.

Orville, P. M. (1963) Alkali ion exchange between vapor and feldspar phases: *Am. J. Sci., 261*, 201–237.

Pampeyan, E. H. (1963) Geology and mineral deposits of Mount Diablo, Contra Costa County, California: *California Div. Mines and Geol. Spec. Rept. 80*.

Prinz, W. C. (1964) Diagram for determining mineral composition in the system $MnCO_3$-$CaCO_3$-$MgCO_3$: *U.S. Geol. Surv. Prof. Paper 501-C*, C84–C85.

Roedder, Edwin (1962) Ancient fluids in crystals: *Sci. Am., 207*, 38–47.

Schoen, Robert and D. E. White (1965) Hydrothermal alteration in GS-3 and

GS-4 drill holes, Main Terrace, Steamboat Springs, Nevada: *Econ. Geol. 60*, 1411–1421.

Schwarzenbach, G. and M. Widmer (1963) Die Löslichkeit von Metallsulfiden, I. Schwarezes Quecksilbersulfid: *Helvet. Chim. Acta, 46*, 2613–2628.

Shcheglov, I. I. (1962) Modern cinnabar in the Apapel spring: *Akad. Nauk SSSR Dokl. 145*, 1373–1374.

Sigvaldason, G. E. (1963) Epidote and related minerals in two deep geothermal drill holes, Reykjavik and Hveragerdi, Iceland: *U.S. Geol. Surv. Prof. Paper 450-E*, E77–E79.

——— and D. E. White (1962) Hydrothermal alteration in GS-5 and GS-7, Steamboat Springs, Nevada: *U.S. Geol. Surv. Prof. Paper 450-D*, D113–D117.

Skinner, B. J., D. E. White, H. J. Rose, and R. E. Mays (1967) Sulfides associated with the Salton Sea geothermal brines: *Econ. Geol., 62* (in press).

Steiner, A. (1953) Hydrothermal rock alteration at Wairakei, New Zealand: *Econ. Geol. 48*, 1–13.

Swinney, C. M. (1950) The Altoona quicksilver mine, Trinity Co., California: *California J. Mines and Geol. 46*, 395–404.

Tunell, George (1964) Chemical processes in the formation of mercury ores and ores of mercury and antimony: *Geochim. Cosmochim. Acta, 28*, 1019–1037.

Vinogradov, A. P. (1962) Average contents of chemical elements in the principal types of igneous rocks of the earth's crust: *Geochemistry, no. 7*, 641–664.

White, D. E. (1955a) Thermal springs and epithermal ore deposits: *Econ. Geol., 50th Anniv. Vol.*, 99–154.

——— (1955b) Violent mud-volcano eruption of Lake City hot springs, northeastern California: *Bull. Geol. Soc. Am., 66*, 1109–1130.

——— (1957a) Thermal waters of volcanic origin: *Bull. Geol. Soc. Am., 68*, 1637–1658.

——— (1957b) Magmatic, connate, and metamorphic waters: *Bull. Geol. Soc. Am., 68*, 1659–1682.

——— (1961) Preliminary evaluation of geothermal areas by geochemistry, geology, and shallow drilling: *United Nations Conf. New Sources Energy*, Rome, Italy.

——— (1965) Saline waters of sedimentary rocks: *Am. Assoc. Petrol. Geol., Mem. 4*, 342–366.

——— (1967) Ore-forming fluids of diverse origins: *Econ. Geol., 62* (in press).

———, E. T. Anderson, and D. K. Grubbs (1963) Geothermal brine well—mile-deep drill hole may tap ore-bearing magmatic water and rocks undergoing metamorphism: *Science, 139*, 919–922.

———, W. W. Brannock, and K. J. Murata (1956) Silica in hot-spring waters: *Geochim. Cosmochim. Acta, 40*, 27–59.

———, Harmon Craig, and H. Begemann (1966) Summary of the geology and isotope geochemistry of Steamboat Springs, Nevada: *Spoleto Isotope Sympos. Vol.*, Conf. of CNEN-Univ. Pisa, 1963, Italy (in press).

———, J. D. Hem, and G. A. Waring (1963) Chemical composition of subsurface waters: *U.S. Geol. Surv. Prof. Paper, 440-F*, F1–F67.

——— and L. J. P. Muffler (1967) Metamorphism of late Cenozoic sediments to greenschist mineral assemblages, Salton Sea geothermal area, California [abst.]: *Geol. Soc. Am. Special Paper* (in press).

——— and C. E. Roberson (1962) Sulphur Bank, California, a major hot-spring quicksilver deposit: *Geol. Soc. Am., Buddington Volume*, 397–428.

——— and G. E. Sigvaldason (1963) Epidote in hot-spring systems, and depth of formation of propylitic epidote in epithermal ore deposits: *U.S. Geol. Surv. Prof. Paper 450-E*, E80–E84.

———, G. A. Thompson, and C. H. Sandberg (1964) The rocks, structure, and geologic history of the Steamboat Springs thermal area, Washoe County, Nevada: *U.S. Geol. Surv. Prof. Paper 458-B.*

Yates, R. G. and L. S. Hilpert (1946) Quicksilver deposits of eastern Mayacmas district, Lake and Napa Counties, California: *California J. Mines and Geol.,* 42, 231–286.

——— and G. A. Thompson (1959) Geology and quicksilver deposits of the Terlingua district, Texas: *U.S. Geol. Surv. Prof. Paper 312.*

Znamirovskii, V. N. (1963) Mercury mineralization in the southern part of the Siberian platform: *Akad. Naukk SSSR Dokl.,* 148, 684–685.

WATERS

prings, Nevada: *Econ. Geol. 60,*

Löslichkeit von Metallsulfiden, I. *ta, 46,* 2613–2628.
apel spring: *Akad. Nauk SSSR*

minerals in two deep geothermal d: *U.S. Geol. Surv. Prof. Paper*

al alteration in GS-5 and GS-7, *Prof. Paper 450-D,* D113–D117.
Mays (1967) Sulfides associated *ol., 62* (in press).
at Wairakei, New Zealand: *Econ.*

r mine, Trinity Co., California:

formation of mercury ores and *smochim. Acta, 28,* 1019–1037.
mical elements in the principal *chemistry, no. 7,* 641–664.
ermal ore deposits: *Econ. Geol.,*

of Lake City hot springs, north-09–1130.
origin: *Bull. Geol. Soc. Am., 68,*

morphic waters: *Bull. Geol. Soc.*

rmal areas by geochemistry, geol-*nf. New Sources Energy,* Rome,

: *Am. Assoc. Petrol. Geol., Mem.*

ins: *Econ. Geol., 62* (in press).
63) Geothermal brine well—mile-ater and rocks undergoing meta-

956) Silica in hot-spring waters:

6) Summary of the geology and evada: *Spoleto Isotope Sympos.* press).
Chemical composition of sub-0-F, F1–F67.
hism of late Cenozoic sediments eothermal area, California [abst.]:

κ, California, a major hot-spring *Volume,* 397–428.
in hot-spring systems, and depth l ore deposits: *U.S. Geol. Surv.*