

## SULPHUR BANK MINE, CALIFORNIA: AN EXAMPLE OF A MAGMATIC RATHER THAN METAMORPHIC HYDROTHERMAL SYSTEM?

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## ABSTRACT

Sulphur Bank mine hydrothermal system (218°C) is surrounded by the youngest eruptions in the Clear Lake volcanic field, and nearby conductive thermal gradients exceed 100°C/km at 1-3 km depth.  $R/R_A$  values for He in Sulphur Bank gases are 7.5. Hydrothermal fluids are highly enriched in deuterium as well as oxygen-18 relative to local meteoric waters and resemble magmatic waters discharged from many arc volcanoes. However, we show herein that magmatic, connate, and metamorphic fluids are indistinguishable based on  $\delta D/\delta^{18}O$  and Br/Cl plots. Sulphur Bank waters have B/Cl, I/Cl, and  $N_2/Cl$  ratios of metamorphic fluids and Sulphur Bank gases are strongly influenced by marine, organic-rich source rocks. We believe that Sulphur Bank fluids originate during metamorphism of Franciscan Complex rocks after shallow intrusion ( $\geq 4$  km) by magmas of the Clear Lake volcanic field.

## INTRODUCTION

Sulphur Bank mine in California has been called "the most productive mineral deposit in the world clearly related to hot springs" (White and Roberson, 1962). When mining operations ceased in 1957, 4500 tons of mercury and 2,000,000 tons of sulfur had been extracted from workings that discharged mineralized waters as hot as 80°C and poisonous gases composed of  $CO_2$ ,  $CH_4$ ,  $NH_3$ , and  $H_2S$ . Because of proximity to The Geysers steam field, four geothermal exploration wells were drilled at Sulphur Bank in the 1960's. Fluids as hot as 218°C were encountered as shallow as 503 m depth, but variable productivity, aragonite scaling, and environmental obstacles have prevented development (Beall, 1985; Goff and Janik, 1993). Sulphur Bank mine now requires extensive environmental cleanup due to mercury contamination of adjacent Clear Lake.

Although Quaternary volcanic rocks crop out in the mine area, Sulphur Bank thermal fluids have been cited as type examples of metamorphic fluids due to their stable isotope and chemical characteristics (White, 1957; White et al., 1973). However, recent work on the stable isotopes of magmatic waters (Giggenbach, 1992; Shevenell and Goff, 1993) has shown that arc volcanoes discharge waters very similar in isotopic composition to Sulphur Bank waters (D'Amore and Bolognesi, 1994). This paper reviews the volcanology and geochemistry of Sulphur Bank and surrounding waters in the Clear Lake region and emphasizes some similarities and differences between magmatic, connate, and metamorphic fluids.

## GEOLOGY

The regional geology, regional tectonics, and Quaternary magmatic history of the Clear Lake region have been discussed by numerous authors (e.g., Donnelly-Nolan et al., 1993). Sulphur Bank mine occurs at the edge of Clear Lake (Fig. 1) in faulted, contorted greywacke and shale of the Franciscan Complex that is overlain by a thin sequence of unconsolidated conglomerate, silt, and cross-bedded sandstone. An andesite flow of the Clear Lake Volcanics overlies the unconsolidated sediments. No dikes or conduit rocks for the andesite occur in the mine but the andesite can be traced to a scoria cone located 2 km to the east (Hearn et al., 1981). Carbon-14 dating of wood fragments in sediments beneath the andesite yields an age of 44.5 ka.

## VOLCANOLOGY/THERMAL REGIME

Sulphur Bank mine is surrounded by the youngest basaltic to rhyolitic eruptions (90 to -10 ka) in the Clear Lake volcanic field. Although Clear Lake volcanism has occurred within the San Andreas transform zone instead of within an arc, the volcanic rocks are distinctly calc-alkaline and most units display classic mixed-magma features (Stimac and Pearce, 1992). Practically all magmas of this volcanic field, including basalts, also show evidence of contamination with crustal rocks (Stimac et al., *submitt.*). Although the volume of the youngest extrusive rocks near Sulphur Bank is relatively small ( $<1$  km<sup>3</sup>), nearby conductive gradients and heat flow are high, exceeding 100°C/km and 170 mW/m<sup>2</sup> at depths of 1-3 km (Walters and Combs, 1989). Two-dimensional computer simulations of conductive and convective heat transport were tailored to model the Sulphur Bank-Borax Lake area of the Clear Lake volcanic field (Stimac et al., 1994). These models use a finite-difference approach to solve for thermal diffusivity in and around magma bodies. Observed thermal gradients in the Sulphur Bank mine area are consistent with simulations that include a narrow but geologically reasonable zone of hydrothermal convection ( $\leq 200$  m wide) overlying a shallow magma body (3-4 km depth) emplaced within the last 100 k.y. The high gradients documented above cannot be achieved from such limited hydrothermal convection without some combination of young and shallow magmatism.

In contrast to Sulphur Bank, volcanism at the Wilbur Springs district represents some of the earliest eruptions in the Clear Lake volcanic field and is limited to a few small basaltic dikes dated at 1.6 Ma. The Wilbur Springs hydrothermal system has a maximum temperature of 140°C at about 1 km in shale (Knoxville Formation) of the Great Valley sequence and serpentinite of the Coast Range ophiolite (Goff and Janik, 1993). Drilling to 2.8 km did not find temperatures  $>140^\circ C$  or a commercial resource.

## FLUID GEOCHEMISTRY

Thermal/mineral waters of the Clear Lake region are unlike thermal waters in typical volcanic-hosted geothermal systems (Goff et al., 1993a). For example, contents of  $HCO_3^-$ ,  $NH_4^+$ , B, Br, I, and Mg+Ca are generally high due to interactions of fluids with marine sedimentary rocks and serpentinites. Clear Lake region springs range from 10 to 72°C and 300 to 35,000 mg/kg TDS. Except at specific sites such as the Wilbur Springs district, where clusters of related waters occur, Clear Lake region waters show few geochemical similarities among different areas. Exploration drilling has failed to discover commercial geothermal resources.

**Isotopic Composition of Waters:** A plot of SD versus  $\delta^{18}O$  for thermal/mineral waters of the Clear Lake region (Fig. 2) shows the pronounced shift in both  $\delta^{18}O$  and  $\delta D$  displayed by many waters of the region and the apparent mixing between meteoric and non-meteoric end-members (White, 1957; White et al., 1973). White and co-workers pointed out that isotopically enriched thermal/mineral waters from the Clear Lake region were similar to the compositions of California oil field brines and called the majority of saline Clear Lake waters "connate" fluids. Although Sulphur Bank waters are not isotopically distinct from connate fluids of the region (except Complexion Spring), White and coworkers considered Sulphur Bank fluids to be "metamorphic" due to some chemical characteristics described below.

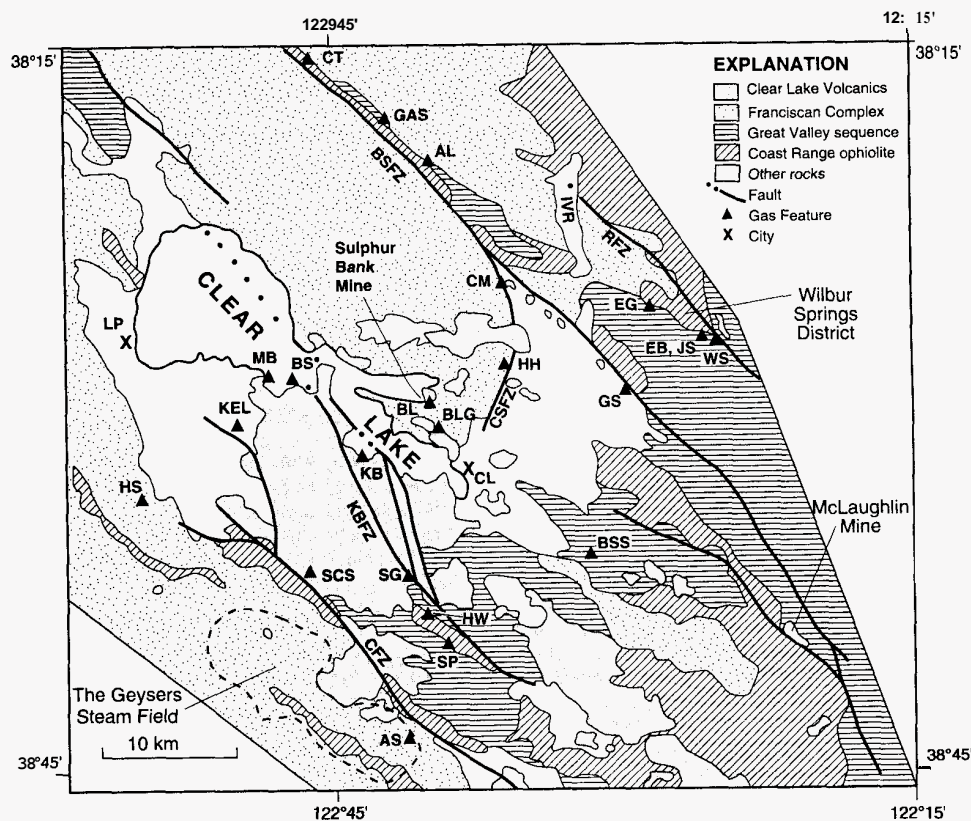


Figure 1: Generalized geologic map of the Clear Lake region, California showing locations of thermal/mineral features discharging gas. BSFZ=Bartlett Springs fault zone; CFZ=Collayomi fault zone; CSFZ=Cross Spring fault zone; KBFZ=Konociti Bay fault zone; RFZ=Resort fault zone; BL=Borax Lake; IVR=Indian Valley Reservoir; LP=Lakeport; CL=Clearlake. Gas sites: AL=Allen Springs; AS=Anderson Hot Springs; BLG=Borax Lake Gas Seep; BS=Big Soda Spring; BSS=Baker Soda Spring; CM=Chalk Mountain Springs; CT=Crabtree Hot Springs; EB=Elbow Hot Spring; EG=Elgin Hot Springs; GAS=Gas Spring; GS=Grizzley Spring; HH=Hog Hollow Spring; HS=Highland Springs; HW=Howard Hot Springs; JS=Jones Hot Spring; KB=Konociti Bay springs; KEL=Kelseyville methane well; MB=Moki Beach springs; SCS=Sulphur Creek Spring; SG=Seigler Hot Springs; SP=Spiers Springs; WS=Wilbur Hot Springs.

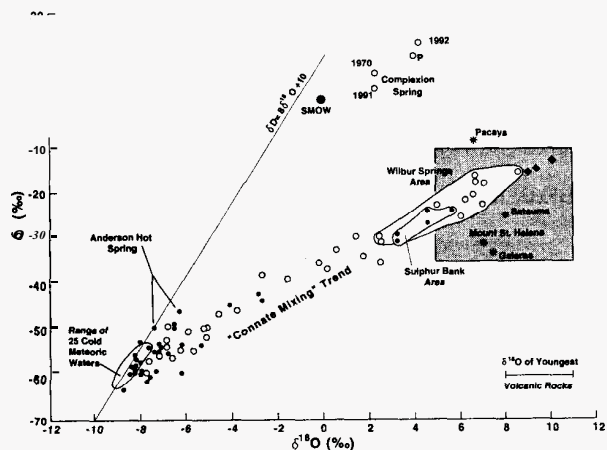


Figure 2: Plot of SD vs.  $\delta^{18}\text{O}$  for thermal/mineral waters of the Clear Lake region (data sources in Goff et al., 1993a and unpub.); isotope data reveal two end-member types (thermal meteoric and connate) with many mixed compositions. Complex Spring, located just east of IVR (Fig. 1), has the most saline fluid in the region but is isotopically unlike other connate fluids (P= data of Peters, 1993). Anderson Hot Spring is a steam- condensate water from the SE Geysers steam field. Data for magmatic waters at arc volcanoes are from Shevenell and Goff (1993) and F. Goff and coworkers (unpub.). Shaded box shows range of "convergent margin magmatic waters" (DAmore and Bolognesi, 1994). The range in  $\delta^{18}\text{O}$  for the youngest Clear Lake volcanic rocks is from Stimac et al. (submitt.). Diamonds represent three volcanic rocks in the Sulphur Bank area for which hypothetical "magmatic" deuterium values are extrapolated from the "connate mixing" trend. Such an extrapolation is not justified (see text).

Recent isotopic work on fluids discharged from arc volcanoes shows that many magmatic waters are isotopically similar to Clear Lake connate waters (Giggenbach, 1992). Magmatic compositions shown on Fig. 2 come from active arc basalt, andesite, dacite, and rhyolite volcanoes (Shevenell and Goff, 1993; F. Goff and coworkers, unpub. data). This raises the possibility that thermal fluids at Sulphur Bank and Wilbur Springs are mixtures of meteoric with magmatic, not connate or metamorphic, water as suggested by D'Amore and Bolognesi (1994). Because Clear Lake magmas are highly contaminated with crust, their  $\delta^{18}\text{O}$  values are more enriched ( $\geq 8\%$ ) than most arc magmas, as shown by our data in Fig. 2. Obviously, stable isotope values alone cannot distinguish among magmatic, connate, and metamorphic waters in the Clear Lake region.

Another explanation for the enriched stable isotope compositions of some Clear Lake region waters was proposed by Donnelly-Nolan et al. (1993), who indicated that "multiple Rayleigh distillation by repeated boiling of a local isolated geothermal system" could create isotope compositions at Sulphur Bank mine and elsewhere. Fig. 3 shows an analysis of this idea. The composition of Sulphur Bank well water is shown by the square and the trend between this composition and local meteoric water falls on a Rayleigh fractionation line of  $185^\circ\text{C}$ . The line for  $200^\circ\text{C}$  is also shown. A reservoir temperature of  $218^\circ\text{C}$  would lie on a nearly horizontal line. Furthermore, the points on the lines show the calculated fraction of water remaining after continuous Rayleigh distillation of local meteoric water. Enriched isotope compositions as found in Sulphur Bank fluids require boiling and steam loss of at least 99% of the original water. As boiling occurs, isotopically depleted steam is removed from the enriched residual water of the reservoir. No boiling hot springs or fumaroles and no isotopically depleted groundwaters (formed by addition of steam condensate) occur at Sulphur Bank mine or

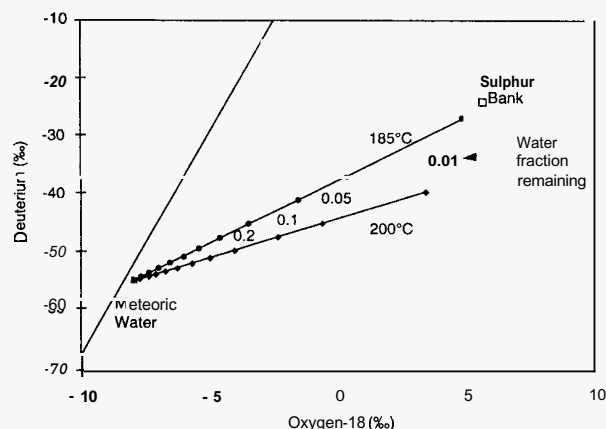


Figure 3: Plot of deuterium vs. oxygen-18 showing shift in isotopic composition of local meteoric water during isothermal boiling at 185 and 200°C. Points show fraction of liquid remaining after steam separation.

anywhere else in the Clear Lake region. Finally, if only 1% or less of the original fluid remained in the rock, the relative permeability of the reservoir would be near zero. No fluid could be produced and the gas content of the residual fluid would be nil.

We believe that Rayleigh distillation cannot explain the enriched isotopic compositions of Clear Lake region fluids. The explanation does not match the geochemistry of thermal manifestations and requires all fluids to be boiled at about the same temperature (185°C), yet the two known reservoirs of any size in the region (Sulphur Bank and Wilbur Springs) circulate at about 215 and 140°C, respectively and their fluids lie on the same isotopic trend (Fig. 2).

**Chemical Composition of Waters:** Peters (1993) noted that connate waters in and near the Wilbur Springs district have Br/Cl ratios similar to seawater. Goff et al. (1993b) commented that all sampled thermal/mineral waters of the Clear Lake region have similar Br/Cl ratios (Fig. 4). Interestingly, condensates of high-temperature magmatic fluids ( $T \leq 885^\circ\text{C}$ ) from the four arc volcanoes (Fig. 4) lie on or close to the seawater trend. Schilling et al. (1978) previously stated that arc volcanic rocks had Br/Cl ratios similar to seawater. Fig. 4 suggests that arc volcanoes produce much of their Br and Cl from recycling of subducted marine rocks but shows that Br/Cl ratios are not a good means to distinguish among magmatic, connate, and metamorphic waters.

White (1957) pointed out that I/Cl and  $\text{NH}_4/\text{Cl}$  ratios of oil field brines and connate waters were high relative to seawater. Marine organisms remove I from seawater (typically  $<0.05 \text{ mg/kg}$ ) during their life cycle but release I and  $\text{NH}_4$  into evolving connate fluids after death, decay, and burial. Fig. 5 shows that all sampled

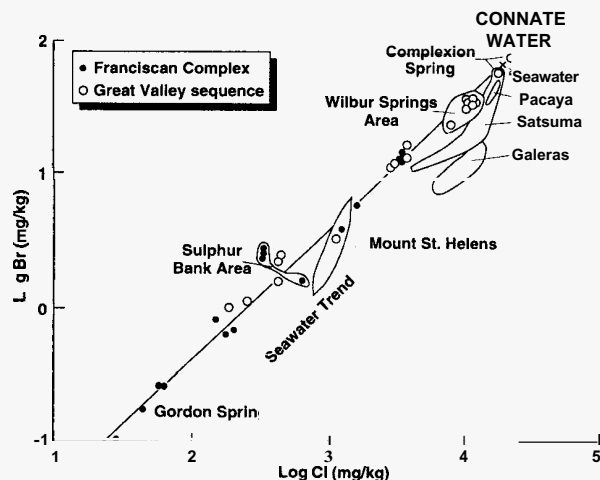


Figure 4: Plot of log Br vs. log Cl for thermal/mineral waters of the Clear Lake region (data sources as per Fig. 2 and unpub.).

thermal/mineral waters of the Clear Lake region have I/Cl ratios significantly greater than seawater and condensates of high-temperature magmatic fluids. Most fluid compositions define a regional trend and Sulphur Bank and Wilbur Springs fluids lie on this trend. Differences in total combined nitrogen ( $\text{N}_{\text{TC}} = \text{NH}_4 + \text{NO}_2 + \text{NO}_3$ ) among Clear Lake region waters, magmatic waters, and seawater are also striking. The value of  $\text{N}_{\text{TC}}/\text{Cl}$  for seawater is 0.000014, much less than ratios of 0.015 to 0.037 found in Wilbur Springs fluids and ratios of 0.53 to 0.80 found in Sulphur Bank fluids. Values of  $\text{N}_{\text{TC}}/\text{Cl}$  for the magmatic fluids range between seawater and Wilbur Springs levels. No other waters in the Clear Lake region remotely approach the high  $\text{N}_{\text{TC}}/\text{Cl}$  values found in Sulphur Bank fluids. Thus, I and  $\text{N}_{\text{TC}}$  may be used to distinguish among magmatic, connate, and metamorphic waters.

Fig. 6 shows that the B/Cl ratios of the various water types are also strikingly different. Ratios of B/Cl in Sulphur Bank waters and

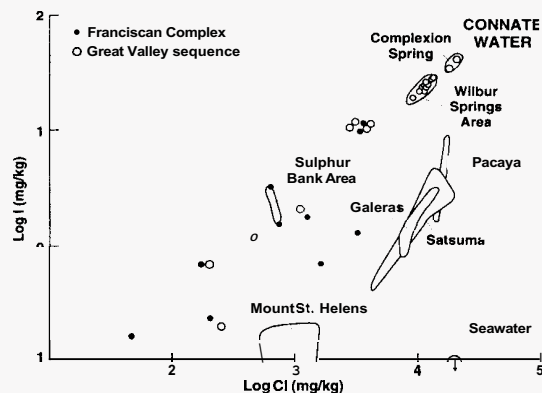


Figure 5: Plot of log I vs. log Cl for thermal/mineral waters of the Clear Lake region (data sources as above).

nearby fluids from other deep exploration wells are about 1:1 by weight whereas values of most other thermal/mineral waters in the Clear Lake region are considerably less. These differences in B/Cl led White et al. (1973) to use B to distinguish "metamorphic" from "connate" waters. The B/Cl ratio of seawater is extremely low while magmatic condensates have values between seawater and connate water. The B/Cl ratios of Sulphur Bank fluids are very similar to those in the geothermal reservoir fluids of Ngawha, New Zealand (Sheppard, 1984).

**Gases:** Although they contain the gas species typical of geothermal environments (Fig. 7), most Clear Lake region gases are different from those derived from high-temperature ( $\geq 200^\circ\text{C}$ ) reservoirs because they contain relatively low  $\text{H}_2\text{S}$ , relatively high  $\text{CH}_4$  and, in several cases,  $>99 \text{ mol-}\%$   $\text{CO}_2$  (Goff and Janik, 1993). In addition, most Clear Lake region gases have  $\text{N}_2/\text{Ar}$  molar ratios between 84 and 38, the ratios in air and air-saturated water, respectively. Such

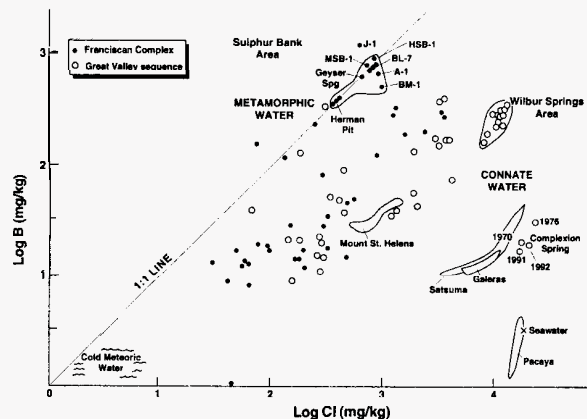


Figure 6: Plot of log B vs. log Cl for thermal/mineral waters of the Clear Lake region (modified from Goff et al., 1993a; data sources as above).

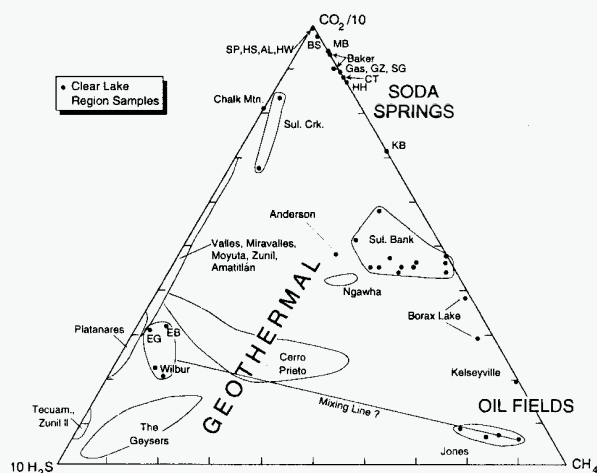


Figure 7: Triangular plot of  $10\text{H}_2\text{S}-\text{CH}_4-\text{CO}_2/10$  comparing gases in the Clear Lake region to gases from other geothermal systems (modified from Goff and Janik, 1993 and unpub.). Abbreviations are explained in Fig. 1.

ratios indicate a meteoric source fluid or near-surface mixing with air and shallow groundwaters. Well over half of the Clear Lake region sites produce gas with no apparent geothermal character. Spring waters at these sites have traditionally been called "soda springs" because of their cool temperatures and early use as naturally carbonated beverages.

Gases discharged at Sulphur Bank mine and the nearby gas well at Borax Lake contain less  $\text{H}_2\text{S}$  than most geothermal gases, but they do resemble gases from the geothermal system at Ngawha (Sheppard, 1984). Rocks at Ngawha resemble the marine greywackes of the Franciscan Complex that underlie Sulphur Bank mine and vicinity. Gases discharged from Sulphur Creek (on the Collayomi fault zone), from Chalk Mountain, and from most locations in the Wilbur Springs district have compositions that resemble typical geothermal gases. Interestingly, most Wilbur Springs gases lie at the  $\text{H}_2\text{S}$ -rich end of a projected mixing line through several samples of gas from Jones Hot Spring, which issues <200 m west of Elbow Hot Spring. The differences in results among various samples from Jones are too large to be analytical errors. We believe that this spring must have two gas sources even though composition of its connate water is relatively constant. One gas source is clearly geothermal in character, whereas the dominant gas source resembles oil field gases.

Gases from other geothermal systems shown on Fig. 7 originate from high-temperature geothermal reservoirs ( $\geq 200^\circ\text{C}$ ), with the possible exceptions of Platanares and Moyuta. Source rocks generally have a profound influence on gas geochemistry in geothermal systems. Gases from The Geysers, Ngawha, Cerro Prieto (Mexico), and Platanares (Honduras) originate in sedimentary source rocks that have some similarities to source rocks in the Clear Lake region (Goff and Janik, 1993). Geothermal fluids at The Geysers issue from rocks of the Franciscan Complex and a young ( $\leq 2.4$  Ma), shallow, composite intrusion (The Geysers felsite intrusion of Thompson, 1992). The relatively high  $\text{H}_2\text{S}$  content of The Geysers steam may be a partial reflection of a magmatic source (Goff and Janik, 1993). Gases from Valles caldera (New Mexico), Miravalles (Costa Rica), Moyuta, Zunil, Amatitlan, and Tecuamburro (all Guatemala) originate from volcanic and/or granitic host rocks at Quaternary volcanoes and have relatively low  $\text{CH}_4$  and other organic components.

If gases from active volcanoes were plotted on Fig. 7 (by calculating  $\text{SO}_2$  as  $\text{H}_2\text{S}$ ), they would be located in the extreme  $\text{H}_2\text{S}$ -rich corner of the diagram. Obviously, Sulphur Bank mine gases do not resemble high-temperature gases from active volcanoes.

**Mantle Contributions:** Preliminary results of a  $^3\text{He}/^4\text{He}$  investigation of the region are described by Goff et al. (1993b) and Goff and Janik (1993). The known  $\text{R}/\text{R}_\text{A}$  values for helium in the Clear Lake region range from 0.7 to 7.9. Values within the area from Sulphur Bank mine to Borax Lake are 7.5 to 7.9 respectively, indicating a definite mantle or young magmatic source. The coincidence of these values

with the  $218^\circ\text{C}$  hydrothermal system at Sulphur Bank and close proximity to the youngest eruptions in the Clear Lake volcanic field is noteworthy.

$\text{R}/\text{R}_\text{A}$  values of 4.0 to 5.2 have been obtained from Baker Soda Spring ( $23^\circ\text{C}$ ), also indicating a mantle signature. This spring issues from a NW-trending fault zone (not shown on Fig. 1) which is subparallel to other major fault zones of the region (Goff and Janik, 1993). The spring is located about 12 km SE of the youngest exposures of the Clear Lake Volcanics. A  $\text{R}/\text{R}_\text{A}$  value of 5.6 was obtained from gas discharges ( $25^\circ\text{C}$ ) at Chalk Mountain, a small dacite plug estimated at 0.9 Ma in age. Chalk Mountain and a string of other Clear Lake volcanic remnants are intruded along the Bartlett Springs fault zone (BSFZ), a major tectonic feature of the northern California Coast Ranges (Benz et al., 1992). Several thermal gradient wells drilled near Chalk Mountain indicate that the area has no geothermal potential; thus no apparent subsurface magma can explain the high  $\text{R}/\text{R}_\text{A}$  value. A  $\text{R}/\text{R}_\text{A}$  value of  $\leq 3.0$  was obtained from Gas Spring ( $10^\circ\text{C}$ ), also on the BSFZ. No known exposures of the Clear Lake Volcanics occur this far north; thus, the high  $\text{R}/\text{R}_\text{A}$  values along this fault zone are suggestive of mantle leakage. Similar associations between relatively high  $\text{R}/\text{R}_\text{A}$  values and tectonic features, instead of volcanic features, have been noted in Honduras and Guatemala (Kennedy et al., 1991; Janik et al., 1992).

$\text{R}/\text{R}_\text{A}$  values of 1.3 to 1.7 occur in the Wilbur Springs district indicating considerably less mantle input. As mentioned above, the youngest volcanism in the area occurred at 1.6 Ma and exposures consist of a few dikes located  $\geq 1$  km from thermal features. Probably magmatic activity has long since waned and the present helium signature represents mantle leakage along a major fault zone.

$\text{R}/\text{R}_\text{A}$  values from sites within the main Clear Lake volcanic field (2.0 to 0.2 Ma) range from only 0.8 to 1.8. The lowest value comes from Sulphur Creek Spring ( $24^\circ\text{C}$ ), just west of the Collayomi fault zone which acts as a hydrologic barrier between The Geysers steam field and the Clear Lake region (Goff et al., 1977).  $\text{R}/\text{R}_\text{A}$  values in the steam field range from 6.6 to 9.5 (Torgersen and Jenkins, 1982).

Fig. 8 compares relatively inert components of Clear Lake region gases to those from active volcanoes and selected geothermal systems. This plot, modified from Giggenbach and Goguel (1989) uses  $\text{N}_2$ , Ar, and He as a means for separating gases of predominantly mantle, arc (sedimentary), and meteoric origins, particularly when combined with  $^3\text{He}/^4\text{He}$  data (Goff and Janik, 1993). For convenience,  $\text{R}/\text{R}_\text{A}$  values are shown in parentheses next to the data points. The majority of Clear Lake region gases plot close to the values for air or air-saturated meteoric water (ASMW) indicating a probable influence from near-surface processes.

Gases from Jones Hot Spring, Kelseyville well, and Crabtree gas seep show the influence of sedimentary organic sources. The  $\text{R}/\text{R}_\text{A}$  values of Jones/Wilbur Hot Springs and Crabtree seep are relatively low indicating little mantle input. The gas from Chalk

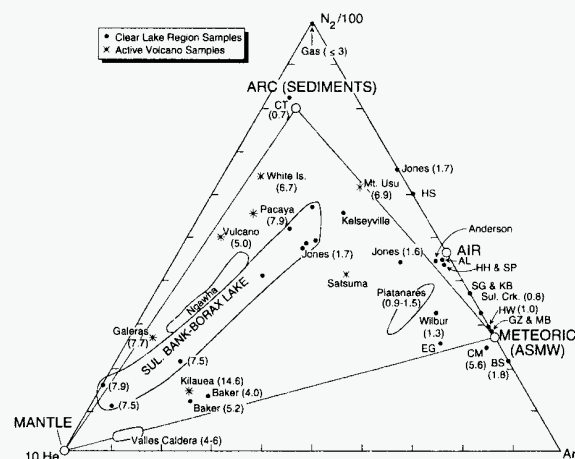


Figure 8: Triangular plot of  $10\text{He}-\text{Ar}-\text{N}_2/100$  comparing gases in the Clear Lake region to volcanic and geothermal gases.  $\text{R}/\text{R}_\text{A}$  values are shown in parentheses (modified from Goff and Janik, 1993 and unpub.). Abbreviations are explained in Fig. 1.

Mountain is heavily influenced by meteoric water even though the  $R/R_A$  value is high. On the other hand, some gases from the Sulphur Bank-Borax Lake area and gas from Baker Soda Spring have definite mantle characteristics due to excess total He and high  $R/R_A$  values.

Gases from Sulphur Bank-Borax Lake show obvious three-component mixing between mantle, sedimentary, and meteoric sources. Data points shown with  $R/R_A$  values were collected in March 1991, during the end of a long drought. Other samples were collected in December 1993, when conditions were considerably wetter. Gas analyses reported in Sheppard (1984) from the Ngawha geothermal wells are similar to Sulphur Bank-Borax Lake gases.

Of the volcanic gases plotted on Fig. 8, most have high relative  $N_2$  due to their arc settings and wedges of subducted sediments, and also have relatively high  $R/R_A$  values. Galeras volcano has surprisingly high total He for an andesitic arc volcano. Kilauea has high total He due to its hot spot setting. The geothermal system of Valles caldera has an obvious mantle contribution even though it is an expression of voluminous high-silica rhyolite volcanism. In contrast, the Platanares geothermal reservoir is not associated with any Quaternary volcanism; the system is strictly tectonic. Platanares gases have an obvious association with meteoric fluids due to mixing of reservoir waters with dilute groundwaters (Janik et al., 1991) and have  $R/R_A$  values of 0.9 to 1.5. Gases from the Wilbur Springs district resemble those from Platanares on this plot.

**Carbon Sources:** Results of  $\delta^{13}C$ -CO<sub>2</sub> analyses for the Clear Lake region are compared to other volcanic and geothermal sources in Fig. 9. All CO<sub>2</sub> samples from the Clear Lake region, including The Geysers, have  $\delta^{13}C$  values with a distinct "organic" character ( $\leq -9\text{‰}$ ) and are more depleted than "mantle" carbon values of  $-8$  to  $-3\text{‰}$  (represented by diamonds, Fig. 9). Interestingly, samples from the two locations in the Clear Lake region known to host liquid-dominated geothermal reservoirs (Sulphur Bank mine and Wilbur Springs district) have  $\delta^{13}C$ -CO<sub>2</sub> values closest to the most depleted mantle and arc volcano values. Quite possibly, the carbon in these samples comes from a combination of mantle and organic sources. However, the carbon isotope values of secondary carbonates from veins, fractures, and faults in regional basement rocks of the Clear Lake region have not been investigated to see if they represent viable carbon sources. Dissolution of vein calcite and possibly aragonite present in the Franciscan Complex has apparently created substantial matrix porosity throughout The Geysers steam field (Hulen et al., 1992) and may be a significant source of carbon for The Geysers and throughout the Clear Lake region. Lambert and Epstein (1992) report carbon-13 values of  $-8$  to  $-15\text{‰}$  for 18 cuttings samples of hydrothermal calcite from steam zones in The Geysers. These values overlap the range of 43 carbon-13 analyses of CO<sub>2</sub> from The Geysers steam wells.

The  $\delta^{13}C$ -CO<sub>2</sub> values of Sulphur Bank mine and Wilbur Springs district gases are most similar to those found in gases from geothermal systems hosted in sedimentary rocks (Platanares, Ngawha, Cerro Prieto). CO<sub>2</sub> produced from reservoirs in volcanic rocks (typical arc geothermal systems) or from reservoirs coexisting with substantial amounts of marine carbonate (Valles caldera) have more enriched isotope compositions than any CO<sub>2</sub> found in The Geysers-Clear Lake region.

## CONCLUSIONS

Sulphur Bank mine is surrounded by the youngest silicic to basaltic rocks in the Clear Lake volcanic field and drilled reservoir temperatures are as hot as  $218^\circ\text{C}$  at 503 m depth. Of all the geochemical parameters discussed in this paper only the high total He content of some Sulphur Bank-Borax Lake gas samples and their corresponding  $R/R_A$  values of 7.5 to 7.9 conclusively indicate that a mantle or magmatic component is present in the reservoir fluid and is discharged along adjacent faults. Stable isotope values and Br/Cl ratios of Sulphur Bank fluids resemble those found in both magmatic and connate waters and resemble those found in the numerous, tepid, mineralized ("connate") springs of the Clear Lake region, which have no magmatic associations. Isotopically enriched fluids of the Clear Lake region do not result from widespread boiling (Rayleigh distillation) of local meteoric waters as proposed by Donnelly-Nolan et al. (1993).

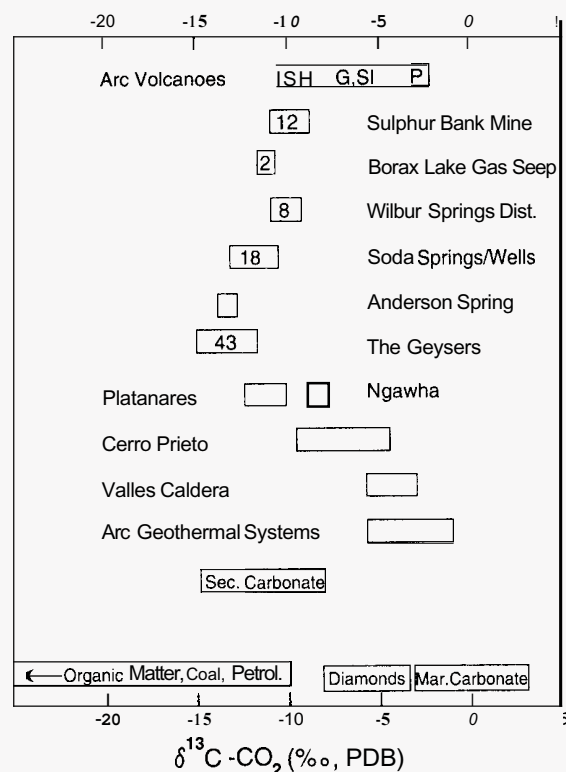


Figure 9: Diagram showing  $\delta^{13}C$ -CO<sub>2</sub> of Clear Lake region gases compared to values from volcanic and geothermal gases and to values from common carbon sources (modified from Goff and Janik, 1993 and unpub.). Arc volcanoes: G=Galeras (andesite); P=Pacaya (high-alumina tholeiite); SH=Mount St. Helens (dacite); SI=Satsuma Iwo-jima (rhyolite). Numbers in boxes refer to numbers of analyses.

Sulphur Bank and other thermal/mineral fluids of the Clear Lake region have high B/Cl, I/Cl, and  $N_2$ /Cl ratios characteristic of connate fluids. In fact, ratios of B/Cl and  $N_2$ /Cl in Sulphur Bank fluids are so high that White and co-workers called them "metamorphic" waters. The latter waters are most common in rocks of the Franciscan Complex whereas connate waters circulate mostly in rocks of the Great Valley sequence.

Sulphur Bank gases do not resemble most geothermal gases or any magmatic gases in bulk composition because of high relative CH<sub>4</sub> (and NH<sub>3</sub>) and low relative H<sub>2</sub>S. Carbon-13 values of Sulphur Bank CO<sub>2</sub> are depleted (about  $-10.5\text{‰}$ ) compared to values from most arc volcanoes, arc geothermal systems, and the mantle. The gases and carbon isotopes are associated with sedimentary rocks containing organic components.

The host rocks, volcanic style, and fluid compositions of Sulphur Bank geothermal system are remarkably similar to those at Ngawha, New Zealand; thus, a comparative study of the two systems would be instructive. Although the heat source for, and some of the volatiles in, the Sulphur Bank system can only be magmatic (Stimac et al., 1994), the evidence for magmatic water in the geothermal system (i.e. D'Amore and Bolognesi, 1994) is not compelling. We believe that Sulphur Bank fluids are derived from rocks of the Franciscan Complex during intrusion and heating by magmas of the Clear Lake volcanic field and are best called "metamorphic" waters as defined by White et al. (1973).

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