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# Oxygen Isotope Geochemistry of
# The Geysers Reservoir Rocks, California

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## ABSTRACT

Whole-rock oxygen isotopic compositions of Late Mesozoic graywacke, the dominant host rock at The Geysers, record evidence of a large liquid-dominated hydrothermal system that extended beyond the limits of the present steam reservoir. The graywackes show vertical and lateral isotopic variations that resulted from gradients in temperature, permeability, and fluid composition during this early liquid-dominated system. All of these effects are interpreted to have resulted from the emplacement of the granitic "felsite" intrusion 1-2 million years ago. The $\delta^{18}O$ values of the graywacke are strongly zoned around a northwest-southeast trending low located near the center of and similar in shape to the present steam system.

Vertical isotopic gradients show a close relationship to the felsite intrusion. The $\delta^{18}O$ values of the graywacke decrease from approximately 15 per mil near the surface to 4-7 per mil 300 to 600 m above the intrusive contact. The $\delta^{18}O$ values then increase downward to 8-10 per mil at the felsite contact, thereafter remaining nearly constant within the intrusion itself. The large downward decrease in $\delta^{18}O$ values are interpreted to be controlled by variations in temperature during the intrusive event, ranging from 150°C near the surface to about 425°C near the intrusive contact. The upswing in $\delta^{18}O$ values near the intrusive contact appears to have been caused by lower rock permeability and/or heavier fluid isotopic composition there.

Lateral variations in the isotopic distributions suggests that the effects of temperature were further modified by variations in rock permeability and/or fluid-isotopic composition. Time-integrated water:rock ratios are thought to have been highest within the central isotopic low where the greatest isotopic depletions are observed. We suggest that this region of the field was an area of high permeability within the main upflow zone of the liquid-dominated hydrothermal system. The lowest water:rock ratios and permeabilities are found in the Northwest Geysers where the least depleted rocks occur.

## INTRODUCTION

Recent isotopic studies of steam from The Geysers geothermal field in northern California (Fig. 1) have documented large variations in both its $\delta D$ and
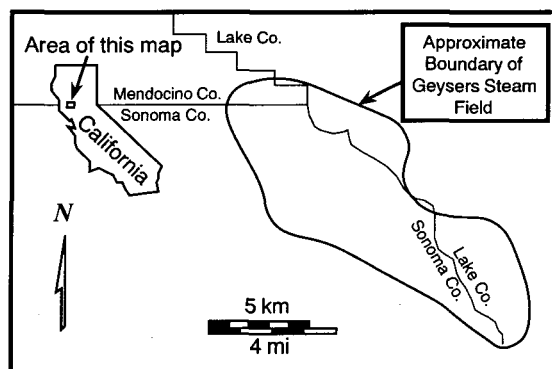


**Figure 1.** Location map of The Geysers.

$\delta^{18}O$ values (Gunderson, 1989; Truesdell et al., 1992). In the southern part of the field, $\delta D$ values of the steam range from -50 to -60 per mil and are similar to local meteoric waters, while in the northwest part of the field the $\delta D$ values of the steam are lighter (-40 to -50 per mil). The corresponding $\delta^{18}O$ values range from a low of -7 per mil in the south, again similar to meteoric waters, to as much as +3 per mil in the northwest.

Gunderson (1989) showed that there is a correlation between the oxygen isotopic compositions of the steam and the average isotopic composition of the reservoir rocks in the same wells. Based on this correlation, he suggested that the isotopic composition of the steam is partly controlled by equilibrium with the enclosing rocks. Because of the low porosities of the reservoir rocks (Gunderson, 1990), the isotopic composition of a relatively small amount of steam, which was initially held as liquid water in the pores and fractures, will be buffered by much larger volumes of rock.

Although the studies of Gunderson (1989) demonstrated the importance of the isotopic variations in the reservoir rocks, insufficient data were available at that time to characterize their extent and magnitude. In this paper, we expand significantly on earlier isotopic investigations of the rocks and vein minerals from The Geysers. These data are first used to document the isotopic structure of The Geysers on a field-wide basis. We then discuss possible factors that controlled the observed isotopic variations within the thermal system.

## ANALYTICAL TECHNIQUES

Whole-rock oxygen isotope analyses were performed on 551 samples of graywacke and 39 samples of felsite from 68 wells drilled throughout the field. With the exception of one well, where 30 m composite samples were analyzed, the analyses were performed on cuttings samples that were collected at intervals of 6 m. In addition to the whole rock analyses, $\delta^{18}O$ values were obtained on single crystals of vein quartz and calcite from 6 intervals in 4 wells in order to evaluate the isotopic composition of the fluids that precipitated these minerals. These samples had previously been used for fluid inclusion studies (Moore, 1992).

Prior to the whole-rock analyses, the cuttings were rinsed in cold water to remove any drilling mud and cleaned of drill steel with a hand magnet. The bulk rock samples were treated with acid to remove any carbonate and then reacted with bromine pentafluoride to extract oxygen from the silicate minerals (Clayton and Mayeda, 1963). The evolved $O_2$ was converted to $CO_2$ by combustion with graphite. The results are reported in parts per mil relative to SMOW. The NBS-28 quartz standard yielded an average $\delta^{18}O$ value of 9.5 per mil. Analytical precision based on multiple analyses of the standard was + 0.2 per mil. The samples were analyzed at Unocal's Science and Technology Center in Brea, California.

## GEOLOGIC RELATIONSHIPS

The Geysers steam field lies within the lithologically heterogeneous Franciscan Formation of Jurassic to Cretaceous age. This diverse unit is dominated by graywackes that are interlayered with argillite, chert, greenstone, and serpentinite (McLaughlin, 1981). The main steam reservoir is found dominantly within nonfoliated graywacke and an underlying granitic pluton that was emplaced more than 1.3 million years ago (Schriener and Suemnicht, 1981; Thompson, 1989; Dalrymple, 1992; Hulen and Nielson, 1993). This pluton, which is informally termed the felsite, is centrally located within the steam field and is generally considered to have provided the heat for a large liquid-dominated hydrothermal system that evolved into the present vapor-dominated regime (McLaughlin, 1981; Sternfeld, 1981; Thompson, 1989; Thompson and Gunderson, 1989; Moore, 1992). Highly foliated graywacke, and discontinuous lenses of mafic igneous rocks and chert occur primarily within the low permeability caprock of the system.

Alteration of the graywacke is related to two major events: early subduction-related regional metamorphism, and later contact metamorphism and associated hydrothermal alteration. During the Mesozoic, the Franciscan Formation underwent northeast-directed subduction that was accompanied by low-temperature, moderate- to high-pressure metamorphism (McLaughlin, 1981). The resulting metamorphic assemblages are found throughout the tectonic melanges and disrupted formations of the Geysers reservoir and caprock and are ubiquitously associated with quartz and calcite veining (Thompson, 1989).

More recent alteration of the Franciscan rocks at The Geysers is associated with the large liquid-dominated hydrothermal system that developed during the emplacement of the felsite. Alteration of the country rocks around the pluton included both recrystallization of the rock-forming minerals and deposition of a complex set of vein and selvage minerals. Recrystallization of the graywackes and argillites is most pronounced within distances of 300 to 600 m from the intrusion, where high temperatures caused the groundmass clays to recrystallize to phengite and biotite forming a biotite hornfels. At greater distances from the felsite, where temperatures were lower, the sheet silicates consist of equal amounts of illite and chlorite. At the shallowest depths, smectites and mixed-layer clays are present. Aside from these differences, the primary mineralogy of the altered graywackes is relatively uniform throughout The Geysers, consisting generally of about 45% quartz, 30% plagioclase feldspar, 20% sheet silicates, and 5% potassium feldspar.

During contact metamorphism and hydrothermal alteration of the Franciscan rocks, calcite in the early quartz-calcite veins was removed by dissolution and reacted to produce calc-silicate minerals (Gunderson, 1989; Hulen et al., 1991, 1992). Consequently, calcite is now generally restricted to the upper 300 m of the reservoir and the overlying caprock (Sternfeld and Elders, 1982; Thompson and Gunderson, 1989; Sternfeld, 1989; Gunderson, 1990; Hulen et al., 1991, 1992). With decreasing metamorphic grade and increasing distance from the intrusion, the following assemblages developed in the reopened Franciscan veins and in the newly formed fractures (Moore, 1992):

1. tourmaline + biotite + actinolite + clinopyroxene + epidote + quartz+ potassium feldspar (restricted to the biotite-hornfels zone);
2. actinolite + ferroaxinite + epidote + quartz + prehnite + potassium feldspar;
3. epidote + chlorite + quartz + potassium feldspar; and
4. quartz + potassium feldspar + calcite

Calcite and quartz related to The Geysers hydrothermal system can be distinguished from the older minerals by their morphologies and optical characteristics. In general, the Franciscan minerals are commonly anhedral in shape and clouded with numerous fluid inclusions, whereas quartz and calcite precipitated during the younger event contain only sparsely distributed fluid inclusions and often display well developed crystal forms.

## ISOTOPIC RESULTS

The $\delta^{18}O$ whole-rock values of the graywackes ranged from +2.3 to +15.6 per mil, while those of the felsite ranged from +4 to +10.5 per mil (Figure 2). The isotopic distributions are shown on plan maps and cross sections in Figures 3 and 4, respectively. The plan maps were constructed by averaging the isotopic values in each of the 610 m slices shown. In contrast, each of the
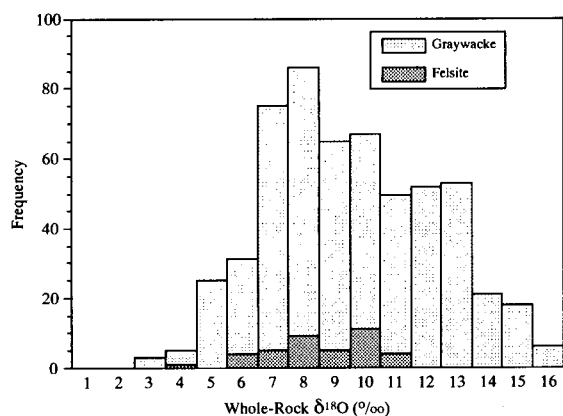
**Figure 2**. Range of isotopic compositions in per mil of graywacke and felsite samples.

| Well | Elevation | Wt % NaCl | O-18 (Qtz) | O-18 (Cc) | F.I. Temp | O-18 Calc | Comment |
|---|---|---|---|---|---|---|---|
| Thorne-6 | -469 | 0.0 | | 5.2 | 172 | -5.94 | 1 |
| Thorne-6 | -488 | 0.0 | 5.80 | | 253 | -2.95 | 2 |
| Thorne-6 | -516 | 0.2 | | 5.5 | 189 | -4.633 | 2 |
| CA 956-A4 | 376 | 0.1 | 5.20 | | 226 | -4.90 | 1 |
| DV-2 | -203 | 4.3 | 7.58 | | 282 | 0.05 | 3 |
| SB-26 | -175 | 0.6 | 6.06 | | 306 | -0.59 | 4 |
| PS-24 | -405 | 1.2 | 12.10 | | 223 | 1.84 | 2 |
| L'Esp[2] | -2462 | 15.7 | 10.13 | | 420 | 6.49 | 1 |

1-average of primary or pseudosecondary inclusions
2-average highest temperature secondary planes
3-average all inclusions probably pseudosecondary
4-data from Sternfeld (1981); average of all inclusions

**Table 1.** Oxygen isotopic compositions in per mil of quartz (Qtz) and calcite (Cc). Also shown are the average fluid inclusion homogenization temperatures (F.I. Temp) and range of salinities in weight percent NaCl equivalent (WT % NaCl). The sample elevations relative to mean sea level are given in meters (m). The calculated compositions in per mil of the waters in equilibrium with the minerals are denoted by O-18 calc.

individual data points was contoured in the cross sections. Thus, the cross sections display details that are not apparent in the plan maps.

Oxygen isotope analyses of the mineral separates are presented in Table 1. These samples yielded $\delta^{18}O$ values that ranged from +5.2 to +12.1 per mil for quartz and +5.2 to +5.5 per mil for calcite. The samples from Thorne 6 and CA 956A-4 are representative of the caprock in the southeastern part of the field while quartz from SB-26 and PS-24 are from the caprock in the central and northwestern parts of The Geysers respectively. Quartz from DV-2 is from a quartz-epidote vein deposited in tourmaline-bearing felsite within the steam reservoir. The isotope data from L'Esp 2 is from a quartz vein in graywacke that was metamorphosed to a biotite-rich hornfels. This sample is from the high-temperature reservoir.

## DISCUSSION

### Distribution of Oxygen Isotopes

Figures 3 and 4 show that $\delta^{18}O$ values of the Geysers graywackes are laterally and vertically zoned

within the steam field. Samples from shallow depths display isotopic values typical of Franciscan rocks outside the geothermal field (Lambert and Epstein, 1992) while strongly depleted values are found above the top of the felsite intrusion near the center of the field. As discussed in greater detail below, the $\delta^{18}O$ values of the rocks show a clear spatial relationship to both the boundaries of the producing steam field and the felsite intrusion. Thus, the data provide independent evidence that intrusion of the felsite was responsible for the development of a large hydrothermal system that eventually diminished in size and evolved into the present steam reservoir.

The near-surface $\delta^{18}O$ values of Franciscan graywacke (above +610 m relative to mean sea level (msl)) obtained in this study range from +12 to +15.6 per mil and are similar to values obtained by Lambert and Epstein (1992) from shallow levels of The Geysers wells LF-19 and LF-15. In these wells, the graywackes yielded $\delta^{18}O$ values of +13 to +16 per mil and displayed no systematic variation within the depth range studied. Detrital quartz grains from the same depths yielded values ranging from +14.2 to +19.8 per mil. From these data, Lambert and Epstein (1992) concluded that the isotopic composition of the quartz was the result of regional metamorphism and that the shallow graywackes were essentially unaltered by recent hydrothermal activity. The lack of any significant variation in the near-surface oxygen isotope values obtained in our study further supports the conclusion that the isotopic composition of the graywacke was not differentially affected by hydrothermal alteration prior to emplacement of the felsite.

Below +610 m msl, the graywackes generally display depleted $\delta^{18}O$ values. With increasing depth, and toward the center of the field, the $\delta^{18}O$ values become progressively more depleted. Between +610 m and sea level, the lowest $\delta^{18}O$ values are found toward the southeastern end of the field above the shallowest part of the felsite intrusion (Fig. 5a). With increasing depth, this isotopic low is shifted northward, defining an elongate northwest-southeast area that is more centrally located within the steam field. Data below -1829 m msl reveal the presence of small, isolated isotopic lows.

In cross section, it is evident that the greatest isotopic depletions are found at distances of 300 to 600 m above the felsite (Fig. 4). These depletions occur within the biotite hornfels in both the normal and high-temperature reservoirs, and are characterized by $\delta^{18}O$ values that typically range from +4 to +7 per mil. As the felsite is approached, $\delta^{18}O$ values within the graywacke increase from these low values up to about +8 to +10 per mil at the intrusive contact. Within the intrusion itself, the whole-rock oxygen isotopic values generally remain fairly constant.

Figure 5a shows that the isotopic contours display a close relationship to the shape of the pluton, the steam reservoir, and major zones of surficial alteration. This coincidence suggests that these features are related to each other and that they were all influenced by the same structural controls. In contrast, there appears to be little relationship between the isotopic variations at
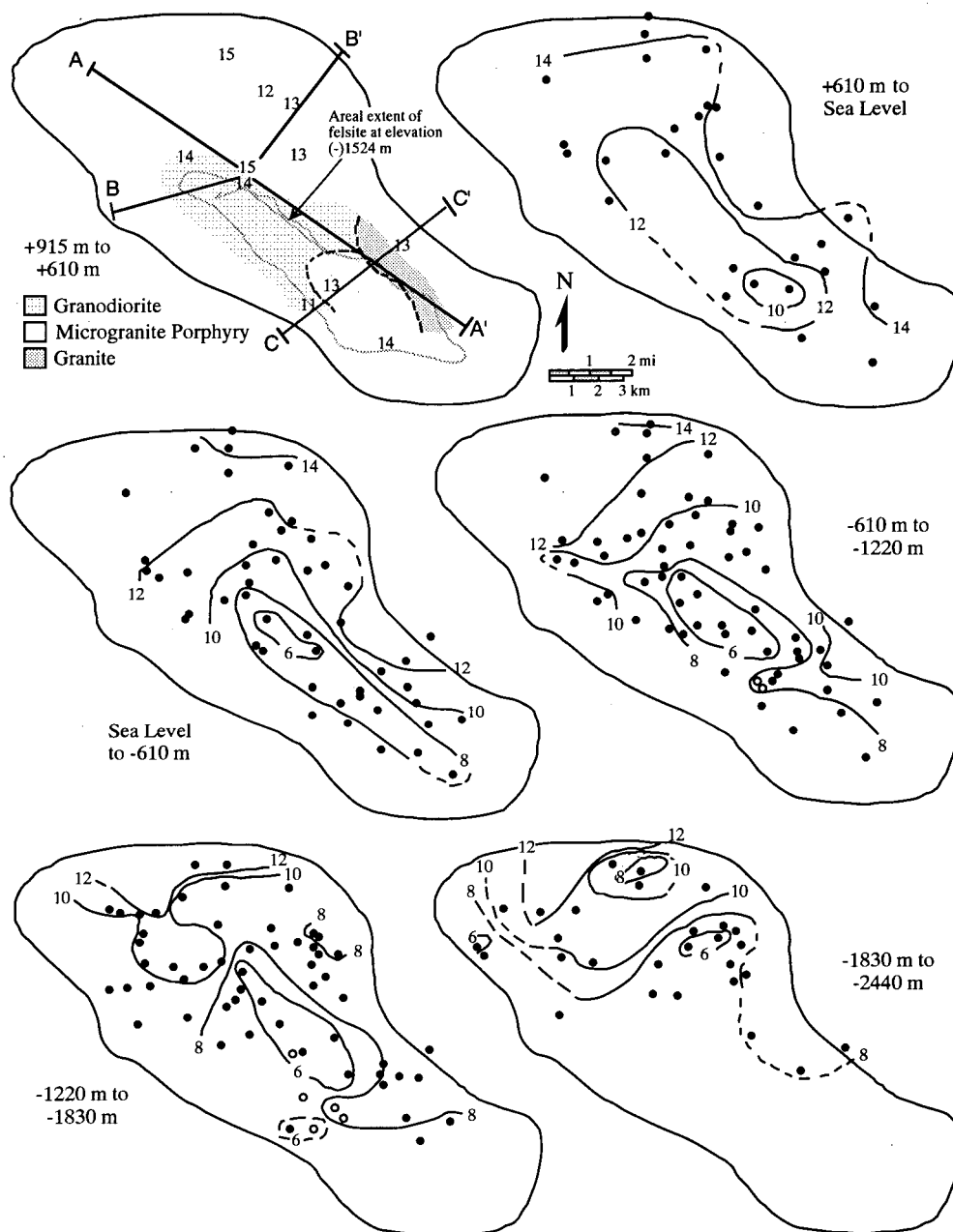
**Figure 3.** Distribution of the average $\delta^{18}O$ values in per mil of graywacke and felsite. The individual diagrams represent successive slices through The Geysers field. All elevations are shown relative to mean sea level. The solid dots represent samples of graywacke or mixtures of graywacke and felsite. Open circles denote felsite samples. The upper left hand diagram shows the distribution of the main granitic phases of the felsite (Hulen et al., 1993), the extent of the felsite at an elevation of −1524 m (Thompson, 1989), the locations of the cross sections given in Figure 4, and the average isotopic composition of graywackes between elevations of +915 and +610 m.

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greater depth and regions of intense tourmaline mineralization in the felsite and hornfels (Fig. 5b). The lack of a clear isotopic signature in the overlying graywckes is surprising because the abundance of tourmaline implies that these were areas of locally high fluid flow that should have affected a large volume of the rock. This apparently was not the case. Instead, the isotopic data suggest that the fluids which deposited the tourmaline

were unable to penetrate much above the top of the hornfels. This conclusion is further supported by fluid inclusion data which shows no evidence for the hypersaline fluids found in tourmaline-bearing veins at distances of more than 600 m from the intrusion (Moore, 1992). The upward mobility of these fluids could have been limited in part by ductile behavior of the hornfels, which is suggested both by the presence of highly con-
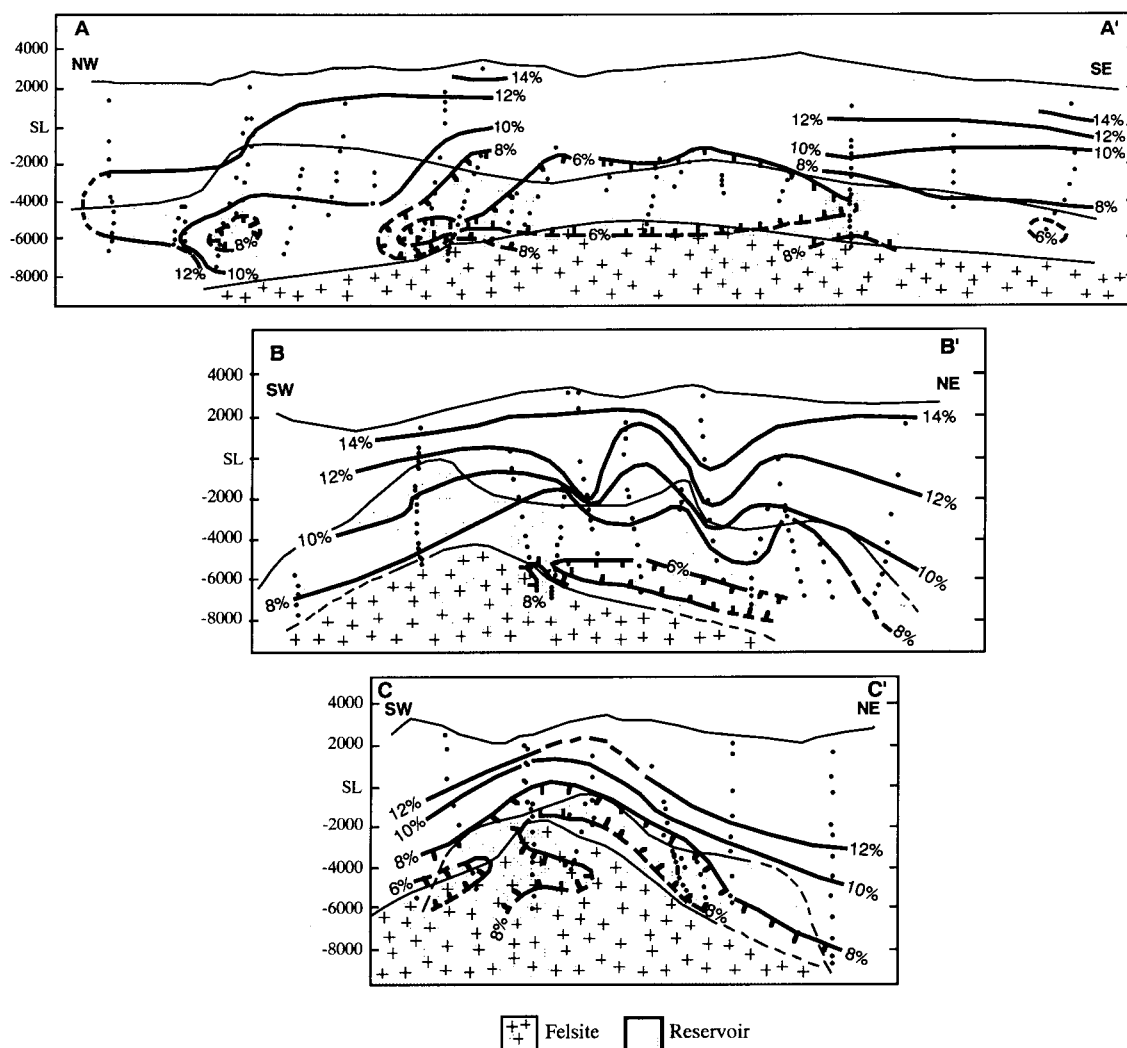
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**Figure 4.** Cross sections through The Geysers field showing the distribution of $\delta^{18}O$ values in per mil with respect to the top of the steam reservoir and the felsite. All values were contoured in this figure. See Figure 3 for cross section locations.
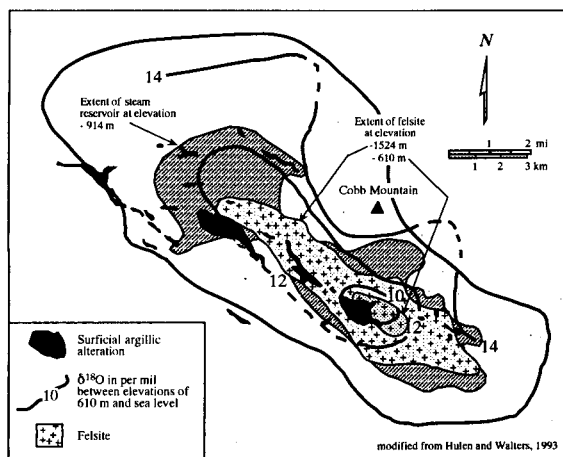


**Figure 5a.** Spatial relationships between the steam reservoir, felsite, surficial hydrothermal alteration, and the average $\delta^{18}O$ values in per mil of graywacke samples from +610 m msl to sea level. Modified from Hulen and Walters (1993)
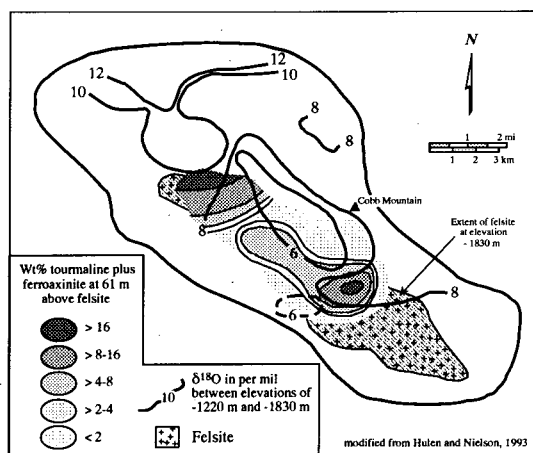
**Figure 5b.** Relationship between regions of strong tourmaline and ferroaxinite mineralization, the felsite, and the average $\delta^{18}O$ values in per mil of rocks from elevations between −1120 and −1830 m msl.

voluted Franciscan veins (Hulen, pers. comm., 1993) and by fluid inclusion data that imply high temperatures and lithostatic pressures (unpub. data).

At the depths shown in Figure 5b, the isotopically dominant feature, the central low, is developed within the graywacke in the contact metamorphic halo above the biotite-orthopyxone granite (refer to Fig. 3). This is the most extensive and apparently the oldest of the three major intrusive phases mapped by Hulen and Nielson (1993). The strong northwest elongation of the low parallels the major structural grain of the region, implying that this region was an area of preexisting and relatively intense fracturing that may have been enhanced by intrusion of the felsite.

**Origin of Isotopic Variations**

As noted above, the general pattern of oxygen isotopic depletions in the rocks strongly suggests a relationship to felsite emplacement. The specific vertical and lateral variations that make up this pattern are interpreted to have been caused by variations in the temperature, rock permeability, and composition of the fluids during the evolution of the hydrothermal system at The Geysers .

The most important isotopic feature shown in Figures 3 and 4 is the downward decrease in the $\delta^{18}O$ values from about +14 per mil near the surface to about +4 to +7 per mil within the hornfels at distances of 300 to 600 m above the intrusive contact. Extrapolation of fluid inclusion data suggest that the maximum temperatures ranged from about 425°C near top of the biotite hornfels to 150°C in the shallow cap rocks above the presently producing steam reservoir (Sternfeld, 1981; Moore, 1992). These temperatures, combined with the average mineral composition of the graywacke given above, yield water-rock fractionation factors of 2.4 and 12.7 per mil respectively. These values were calculated from the fractionation factors for water-quartz, -albite, -potassium feldspar, -muscovite, and -chlorite given by Matsuhisa et al. (1979), O'Neil and Taylor (1967), O'Neil and Taylor (1967), O'Neil and Taylor (1969), and Wenner and Taylor (1971) respectively. Thus, the inferred temperature gradient can itself account for a 10 per mil variation in the isotopic composition of the rocks, assuming that they equilibrated with waters of uniform isotopic compositions. This correspondence between the observed and calculated $\delta^{18}O$ values of the graywackes strongly suggests that temperature was the dominant process controlling the isotopic compositions of the rocks. These fractionation factors would require a water with a $\delta^{18}O$ of about +2 per mil.

Within the hornfels, the $\delta^{18}O$ values commonly increase by 1 to 3 per mil as the intrusion is approached. This opposite trend suggests that effects other than temperature influenced the oxygen isotope composition of the rocks in the immediate vicinity of the felsite. The most likely factors that could lead to this increase in $\delta^{18}O$ are a downward decrease in the water:rock ratios caused by decreasing permeabilities and equilibration of the rock with an isotopically heavier water. Both of

these possibilities are reasonable, as measured matrix permeabilities of hornfels core samples are indeed considerably lower than the overlying graywackes, while isotopically heavy magmatic water could have readily been derived from the felsite. Evidence for the presence of such water is provided by the isotopic data and salinities of the inclusion fluids from the hornfels near the intrusive contact (see below), and by the presence of boron-rich waters.

The lateral isotopic gradients that result in the "bull's eye" pattern seen at intermediate depths in Figure 3 have two possible origins. The isotopically light "bull's eye" may have resulted from interaction with waters that were isotopically lighter than those found near the edges of the thermal system, or, more likely, from higher water:rock ratios in the center of the system. Higher water:rock ratios would imply that the isotopically lightest part of the system had the greatest permeabilities during the early development of the hydrothermal system at The Geysers. The present rates of steam production in the central part of The Geysers, however, are not anomalously high, suggesting that increased permeabilities are no longer present in this region.

Table 1 shows calculated $\delta^{18}O$ values of waters in equilibrium with vein calcite and quartz from Geysers cores and cuttings. These values, which ranged from -5.9 to +6.5 per mil, were calculated using the fractionation factors for quartz-water and calcite-water from Matsuhisa et al. (1979) and Freidman and O'Neil (1977) respectively, and pressure-corrected homogenization temperatures from the fluid inclusion data of Moore (1992) and Sternfeld (1981). Waters from the caprock in the southeastern part of the field (Thorne 6 and CA 958-3) display a relatively narrow range of $\delta^{18}O$ values between -5.9 and -3.0 per mil, while the fluid from the caprock in PS-24 and SB-26 (northern third of the Geysers), are substantially heavier (+1.8 and -0.6 per mil respectively). All of these samples are thought to belong to paragenetic sequence 4 (see above).

The low $\delta^{18}O$ values in the southeastern part of the field suggest that the fluids contained a large component of meteoric water. In contrast, the isotopically heavier waters from the northwestern third of the field are similar to the +2 per mil values determined for the early fluids from the rock-water fractionation factors (see discussion above). These heavier $\delta^{18}O$ values imply lower water:rock ratios, if it is assumed that the northwestern fluids were also meteoric in origin, or derivation from a different source. We favor the latter hypothesis. This conclusion is consistent with the relatively high fluid inclusion salinities of 1.2 equivalent weight percent NaCl determined for this sample from PS-24 and with the even higher salinities of up to 4 equivalent weight percent NaCl contained in fluid inclusions from other samples from the caprock in the Northwestern Geysers (Moore et al., 1989). These relatively high salinities suggest that the waters may be connate in origin or mixtures of magmatic and connate or meteoric water. The occurrence of these various water types in the region around The Geysers has recently been reviewed by Donnelly-Nolan et al. (1992).

In contrast to the shallower samples, the water responsible for deposition of the quartz veins in the biotite hornfels in L'Esp-2 had a $\delta^{18}O$ value of +6.5 per mil. This value lies within the region of primary magmatic waters (Sheppard et al., 1969). Such an origin is consistent with salinities of up to 31 weight percent NaCl in fluid inclusions from this sample and the occurrence of hypersaline inclusion fluids in other samples of the felsite and hornfels. Thus, the data demonstrate that the fluids responsible for the initial alteration of the hornfels were compositionally and isotopically different than the fluids that circulated through the upper portions of the hydrothermal system.

## CONCLUSIONS

The whole-rock $\delta^{18}O$ values of graywackes from The Geysers display systematic variations with respect to depth, location within the field, and grade of alteration. The dominant feature is an overall downward decrease in the $\delta^{18}O$ values of the graywackes as the underlying granitic intrusion is approached, with the lowest values in the center of the current steam system. The shallowest samples are characterized by $\delta^{18}O$ values of +12 to +15.6 per mil, which are typical of the weakly altered graywackes studied by Lambert and Epstein (1992), Sternfeld (1981), and Cole (1985). These high $\delta^{18}O$ values are found throughout the field at shallow depths, suggesting pre-intrusion isotopic homogeneity of the graywackes. Biotite hornfels, found at distances of up to 600 m from the intrusion, commonly displays the greatest isotopic depletions. This rock type occurs in both the normal and high-temperature reservoirs and is characterized, throughout most of the field, by $\delta^{18}O$ values that are as depleted as +4 to +7 per mil. Variations in temperatures determined from fluid inclusion and mineralogic data yield calculated rock-water fractionation factors that can account for $\delta^{18}O$ variations of 10 per mil. Thus, temperature variations provide an explanation for the overall vertical decrease in the $\delta^{18}O$ values of the rocks. As the intrusion is approached, the $\delta^{18}O$ values in the hornfels increase to a maximum of +8 to +10 per mil at the granitic contact. Corresponding values within the intrusive are similar and remain fairly constant with depth. We suggest that the effects of increasing temperature on the $\delta^{18}O$ values within the hornfels were offset by interaction with isotopically heavy waters of magmatic origin and possibly decreasing permeabilities.

Lateral variations in the pattern of isotopic values of the greywackes mimic the shape of the underlying felsite and display a strong zonation around a central low. The axis of this low, which is elongate in a northwest-southeast direction, is located in the center of the producing steam field slightly to east of the axis of the underlying granitic pluton and to the north of the shallowest portion of the intrusion. This low is interpreted as representing the central upwelling region of the early hydrothermal system that formed in response to the intrusion of the granite. The isotopic depletions in the graywackes imply that this region was characterized by the highest time-integrated water-rock ratios and permeabilities.

Rocks from the northwestern third of The Geysers field are consistently more enriched in oxygen-18 than the remainder of the system. As shown by Gunderson (1989), these gross lateral variations are also correlative with the isotopic composition of the early produced steam. These relationships suggest that lower water:rock ratios and hence lower permeabilities have characterized this part of the field throughout the evolution of The Geysers thermal system.

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