Diverse Origins of Hydrothermal Ore Fluids

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Abstract

Chemical, isotopic, and physical data from fluid inclusions, ore and gangue minerals, and active geothermal systems indicate the general characteristics and probable origins of the dominant ore-transporting waters of many systems. Evaluation of such data from a wide variety of mining districts and hot-spring systems indicate that five classes of waters, here called meteoric, ocean, "evolved connate," metamorphic, and magmatic, account in varying proportions for hydrothermal fluids.

More than 40 localities are reviewed in this study, including: (1) 6 Hg systems involving metamorphic or "evolved-connate" waters; (2) 15 epithermal Au-Ag districts and 2 probably similar active hydrothermal systems involving meteoric water and perhaps as much as 5 or 10 percent of magmatic water; (3) 10 ore districts and 2 active systems with abundant base metals ±Ag, involving waters of diverse origins, including ocean, "evolved-connate," meteoric, and magmatic, usually with salinities above 4 percent; and (4) 5 copper-molybdenum deposits, generally involving early dominance by magmatic water but with increasing proportions of meteoric water during sulfide and postsulfide stages.

Individual constituents, including the metals, Cl, S, and CO_2, may come from the same or different sources than the dominant water. Igneous intrusions frequently provide the energy and perhaps the S and C of the ore deposits, but a magmatic origin of the metals, H_2O, and other constituents is commonly assumed uncritically.

Ore deposition may require favorable combinations of circumstances that differ from place to place, but with some combinations being especially favorable. No simple model of origin is likely to explain all or even most metalliferous ore deposits.

Introduction

In an earlier review chemical and isotopic data adequate for determining the origin of the fluids existed for only 5 ore systems (White, 1968). Two of the 5 are active systems and potentially ore-forming (Salton Sea and Red Sea brine systems).

In the last several years the number of districts, separate deposits, and active metal-rich geothermal systems that can be tentatively categorized by origin, at least with respect to that of the dominant water, has increased from about 27 in the early summer of 1973 to more than 40 by the time of the November 1973 S.E.G. Isotope Symposium!

The most useful sources of data in deducing origin of fluids are from: (1) fluid inclusion studies of ore and gangue minerals of ore deposits, which provide temperatures of deposition and chemical compositions of fluids and daughter minerals (Roedder, 1972; Roedder et al., 1963; Hall and Friedman, 1963); (2) isotopic analyses of the fluids and associated minerals (this volume); and (3) studies of natural waters and active geothermal systems. Chemical and isotopic compositions of the latter have helped to establish the most probable origin of many thermal and mineral waters. In active systems, adequate volumes of water, properly collected, are sel-

dom a serious constraint in analyzing for any desired constituent or isotope. Thus, detailed analysis of such waters has established criteria applicable to fluid inclusions, where an adequate supply of fluid is a serious constraint. Geochemical relationships from active thermal and mineral water systems that have already been applied to fluid inclusion compositions include the ratio of Na/K and Na-K-Ca relations as functions of temperature (White, 1965, 1968, in press; Rye and Haffty, 1969; Fournier and Truesdell, 1973), and B/Cl (Roedder et al., 1963).

The analyses of the light stable isotopes of water, D/H, and $^{18}O/^{16}O$, provides the most diagnostic data for determining the origin of waters, and such data are emphasized in this review. The δD and $\delta^{18}O$ contents of meteoric waters decrease with latitude, altitude, and distance from the ocean (Craig, 1961). Most meteoric waters, if heated in contact with most rocks, are depleted in ^{18}O; water and rocks tend to exchange ^{18}O, with the extent of exchange being dependent on initial ^{18}O contents, temperature, proportions of water and rocks, the specific water-mineral fractionation factors, and extent of equilibration attained (Craig, 1963; Taylor, 1973, 1974). The δD values of the waters of each geothermal system, in contrast, are generally nearly

identical to the δD values of the meteoric waters of the same area (Craig, 1963), thus indicating that meteoric water is the dominant source of supply of most geothermal systems. The precision of measurements and the slight isotopic differences within the thermal and the meteoric waters of each area permit, in general, at least 5 to 10 percent of nonmeteoric water of different isotopic composition to be involved in the thermal system without detection.

Definitions

Genetic terms for different kinds of water include: (1) meteoric—nonmarine water recently involved in atmospheric circulation; its age since last contact with the atmosphere is slight as compared to the age of the enclosing rock; (2) ocean—water of the oceans of the time, or recently derived from an ocean; (3) connate—"fossil" water, generally initially ocean water in the pores of young marine sediments but out of contact with the atmosphere for at least an appreciable part of a geologic period; (4) metamorphic—water that is or that has been associated with rocks during their metamorphism; (5) magmatic—water that is in or has come from magma, regardless of ultimate origin; and (6) juvenile—"new" water that is in or is derived from the mantle and has not previously been a part of the hydrosphere.

Each of these types of water may migrate into new chemical and physical environments, evolving chemically and isotopically in response to changes that include mixing with other types and probably the effects of membrane filtration. The genetic terms, approximately as defined above, are in common use except for connate, which has been defined and redefined many times (White, 1965, p. 345–346). Connate water of marine sediments differs from other types mainly in the fact that its *initial* composition as ocean water can be assumed within rather close limits, and any significant chemical and isotopic change is therefore obvious. In order to emphasize the expected changes, the term "evolved connate" is used in this report.

Mercury Deposits Associated with Thermal and Mineral Waters

California

Thermal and mineral waters of the California Coast Ranges are closely associated with many mercury deposits (White, 1967; Barnes et al., 1973a; 1973b; White et al., 1973), especially in regions underlain by rocks of the Franciscan group. Some of these waters, generally the more dilute, plot isotopically close to the meteoric-water line of Craig (1961) and are mainly of meteoric origin. These include Aetna, Skaggs, and Amedee Springs, and

the Cordero mercury mine (see fig. 1; White, 1967; Barnes, 1973b; and Berry, 1973, for geologic setting, chemical data, and fluid-pressure environments). Other waters, generally more saline, are isotopically very different from nearby meteoric waters. In contrast to the high-temperature waters that show only an "^{18}O-shift" from associated meteoric waters (Craig, 1963), many of the Coast Range waters are strongly enriched in both ^{18}O and D relative to their nearest meteoric waters. White et al. (1973) have shown that the most saline waters of the Wilbur Springs and Suphur Bank mercury districts are enriched by 25 to 40 per mil in δD and about 13 per mil in δO^{18} relative to the local meteoric waters of each area (Fig. 1). Some of the springs discharge on or near the crests of ridges and cannot be recharged by meteoric water in normal environments controlled by hydrostatic-pressure gradients. Most of the anomalous waters occur in or are underlain by rocks of the Franciscan group, where fluid pressures are characteristically close to lithostatic (Berry, 1973, figs. 16 and 17). For these reasons, the more saline of these waters are considered to be nonmeteoric.

The chemical compositions of the Sulphur Bank type are exceedingly high in B, CO_2, and NH_3 relative to other constituents but are only modestly high in Cl; they are best explained as resulting from progressive metamorphism at depth. Wilbur Springs water is chemically and isotopically similar to oil-field waters of the Great Valley of California (average of 6 isotope analyses shown on Fig. 1; see White et al., 1973, for specific data) except for some further enrichment in B, CO_2, and NH_3 that may be of metamorphic origin. Regardless of any metamorphic contribution, the bulk of Wilbur Springs water is interpreted as "evolved connate," derived by compaction and loss of pore water from marine sediments. The "evolved connate" component seems to decrease westward from the Great Valley fault as the metamorphic component increases. In places in the region north and west of Sulphur Bank, the metamorphic fluid may consist dominantly of CO_2-rich vapor with little or no associated saline water.

Both types of nonmeteoric water are diluted near the surface by meteoric water in proportions that range from very low to such an overwhelming dilution that the nonmeteoric component is difficult to recognize isotopically. The chemical compositions, however, are more sensitive indicators of origin than isotopic differences, as indicated by the Aetna and Skaggs data of Figure 1 (White, 1967; Barnes et al., 1973a). This figure also shows the isotopic composition of mine-drainage water (average of 4 analyses) from the Abbott mercury mine, which is best ex-
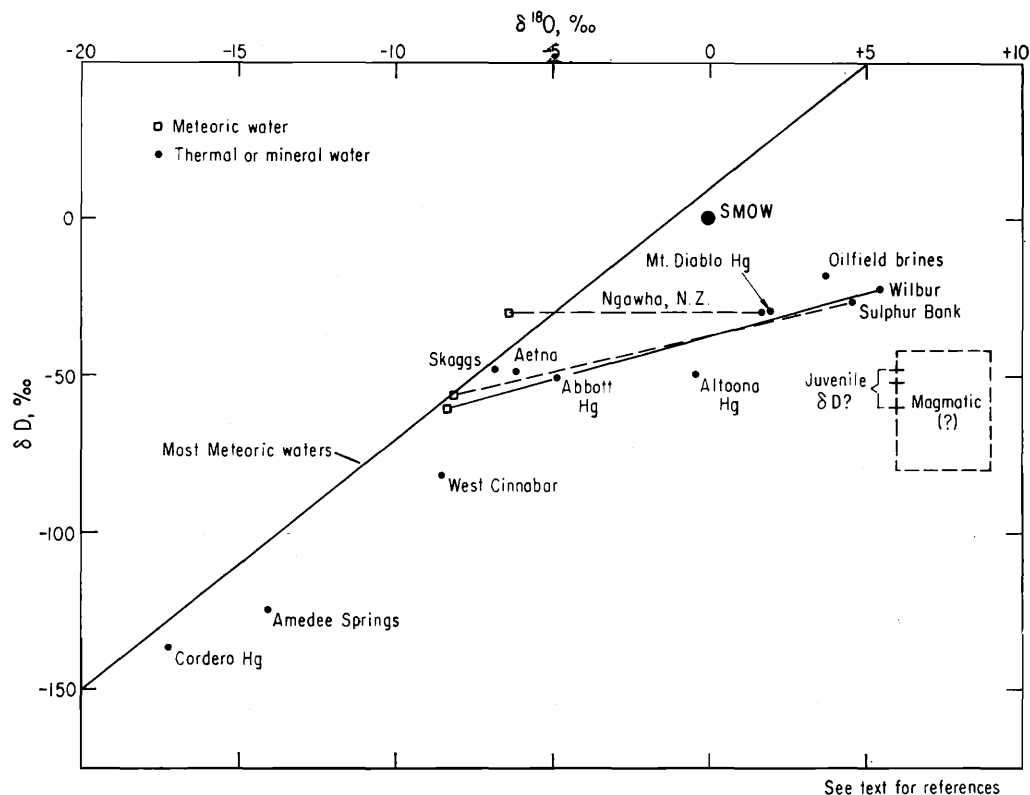
Fig. 1. Isotopic compositions of thermal and mineral waters associated with mercury deposits (modified from White et al., 1973).

plained as a thermal saline water intermediate between the Wilbur and Sulphur Bank types, diluted by meteoric water (White et al., 1973).

Also shown are isotope analyses of waters from the Altoona, Mt. Diablo, and West Cinnabar mercury deposits of the California Coast Ranges, which are described briefly by White (1967) along with chemical analyses of present-day fluids.

All of the waters discussed above seem to be unrelated to magmatic water. The full range in isotopic composition of magmatic waters is not yet known with certainty, but the box shown as "magmatic(?)" on Figure 1 includes the best estimates of many authors, including Rye (1966), Epstein and Taylor (1967), Sheppard et al. (1971), Sheppard and Taylor, (1974), Rye and Sawkins (1974), and Rye et al. (1974); its limits seem certain to increase somewhat as more is learned about the ultimate sources of the waters in magmas and about the probable limits of exchange reactions as magmatic water evolves before and after separation from its igneous affiliate.

Present indications of the δD values of juvenile water from the mantle are tightly clustered near −50 per mil; δD of condensed fumarolic water from Surtsey, Iceland, is −53 per mil (Arnason and

Sigurgeirson, 1968); δD in glassy rims of young pillow lavas erupted at high pressures in the ocean (minimal vesiculation) is −60 per mil (Moore, 1970); and δD of water driven from phlogopites of possible mantle origin is estimated to be −48 ±20 per mil (Sheppard and Epstein, 1970). These three values are totally independent and are in rather remarkable agreement.

The Amedee hot springs of California have been described by Tunell (1964), Dickson and Tunell (1968), and White (1967). The springs are of interest because metacinnabar, cinnabar, native mercury, and zeolites are precipitating in spring vents and discharge channels. The waters are relatively low in dissolved constituents and are dominated by meteoric waters.

Nevada

The warm well waters north of the Cordero mercury deposits were mentioned briefly by White (1967). An isotopic analysis shown on Figure 1 indicates strong dominance by water of meteoric origin.

Mercury is also being deposited at Steamboat Springs, Nevada (White, 1967), but the system is

similar in many respects to "epithermal" gold-silver deposits and is discussed in the next section.

New Zealand

The thermal springs of the Ngawha mercury mine area of New Zealand are remarkably similar chemically to those of the Sulphur Bank mine, and both districts are characterized by mercury deposits clearly related to the hot springs (McDonald, 1966; White, 1967; White et al., 1973). The Ngawha waters are nearly identical in δD value to the meteoric waters of the same area (generalized on Fig. 1), but the thermal waters are higher in $\delta^{18}O$ by about 8 per mil. McDonald concluded that Ngawha is another example of "^{18}O-shifted" meteoric water, but the striking similarities between Ngawha and Sulphur Bank and their similar isotopic compositions suggest that the Ngawha waters are dominantly nonmeteoric, emerging in an area where the meteoric waters are by coincidence nearly identical in δD.

"Epithermal" Gold-Silver Deposits

"Epithermal" is a convenient and long-used name for a large group of deposits valuable mainly for their gold and silver content, generally of Tertiary age, and localized in intermediate and silicic volcanic rocks (Nolan, 1933). Where ages are known, the volcanic rocks tend to be only slightly older than the ore deposits (O'Neil and Silberman, 1974; Silberman and McKee, 1974).

White (1955, p. 103–116, 138–141) emphasized the similarity in metal association and hydrothermal alteration between the "epithermal" gold-silver deposits and hot-spring systems such as Steamboat Springs, Yellowstone Park, and New Zealand. Isotope data reviewed here provides further support for this conclusion.

Steamboat Springs, Nevada

Evidence previously presented (White, 1955) and the isotope data summarized here (White et al., 1963; unpub. data) indicate that Steamboat Springs is the clearest example of a present-day active "epithermal" Au-Ag system. Banded and crustified veins of chalcedony, quartz, and calcite commonly range up to several feet in thickness and contain a few rich veinlets of pyrargyrite (Ag_3SbS_3). The hot-spring system is now known to have been active over a period of at least 1 million years and probably as much as 3 million years (Miles L. Silberman, unpub. data), but continuous activity cannot be proven (White et al., 1964).

Temperatures range up to 172°C but temperatures in the past, calculated from isotope relationships (J. R. O'Neil and White, unpub. data), exceeded 200°C at depths below 300 feet.

The ranges in isotopic compositions of the thermal and cold meteoric waters of the area are shown in Figure 2. The thermal waters show an average "$\delta^{18}O$-shift" of about 2.5 per mil. Their isotopic compositions could be explained entirely by water of meteoric origin, with differences in ^{18}O value resulting entirely from water-rock exchange at high temperatures. However, the relative abundance of highly soluble elements of low crustal abundance (such as Li, B, As, Sb, and Cs) and the great life of the system (probably hundreds of thousands of years, if not several millions) create great problems in maintaining the supply of these elements by rock leaching and favor, instead, a continuing small supply of magmatic water enriched in these constituents (White, 1969). The highest content of magmatic water that could be present in this system, assuming $\delta^{18}O$ values of -15 per mil for meteoric water, -12.5 per mil for the hot water, and $+7.5$ per mil for magmatic water, is 11 percent. The actual content, assuming that much of the $\delta^{18}O$ shift results from water-rock exchange, would be much less and is probably less than 5 percent.

Broadlands, New Zealand

Siliceous sinter deposited at the surface from hot springs and from discharge streams of erupting wells of the active Broadlands geothermal system of New Zealand are high in Ag, As, Sb, Hg, and Au (Weissberg, 1969; Browne, 1971; Browne and Lovering, 1973). In contrast, sphalerite, galena, and minor chalcopyrite are associated with pyrite and pyrrhotite in drill core from depths of 920 to 7,593 feet, where present temperatures are 120° to 298°C. These relationships suggest metalliferous zoning in depth. The chemistry of the fluids has been investigated extensively (Browne and Ellis, 1970; Mahon and Finlayson, 1972). Recent literature has emphasized the base metals, with contents in core of a few percent of zinc and a few tenths of one percent lead, but such relatively low contents are much more characteristic of "epithermal" Au-Ag deposits (Nolan, 1933) than of base metal deposits.

The Broadlands waters have been analyzed isotopically by Giggenbach (1971). The deep water prior to dilution or steam loss has a δD of about -40 per mil and $\delta^{18}O$ of -4.5 per mil and is compared on Figure 2 with the least evaporated local stream waters, which are slightly lower in δD. Giggenback suggests that these stream samples, collected in late winter, may be depleted in δD from average meteoric water. Broadlands water is chiefly meteoric water with no isotopic evidence for any magmatic contribution.
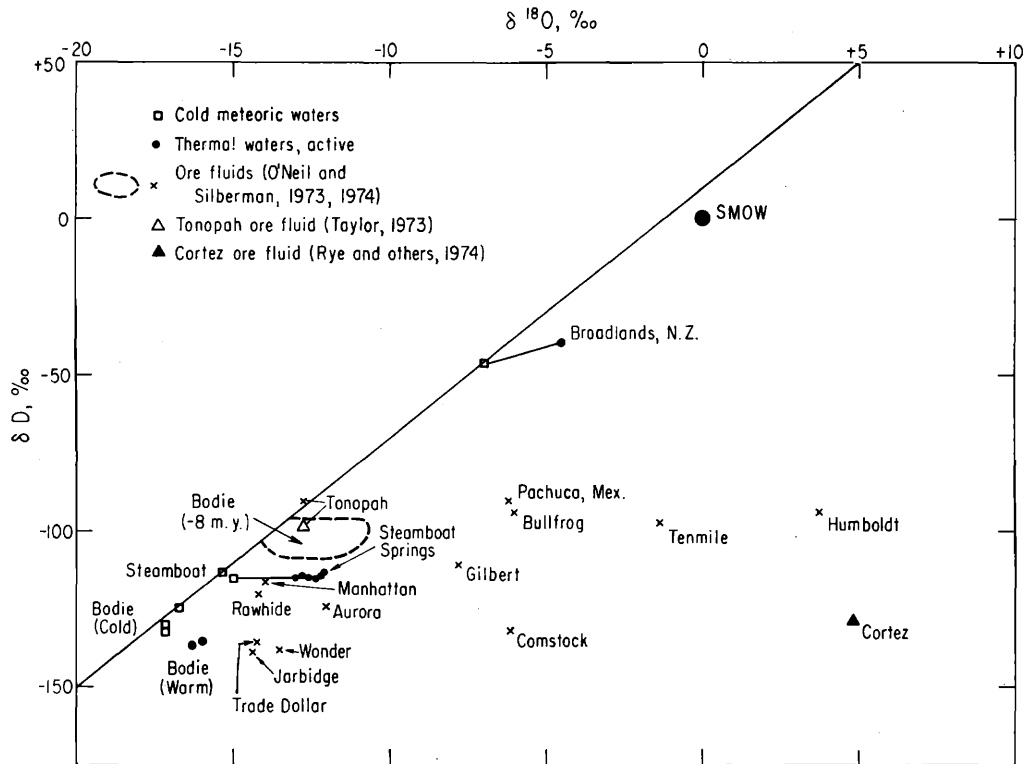
FIG. 2. Isotopic compositions of waters of "epithermal" gold-silver deposits.

Present salinities of the Broadlands waters range only up to about 0.3 percent, which is surprisingly low in view of evidence (reviewed in following sections) suggesting base metal transport by brine of high salinity. Freezing temperatures of fluid inclusions in sphalerite, quartz, and adularia from Broadlands drill core indicate that early fluids were more saline than present waters and range from 5,100 to 13,600 ppm of equivalent NaCl (Browne, Roedder, and Wodzicki, 1974).

Bodie, California

This "epithermal" mineral deposit has been extensively studied by isotopic methods (O'Neil et al., 1973; O'Neil and Silberman, 1974). The compositions of waters of fluid inclusions were determined by direct analysis of δD in inclusions in quartz and by calculating the $\delta^{18}O$ of the water, utilizing the analyzed $\delta^{18}O$ of quartz, the temperature of deposition (215° to 245°C, O'Neil et al., 1973), and quartz-water fractionation factors at these temperatures. All of these water compositions plot within the area of Figure 2 marked Bodie. The similar range of isotopic compositions of Bodie ore fluids of 8 m.y. ago and of the present Steamboat Springs system (Fig. 2) and their similar proximity to the meteoric water line is indeed striking. The difference in δD

between the indicated meteoric waters of the former Bodie system and of the cold-spring waters of the present Bodie area seems best explained by changes in climate over the 8-million-year interval, perhaps related in large part to the rise of the Sierra Nevada range in the interim (O'Neil et al., 1973).

Other "epithermal" gold-silver deposits

Other deposits of this type have been studied extensively but generally not intensively. Taylor (1973) determined $\delta^{18}O$ in many samples of quartz and altered rock from Tonopah and proved that a considerable volume of volcanic rocks has lost 5 to 15 per mil of its original ^{18}O content; reaction with meteoric water provides the only plausible explanation (Taylor, 1973, 1974). Taylor also determined the δD values of hydrothermally altered rocks containing mixtures of illite and chlorite in unknown proportions and he calculated the δD and $\delta^{18}O$ of the coexisting water (assuming reasonable temperatures and water-mineral fractionation factors) as −100 per mil and −13 per mil, respectively (shown as $\triangle$ within the area marked "Bodie"). The Comstock Lode, Goldfield, and Aurora were also studied by Taylor but in less detail. δD of the ore fluids was not determined, but $\delta^{18}O$ values were calculated, utilizing data from quartz, reasonable temperatures of

deposition (200° to 300°C assumed), and quartz-water fractionation factors at these temperatures. Taylor's calculated ranges in $\delta^{18}O$ of most ore fluids of these systems, excluding the Comstock, are rather similar to those of Bodie (O'Neil et al., 1973), but Taylor's Comstock values are about 5 per mil higher in $\delta^{18}O$. Even though δD is lacking from most of Taylor's data, all of these ore fluids are so low in ^{18}O that they must be chiefly meteoric water.

O'Neil and Silberman (1974) provide additional information on δD and $\delta^{18}O$ variations of the group, including ages and calculated waters of about 15 deposits; $\delta^{18}O$ values of the waters are calculated for an additional 8 deposits. Only 1 or 2 samples of quartz and inclusion fluids were analyzed from most deposits, with as many as 5 samples from others. O'Neil and Siberman recognize that reliable evaluation of each district cannot be made from only a few analyses but their data permit preliminary evaluation of the group, especially in view of the fact that their calculated $\delta^{18}O$ values of the ore fluids are in close agreement with those of Taylor (1973). Most of the waters of epithermal Au-Ag deposits, plotted as x's on Figure 2, are within 5 per mil in $\delta^{18}O$ from the meteoric water line. Two deposits that had the highest fluid $\delta^{18}O$ values are in sedimentary or metamorphic rocks, probably with initial $\delta^{18}O$ values much above the volcanic rocks of the type. A single sample from the Comstock (O'Neil and Siberman, 1974, not plotted) indicates an isotopic composition notably different from meteoric water and suggests a large magmatic component.

The gold deposits of the Cortez district, Nevada, are disseminated in Paleozoic sedimentary rocks but are similar in some other respects to "epithermal" Au-Ag deposits. Rye et al. (1974) present the isotopic analysis of a water that deposited a quartz veinlet in ore (Fig. 2; temperature of deposition, 200°C). Fluids that deposited the chalcedony of the ore body ranged in $\delta^{18}O$ from −6.8 to −0.7, but no δD data were obtained. The δD value from fluid inclusions in the quartz, −128 per mil, is close to the average δD value of the present meteoric waters, ∼ −130 per mil. Rye et al. conclude that the ore fluids were mainly meteoric water of variable extent of exchange of $\delta^{18}O$ with the sedimentary host rocks. The ^{13}C, ^{34}S, and lead isotope data from Cortez suggest derviation of these constituents and presumably also the gold from the sedimentary rocks associated with the ores.

Base Metal Deposits

No effort is made here to subdivide base metal ore deposits into genetic types. Abundant evidence is now available from this review and other papers of this symposium to indicate that temperature alone or pressure alone is not a valid criterion. Several active geothermal systems with fluids high in base metals are first reviewed, then deposits closely associated with volcanic and plutonic igneous rocks are considered and are followed by deposits that show no obvious relationship to igneous processes.

Salton Sea geothermal brine

The characteristics of this remarkable hot-brine geothermal system were first described in 1963 and its geologic setting, chemical and isotopic composition, probable origin, and other pertinent literature were reviewed by Craig (1966) Helgeson (1968), and White (1968) and are not repeated here.

The isotopic compositions of two samples of total fluid are shown on Figure 3A along with 4 analyses of cold to warm waters considered most representative of the meteoric waters of the system (Craig, 1966; White, 1968). All of these meteoric waters are 1.5 to 2 per mil higher in δO^{18} than would be expected from the trend line of most meteoric waters, perhaps because of nonequilibrium evaporation of the meteoric waters in the desert environment prior to seepage underground.

Strong evidence (Craig, 1966; Clayton et al., 1968; White, 1968) indicates that meteoric water is the main if not the only source of recharge; NaCl-rich evaporites are dissolved, the brine is then heated at least to 360°C, and heavy metals, calcium, potassium and some other constituents are leached from the local delta sediments, including most of the strontium and lead now dissolved in the brine (Doe et al., 1966). Exchange of ^{18}O has enriched the brine water by about 10.5 per mil as the clastic sediments have lost ^{18}O (Clayton et al., 1968) by about 10 per mil. The volume proportions of water to rock required for the exchange is approximately 1/1. Magmatic water alone is far too high in ^{18}O to produce the observed changes. Any magmatic water of initial $\delta^{18}O$ value of 6 to 9 per mil (Fig. 1) would increase in ^{18}O in contact with the delta sediments of initial $\delta^{18}O$ of ∼ +18 per mil. Instead, the actual water must be low enough in ^{18}O to decrease the $\delta^{18}O$ of the sediments to ∼ 8 per mil. Meteoric water alone can best do the job, requiring about 50 km³ for the probable volume of the reservoir (White, 1968, p. 314). If any magmatic water is present, the demand for total water increases and is about 200 km³ for equal parts of meteoric and magmatic water.

Four samples of pyrite from the host rocks and 4 samples of pipe scale high in silver and copper sulfides (Skinner et al., 1967; White, 1968) range in $\delta^{34}S$ from −1.4 to +3.0 per mil, permitting but not

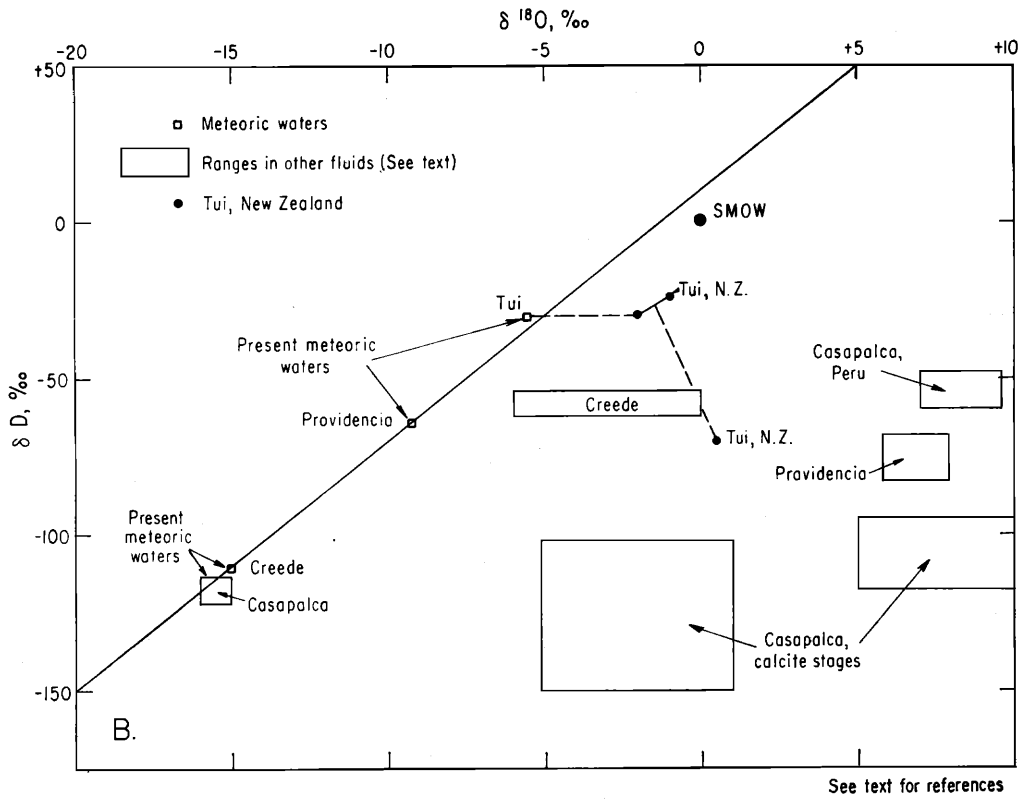$\delta\ ^{18}O,\ ‰$
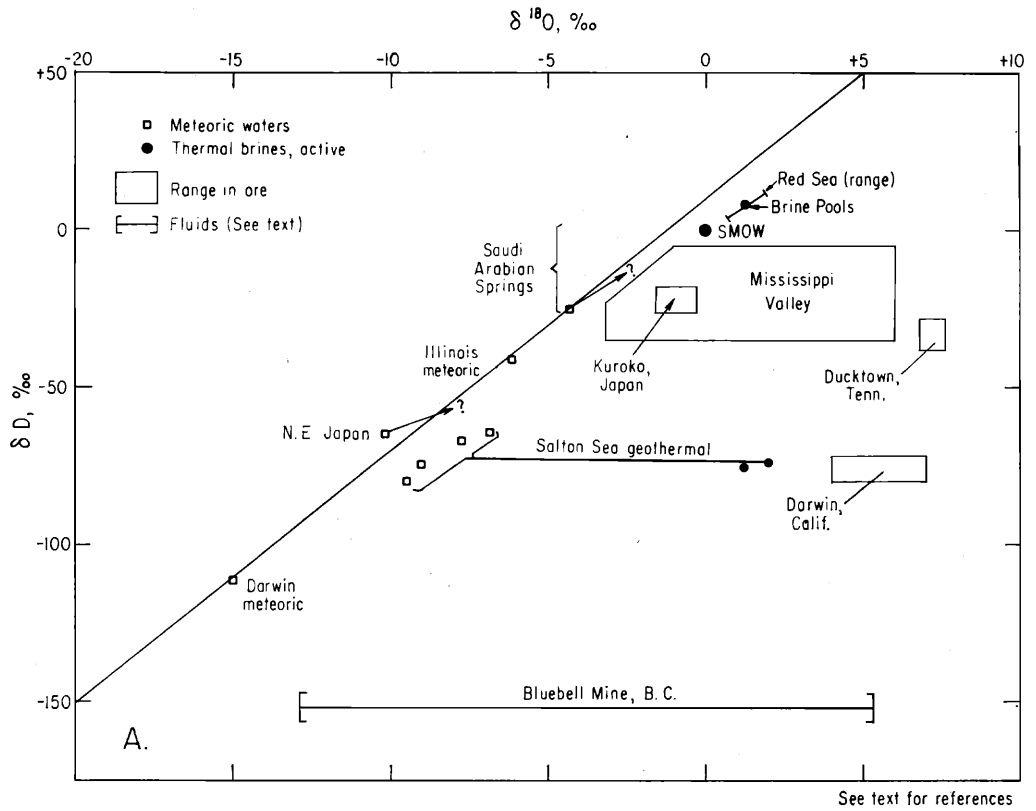

$\delta\ ^{18}O,\ ‰$

Fig. 3. A and B. Isotopic compositions of waters of base metal deposits.

proving, a deep-seated source for the sulfide. Most of the CO_2 of the fluids of the system is released in metamorphic reactions involving clastic calcite and dolomite (Clayton et al., 1968; Muffler and White, 1968) although some CO_2 of deep-seated origin may also be present.

Only meager heavy metal sulfides (other than pyrite) have been identified in cuttings and minor core recovered from the geothermal wells of the area. The brine system is of special interest, not because of known ore concentrations, but because it provides mechanisms and environments that could have produced large ore concentrations if more sulfide sulfur were available.

Red Sea hot-brine pools

Pools of hot brine localized in basins on the median trench of the Red Sea were discovered in 1964 and 1965 (Degens and Ross, 1969). Thirteen pools or basins of present or former activity are now known (Backer and Schoell, 1972). The brine pools, in spite of temperatures as high as 60.1°C and with active inflow as high as 104°C (Ross, 1972, Schoell and Hartmann, 1973), are gravitationally stable on the sea floor because of their high salinity ($\sim$ 26 per mil) and consequently their high density ($\sim$ 1.14 at 100°C). Thus, the brine pools have no evident sea-surface anomalies.

The pools (especially Atlantis II) and surrounding environments have been studied extensively, in considerable part because of the high metal contents of chemical sediments precipitated from the brines (Bischoff in Degens and Ross, 1969). Isotopic relationships are reviewed in many individual chapters of Degens and Ross (1969).

Craig's study (in Degens and Ross, 1969) of the chemical and isotopic compositions of the waters provides major keys for understanding these fascinating deposits. The isotope data from the brine pools are shown in Figure 3A relative to the total analyzed range in isotopic compositions of normal Red Sea waters. The plot shows that the brine pools are almost exactly at the midpoint of the known variations. The waters of the Red Sea are extensively evaporated relative to average ocean water because of the hot, dry environment and thus are enriched in the heavy isotopes. Craig found that waters with isotopic compositions of the brine water, less enriched in heavy isotopes, occur only near the southern sill of the Red Sea. He concluded that the brine pools were supplied by the Red Sea near the southern sill, presumably sinking under the sea floor and dissolving known NaCl-rich evaporites from the Red Sea's margins. Subsurface flow of 500 to 900 km is required by Craig's model, presumably along

the median trench of the Red Sea, with the brine somehow avoiding some basins of greater depth than those known to have hot brine.

Other models can account for the chemical and isotopic compositions of the hot brines but avoid the serious hydrologic problems of Craig's model. As one example, the hot brines may be recharged from adjacent flanks of the Red Sea, dominantly by highly evaporated sea water but with a smaller fraction of meteoric water from mainland Saudi Arabia. Six of seven isotope analyses of thermal and cold waters of coastal Saudi Arabia from $\sim$80 to 300 km east and southeast of the brine pools (unpub., D. E. White and J. R. O'Neil) lie precisely on the Red Sea line of Figure 3A but extending through SMOW to its intersection with the "meteoric water lines" at $\delta D = -25$ per mil. Any one of these waters could mix with highly evaporated Red Sea water without shifting the mixture from the common line; depending on the sample, 10 to 40 percent of meteoric water mixing with the main mass of Red Sea water would attain the brine pool composition. Probably after subsurface mixing of the two waters, NaCl-rich evaporites are dissolved and the brine then reacts with basaltic rocks, acquiring heavy metals, calcium, and some other constituents.

Regardless of the actual mechanism and specific sources of recharging water, the Red Sea is clearly the major source of the hot-brine water.

Creede, Colorado

The Creede district is the most thoroughly studied of the base metal deposits, formerly called "epithermal" (Bethke et al., 1973). The measured and calculated isotopic compositions of the ore-fluid waters are generalized on Figure 3B along with the isotopic composition of present meteoric water of the district. The ore and gangue minerals were deposited at temperatures of 190° to 265°C (median, 250°C); salinities ranged from 4 to 12 equivalent wt percent NaCl; the sulfides precipitated from solutions in which Σ sulfate $> \Sigma$ sulfide; $\delta^{34}S$ of the sulfide minerals is within the narrow range of -4.1 to $+1.7$ per mil, and $\delta^{34}S$ of sulfate of barite is $+19.8$ to $+31.3$ per mil.

Bethke and his associates conclude that the water of the ore fluids was dominantly meteoric in origin with δD value near -58 per mil, but $\delta^{18}O$ varied within a range of at least 6 per mil, presumably depending on extent of ^{18}O exchange with the volcanic country rocks.

The indicated δD of the meteoric water of the area in late Oligocene time was about 50 per mil higher than that of present-day meteoric water of the area (Fig. 3B). The indicated change in climate was

similar to, but larger than, the indicated change in the Bodie area over the last 8 million years.

Tui mine, Te Aroha, New Zealand

The Tui mine contains lead-zinc-copper-silver sulfides as open-space vein fillings with hematite, barite, cinnabar, and carbonates in hydrothermally altered andesites (Weissberg and Wodzicki, 1970); the deposit is on the margin of the "epithermal" Haurakigold district.

Robinson (1974) concludes that thermal waters of nearby Te Aroha hot springs and of postore stage 3 of the Tui mine are similar in δD to existing meteoric water (Fig. 3B) but are enriched in $\delta^{18}O$ by 3.5 to 4.5 per mil by "^{18}O-shifting". Fluid inclusions from earlier ore-stage galena, in contrast, are much lower in δD and slightly higher in $\delta^{18}O$. The ore fluid is similar in δD to hypothesized magmatic water but its $\delta^{18}O$ seems low for such an origin.

Robinson concludes from isotopic evidence that the sulfur is from graywackes underlying the andesites, perhaps with some magmatic sulfur; lead seems to have been derived from the graywackes. Weissberg and Wodzicki (1970) also utilize isotopic evidence but favor derivation of both lead and sulfur from magmatic sources.

Providencia, Mexico

The ore deposits of Providencia, Zacatecas, consist of pipe-like bodies of sphalerite, galena, and pyrite in Mesozoic limestone near a granodiorite stock (Sawkins, 1964; Rye, 1966). The age of the stock is about 40 m.y. and the ore deposits are about 38 m.y. according to Ohmoto et al. (1966).

Temperatures of filling of fluid inclusions in sphalerite, quartz, calcite, and fluorite are largely between 400° and 300°C, generally trending downward with time but with local reversals of as much as 20°C; late-ore stages of deposition continued down to 200°C (Sawkins, 1964; Rye 1966). Salinities of inclusion fluids generally range from 5 to 20 equivalent wt percent of NaCl, but some are as high as 40 percent with no obvious correlation with other parameters.

The D, ^{18}O, and ^{13}C values of fluid inclusions and hydrothermal calcites were analyzed by Rye (1966) and Rye and O'Neil (1968). The ^{18}O and ^{13}C content of the calcites increase progressively with time during the first 4 of 5 recognized stages of deposition, with each generation showing little scatter. The relationships indicate that these calcites did not exchange ^{18}O with late fluids and that ^{18}O and ^{13}C of the fluids remained approximately constant, with temperature as the principal variable. In the final calcite stage, ^{13}C decreased but ^{18}O continued to increase.

The δD values of the fluids were determined directly from fluid inclusions, ranging from −68 to −83 per mil. Most of Rye's data on $\delta^{18}O$ of the fluids were calculated, utilizing ^{18}O of the calcites, filling temperatures of inclusions, and calcite-water fractionation factors. Most calcites precipitated from waters of nearly constant $\delta^{18}O$ with time, ranging from 6.4 to 7.9 per mil. Direct analysis of $\delta^{18}O$ of water in fluid inclusions in sphalerites, with filling temperatures of 365° to 290°C from 3 ore bodies, ranged from 6.2 to 5.8 per mil (Rye and O'Neil, 1968), or slightly less than calculated values, but providing a satisfactory check on the calculated values.

The total indicated range in δD and $\delta^{18}O$ of the Providencia fluids is shown on Figure 3B. The range in $\delta^{18}O$ is close to, but slightly lower than, that expected of water in equilibrium with normal granitic rocks at magmatic temperatures, suggesting that some retrograde exchange at submagmatic temperatures has occurred (R. O. Rye, written commun., 1974). Also shown on Figure 3B is the approximate isotopic composition of present-day meteoric water near Providencia. The δD contents of the ore fluids and present meteoric waters are nearly identical, so other evidence is needed to prove that the ore fluid was predominently magmatic. The waters of fluid inclusions in postore and postoxidation calcites have δD values near −100 per mil, thus indicating that the meteoric water of the area has not been constant since ore deposition. Also, if meteoric water of initial $\delta^{18}O$ of −10 per mil had been an important part of the ore fluid, the observed range in $\delta^{18}O$ from 5.8 to 7.9 per mil throughout the hydrothermal activity is remarkably small and is the tightest clustering of values yet observed in a detailed study of a complex deposit (R. O. Rye, written commun., 1974). This deposit and the Salton Sea geothermal system illustrate the difficulties that exist in distinguishing between meteoric and magmatic waters in areas where the δD of the meteoric water is in the range of −50 to −80 per mil.

Casapalca, Peru

The base metal and silver deposits of Casapalca, Peru, contain pyrite, sphalerite, galena, and tetrahedrite in a gangue of quartz and minor calcite.

Fluid inclusion and paragenetic studies (Rye and Sawkins, 1974) indicate sulfide ore deposition over a temperature range of ∼370° to 280°C; salinity varied erratically from 4 to 40 equivalent weight percent NaCl; and local boiling of the ore fluids occurred. Isotope data indicate that $\delta^{18}O$ values of the sulfide-depositing ore fluids ranged from 3.6 to 9.6 per mil and that δD ranged from −48 to −60 per mil (Fig. 3B). In contrast, δD of postsulfide

inclusion fluids and of present meteoric waters has ranged from −96 to −151 per mil, or about 50 to 70 per mil lower than the ore fluids. Rye and Sawkins conclude that the main-stage ore fluids were "deep-seated" (probably magmatic?) in origin and that involvement of meteoric waters was restricted to the postsulfide stages of hydrothermal activity. This late activity extended from temperatures of about 280°C down to 200°C (and possibly continued without pause to the present time). Rye and Sawkins discounted the possibility that the local meteoric water during main-stage mineralization was much higher than now in δD or that climatic changes were abrupt and drastic enough to account for the deuterium contents of all postore fluids.

$\delta^{13}C$ of the hydrothermal fluids averaged about −6 ± 0.5 per mil during sulfide stages of deposition and ranged from −8.6 to −2.2 per mil during postsulfide calcite deposition. Sphalerite ranged in $\delta^{34}S$ from −0.4 to +2.4 per mil, thus indicating a very narrow range in $\delta^{34}S$ of the ore fluids that averages about 1.5 per mil. The ^{13}C and ^{34}S data in ore-stage fluids are interpreted as indicating a deep-seated origin, presumably from the mantle (Rye and Sawkins, 1974).

Pasto Bueno, Peru

The Pasto Bueno tungsten-base metal deposit consists of quartz veins near the upper intrusive contact of a 9.5-m.y.-old quartz monzonite stock (Landis and Rye, 1974). Fluid inclusion studies indicate high salinity (>20 wt percent NaCl), high temperature (400° to 500°C), and sporadic boiling of the fluids during the greisen and early vein stages. Ore fluids of the main vein and later vug stages had temperatures of 290° to 175°C and salinities of 17 to 2 wt percent NaCl.

The δD and $\delta^{18}O$ data are interpreted by Landis and Rye (1974) as indicating waters of magmatic origin during the greisen stage but as mixtures of meteoric and magmatic waters during the vein and vug stages; δD varied greatly during the later stages but $\delta^{18}O$ was nearly constant, interpreted by these authors as deep circulation of meteoric water, with $\delta^{18}O$ being buffered by large volumes of rock. Wolframite was deposited during periods dominated by meteoric water, but only magmatic water is indicated for the sulfide stages.

$\delta^{13}C$ of the hydrothermal CO_2 ranged from −4.1 to −11.9 per mil and is interpreted as indicating both sedimentary and deep-seated sources. $\delta^{34}S$ of sulfides ranged from −2.5 to +3.9 per mil, suggesting a deep-seated or mantle origin for the sulfur (Landis and Rye, 1974).

Kuroko deposits of Japan

Much attention has been given to these deposits in recent years because they are the clearest examples of massive sulfide deposits formed on or near the sea floor and in close association with silicic submarine extrusive volcanic rocks. Their characteristics, age, zoned mineralogy, stratigraphic relationships, and isotope geochemistry are summarized by Sakai and Matsubaya (1970, 1974) and Ohmoto and Rye (1974).

Most recent studies conclude that the ores were precipitated directly on the sea floor, thus requiring drastic changes in fluid compositions and saturated phases with time to account for the striking vertical (and horizontal) mineral zonation. However, this zonation and the coarse-textured crystallization may be better explained by continuing accumulation of chemical precipitates on or near the sea floor, but accompanied by continuing extensive diagenetic redistribution and reconstitution of constituents within each pile as activity continued. Changes may also have occurred after each pile was buried by new volcanic cover.

Inclusion fluids from sulfides are all within a narrow isotopic range, with δD from −26 to −18 per mil and $\delta^{18}O$ from −1.5 to −0.3 per mil (Fig. 3A). The isotope studies conclude that the ore fluids were probably dominantly sea water that convected deeply into the newly erupted volcanic rocks and probably mixed with some meteoric water from the nearby land areas. Ohmoto and Rye (1974) calculate that a small content of magmatic water may have been involved, but mixtures of sea water and meteoric water, combined with water-rock exchange of ^{18}O, seem more probable. Sakai and Matsubaya (1974) also consider the possible involvement of the kind of water here called "evolved connate."

Sulfur isotope data (Kajiwara, 1971; Sakai and Matsubaya, 1970; Rye and Ohmoto, 1974) and thermodynamic considerations are also satisfied by a convecting sea-water model that assumes initial $\delta^{34}S$ of +20 per mil from sea-water sulfate.

Darwin, California

The geology and ore deposits of the Darwin district are described by Hall and MacKevett (1962). The ore deposits are in carbonate rocks and siltstone of late Paleozoic age intruded by a quartz-monzonite stock. Rocks within 4,000 feet of the stock are metamorphosed to marble and calc-silicate rocks, and the sulfide ore deposits are localized in the metamorphic rocks.

The isotope geochemistry of the deposits, studied by Rye et al. (1974), has shown that δD of the fluids ranged from −62 to −70 per mil. The $\delta^{18}O$ values

of calcite, when utilized with water-calcite fractiona-
tion factors at temperatures indicated by fluid in-
clusions and other data, indicate that $\delta^{18}O$ of the ore
fluids ranged from about $+4$ to $+7$ per mil. These
narrow ranges (Fig. 3A) are compatible with a
magmatic origin and provide no evidence for in-
volvement of meteoric water (present $\delta D \sim -110$
per mil).

$\delta^{34}S$ of all sulfides range from $+4.4$ to -5.7 per
mil (Rye et al., 1974). The differences between co-
existing galena and sphalerite are consistent and in-
dicate equilibrium deposition at temperatures averag-
ing $\sim 330°C$. The data indicate that $\delta^{34}S$ of total
hydrothermal sulfur was close to $+1$ per mil, with
variations being due to differences in P_{O_2} and pH
of the fluids (Rye et al., 1974).

The $\delta^{13}C$ contents of hydrothermal calcites range
from -3.6 to -5.8 per mil (PDB), which is slightly
lower than most limestone carbon ($+4$ to -4 per
mil). This suggests that most hydrothermal CO_2 is
not from the limestone host but is of deeper origin;
this range is within the commonly assumed magmatic
or mantle range.

Bluebell mine, British Columbia

Ohmoto and Rye (1970) have studied the fluid
inclusions and isotope geochemistry of the lead-zinc
deposits of the Bluebell mine and they also briefly
reviewed earlier work (Ohmoto, 1968) on the
geologic setting, mineralogy, and paragenesis of the
deposits.

The massive sphalerite-galena ores are largely re-
placements of limestones at temperatures above
450°C. Most of the published data, however, con-
cern the last 10 percent of ore, sulfides, and gangue
quartz and carbonates deposited in vugs at tempera-
tures from $\sim 450°C$ down to $\sim 320°C$. Salinity of
the fluids changed gradually from about 10 weight
percent equivalent NaCl down to ~ 3 percent. The
$\delta^{18}O$ of the fluids during the vug stage also changed
gradually from $\sim +5$ to -13 per mil as tempera-
tures decreased. During these progressive changes,
however, δD remained almost constant at -152 ± 5
per mil (Fig. 3A). The ^{13}C composition of the
fluids was also nearly uniform at -5.5 per mil.

The nearly constant δD of the late-stage ore solu-
tions is interpreted by Ohmoto and Rye as indicat-
ing a dominantly meteoric origin for the water, with
$\delta^{18}O$ variations reflecting the mixing of two meteoric
waters, one of which had previously exchange ^{18}O
by reaction with high-^{18}O rocks at high tempera-
tures. According to H. Ohmoto (written commun.
1974), recent unpublished δD and $\delta^{18}O$ data on the
earliest sulfide-stage fluids are identical in range to

the late-stage fluids and all are dominated by meteo-
ric water.

Mississippi Valley deposits

These deposits have been described and reviewed
many times; the isotope data and earlier literature
are summarized by Heyl et al. (1974). The origin
of the deposits has been especially controversial, in
considerable part because of the absence or scarcity
of igneous rocks within the region. At least 10 dif-
ferent origins or significant variants have been
proposed (reviewed by White, 1968). The tenuous
possibilities for igneous affiliation were not dif-
ficult to explain by syngenetic and other nonmag-
matic models but provided serious problems for many
geologists who assumed that hydrothermal ore fluids
must be magmatic.

Fluid inclusion and isotope studies, largely by Hall
and Friedman (1963, 1969) and Roedder (1972),
are almost wholly responsible for our recent advances
in understanding and negate most of the possible
origins previously suggested. Temperatures of
homogenization of fluid inclusions are relatively low
in most deposits, ranging from $\sim 70°$ to $135°C$ in
sphalerite and somewhat lower in postore calcite, but
are as high as 180°C in fluorite and sphalerite of
southern Illinois and Kentucky (Pinckney, 1966;
Roedder, 1972).

The inclusion fluids consist of Na-Ca-Cl brines,
generally with 5 to 10 times the salinity of sea wa-
ter during the fluorite and sulfide stages but declin-
ing to less than 3 times that of sea water during
postore calcite and sulfate stages in southern Illinois
(Hall and Friedman, 1963; Roedder et al., 1963;
Roedder, 1972). The salinities and constituent pro-
portions are remarkably similar to oil-field brines of
the Mississippi Valley (Hall and Friedman, 1963)
through the ore-forming stages (except for tem-
perature-dependent constituents such as potassium),
but dilution by meteoric water evidently occurred
during deposition of the postore gangue minerals.

The δD values of the fluid inclusion brines range
from about -5 to -35 per mil (original data of Hall
and Friedman, 1963, converted to SMOW standard).
The $\delta^{18}O$ of late-stage fluids, as calculated from hy-
drothermal carbonate minerals from the upper Mis-
sissippi Valley, ranged from $+0.4$ to -1.6 per mil
and from the Tri-State District, were about -3
per mil (Hall and Friedman, 1969). In addition,
Hall (written commun., 1973) calculated a $\delta^{18}O$ of
$+4 \pm 2$ per mil for the fluid that deposited hydro-
thermal quartz of the Deardorff mine of southern
Illinois.

The area within the solid lines shown on Figure
3A as "Mississippi Valley" is defined by the data

from southern Illinois, cited above, but arbitrarily limited on the upper left by the meteoric-water line. This range of data also includes nearly all isotope analyses of present Illinois oil-field brines of high salinity (>2 gm-equivalents per liter, or ~7 to 12 percent salinity; Clayton et al., 1966) which were plotted individually by White (1968, p. 306) and are not repeated here.

Heyl et al. (1974) review the isotope data and conclude that the main ore fluids were heated oil-field brines, perhaps circulating in fracture systems deep into pre-Paleozoic basement rocks, to explain the lead isotope data. However, Doe and Delevaux (1972) conclude that the lead of southeast Missouri is probably derived from the Lamotte sandstone underlying the ore horizon and is not from carbonate or basement rocks. Heyl et al. (1974) interpret the $\delta^{34}S$ data as indicating connate or evaporite sulfate of marine origin, with possible isotopic disequilibrium between sulfide and sulfate sulfur. Each district in the Valley has a distinctive isotopic pattern that reflects direction of fluid flow, heat source, and localization of major deposits. The abundance of fluid inclusions of petroleum provides additional support for the "evolved-connate" model.

Jackson and Beales (1967) suggested that mixing of two fluids is one means of avoiding the serious problem of transporting lead and zinc with sulfide in the same fluid at low temperatures. Sulfide-deficient brines of deep circulation could have provided the metals, with other brines supplying the sulfide resulting from bacterial reduction of SO_4 in local carbonate reservoirs low in iron. Other models have also been proposed (individual authors in Brown, 1967), several of which depend on metastability.

The problem of accounting for the anomalous temperatures of the Mississippi Valley deposits, which are too high for normal geothermal gradients (White, 1968, p. 311), still has no clear answer but is probably best satisfied by deriving the metal-bearing fluids from the deep sedimentary basins and perhaps also by involving deep circulation into crystalline basement rocks. Regional geothermal gradients significantly above present gradients at the time of mineralization are also a possibility but are not yet supported by any independent evidence.

Ducktown, Tennessee

The massive sulfide ore deposits of Ducktown, Tennessee, consist of pyrrhotite, pyrite, chalcopyrite, sphalerite, specularite, and magnetite associated with high-grade metamorphic silicate-carbonate mineral assemblages. Addy and Ypma (1973) favor a premetamorphic and probably syngenetic origin for the original deposits, which were later metamorphosed

along with the enclosing rocks; late-stage metamorphic or hydrothermal modifications are also indicated.

The rocks in the alteration zone surrounding the massive sulfide ore bodies are depleted in $\delta^{18}O$ by about 2 per mil as compared to the more distant country rocks (Addy and Ypma, 1973). δD values in hydrous minerals found in both the alteration zone and country rock are nearly identical for each mineral, ranging from −68 to −77 per mil for biotite, −62 to −69 per mil for chlorite, and −49 to −54 per mil for muscovite.

The isotopic composition of the water of the ore zone ranged from +6.8 to 7.6 per mil in $\delta^{18}O$, −28 to −38 per mil in δD, and −10 to −16 per mil in $\delta^{13}C$ (Addy and Ypma, 1973). This range in δD and $\delta^{18}O$ is shown on Figure 3A. The authors imply a metamorphic origin for the fluids that last affected the ore deposits.

The isotopic compositions of several indicated metamorphic waters are considered briefly here and in relation to some mercury deposits of California. A broad discussion of the chemical and isotopic compositions of metamorphic waters is outside the scope of the present paper, but the interested reader is referred to two important forthcoming papers on such waters by Rye and Schuiling (in press) and Rye and Rye (1974).

Copper-Molybdenum Deposits

Porphyry copper deposits

Some data on the temperatures of filling and the salinities of fluid inclusions of porphyry copper deposits have been published by Roedder (1971) and Nash (1971). The isotopic compositions of the fluids associated with three porphyry copper deposits have been calculated by Sheppard et al. (1971), utilizing analyzed δD and $\delta^{18}O$ of hydrous hydrothermal minerals and available data on temperatures of formation and water-mineral fractionation factors; no direct analysis of the fluids from fluid inclusions has yet been published.

δD and $\delta^{18}O$ of hydrothermal biotites from three districts, Santa Rita, Bingham, and Ely (Sheppard et al., 1971, p. 523), are all nearly identical. If the same temperatures of formation (assumed 650°C) and fractionation factors are used, the calculated compositions of the waters that were associated with these biotites are also nearly identical. The calculated waters (Sheppard et al., 1971) plot within the area shown on Figure 4 and are also within the range for magmatic waters suggested by Figure 1 and its supporting references.

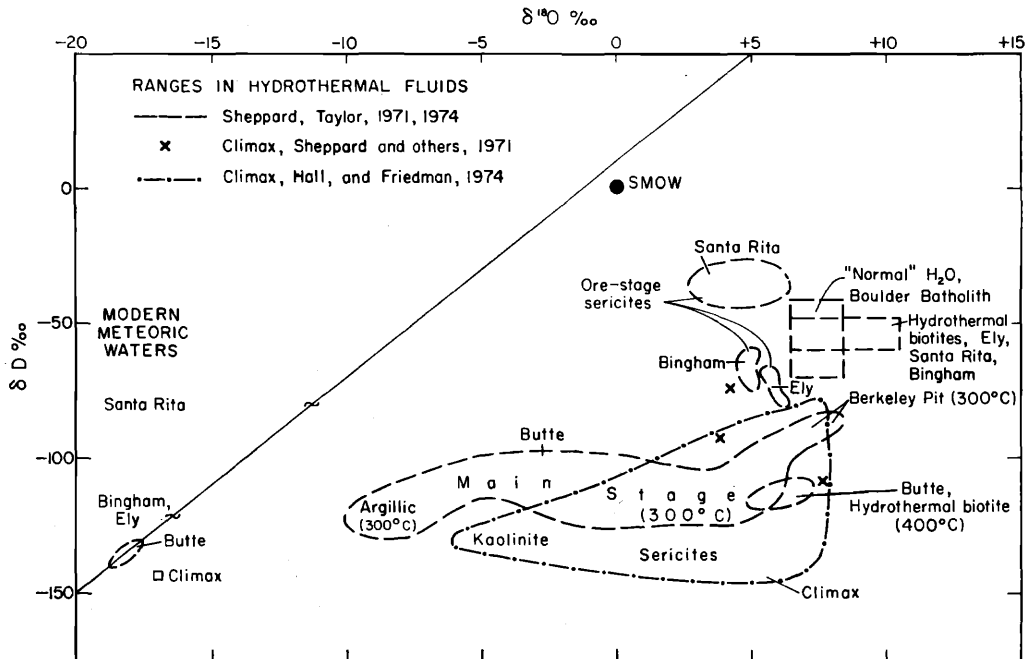Water compositions of the main-stage ore fluids were also calculated by Sheppard et al. (1971) from

FIG. 4. Isotopic compositions of waters of some copper and molybdenum deposits.

isotope analyses of the closely associated sericites. The water compositions for the sericites of the three districts are shown on Figure 4; they differ somewhat, with Santa Rita fluids being higher in δD by about 30 per mil than those of Bingham and Ely. Also shown on Figure 4 are the approximate isotopic compositions of modern meteoric waters of the same districts. Those of Santa Rita are about 40 per mil higher in δD than those of Ely and Bingham.

The ore-stage fluids of Bingham and Ely could be explained by mixtures of meteoric and magmatic waters but are dominated by the latter. The Santa Rita fluids, however, cannot be explained by any known mechanism involving meteoric water similar in composition to those of modern waters. Sheppard et al. (1971) suggest that the meteoric water of the time was 40 to 50 per mil higher in δD than modern waters. The ore-stage meteoric water presumably increased in ^{18}O by water-rock exchange and perhaps also by mixing with some magmatic water.

Butte, Montana

The ore deposits of Butte, Montana, have probably been studied more extensively than any other mining district, but the first data that permit isotope characterization of the ore fluids of the Butte district were obtained by Sheppard et al. (1971) and Sheppard and Taylor (1974). All water compositions were calculated by Sheppard and Taylor from hydrous hydrothermal minerals, utilizing available temperatures of formation and water-mineral fractionations, and are generalized on Figure 4.

The waters associated with Butte's early hydrothermal biotite differ greatly from those of the three porphyry copper deposits reviewed above. The calculated δD content of Butte's waters averages about −115 per mil, which is closer to modern meteoric water (∼ −135) than to the "magmatic waters" of Figure 1 (∼ −60 ± 20 per mil) or the "normal" water coexisting with biotite and hornblende of the Boulder batholith (∼ −55 ± 15 per mil; Sheppard and Taylor 1974).

The large amoeba-shaped area of Figure 4 includes most compositions calculated for main-stage ore fluids, including fluids of Berkeley Pit ores, and for advanced argillic alteration elsewhere (300°C assumed for all calculated hydrothermal water compositions by Sheppard and Taylor). The most conspicuous feature of the Butte fluids is their large range in δ^{18}O in comparison to their small range in δD. The large variations in δ^{18}O indicated by the hydrous minerals are also supported by the data from hydrothermal quartz (Garlick and Epstein, 1966). Sheppard and Taylor (1974) conclude that meteoric waters were dominant in all stages of mineralization, and they found no specific evidence for ore-stage involvement of the "normal" (magmatic?) water that equilibrated with igneous biotite and hornblende of the Boulder batholith (Fig. 4).

What are the possibilities for large original variations in both D and ^{18}O in the ore fluids with time, but with late-stage meteoric waters permeating all mineralized rocks at high temperatures and exchanging hydrogen more readily than oxygen and more extensively at Butte than in the porphyry copper deposits? Sheppard and Taylor favor a search for early hydrothermal biotites that might not be affected by main- and late-stage processes. Perhaps critical evidence can also be provided by direct analysis of the δD contents of fluid inclusions in quartz and sulfide minerals.

Climax, Colorado

The ore deposits of Climax, Colorado, are similar in some respects to porphyry copper deposits except for the great dominance of molybdenum over copper. The geologic setting and general characteristics of the deposits are described by Wallace et al. (1968) and summarized by Hall et al. (1974).

The isotopic compositions of fluids associated with Climax were first calculated by Sheppard et al. (1971) from D and ^{18}O contents of hydrothermal micas and quartz, utilizing assumed temperatures of formation and experimental water-mineral fractionation factors.

Hall et al. (1974) made a detailed study of fluid inclusions and isotopic compositions of hydrothermal minerals of the Climax deposits. Temperatures of filling and δD values of fluid inclusions were measured. The large triangular area shown on Figure 4 is generalized from isotopic data on water compositions measured and calculated by Hall et al. (1974). The apex of the triangle is controlled by a pegmatitic muscovite with a calculated water composition close to the area of "magmatic" waters of Figure 1. The left corner of the triangle is based on calculated waters associated with hydrothermal kaolinites, and the waters associated with sericites of the Climax ore bodies plot throughout the main body of the triangle (Hall et al., 1974).

Two of the three water compositions calculated by Sheppard et al. (1971) also plot within the triangle (shown as x's on Fig. 4) and the third calculated water plots just to the left of the apex of the triangle. Thus the agreement between measured and calculated δD contents of the ore fluids, as indicated by the two studies, is reasonably satisfactory.

Hall et al. found that salinity and D contents of the inclusion fluids are mutually related, with early ore fluids having salinities as high as 18 percent equivalent NaCl with δD of -92 percent and some late fluids having salinities of < 1 percent NaCl and δD of -145 per mil.

Hall et al. (1974) conclude that progressive mixing of isotopically heavy and light waters occurred with time. The late-stage light water was similar to modern meteoric water; the early heavy water was probably either magmatic water or meteoric water with a much higher δD value than modern meteoric water (by about 60 per mil). The lower right corner of the triangle of Figure 4 constitutes an intriguing genetic problem. If resulting from interaction with meteoric water, a very low ratio of water to rock is required; the rock must be high in ^{18}O and not previously reacted with meteoric waters. A high salinity would be expected if leaching supplies most of the salts of hydrothermal fluids, as proposed by Ellis and Mahon (1967), but would not be expected if the salts in such systems are largely supplied by a small proportion of very saline magmatic fluid, as favored by White (1969). Thus, the occurrence of high-δD values in fluids with high salinity and vice versa (Hall et al., 1974) seem to favor magmatic water as the major supplier of dissolved salts, rather than previously unleached rocks.

General Characteristics of Ore Fluids

This paper emphasizes the isotopic compositions of the waters of ore fluids, viewed as the most diagnostic approach for determining the origins of the fluids and their dissolved constitutents. A comprehensive review of *all* chemical and isotopic data on the fluids is not attempted here but representative data are included to indicate the general trends. Table 1 summarizes the general characteristics of the fluids of the ore deposits considered here.

TABLE 1. General Characteristics of the Ore Fluids Reviewed in This Report

	Hg	Epithermal Au-Ag	Base Metals $\pm$ Ag	Porphyry Cu, Mo
Salinity, %	<3?	<2	>2 to ~40	~5 to 60
Dominant dissolved constituents	Na, HCO_3, CO_2, B, NH_3	Na, Cl, HCO_3, SiO_2	Na-Ca-Cl	Na-Ca-Cl
Temp. range, °C	<200?	150 to 300	75 to ~500	>250
Driving energy	Magmatic heat & gravity	Magmatic heat	Magmatic heat + gravity?	Magmatic heat

Salinity

Salinities of fluids presently associated with Hg deposits (White, 1967; Barnes and others, 1973a) are less than ~3 percent, but these deposits are all relatively small and are in geologic settings that are not typical of many other Hg deposits. However, the three analyses of fluid inclusions in quartz from Hg-Sb deposits of the USSR (Roedder, 1972, p. JJ159) are similarly low in salinity (<1%).

The fluids of epithermal Au-Ag deposits are also low in salinity and generally do not exceed 2 percent (J. T. Nash, 1972). Probably because the salinities and densities of Hg and Au-Ag ore fluids are so low, such waters are relatively common near the earth's surface and discharge as thermal springs (White, 1955, 1967).

In contrast, the fluids of base metal deposits generally have salinities above 2 percent and most commonly are from 5 to 40 per mil (Roedder, 1972, p. JJ159-160, and data reviewed here); such high-density fluids are almost never discharged at the surface as thermal springs (White, 1967), thus in part explaining why early hot-spring studies contributed so little to the understanding of the origin of base metal ore deposits. Normally such saline waters are discharged only after very extensive dilution with meteoric water. The fluids of associated fluorite and barite stages of base metal deposits are also generally brines, but some other postmineral fluids are dilute and low in density, thus indicating eventual flushing and replacement of brines by meteoric waters.

The fluid inclusions of porphyry copper deposits are generally saline brines ranging from ~5 to 60 percent in salinity (Roedder, 1971; Nash, 1971, and oral commun.) but main-stage and postore fluids are generally in the low part of this range.

No systematic study of the salinities of Butte fluids has been published. Hall et al. (1974) found that the salinity of Climax hydrothermal fluids is directly related to deuterium content, with salinity ranging up to 18 percent. The fluids of lowest δD content are also least saline and are similar to meteoric water.

Dominant dissolved constituents

Present thermal and mineral waters of mercury deposits (White, 1967; Barnes et al., 1973b) are nearly all high in $NaHCO_3$, B, NH_3, and free CO_2; some are relatively high in chlorine but others are very low. The isotopically analyzed waters that are closest to the meteoric water line (Fig. 1) are generally dilute and may have little relationship to the earlier ore fluids.

Only a few fluid inclusions of mercury deposits have been chemically analyzed but the three listed by Roedder (1972, p. JJ159) are all $NaHCO_3$ waters, with $HCO_3 >> Cl$. Roedder (1972, p. JJ136) has also identified liquid CO_2 inclusions in quartz from a mercury deposit. Thus the scanty data, not yet conclusive, point to high contents of CO_2 (and, therefore, moderate to low in pH) as an important chemical characteristic of mercury ore fluids.

Dominance of Na, Ca, and Cl characterizes the analyzed waters and fluid inclusions associated with base metal and copper deposits (Hall and Friedman, 1963; White, 1967, 1968; Rye and Haffty, 1969; and Roedder, 1972). Because the minute quantities of fluids from inclusions are difficult to analyze, most recent studies report total dissolved constituents as "equivalent NaCl" from freezing-stage data (Roedder, 1972), and relatively little effort is spent in analyzing individual chemical constituents.

Natural thermal and mineral waters high in base metals and Cu are characterized by high salinity and relatively high Ca/Na ratios (White, 1967, 1968) and thus are consistent with available data from fluid inclusions of ore deposits (Roedder, 1972).

Temperature range

For many years temperature was viewed as being exceedingly important and perhaps dominant in controlling metal transport and deposition. Recent abundant data on filling temperatures of fluid inclusions indicate much overlap in depositional temperatures of deposits of differing type. Although temperature undoubtedly is an important factor, other characteristics of the chemical environment such as salinity, pH, f_{O_2}, f_{CO_2}, and proportions of metals and sulfide species (Rye and Ohmoto, 1974) are probably of greater importance.

The temperatures of mercury deposition are likely to have been relatively low (White, 1967, p. 610), probably below 200°C in most deposits and near 100°C in some deposits; data on filling temperatures of fluid inclusion in mercury deposits are lacking and are much needed. Most epithermal Au-Ag deposits formed between 135° and 330°C (Nash, 1972), with 200° to 300°C probably being most common.

Fluid inclusion studies of base metal deposits demonstrate that some deposits formed at temperatures as low as 75°C but others probably ranged as high as 500°C (Ohmoto and Rye, 1970; Landis and Rye, 1974), with 250° to 400°C being most common. Thus, the base metal deposits span almost the total temperature range of hydrothermal ore deposits. Obviously, other characteristics of these fluids must be more important than temperature alone.

Copper and molybdenum of Butte, Climax, and the porphyry copper deposits were largely emplaced by brines at temperatures above 300°C, but postore

minerals formed at much lower temperatures, perhaps as low as 100°C.

Nearly all of the temperatures cited above are within the range now being explored in the worldwide search for utilizable geothermal energy. Brine systems provide the only known examples of temperatures much above 300°C, with two at least as high as 360°C (Helgeson, 1968; White, in press). The dilute systems with salinities below 1 percent rather commonly attain 250° to 300°C, but higher temperatures have not yet been identified.

Driving energy

Magmatic heat has probably been essential in supplying the energy of most hydrothermal systems. Localized heating results in thermal expansion of pore liquid and promotes convection and deep circulation of meteoric water. Sufficient thermal expansion of a brine, regardless of its salinity, permits a convection system to be set up, provided that permeability is adequate. Dilute and initially cold meteoric water can displace brine in some circumstances; the two waters can mix, or the dilute water can remain above the brine in a gravitationally stable relationship, depending on local conditions (Helgeson, 1968; White, 1968, p. 329–330).

Gravity is the dominant factor in explaining the escape of fluids from sediments undergoing compaction and of fluid escaping during progressive metamorphism.

Sources of Constituents of Ore Fluids

Water

As mentioned previously, the sources of the waters of ore fluids are the principal focus of this paper (Table 2). The present waters most intimately associated with the mercury deposits of the California Coast Ranges differ significantly in isotopic composition from the meteoric waters of each area (White et al., 1973; Fig. 1); their characteristics are best explained by metamorphic and "evolved-connate" origins. Only sparse data are yet available from fluid inclusions of mercury ore deposits, but these

suggest similarities to the active systems of California and New Zealand that have been studied.

The waters of most epithermal Au-Ag deposits are clearly dominated by meteoric water to such an extent (Fig. 2) that participation of any other water has been questioned. As much as 5 percent of magmatic water would be high enough to explain the persistence of soluble chemical constituents in systems probably active for hundreds of thousands of years but would be low enough to be unrecognizable in most systems by differences in D content as compared to nearby meteoric waters. O'Neil and Silberman (1974) help to confirm this tentative conclusion by finding one example of ore from the Comstock Lode with fluid inclusions appropriate in δD value for magmatic water. Small proportions of other kinds of waters are also likely to be involved, such as "evolved-connate" and metamorphic waters, but supporting evidence is presently lacking.

Base metal ore deposits as a group differ greatly in detailed characteristics, indicated temperatures of deposition, and indicated origin of dominant water. The Red Sea brine pools provide clear evidence of dominance by Red Sea water; whether this is the sole supply or whether a small part is derived from adjacent land areas or from some other source is not known. Similar questions concern the Kuroko ore fluids of Japan; ocean water is surely dominant but a small percentage of some other water seems probable (Sakai and Matsubaya, 1974; Ohmoto and Rye, 1974). Mississippi Valley ore fluids must have been dominantly "evolved connate", but a little magmatic water could be present in southern Illinois and Kentucky (Heyl et al., 1974). Meteoric water alone, with salts being supplied by evaporites, probably explain the Salton Sea geothermal system (White, 1968) and perhaps also the Bluebell deposit of British Columbia (Ohmoto and Rye, 1970). Late-stage flushing by meteoric water is almost universally indicated, with Providencia being the principal likely exception.

The deposits formerly classed as "epithermal" base metal, including Creede, Colorado (Bethke et al.,

TABLE 2. Sources of Constituents of Ore Fluids of Various Metals

	Hg	"Epithermal" Au-Ag	Base metals ± Ag	Porphyry Cu, Mo
H_2O	Varied	Meteoric + magmatic?	Varied	Magmatic + meteoric
Cl	Varied	Magmatic?	Varied	Magmatic + others?
S	Magmatic + others?	Magmatic?	Varied	Magmatic
C	Varied	Magmatic?	Magmatic + others?	Magmatic + others?
Metals	Metamorphic + magmatic?	Magmatic?	Varied	Magmatic + others?

1973), and Tui, New Zealand (Robinson, 1974), may be similar to the "epithermal" Au-Ag deposits except that the ore fluids of the latter may generally be less saline. Meteoric water was probably dominant in these base metal ore fluids, but some water of magmatic origin may have been involved, especially in the Tui deposits. Casapalca, Providencia, and Darwin provide the clearest evidence for high proportions of probable magmatic water; meteoric waters were either absent or were largely restricted to postore stages.

The fluids initially responsible for the ore-metal concentrations of Ducktown, Tennessee, left no direct evidence of their nature or origin. Some evidence favors syngenetic or early diagenetic processes, perhaps similar to those of the Kuroko deposits of Japan and the Red Sea geothermal systems, with sulfide being provided locally on the sea floor, at least in part by bacterial reduction of sulfate. Regardless of the mechanism of initial emplacement of the Ducktown ore metals, the fluids involved in any late redistribution and reconstitution were almost certainly metamorphic in origin.

The fluids associated with Climax and with porphyry copper deposits were initially dominated by magmatic waters, but some meteoric involvement is indicated during ore-emplacement stages and became increasingly dominant during postore stages. No positive evidence is yet available for magmatic water in the Butte hydrothermal sytem, although in places the Boulder batholith still retains the imprint of probable magmatic water that differed in D content from the meteoric waters of the area. In all hydrous minerals of these Cu-Mo deposits, exchange of D from early magmatic-dominated waters by H from later meteoric-dominated waters may be an important phenomenon, especially where pervasive penetration by later waters occurred at temperatures above 300° C.

Chloride

Most ore fluids contain chloride as the dominant anion, with relative dominance generally increasing with salinity. The origin of the chloride cannot be determined directly but possible origins must be consistent with geologic environment and deduced origin of the water. Thus, if a magmatic origin of the water is indicated, the chloride is also likely to be magmatic; if ocean or "evolved-connate" waters are indicated, the chloride is presumably from sea water; and if chloride is anomalously high for the deduced origin of a water, NaCl-rich evaporites are a likely explanation for the anomaly. For the Red Sea and Salton Sea systems (~26 percent salinity), this assumption is strongly supported by Br/Cl ratios in

both systems; bromine is so low that NaCl-rich evaporites provide the most reasonable source for the excess halogens.

Reliable analytical methods are needed for bromine and chlorine in fluid inclusions. The oil-field brines of the Illinois basin, for example, are higher in Br/Cl ratio than sea water. Similar Br/Cl ratios in fluid inclusions of Mississippi Valley ore deposit would add strong support for the models involving "evolved-connate" waters.

The source of the chlorine of the brines of the Bluebell deposit is not yet certain. Meteoric water plus evaporites seem to be supported by recent conclusions (Rye and Ohmoto, 1974) that part of the sulfur is derived from evaporite sulfate.

Sulfur and carbon

These constituents are not considered in detail here, but their isotope geochemistry is reviewed by Rye and Ohmoto (1974). These constituents may differ in origin from the dominant water, the halogens, or the metals of an ore fluid, but the deduced origins of each must be compatible with, even though different from, the others. The active Salton Sea geothermal system provides an especially clear example of varied origins if present deductions (White, 1968) are correct: The water is dominantly or entirely meteoric; the halogens are largely from evaporites; the carbon of CO_2 is largely but perhaps not entirely from metamorphic reactions of clastic carbonate and silicate minerals; the sulfide may be from a volcanic and ultimately a mantle source; and the lead, strontium, and some other metals are largely from exchange reactions involving Colorado River delta sediments or their metamorphosed equivalents.

Elsewhere in near-magmatic environments, magmatic sources of sulfur and CO_2 are commonly indicated by isotopic evidence, but other origins must also be considered. An example is the Kuroko deposits of Japan, which are closely associated with volcanism but oceanic sulfate partially reduced to sulfur is indicated by the isotope data. In fact, most syngenetic or diagenetic base metal and copper deposits were probably emplaced at such low temperatures that adequate sulfide probably could not be transported with the metals in the same solution. Other models that should be considered for such deposits involve the mixing of two solutions with one providing the metals and the other providing the sulfide (Jackson and Beales, 1967); bacterial production of sulfide from sulfate; inorganic reduction of sulfate by one of several mechanisms; inorganic decomposition of sulfur-containing organic compounds (Skinner, 1967); and transport in supersaturated solutions.

Metals

Lead and strontium are the only metals of ore deposits that have isotope variations utilizable as tracers for origin, but these two metals are immensely useful in indicating the probable origins of associated metals that lack significant isotope variations. The isotopes of lead are reviewed by Doe and Stacey (1974) and Zartman (1974), and those of lead and strontium with respect to Mississippi Valley deposits by Heyl et al. (1974).

Hot magmatic rocks may be the sources of the metals of many ore deposits, even in systems dominated by water of some nonmagmatic origin. A given fluid adequate in temperature and composition to remove metals from a magmatic environment, however, is also competent to extract metals from other rocks with which the fluid is in intimate contact. The Salton Sea and Red Sea brines again provide convincing examples that such processes do occur.

Conclusions

This review provides abundant support for earlier conclusions that ore fluids do indeed have varied origins. The generation of an ore deposit requires favorable combinations of circumstances. Source rocks must supply the metals; an adequate physical and chemical environment permits selective concentration of metals in a fluid phase; and the fluid must then migrate to some other environment where chemical and physical conditions are appropriate for selective deposition. In some environments perhaps only physical or chemical changes are required (not considered in detail here), or only dilution by meteoric water may be adequate to produce ore deposition. In other environments a necessary constituent such as sulfide may be required from a second fluid or by inorganic or bacterial reduction of sulfate.

The mixing of two fluids may frequently be involved, but this possibility has not yet been accepted by most geochemists and economic geologists. Of the forty deposits and districts considered in this review, only Providencia and Darwin provide evidence that mixing was probably *not* involved; data from Casapalca indicate postore flushing by meteoric water; four mercury deposits (Ngawha, Sulfur Bank, Mt. Diablo, and Altoona), Ducktown, and the Salton Sea geothermal system provide no evidence for or against the mixing of solutions. However, in contrast, Wilbur Springs, Abbott, the Kuroko deposits, Tui, Pasto Bueno, three porphyry copper deposits, and Climax all show isotopic or chemical evidence interpreted by the authors of individual studies as indicating the mixing of waters *during* ore deposition; the Red Sea brine system, Bluebell, and the

Mississippi Valley deposits may have involved the mixing of waters but the evidence is less conclusive; and the ore fluids of all epithermal Au-Ag deposits, Creede, and Butte are interpreted to be either *entirely* meteoric, or dominantly meteoric with small fractions of other waters (magmatic?) not distinguishable by isotopic evidence.

The mixing of solutions would help to explain the abrupt bottoming of many ore deposits. Especially if one solution is higher in temperature, more saline, and higher in contents of ore metals than the second solution, the intermediate temperature and salinity of mixture would decrease the stability of metal-chloride complexes (Helgeson, 1964) and favor precipitation of sulfides.

The problems of finding ore and predicting behavior would be far easier if simple models actually prevail. But our long-continued search for adequate simple models is not yet satisfied; if these tentative conclusions are correct, we must accept diversity.

Acknowledgments

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