

NOTICE CONCERNING COPYRIGHT RESTRICTIONS

This document may contain copyrighted materials. These materials have been made available for use in research, teaching, and private study, but may not be used for any commercial purpose. Users may not otherwise copy, reproduce, retransmit, distribute, publish, commercially exploit or otherwise transfer any material.

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specific conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use," that user may be liable for copyright infringement.

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

ISOTOPIC AND CHEMICAL CONSTRAINTS ON RESERVOIR FLUIDS
FROM THE COSO GEOTHERMAL FIELD, CALIFORNIA

A.E. Williams and M.A. McKibben

Center for Geothermal Resources Research
I.G.P.P. Univ. of Calif., Riverside, CA 92521

ABSTRACT

Sampling of reservoir fluids from more than 45 geothermal production wells has provided excellent light stable isotopic and chemical constraints on field-wide reservoir characteristics. Hydrogen, oxygen, carbon and sulfur isotopic compositions give information on the sources of these components and constrain fluid-rock interactions and reservoir processes which have occurred in the system. Studies of reservoir fluid chemical variations indicate a very complex reservoir. Two discrete two-phase regions appear to exist, as well as three distinct single-phase (liquid) regions of the field. This apparent compartmentalization of Coso reservoir chemistry can be interpreted to reflect one or more of the following: 1) a very young reservoir, 2) one that is poorly interconnected or 3) one strongly affected by local wall rock variations or reservoir processes.

INTRODUCTION

The recent development of production facilities in the Coso geothermal system has permitted unprecedented geochemical observations of a large portion of the reservoir in nearly its natural state. Unlike most active geothermal systems developed to date, the rapid expansion of facilities at Coso allowed 3-dimensional sampling of fluids from much of the reservoir prior to extensive modification of fluid compositions and distributions by long term production and/or injection induced effects.

Although the Coso field has been known for some time because of surface expressions at both Coso Hot Springs and at the Devils Kitchen area, data concerning the deep reservoir chemistry has been only recently acquired. Preliminary studies of reservoir fluid chemistry and stable isotopic

compositions from two early wells (CGEH #1 and COSO #1) were first reported in Fournier et al. (1980) and Fournier and Thompson (1980), respectively.

Since water-rock interaction does not significantly modify the deuterium/hydrogen isotopic composition (D/H) of geothermal fluids, it is commonly utilized to determine the original source of meteoric ground waters which recharge active geothermal systems. The favorable comparison of two fluid samples from the CGEH #1 well with groundwaters produced in the Sierra Nevada led Fournier and Thompson (1980) to propose a distant Sierran recharge site for the fluids in the Coso field.

From their limited sample set (two wells) Fournier et al. (1980) recognized the presence of a Cl⁻-rich (~2300 mg/kg) liquid-dominated geothermal system which appeared to be relatively homogeneous in chemical composition. Minor variations in the chemical compositions of the fluids sampled from these two wells appeared to be primarily due to temperature dependent cation exchange reactions in the regions tapped by these two wells. Reservoir temperatures of 240-250°C and 205°C were inferred for the COSO #1 and CGEH #1 regions respectively. Their results seemed to indicate that the fumarole and acid-sulfate surface manifestations seen at Coso Hot Springs and the Devils Kitchen were only a shallow effect disguising an alkali-chloride liquid dominated system at depth.

More recently, Moore et al. (1989) reported a more detailed picture of the deep reservoir chemistry at Coso as indicated by sampling of 27 wells. Their results indicated a widespread and variable presence of reservoir steam (a two-phase reservoir) and relatively large variations in chemistry across the field. A consistent decrease in Cl⁻ and CO₂ concentrations from deep southwest wells to shallow wells in the north was

observed. This, and other chemical observations were interpreted by Moore et al. (1989) as indicating mixing of rising hot, saline, CO₂ rich geothermal fluids with cooler, dilute, shallow groundwaters which were higher in Ca, SO₄ and HCO₃. The natural convective reservoir upflow was therefore interpreted as being roughly southwest to northeast. Similar hydrologic trends were also inferred by Moore et al. (1989) for computed salinity-temperature relationships of fluid inclusions trapped in minerals sampled from 12 thermal gradient and production wells.

ANALYTICAL RESULTS

Hydrogen and Oxygen in Liquid and Steam

Over the past few years, samples of reservoir fluids from more than 35 Coso geothermal wells representing all developed regions have been collected and analyzed for D/H and ¹⁸O/¹⁶O. Our sampling was coordinated with routine geochemical sampling of wells by the California Energy Company (CEC) and consisted of well-head collection of both liquid and steam condensate using CEC's truck-mounted cyclone mini-separator/cooling coil apparatus.

Deuterium/hydrogen isotope ratios (δD) of fluid samples were analyzed by the standard zinc reduction technique, followed by mass spectrometry.

Oxygen isotopic compositions ($\delta^{18}O$) for the Coso fluids were analyzed by equilibration of CO₂ gas with samples at a constant temperature of 25°C, followed by mass spectrometry of the CO₂.

δD and $\delta^{18}O$ values for liquid and steam condensate from Coso wells typically indicate isotopic equilibrium at the temperature of separation at the wellhead. We have therefore assumed equilibrium and recalculated reservoir δD and $\delta^{18}O$. This assumption is probably valid for production from single phase reservoir regions or from two-phase reservoirs which are well mixed. Figure 1 presents calculated δD vs $\delta^{18}O$ values of the reservoir liquid phase for 23 sample suites for which adequate isotopic and mass balance information is presently available. Published information from Fournier and Thompson (1980) constraining groundwater source regions and Coso geothermal wells have been included in this figure.

Carbon in Gas

During sampling of several wells for steam condensate, bulk samples of non-condensable gases were collected into evacuated sample containers. After laboratory separation of other gases, the CO₂ was directly analyzed by mass spectrometry. All carbon isotopic compositions ($\delta^{13}C$) are relatively consistent (Fig. 2), with samples from 10 wells representing all areas of the active production field ranging only from -4.57 to -5.97‰ relative to PDB. A similar value (-4.32) was also obtained from sampling of steam and gas emanating from a shallow steam well in the Coso Hot Springs area.

Sulfur in Liquid and Gas

During sampling of well-head fluids from Coso wells, separate samples of steam condensate and liquid were collected specifically for analyses of sulfur isotope ratios ($\delta^{34}S$) in H₂S and SO₄ respectively.

H₂S sampling was performed by bubbling steam condensate and non-condensable gas through a two stage precipitator containing a cadmium chloride solution. In this manner, geothermal sulfide was quantitatively collected as a CdS precipitate.

Sulfate sampling on the other hand, was accomplished by collecting a large quantity of flashed geothermal liquid into a diluent. Sulfate stabilized in this manner was precipitated as BaSO₄ and collected by filtration for subsequent analysis.

All sulfide and sulfate $\delta^{34}S$ data are presented with respect to the CDT standard and are shown as histograms in Figures 3a and 3b.

Fluid Geochemistry

Although our research group has collected and analyzed a few samples of Coso geothermal fluids as laboratory intercalibrations, we have depended on the routine sampling and chemical analysis of fluids and gases performed by CEC for the bulk of our database. At this time, 151 analyses of fluids from 47 Coso geothermal wells are being utilized for our interpretations. These analyses show significant and consistent regional variations in the chemistry of both the fluids and the non-condensable gases analyzed. Space does not permit a comprehensive discussion of all elemental variations observed, so several representative graphs and a generalized discussion have been included below.

INTERPRETATION (STABLE ISOTOPE)

As observed in the δD vs $\delta^{18}O$ diagram (Fig. 1), Coso reservoir fluid isotopic compositions generally indicate a tight clustering of δD at approximately -98‰ relative to SMOW as well as a somewhat looser grouping of $\delta^{18}O$ (from -5 to nearly -8‰). Hydrogen isotopic ratios in liquid dominated active geothermal systems worldwide have been observed to suffer only minor changes during water-rock interaction, making them ideal tracers of the original surface source of the circulating meteoric fluids. Using this line of reasoning, Fournier and Thompson (1980) interpreted the isotopically light δD of two samples from the CGEH #1 well (-107‰ , dark circles on Fig. 1) as indicators of a Sierran meteoric water source. The dominantly heavier (>-100) ratios shown by all samples collected from the Coso production field (filled squares) have caused us to seek an alternate interpretation. As observed in Fig. 1, δD compositions of -90 to -100 were found by Fournier and Thompson (1980) to be typical of groundwaters produced by the somewhat lower elevation rain and snowfall in the Coso and Argus ranges. It is therefore most reasonable to conclude that fluids sampled from the Coso geothermal reservoir originated as meteoric waters in the Coso or Argus ranges or at least at elevations significantly lower than those dominating the Sierran isotopic signatures.

A large oxygen isotopic shift is implied by the difference between the $\delta^{18}O$ values of Coso geothermal fluids and their original meteoric source (Fig. 1). This shift is typically interpreted as an effect of isotopic exchange between the hot fluids and the rocks through which they flow. The large $\delta^{18}O$ shift of Coso fluids ($+6$ to $+8\text{‰}$) is quite typical of high temperature active geothermal systems but is somewhat surprising in a fracture dominated system where intimate contact of the fluid with large volumes of the wall rock may be limited. We hope to gain additional insight into such water-rock interaction constraints by performing analyses of $\delta^{18}O$ in a wide variety of fractured and unfractured reservoir rocks from the Coso field.

A moderate temperature shallow water well sample from the Coso Wash area east of the production field also showed an ^{18}O shift and δD similar to those observed for Coso reservoir fluids. This may be an indication of natural reservoir discharge toward the east providing both heat and fluid supply beneath the Coso Hot Springs and Coso Wash.

Localized variations in isotopic compositions of both hydrogen and oxygen produced by reservoir boiling and phase separation in the two-phase Coso field appear to be small relative to those produced by water-rock interaction.

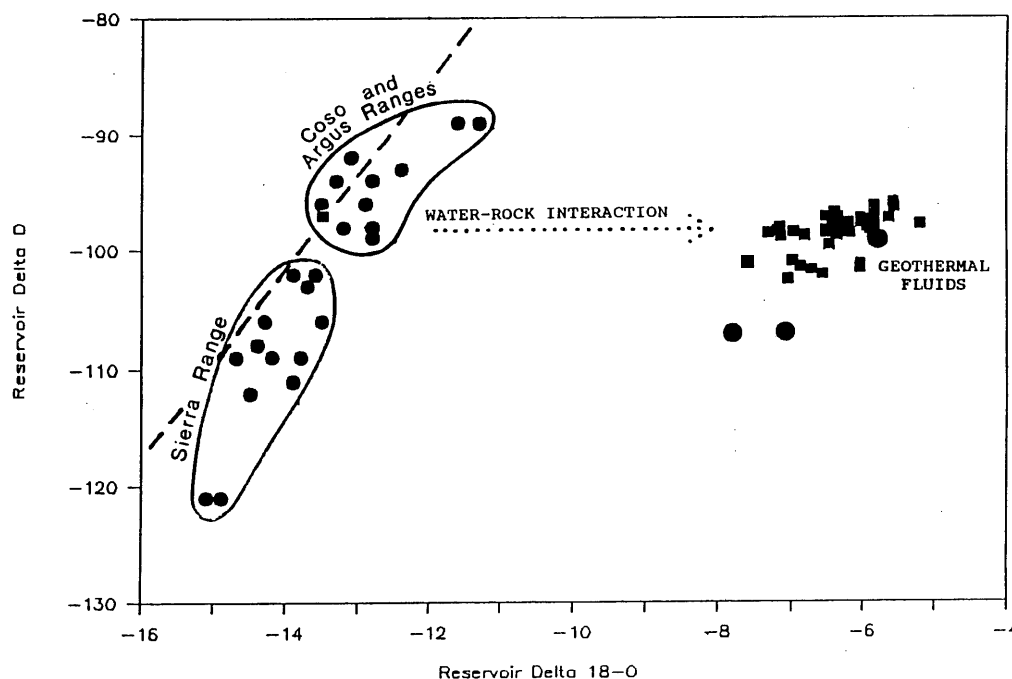


FIGURE 1. Reservoir δD vs. $\delta^{18}O$ for Coso fluids. On the left are ground-water samples which lie along the meteoric water line (diagonal dashed line). Dotted line is an inferred water-rock interaction trend producing the observed reservoir fluid compositions to the right. Squares -this study; Circles -Fournier and Thompson (1980).

Carbon isotopic compositions ($\delta^{13}\text{C}$) in the range -4 to -6‰ relative to PDB (Fig. 2) are quite typical for geothermal environments dominated by igneous rock or organic-poor clastic sediments (Taylor, 1986). Organic-rich sediments would contribute extremely light carbon while marine limestones produce somewhat heavier $\delta^{13}\text{C}$ values. Because of the narrow range and nearly "igneous" signature of the carbon sampled from the Coso reservoir, we infer that there has probably been little or no contribution of carbon from either isotopically heavy or light source rocks in the subsurface (marine limestones or organic-rich sediments).

$\delta^{34}\text{S}$ values of H_2S in steam show a bimodal distribution (Fig. 3a.), with the majority of values clustering around a mode of $+2\text{‰}$. A lesser number of isotopically light values have a mode of -2‰ . $\delta^{34}\text{S}$ values of SO_4 in liquid show a wider variation (Fig. 3b). The isotopically lightest values (1.0 , 1.7‰) are from surface springs at Coso Hot Springs. The remainder of the values are from geothermal wells and show a mode of $+9\text{‰}$.

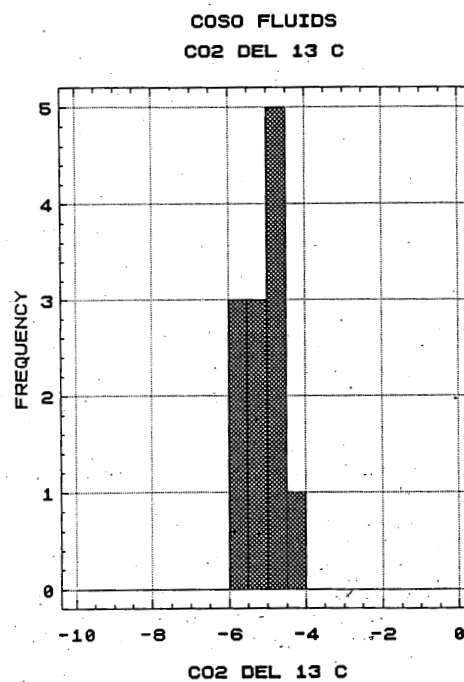


FIGURE 2. Frequency histogram illustrating $\delta^{13}\text{C}$ values of gas sampled from geothermal wells in the Coso field.

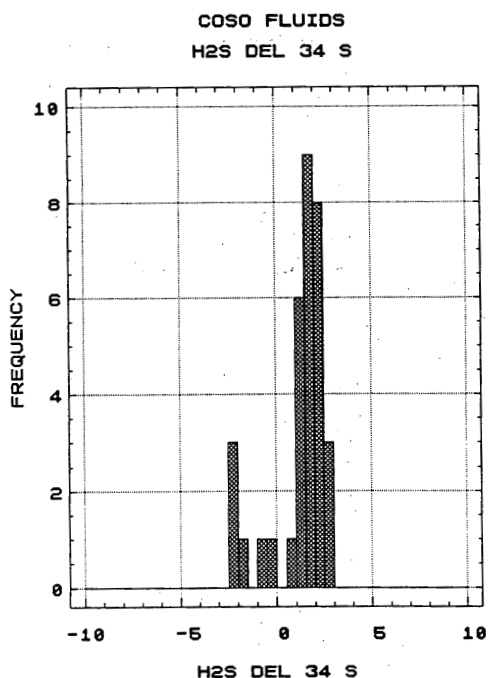


FIGURE 3a. Frequency histogram illustrating $\delta^{34}\text{S}$ values of hydrogen sulfide sampled from Coso geothermal wells.

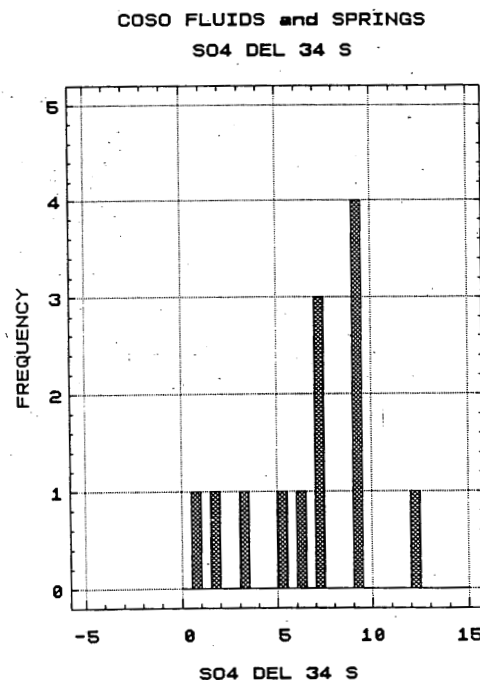


FIGURE 3b. Frequency histogram illustrating $\delta^{34}\text{S}$ values of aqueous sulfate sampled from Coso wells and hot springs.

The isotopically heavy $\delta^{34}\text{S}$ values of reduced sulfur in the majority of geothermal fluids are consistent with whole-rock $\delta^{34}\text{S}$ values of magnetite-series batholithic rocks of the eastern Sierra Nevada (Ishihara and Sasaki, 1989). Thus, it is possible that most of the H_2S in the Coso geothermal system is derived from the granitic host rocks. On-going sulfur isotopic analyses of the granitic rocks within the field will allow us to test this hypothesis.

The few isotopically light H_2S values are found in wells from single-phase (liquid) reservoir areas in the field. However, the typically heavy values from two-phase reservoir regions show little correlation with the reservoir steam fraction produced, suggesting that there is negligible sulfur isotopic fractionation accompanying H_2S partitioning between liquid and steam phases at these temperatures. Qualitative sulfur isotope partition and reaction models are being applied to clarify the observed relationships.

The apparent sulfur isotope fractionation (+1 to +12‰) between H_2S and SO_4 coexisting in Coso well-head samples is far smaller than that expected for equilibrium partitioning at reservoir temperatures (approximately +20 to +25‰, Ohmoto and Lasaga, 1982). This lack of isotopic equilibrium between H_2S and SO_4 in Coso fluids may be caused by mixing, boiling and/or short residence times. At temperatures of 250-300°C and pH 4-7, the time for these species to attain sulfur isotopic equilibrium is between 3 and 40 days (Ohmoto and Lasaga, 1982). Therefore the process producing the disequilibrium observed must be occurring continuously in very close proximity to the Coso production reservoir.

If the analyzed H_2S and SO_4 have different origins, such as mixing of local groundwaters with deep geothermal fluids, or mixing of reservoir liquid and steam phases from different isolated aquifers, the residence times of the mixture in the reservoir must be less than 3 to 40 days. Reservoir boiling may also produce disequilibrium by non-equilibrium oxidation of some portion of the H_2S to SO_4 (Drummond and Ohmoto, 1985). As mentioned above, any such mechanism must occur in a short time period prior to or during extraction of the fluid from the reservoir or re-equilibration of the isotopes would occur.

INTERPRETATION (GEOCHEMISTRY)

Our inspection of the more complete database provided by CEC supports the observation of Moore et al. (1989) that there is a wide range of steam content (from single-phase liquid to nearly dry steam) in the reservoir being produced at Coso. The distribution of such variations in steam content can be further refined by examining the calculated reservoir steam content as a function of 3-dimensional location within the reservoir. Data from the northern portion of the field illustrate a consistent increase in reservoir steam content with decreasing depth. This trend and the presence of extremely steam-rich shallow production could imply the presence of a steam "cap" produced by upward migration of reservoir steam. Large degrees of boiling of the directly underlying fluids are not, however indicated since these liquids tend to be similar to or less saline than those sampled in other portions of the field.

Data from the typically deeper geothermal wells sampled in the southern region of the Coso field show no such obvious trend of depth with reservoir steam content. In this region, geographical locations are of greater importance, with steam-rich wells being located in the southwestern portion of the field and single-phase (liquid) wells located in the southeastern area. As we discuss later, salinities in the southwestern wells are consistently higher than in other portions of the field, possibly indicating large degrees of in-situ boiling as the source of much of the steam in the reservoir.

Although non-condensable gas contents of Coso geothermal wells vary considerably, calculating gas ratios for both reservoir liquid and steam phases permits relatively straightforward interpretation. For example, Figure 4a shows the consistency of the methane/carbon dioxide ratio calculated for the steam phase in two-phase wells. Use of various gas geothermometers (D'Amore and Truesdell, 1985) indicates quite reasonable temperatures and steam saturations for Coso well data, providing some verification of other reservoir geothermometers and enthalpy estimates of reservoir steam fraction.

Non-condensable gas contents and ratios in steam-poor regions of the field also permit distinction of different recognizable liquid types. The plot of hydrogen sulfide vs. carbon dioxide concentrations (Fig. 4b) in steam-poor wells indicates not only the ease of identification of even a small (< 5%)

contribution of steam (by the elevated H₂S content observed for southwestern wells), but also the extreme bimodality of the aqueous CO₂. All single phase wells from the northern portion of the field cluster in the low H₂S-low CO₂ region of the diagram while single-phase wells from the southeastern region plot at significantly higher CO₂.

Regional variations in reservoir chemistry can also be observed in the data from chemical analyses of the geothermal liquid phase. For the purposes of this discussion we crudely divide solute species into two categories, conservative and reactive.

Conservative elements, once dissolved, tend to remain with the liquid phase, relatively inert to boiling and mineral precipitation effects. As examples of conservative elements we have included Figure 5a, a plot of fluorine vs. chlorine content of the calculated reservoir liquid phase. If fluids remain undersaturated in fluorite, both of these solutes can be considered "conservative". In that case, boiling effects will enrich both elements along lines radial to the origin. This is typified by the roughly

linear array of data points from the southern wells, with the most dilute compositions occupied by the southeastern single-phase wells, and those most concentrated by steam loss at the highest fluorine and chlorine contents. It should be noted that this spread of data, if produced by boiling alone requires loss of as much as half of the reservoir fluid mass to the steam phase. Conservative element variations which do not follow radial trends are most conveniently explained by differences in fluid source. For instance, the extreme difference in fluorine/chlorine ratio between the northwestern wells (Fig. 5a) and the southern wells may indicate the leaching of these solutes from rocks containing different relative amounts of F and Cl. If this is the case, fluids in these regions have followed distinctly different paths in reaching the present reservoir and have never been well mixed by reservoir convection. Localized reservoir mixing may be indicated (Fig. 5a) by the elongation of the field for the northern deep wells which connects fields of the fluorine-rich northwestern wells with the fluorine-poor southern well boiling trend.

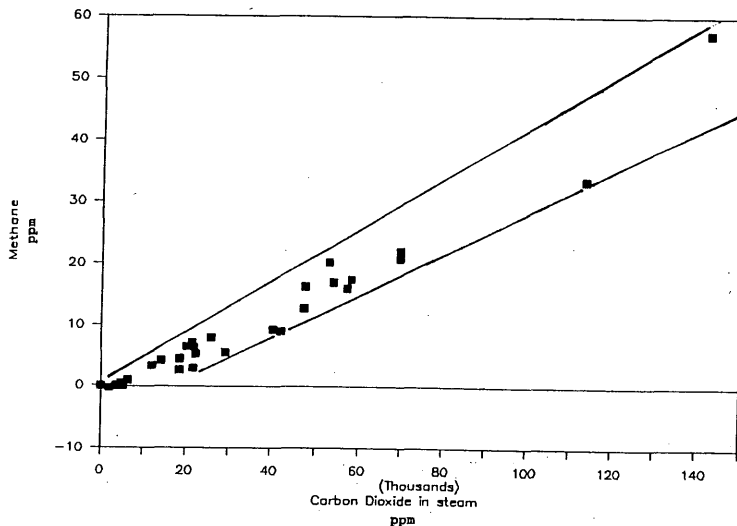


FIGURE 4a. Methane in reservoir steam plotted against carbon dioxide in reservoir steam for all available analyses of fluids produced from Coso two-phase reservoir regions.

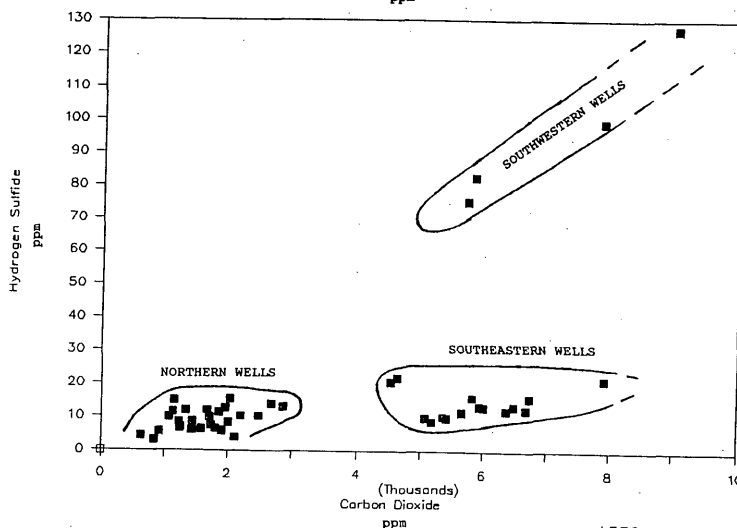


FIGURE 4b. Reservoir hydrogen sulfide plotted against dissolved reservoir carbon dioxide for all Coso wells showing little or no reservoir steam.

Trends in the concentration of "reactive" elements can assume orientations other than those produced by boiling enrichment or mixing. Selective precipitation and/or dissolution of mineral phases in the reservoir and selective partitioning into the steam phase during boiling can create relatively complex relationships. Figure 5b has been included as an example. In this diagram, we have plotted concentrations of a reactive element (strontium) against a conservative element (chlorine). The presence of trends (ie. northern deep wells) which are neither radial to the origin nor mixing lines between two end member fluids indicates the complicating presence of an additional process (that of dissolution/precipitation of a mineral phase). The nearly radial trend of the southern wells on this Sr vs. Cl diagram implies that strontium behaves nearly as a conservative element in this part of the field and is dominantly influenced by boiling enrichment but not by mineral effects. For northern wells, however, very steep slopes indicate the preferential addition of Sr by dissolution of some strontium bearing phase. Since the trends visible on a

calcium vs. chlorine plot are nearly identical to those in Fig. 5b, we infer that the effect is due to a Sr bearing calcium mineral, most likely calcite. The shallowest wells in the northern region have consistently high Sr (Fig. 5b) and Ca concentrations while the deep northern wells and the deepest of the northern wells have the lowest concentrations.

It is apparent from the sample diagrams shown here that distinctive chemical compositions are observed for reservoir fluids in various regions of the field. In fact, a set of five distinct geographical regions can be identified solely on the basis of their geochemical signatures. Several bordering areas seem to be regions of mixing between these distinctive fluids while other zones have as of yet, not been analyzed adequately to document interactions between adjoining distinctive fluids. In addition to this simple classification of individual distinct regions of the Coso reservoir, constraints on the natural development of the fluid distribution can also be inferred. The presence of large, regionally consistent chemical variations

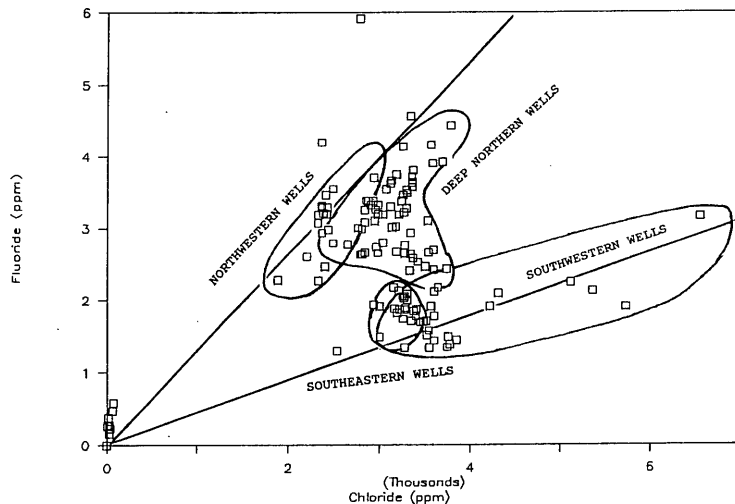


FIGURE 5a. Reservoir fluorine concentration plotted against reservoir chlorine concentration for all Coso samples. Regional groupings have been illustrated, as have radial theoretical "boiling" relationships.

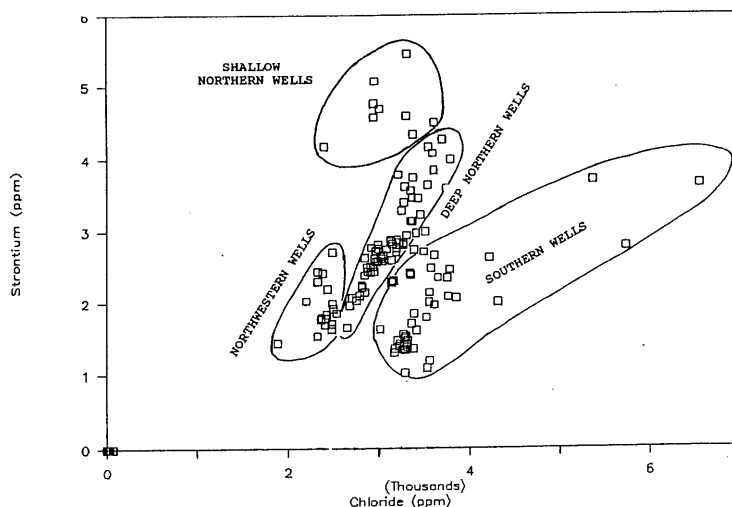


FIGURE 5b. Reservoir strontium concentration plotted against reservoir chlorine concentration for all Coso samples. Regional groupings have been illustrated.

indicates that reservoir mixing processes have been unable to homogenize fluid compositions in the Coso reservoir. Several interpretations for this lack of homogeneity are possible. First, the observations could indicate that the Coso reservoir is very young and that insufficient time has passed for convective mixing to occur. Second, the rate of convective mixing could be slow due to limited interconnectivity in this fracture dominated reservoir. Finally, the chemical variations could indicate that local water-rock interactions and reservoir processes (such as boiling) create chemical differences too rapidly for mixing to remove them. Of course, it is most reasonable to assume that all of these factors play some role in maintaining the regional variations observed.

The wide diversity and regionally compartmentalized nature of the Coso reservoir chemistry provides an ideal set of natural tracers with which to track production and injection induced transport within the system. In this respect the Coso field is unique, since widespread reservoir sampling has provided an excellent baseline against which to compare reservoir chemical surveys as thermal fluid withdrawal and injection progress. We hope that comparable routine sampling and analysis of the Coso reservoir fluids will be carried out as the field makes the transition from development into routine power production. If this is done, chemical variations with time may provide data (natural equivalents to tracer tests) needed to produce a high quality 3-dimensional reservoir model.

ACKNOWLEDGEMENTS

This is report 90-4 of the Center for Geothermal Resources Research, IGPP, Univ. of Calif., Riverside. We thank J. Moore and C. Austin and numerous CEC employees for the access to samples, analyses and information provided by CEC and the U.S. Navy. Additional thanks are expressed to R. Rye, T. Coplen and C. Kendall of the U.S.G.S. for their help in obtaining crucial isotopic analyses. This work was funded through research grants from the National Science Foundation (grant No. EAR-8804864 and EAR-8815503).

REFERENCES

- D'Amore, F. and A.H. Truesdell (1985) Calculation of geothermal reservoir temperatures and steam fractions from gas compositions; Geoth. Resources Council Trans. vol. 9, 305-310
- Drummond, S.E. and H. Ohmoto (1985) Chemical evolution and mineral deposition in boiling hydrothermal systems; Economic Geology, vol. 80, 126-147
- Fournier, R.O. and J.M. Thompson (1980) The recharge area for the Coso, California geothermal system deduced from δD and $\delta^{18}O$ in thermal and non-thermal waters in the region; U.S. Geol. Survey Open File Report 80-454
- Fournier, R.O., J.M. Thompson and C.F. Austin (1980) Interpretation of chemical analysis of waters collected from two geothermal wells at Coso, California; Jour. Geophys. Res. vol. 85, 2405-2410
- Ishihara, S. and A. Sasaki (1989) Sulfur isotopic ratios of the magnetite-series and ilmenite-series granitoids of the Sierra Nevada batholith - a reconnaissance study; Geology, vol. 17, 788-791
- Moore, J.N., M.C. Adams, B.P. Bishop and P. Hirtz (1989) A fluid flow model of the Coso geothermal system; Data from production fluids and fluid inclusions; Univ. of Utah Earth Sci. Lab. Report ESL-89001-JP
- Ohmoto, H. and A.C. Lasaga (1982) Kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems; Geochim. et Cosmochim. Acta, vol. 46, 1727-1746
- Taylor, B.E. (1986) Magmatic volatiles: isotopic variation of C, H, and S; Reviews of Mineralogy, vol. 16, 185-225