UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

Chemical Analyses of Water from the GTA-1 Well, Parkfield, California, and Other Nearby Spring and Well Waters

J. Michael Thompson and L. Douglass White

U.S. Geological Survey

Open File Report 91-0003

1991

Abstract

The GTA-1 well, located on the eastern side of Car hill near Parkfield, California, was drilled to monitor water conductivity and the dissolved gases carbon dioxide, hydrogen and radon. In addition, water from the GTA-1 well was periodically sampled for chemistry and water isotopes seeking changes that may be associated with the predicted future Parkfield earthquake. As yet no significant changes have been detected. Water isotopes in the area generally plot along the meteoric water line. The chemistry of the GTA-1 well closely resembles water from an irrigation well in Cholame Valley.

Introduction

Based on the pattern of recurrence of earthquakes in the Parkfield area, a magnitude 6 earthquake is expected to occur before 1993 (Bakun and McEvilly, 1984 and Bakun and Lindh, 1985). One objective of this study is to evaluate whether or not detectable changes in water chemistry occur before that predicted earthquake. In order to monitor for chemical changes in groundwater, a well (GTA-1) was drilled into the San Andreas fault zone at 23S/14E-35, NE 1/4 section. The GTA-1 well-water has been sampled periodically for chemistry and isotopes.

A second objective is to investigate mixing of groundwaters. Roeloffs and others (1989) reported that 12 of 18 creep events at Middle Mountain were accompanied by water level changes in a nearby observation well. Changes in water level may result in mixing of normal groundwater with perched aquifer waters. To investigate this more completely, two wells relatively close together and having different water chemistries were sampled and analyzed periodically, the GTA-1 well and the Haliburton well, to ascertain if the concentration of any major ions (Na, Ca, Mg, K, HCO_3, SO_4 and Cl), SiO_2, B, conductivity and/or water isotopes changed in a manner consistent with mixing.

A third objective is to look for evidence of deep rock-water interaction. In an experimental study, Kita and others (1982) demonstrated that H_2 could be produced from damp, freshly crushed quartz or granite in an experimental bomb at temperatures ranging from 25 to 270 °C. The reactions producing H_2 are free radical ones. To generate H_2, which is a chain termination reaction, two hydrogen radicals ($H\cdot$) must bond. Also generated in their mechanism is $SiO_2\cdot$ as a possible intermediate. At Parkfield the dominant rock is serpentine. Would $MgO\cdot$ and $SiO_2\cdot$ (free radicals) be produced in a serpentine as $SiO_2\cdot$ were produced in granites? If so, would the concentration of dissolved Mg^{2+} and SiO_2 may rise in response to free radical reactions driven by an applied stress. Monitoring Mg and SiO_2 concentrations may be a means of investigating the state of stress required to generate free radicals.

History

In July, 1987, the GTA-1 well was spudded in on the eastern side of Car hill (23S/14E-35AB) outside of Parkfield, California. The well was drilled as part of the U.S. Geological Survey's Parkfield earthquake-prediction experiment to monitor radon (Chi-yu King, project chief) and hydrogen, carbon dioxide and conductivity (M. Sato, project chief). Periodically, samples of the well water were collected for chemical and isotopic analyses. The results of those analyses are reported here.

The well monitoring was part of the Earthquake Hazard Reduction Program of the U.S. Geological Survey. Well drilling began about July 13, 1987, and the well was completed about July 28, 1987. Polyvinyl chloride (PVC) plastic casing, 22 cm (8 5/8 inches) outside diameter, was installed on July 23, to 129 m (424 feet), the well bottom. The following morning about two m of casing were found protruding above ground level. The PVC casing was removed, the well cleaned out and 16.8 cm (6 5/8 inch) steel casing was installed on July 27, 1987, to a bottom hole depth of 125 m (410 feet).

After the well was completed, a small well house was constructed over the well. Radon detecting instruments were installed inside the well-house in the Fall of 1987. The hydrogen, carbon dioxide and conductivity monitoring equipment was installed in December, 1987. Initially all experimental parameters were measured in duplicate. However, the well was unable to produce sufficient water to meet the requirements of all the equipment. Duplication ceased in Fall, 1988.

The duplicate instruments were removed and set-up at a nearby, unused irrigation well. This well is located approximately 1/4 mile from the trace of the San Andreas at 23S/14E-27,SE 1/4 section and was instrumented in December, 1988. This well produces sufficient water to meet the requirements of the radon monitoring system and the water conductivity, dissolved carbon dioxide, and hydrogen monitoring system.

The U.S. Geological Survey leased a ranch near Parkfield to provide housing for computers and other equipment and office space for employees working on the Parkfield Earthquake Prediction Experiment. Water for the ranch house, the Haliburton Ranch, is provided by a shallow, ≈20 m (≈60 feet) well. This water, too, was periodically collected and analyzed.

Field Methods

Only a relatively small number of spring and well waters were collected for this study because of limited funds. Water from the GTA-1 well, Haliburton Ranch, Miller Ranch and miscellaneous irrigation wells and various springs were collected without filtering and field determinations were not made. Field pH measurements were usually made with E. Merck colorphast pH strips. The waters were acidified immediately after collection with trace-metal grade (single distilled) hydrochloric acid.

Samples of some nearby springs were collected on May 3, 1988. One sample, Kerr Spring, was revisited on June 13, 1988, in order to collect a sample for carbon-13 analysis of the dissolved bicarbonate as well as major ion chemistry. Bicarbonate carbon-13 was previously collected from the GTA-1 well. Lastly, a seep from an old oil well, located at 23S/14E-5, SE 1/4 section, was collected by E. Roeloffs and A. Records in January 1990.

Methods of Analysis

Sodium was determined by atomic emission spectroscopy (AES) in an air acetylene flame at 589.0 nm with added K ion (0.1 % v/v).

Potassium was determined by atomic absorption spectroscopy (AAS) in an air acetylene flame at 766.5 nm with added Na ion (0.1 % v/v).

Lithium was determined by either AES or AAS in an air acetylene flame at 670.8 nm with added K ion (0.1 % v/v)

Calcium and ***magnesium*** were determined simultaneously by AAS in an air acetylene flame at 422.7 nm and 285.2 nm, respectively, with added La ion (1 % v/v).

Iron and ***manganese*** were determined simultaneously by AAS in an air acetylene flame at 248.3 nm and 275.5 nm, respectively, with added K ion (0.1 % v/v).

Ammonia was determined by spectrophotometry following procedure 428C described by the American Public Health Association (1975).

Boron was determined by AES in a direct current plasma at 249.7 nm.

Bicarbonate was determined by automated pH titration using standardized sulfuric acid to an endpoint near pH 4.2. The pH at the start of the titration was reported as the laboratory pH.

Chloride was determined by automated potentiometric titration to an endpoint near 310 mV with standardized $AgNO_3$.

Fluoride was determined by ion specific electrode using a 1:1 mixture of CDTA in an acetate buffer at pH 5.5 with 1 M NaCl (Fishman and Friedman, 1985).

Sulfate was determined by turbidity produced from $BaCl_2$ in acidic NaCl (Fishman and Friedman, 1985).

Silica was determined by spectrophotometry using reduced molybdenum blue at 640 nm (Shapiro and Brannock, 1956).

Sulfide was determined by using an iodometric titration. A 100 mL sample was precipitated with 4 mL of 20 percent $Zn(OAc)_2$ to inhibit oxidation. The sample was later acidified with 10 mL of 12N HCl to dissolve any ZnS. A known concentration of I_2 was added to oxidize any sulfide to sulfur. Excess I_2 was titrated with standardized $S_2O_3^{2-}$ to the starch endpoint (Fishman and Friedman, 1985).

Conductivity was determined using a Whatman CDM 300 conductivity meter.

Deuterium was determined following the technique of Biegelson and others (1952).

Oxygen-18 was determined following the technique of Epstein and Mayeda (1953).

Carbon-13 was determined following the procedure described by Huebner (1981).

For those elements determined using atomic spectroscopy, typical relative standard deviations (RSD) for the individual determinations are <2.0 percent for Na, K and Li, range from 2 - 4 percent for Ca and Mg, and range from 5 - 10 percent for B, Sr and Ba. The precisions for Ca, K, Mg, Li and Na in the data set are 7, 9, 6, 12 and 5 %, respectively (Fishman and Friedman, 1985). From standardization titrations, the RSDs for the individual HCO_3 and Cl determinations are ≈1.0 percent, the precision of the data for both is about 4 % (Fishman and Friedman, 1985). The individual measurement RSD for the spectrophotometric silica procedure is estimated to be <2 % based on multiple readings of the same standards and 7 % for the data set (Fishman and Friedman, 1985). RSD for the individual F determinations are about 10 % and are estimated to be about 41 % for the data set.

Chemistry

The results of the chemical and isotopic analyses are presented in Table 1. The data in Table 1 were used to construct Figure 1, a constituent - time plot, and Figure 2, a Schoeller diagram for the GTA-1 well. The Schoeller diagram indicates that the GTA-1 well is a Na-Mg-Ca HCO_3-Cl-SO_4 water. Both Figures 1 and 2 indicate little substantial variation in dissolved chloride concentrations from the GTA-1 well. Chloride was selected because the analytical precision is high and chloride salts are exceedingly soluble in naturals water of this composition.

Figure 3 is a Schoeller diagram of all the Haliburton Ranch well data. This diagram shows that the Haliburton well is a Mg-Ca-Na HCO_3-Cl-SO_4 type water. Figure 4 shows a Schoeller diagram for the GTA-1 well and the Haliburton Ranch well. The diagrams indicate that the waters from the two wells are different. The data in Table 1 show that significant mixing has not occurred between the GTA-1 well and the Haliburton Ranch well because the Cl concentrations in these wells are each essentially constant within analytical uncertainty.

Figure 5 is a Schoeller diagram for the miscellaneous springs in the Cholame Valley. The cations vary widely in concentration and ratios, but the general chemical pattern of the anions is similar. Figure 6 shows a similar plot for Ybarra Spring using additional data reported by Berkstresser (1963) and California Department of Water Resources (1979) indicating that the composition of Ybarra Springs has not changed significantly in 27 years. Because no significant changes in any dissolved constituent, especially Mg and SiO_2 were identified, within analytical uncertainty, at either Ybarra Spring, the Haliburton well or the GTA-1 well, there is no compelling evidence that a deep rock-water interaction is occurring at least as defined by objective 3. Further major ion monitoring may be required to document such changes.

As mentioned above the GTA-1 well water is dominated by Na while other surrounding waters are dominated by Mg. In a serpentinite environment, as is found here, the Mg dominated water is not unusual, while the Na dominated water is. Figure 7 is a Schoeller Diagram for the GTA-1 well and an irrigation well at 23S/14E-35, NE 1/4 section (California Department of Water Resources, 1979). This plot indicates that the water being pumped from the GTA-1 well is remarkably similar to the water from that irrigation well in Cholame Valley at 23S/14E-35, NE 1/4 section, approximately 8.6 miles south along the San Andreas fault. Water from both the GTA-1 and the irrigation well at 23S/14E-35, NE 1/4 section are dominated by Na. This suggests that water within the fault zone is rich in Na and Cl and is different from waters outside the fault zone.

Hydrogen and Oxygen Isotopes

A δD - $\delta^{18}O$ plot is shown in Figure 8. Examination of the plot shows that the GTA-1 well waters are generally about two per mil lighter in oxygen-18 and 10 per mil lighter in deuterium than nearby meteoric waters. This isotopic evidence combined with the chemical evidence suggests that the source of the GTA-1 water is not local and that it originated at a higher elevation and/or at a more northerly latitude. Unfortunately we do not have a current chemical or isotopic analysis of the well-water at 23S/14E-35, NE 1/4 section. Without further chemical and isotopic information, it cannot be determined if the irrigation well water in Cholame Valley originated in the same vicinity as the GTA-1 well water and if the water is a "fault water".

Because the bicarbonate concentrations in the GTA-1 well and Kerr Spring are greater than 600 mg/L, water samples were collected for carbon-13 analyses. The carbon-13 for the GTA-1 well and Kerr Spring were found to be similar, -14.8 and -13.6, respectively. Based on the results of the carbon-13 analyses, two expanations for the source of the bicarbonate are are possible.

The first explanation is that the bicarbonate originates from decomposition of organic material. Staniaszek and Halas (1988) reported on the carbon-13 and water chemistry from three springs near Lublin City, Poland. The bicarbonate concentrations and carbon-13 values they reported are comparable to those found here. They monitored the three springs near Lublin City from October 1982 through May 1983. They reported that the carbon-13 ranged from -12.47 to -14.78 at Baszki Spring, from -13.29 to -14.67 at Dys and from -12.83 to -15.14 at Pliszczynand suggest these values most likely arise from organic decomposition of plant matter. Their carbon-13 values approximate the values reported by van der Merwe and Medina (1989) for Amazonian rain forests.

A second explanation for the source of the bicarbonate is alteration of serpintinite. Table Mountain, a large serpentinite block, is located only 9 km (5.5 miles) NE of the San Andreas fault in this vicinity and may be the rock being altered to talc and carbonate minerals (see below). Huebner (1981) reported that carbon-13 values for Howard Springs and Seigler Springs in Lake County, California, an area where serpeninite is currently being altered to talc and carbonate minerals and which may be underlain by the sedimentary rocks of the Great Valley sequence, were -13 and -15, respectively. The available carbon-13 values are between those reported by Huebner for Howard Springs and Seigler Springs. However, Kerr Spring is situated in the Tertiary and Quaternary deposits comprising the Cholame Hills and GTA-1 well is situated in the Pleistocene sediments of Car Hill. A possible explanation for the similarity in carbon-13 values is that the bicarbonate originated from dissolution of carbonate minerals precipitated during serpentinization (see below).

In most cold waters calcium is the dominate cation. Magnesium concentrations are commonly two to ten times lower than calcium concentrations. In the vicinity of Parkfield, however, the magnesium normality is essentially equal to or greater than the calcium normality, suggesting the presence of dissolving magnesium compounds. Thus, we prefer the Mg originating from dissolution of serpeninites.

Equilibrium Calculations

Equilibrium calculations using the personal computer Program WATEQ4F (Ball and others, 1987) indicate that all waters in the vicinity of Parkfield are very near equilibrium with respect to amorphous silica. For the GTA-1 well, the calculations suggest that the water varies between being saturated and being undersaturated with respect to calcite and dolomite and perhaps magnesite in 1988 (Table 2). However from the 1989 and 1990 chemical analyses, the calculations indicate that the well water is undersaturated with respect to calcite, dolomite and magnesite. Calcite, dolomite, magnesite and amorphous silica are all alteration products of serpentine (Barnes and O'Neil, 1969, Barnes and others, 1973, and O'Neil and Barnes, 1971). Serpentine is common along many California fault zones and is also present at Table Mountain.

Possible reactions controlling the water chemistry are

$$CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^- \quad 1$$
$$Mg_3Si_2O_5(OH)_4 + 6H^+ = 3Mg^{2+} + 2Si(OH)_4 + H_2O \quad 2$$
$$Mg_3Si_2O_5(OH)_4 + 2Si(OH)_4 = Mg_3Si_4O_{10}(OH)_2 + 5H_2O \quad 3$$
$$Si(OH)_4 = SiO_2 + 2H_2O \quad 4$$
$$Mg^{2+} + 2HCO_3^- = Mg(HCO_3)_2 = MgCO_3 + CO_2 + H_2O \quad 5$$

Reaction 1 creates hydronium ions. These hydronium ions can then assist in the dissolution of chrysotile (a serpentine mineral) to form Mg^{2+} and $Si(OH)_4$ (reaction 2). The $Si(OH)_4$ can react with more chrysotile to form talc or dehydrate to form amorphous silica, SiO_2 (reactions 3 & 4). The Mg can react with HCO_3^- to form $Mg(HCO_3)_2$ which can decarboxylate and dehydrate to magnesite (reaction 5).

In general water from the GTA-1 well is clear. However, a black precipitate forms in the plastic tubing with time while the well is pumped. This precipitate appears to be iron sulfide. To determine if the precipitate was a sulfide, a water sample was collected for sulfide analysis. The water was determined to contain 1.8 mg/L sulfide and 4.8 mg/L Fe (total). From the chemistry given in Table 1, WATEQ4F calculates a log AP/KT value of +1.783 indicating that an iron sulfide should be actively precipitating from the well water.

The oil well water sampled by Roeloffs and Records is substantially different from anything previously sampled. The water isotopes are exceptionally heavy and the water has an exceptionally high conductivity. Because the water was collected from an abandoned oil well, most likely the water came from a brine associated with oil (some oil was reported on the surface of the water when it was sampled). Nearby oil fields reportedly produce from the Monterey Formation. Comparison of the oil seep water to waters associated with oil field brines (White and others, 1963; Kharaka, 1986) suggests that the water is similar to Tuscan Springs (Figure 9). Tuscan Springs issues from rocks of the Cretaceous Chico Formation near Red Bluff in Tehama County.

Kharaka (1986) reports that waters in sedimentary basins often have oxygen-18 values greater that nearby meteoric water. This is usually explained by rock-water interaction with heavier rock oxygen-18. He also reports that sedimentary basin waters also have a deuterium shift. Reported causes for the "hydrogen isotope shift" include authigenic mineral formation and membrane filtration. The shift is usually temperature related and may be to either heavier of lighter values.

Suggestions and Recommendations

During this study, other springs along active faults were sampled. These include Coalinga Mineral Springs (20S/13E-34, SE 1/4 section), Alum Rocks Springs (6S/2E-19, NW 1/4 section) and an unnamed spring group (12S/3E-10, NE 1/4 section) that emerged after the Loma Prieta Earthquake near El Pajaro Springs (at Pajaro Gap along California State Highway 129). These springs have very little in common, except that all have elevated bicarbonate concentrations, all have detectable H_2S (as high as 60+ mg/L) and Alum Rock and the unnamed springs along hiway 129 have detectable NH_3 (although only Alum Rock Springs were analyzed for NH_3). All, however, issue along active faults.

Alum Rock and the unnamed springs along hiway 129 have detectable NH_3 (although only Alum Rock Springs were analyzed for NH_3). All, however, issue along active faults.

Irwin and Barnes (1980) discuss the implications of high CO_2 discharges along active faults. Although they recognize that it may be difficult, they recommend that CO_2 discharges be monitored as well as other gases entrained in the CO_2. The use of Rn, H_2, ^3He concentrations and $^3He/^4He$ in predicting earthquakes was reported by Wakita and associates (Rn: Noguichi and Wakita, 1977, Wakita, 1978, Wakita, 1979, Wakita and others, 1980a, Wakita, 1981, Wakita, 1984, Wakita and others, 1985, Wakita and others, 1986; H_2: Wakita and others, 1980b, Kita and others, 1980, and Kita and others, 1982; ^3He and $^3He/^4He$: Wakita and others, 1978, Nagao and others, 1980, Sano and others, 1986, Wakita and others, 1987) These inert and reduced gases originate in the deep crust or mantle.

Little free oxygen is found in waters from deep drill holes indicating that water and gas from deep wells are anoxic. Most chemical species found in such environments have low (negative) oxidation-reduction potentials (Eh values). Thus, elevated concentrations of ammonia and hydrogen sulfide, which are common reduced gases produced by decomposition of organic matter, suggest origins as deep as 3-4 km. These gases dissolve readily in water. Springs having elevated concentrations of such gases apparently had either insufficient time to mix with and totally oxidize these gases to sulfate and nitrite/nitrate or else do not mix at all. Perhaps periodic analyses of springs having elevated concentrations of bicarbonate, ammonia and hydrogen sulfide (such as Warm Springs in southern Alameda County, Alum Rock Park in San Jose, and Coalinga Mineral Spring in Fresno County) may be appropriate in elucidating chemical processes occurring deep in the earth.

Acknowledgements

I thank M. Nathenson, E. A. Roeloffs and J. D. Sims for fruitful discussions and suggestions. I also thank A. Records for collecting GTA-1 well waters. I also appreciated the opportunity provided by M. Sato to sample the waters.

References

American Public Health Association, 1975, Standard Methods for the Examination of Water and Wastewater (14th edition): Washington, D.C., p. 503-505.

Bakun, W. H., and Lindh, A. G., 1985, The Parkfield, California, earthquake prediction experiment: Science, v. 229, p. 619-624.

Bakun, W. H., and McEvilly, T. V., 1984, Recurrence models and Parkfield, California, earthquakes: Journal of Geophysical Research, v. 89, p. 3051-3058.

Ball, J. W., Nordstrom, D. K. and Zachman, D. W., 1987, WATEQ4F--A Personal Computer FORTRAN Translation of the Geochemical Model WATEQ2 with Revised Data Base: U.S. Geological Survey Open-File Report 87-50, 108 p.

Barnes, Ivan, and O'Neil, J. R., 1969, The relationship between fluids in some fresh alpine-type ultramafics and possible modern serpentinizations, western United States: Geological Society of America Bulletin, v. 80, p. 1947-1960.

Barnes, Ivan, O'Neil, J. R., Rapp, J. B., and White, D. E., 1973, Silica-carbonate alteration of serpentine: Wall rock alteration in mercury deposits of the California Coast Ranges: Economic Geology, v. 68, p. 388-398.

Berkstresser, C. F., 1968, Data for the springs in the Southern Coast, Transverse, and Peninsular Ranges of California: U.S. Geological Survey Open-File Report, March 1968, 53 p.

Biegelson, J., Perlman, M. L., and Prosser, H. C., 1952, Conversion of hydrogenic materials to hydrogen for isotopic analysis: Analytical Chemistry, v. 24, p. 1356-1357.

California Department of Water Resources, 1979, Ground water in the Paso Robles Basin: Southern District Report, March 1979, p. 65-66.

Epstein, S., and Mayeda, T., 1953, Variations of the ^{18}O contents of waters from naturals sources: Geochimica et Cosmochimica Acta, v. 4, p. 213-224.

Fishman, M. J., and Friedman, L. C., 1985, Methods for the determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Open-File Report 85-495, 709 p.

Huebner, M., 1981, Carbon-13 isotope values for carbon dioxide gas and dissolved carbon species in springs and wells in the Geyser-Clear Lake region, in R. J. McLaughlin and J. M. Donnelly-Nolan (Eds.), Research in the Geysers-Clear Lake Geothermal area, Northern California: U.S. Geological Survey Professional Paper 1141, p. 211-214.

Irwin, W. P., and Barnes, Ivan, 1980, Tectonic relations of carbon dioxide discharges and earthquakes: Journal of Geophysical Research, v. 85, No. B6, p. 3115-3121.

Kharaka, Yousef K., 1986, Origin and evolution of water and solutes in sedimentary basins: Third Canadian/American Conference on Hydrogeology, Proceedings, Brian Hitchon, Stefan Bachu, and Claude Sauveplane (Eds.), National Water Well Association, Dublin, Ohio, p. 173-195.

Kita, I., Matsuo, S., Wakita, H., and Nakamura, Y., 1980, D/H ratios of H_2 in soil gases as an indicator of fault movements: Geochemical Journal, v. 14, p. 317-320.

Kita, I., Matsuo, S., and Wakita, H., 1982, H_2 generation by reaction between H_2O and crushed rock: An experimental study on H_2 degassing from the active fault zone: Journal of Geophysical Research, v. 87 No. B13, p. 10789-10795.

Nagao, K., Takaoka, N., Wakita, H., Matsuo, S., and Fujii, N., 1980, Isotopic composition of rare gases in teh Matsushiro earthquake fault region: Geochemical Journal, v. 14, p. 63-69.

Noguchi, M., and Wakita, H., 1977, A method for continous measurement of radon in groundwater for earthquake prediction: Journal of Geophysical Research, v. 82, p. 1353-1357.

O'Neil, J. R., and Barnes, Ivan, 1971, C-13 and O-18 compositions in some fresh-water carbonates associated with ultramafic rocks and serpentinites: western United States: Geochimica et Cosmochimica Acta, v. 35, p. 687-697.

Roeloffs, E. A., Burford, S. S., Riley, F. S. and Records, A. W., 1989, Hydrologic effects on water level changes associated with episodic fault creep near Parkfield, California: Journal of Geophysical Research, v. 94, No. B9, p. 12,387-12,402.

Sano, Y., Nakamura, Y., Wakita, H., Notsu, K., and Kobayashi, Y., 1986, $^3He/^4He$ ratio anomalies associated with the 1984 western Nagano earthquake: Possibly induced by a diapiric magma: Journal of Geophysical Research, v. 91, p. 12,291-12,295.

Shapiro, Leonard, and Brannock, W. W., 1956, Rapid analysis of silicate rock: U.S. Geological Survey Bulletin 1036-C, p. 32-34.

Staniaszek, P. and Halas, S., 1988, Chemistry and $\delta^{13}C$ of total dissolved carbon in waters of selected springs nearby Lublin City: Weekly observations from October 1982 to June 1983: Nordic Hydrology, v. 19, p. 121-134.

van der Merwe, N. J., and Medina, E., 1989, Photosysnthesis and $^{13}C/^{12}C$ ratios in Amazonian rain forests: Geochimica et Cosmochimica Acta, v. 53, p. 1091-1094.

Wakita, H., 1978, Earthquake prediction and geochemical studies in China: Chinese Geophysics, v. 1, p. 443-457.

Wakita, H.,1979, Earthquake prediction by geochemical techniques: Record of Progress of Natural Science in Japan, v. 4, p.69-75.

Wakita, H., 1981, Precursory changes in groundwater prior to the 1978 Izu-Oshima-kinkai earthquake in D. E. Simpson and P. G. Richard (Eds.) Earthquake Prediction, An International Review: American Geophysical Union, v. 4, p. 527-532.

Wakita, H., 1984, Groundwater observations for earthquake prediction in Japan: Proceedings of the International Symposium on Continental Seismicity and Earthquake Prediction, p. 494-500.

Wakita, H., Nakamura, Y., Notsu, K., Noguchi, M., Asada, T., 1980a, Radon anomaly: a possible precursor of the 1978 Izu-Oshima-kinkai earthquake: Science, v. 207, p. 882-883.

Wakita, H., Nakamura, Y., and Sano, Y., 1985, Groundwater radon variation reflecting changes in regional stress fields: Proceedings of the U.S.-Japan Seminar on Practical Approaches to Earthquake Prediction and Warning, Earthquake Prediction Research, v. 3, p. 545-557.

Wakita, H., Nakamura, Y., Sano, Y., 1986, Background fluctuation in groundwater radon observation: Journal of Physics of the Earth's Interior, v. 34, p. S81-S89.

Wakita, H., Nakamura, Y., Kita, I., Fujii, N., and Notsu, K., 1980b, Hydrogen release: New indicator of fault activity: Science, v. 210, p. 188-190.

Wakita, H., Fujii, N., Matsuo, S., Notsu, K., Nagao, K., and Takaoka, N., 1978, "Helium spots": Caused by a diapiric magma from the upper mantle: Science, v. 200, p. 430-432.

Wakita, H., Sano, Y., Mizoue, M., 1987, High ^{3}He emanation and seismic swarms observed in a nonvolcanic, forearc region: Journal of Geophysical Research, v. 92, 12,539-12,546.

White, D. E., Hem, J. D., and Waring, G. A., 1963, Chapter F Chemical composition of subsurface waters in Michael Fleischer (Eds.) Data of Geochemistry, Sixth Edition, U.S. Geological Survey Professional Paper 440-F, p. F36.

Table 1. Chemical analyses of GTA-1 well waters and well and springs waters in the vicinity of Parkfield, California. (analysts: J. M. Thompson, chemistry, and L. D. White, isotopes)

Sample no.	Date Collected	Collector*	Water Temp	1 pH	SiO_2	Fe	Mn	Ca	Mg
					<		mg/L		>
GTA-1 well (23S/14E-35AB)									
PJ-87-01	17 Dec 87	JMT	19	7.45	41.2	1.74	0.07	19.2	20.3
PJ-88-01	23 Jan 88	JMT	23	7.4	42.8	3.5	0.1	20.1	22.7
PJ-88-02	19 Feb 88	AR	--	7.85	41.1	0.023	0.044	14.6	21.4
PJ-88-03	1 Apr 88	AR	--	7.37	41.3	0.63	0.06	14.4	21.1
PJ-88-04	19 Apr 88	AR	--	7.46	41.3	0.66	0.06	13.3	21.0
PJ-88-05	25 Apr 88	JMT	--	7.43	41.1	0.64	0.06	13.2	20.9
PJ-88-06	3 May 88	JMT	23.5	7.26	41.3	1	0.06	14.4	21.0
PJ-88-07	13 May 88	AR	--	7.37	37.8	--	--	10.1	20.5
PJ-88-08	12 Oct 88	AR	--	6.98	38.9	--	--	10.9	19.2
PJ-88-09	16 Nov 88	JMT	--	6.89	38.3	--	--	11.1	19.0
PJ-89-01	26 Jan 89	AR	--	6.77	37.8	--	--	10.6	19.0
PJ-89-02	15 Mar 89	AR	--	7.03	37.7	--	--	10.6	19.0
PJ-89-03	16 May 89	AR	--	7.02	37.6	--	--	11.1	20.5
PJ-89-04	9 Jun 89	JMT	--	7.42	37.6	--	--	11.5	20.5
PJ-90-02	29 Mar 90	JMT	23.7	7.05	37.3	4.28	0.09	13.1	24.0
PJ-90-05	30 Mar 90	AR	--	7.06	37.9	9.66	0.76	11.4	20.1
PJ-90-06	11 May 90	JMT	--	6.26	36.7	0.6	0.07	13.2	20.2
Irrigation well similar to GTA1 at 25S/15E-11C3									
	8 Nov 73		17	7.7	--	--	--	42.0	57.0
	18 Oct 76		16	8	--	--	--	48.0	47.0
Haliburton Ranch Domestic well (23S/14E-35AA)									
PJ-88-10	25-Apr 88	JMT	--	7.14	43.9	0.07	0.02	65.6	49.1
PJ-89-05	9 Jun 89	JMT	--	7.3	40.3	0.11	0.02	62.3	41.6
PJ-90-03	29 Mar 90	JMT	15.5	6.34	40.6	--	--	54.8	49.1
PJ-90-07	30 Mar 90	AR	--	6.18	40.9	0.08	0.02	58.3	35.8
PJ-90-08	11 May 90	JMT	--	6.12	40.2	0.06	0.01	54.7	34.8
Miller Ranch well (23S/14E-27AD)									
PJ-89-06	8 Jun 89	JMT	--	7.27	39	--	--	49.9	108.0
PJ-90-04	29 Mar 90	JMT	22	6.43	38	0.03	0.11	49.5	116.9
PJ-90-09	11 May 90	JMT	--	6.12	37.8	1.05	0.17	51.0	112.7
Miscellaneous Springs									
Buckeye Spg	21 Sep 88	AR	--	6.23	20.4	--	--	37.0	17.0
Jack Ranch	3 May 88	JMT	--	6.73	47.6	<.01	0.01	19.3	50.3
Jespersen Spg	3 May 88	JMT	19	6.73	41.3	<.01	<.01	51.6	27.2
Kerr Spg	3 May 88	JMT	17	6.57	45.8	1.25	0.03	169.3	99.8
Kerr Spg	13 Jun 88	JMT	17	6.57	45.3	0.08	0.01	166.	97.2
Ybarra Spg	10 Jun 63	CFB	14	8.2	44	0.014	--	92.0	64.0
Ybarra Spg	13-Jun 67	unk	16	7.8	--	--	--	150.	40.0
Ybarra Spg	3 May-88	JMT	16	7.15	76.8	2.84	0.15	112.	79.7
Middle Mountain Oil well seep (23S/14E-5DC)									
	31 Jan 90	AR&ER	20.3	8.41	42.3	0.05	0.14	137.	60.0

* CFB, C. F. Berkstresser, AR, Andy Records, ER, Evelyn Roellofs, JMT, J. M. Thompson

Table 1. continued

Sample no.	Na	K	Li	HCO$_3$	SO$_4$	Cl	F	B	Meas. Cond.	delta D	delta ^{18}O	delta ^{13}C
	<—			mg/L				—>	µS	<—	in °/oo	—>
GTA-1 well (23S/14E-35AB)												
PJ-87-01	274	2.49	0.03	606	72	138	0.36	3.3	1403	-61.3	-8.16	--
PJ-88-01	271	2.32	0.04	615	63	122	0.31	3.1	1314	-62.9	-8.24	--
PJ-88-02	300	1.37	0.03	640	100	114	0.11	2.8	1281	-61.8	-8.27	--
PJ-88-03	308	1.25	0.03	642	75	108	0.1	2.7	1271	-61.2	-8.12	--
PJ-88-04	298	1.71	0.03	638	91	106	0.1	2.7	1267	-60.1	-7.89	--
PJ-88-05	294	1.27	0.03	638	83	107	0.15	2.7	1269	-61.5	-8.45	--
PJ-88-06	305	0.99	0.03	637	89	106	0.15	2.7	1259	-57.5	-8.25	-14.85
PJ-88-07	280	2.15	0.03	632	76	126	0.19	2.7	1266	--	--	--
PJ-88-08	291	2.11	0.03	627	77	107	0.28	2.9	1277	--	--	--
PJ-88-09	279	2.04	0.03	627	72	109	0.2	2.9	1272	--	--	--
PJ-89-01	280	2.07	0.03	629	72	108	0.21	2.8	1274	--	--	--
PJ-89-02	279	2.15	0.03	626	69	109	0.19	2.8	1271	--	--	--
PJ-89-03	274	2.05	0.03	621	55	109	0.18	2.6	1266	--	--	--
PJ-89-04	272	2.16	0.03	620	60	113	0.21	2.8	1268	-58	-7.7	--
PJ-90-02	256	4.52	0.04	612	63	124	0.201	2.7	1278	-55	8.0	--
PJ-90-05	250	1.97	0.04	599	36	124	0.16	3.0	1266	-58	-7.8	--
PJ-90-06	259	1.96	0.04	603	48	121	0.15	2.6	1279	-59	-8.0	--
Irrigation well similar to GTA-1 at 25S/15E-11C3												
	215	6.2	--	586	30	121	0.3	1.3	1242	--	--	--
	167	3.1	--	558	60	116	0.4	1.2	1232	--	--	--
Haliburton Ranch Domestic well (23S/14E-35AA)												
PJ-88-10	56.9	0.42	0.03	423	79	55.4	0.17	0.09	--	-47.8	-6.49	--
PJ-89-05	62.3	1.36	0.03	405	51	50.5	0.25	0.1	841	-48	-6.4	--
PJ-90-03	56.0	1.15	0.05	400	65	50.5	0.22	0.3	865	-46	-6.6	--
PJ-90-07	54.9	1.25	0.03	402	54	50	0.18	<.1	846	-47	-6.5	--
PJ-90-08	55.5	2.33	0.04	395	57	48.8	0.48	<.1	846	-47	-6.6	--
Miller Ranch well (23S/14E-27AD)												
PJ-89-06	152	2.05	0.02	412	12	452	0.18	0.3	1872	-52	-6.8	--
PJ-90-04	95	3.78	0.04	410	29	347	0.17	0.6	1566	-51	-7.0	--
PJ-90-09	146.2	2.03	0.02	412	16	462	0.13	0.6	1898	-52	-6.9	--
Miscellaneous Springs (see text for location)												
Buckeye Spg	30	1.06	<.01	193	62	19	0.13	<.1	598	--	--	--
Jack Ranch	34.1	0.63	0.01	330	39	25	0.1	0.2	700	-46	-5.98	--
Jespersen Spg	110	1.9	0.15	248	174	56	0.65	0.4	1691	-48.5	-6.27	--
Kerr Spg	86.2	1.7	0.15	274	690	73.6	0.6	0.5	2022	-45.5	-6.45	--
Kerr Spg	86.5	1.58	0.15	368	700	72.5	0.61	0.5	--	-57	-6.34	-13.63
Ybarra Spg	141	3.7	0.18	304	408	95	1	0.8	1438	--	--	--
Ybarra Spg	156	3	--	310	428	99	1	1.6	1483	--	--	--
Ybarra Spg	125	4.6	0.21	405	370	103	0.85	0.8	790	-53	-6.33	--
Middle Mountain oil seep (23S/14E-5DC)												
	8494	91	4.55	2730	1	11430	0.29	392.	31200	-18	6.7	--

Table 2. Results of WATEQ4F log AP/KT calculations for alteration products of serpentine on Parkfield area waters: 0.000, equilibrium, +, saturated and - undersaturated.

Date	Calcite	Dolomite	Magnesite	Am. Silica	Talc
GTA-1 well (23S-14E-35)					
17 Dec 87	-.153	-.000	-.357	-.078	+.073
23 Jan 88	-.099	+.102	-.291	-.106	+.332
19 Feb 88	+.202	+.821	+.128	-.126	+2.8823
5 Mar 88	-.019	+.032	-.091	-.128	+1.507
1 Apr 88	-.263	-.113	-.341	-.121	-.024
19 Apr 88	-.216	+.016	-.206	-.122	+.497
25 Apr 88	-.245	-.092	-.288	-.124	+.311
3 May 88	+.071	+.165	-.394	+.229	+.470
14 Jun 88	-.258	-.100	-.333	+1.879	+8.133
15 Mar 89	-.623	-.729	-.598	-.173	-1.842
29 Mar 90	-.622	-.727	-.597	-.173	-1.843
Haliburton well (23S/14E-35)					
25 Apr 88	-.026	+.035	-.430	-.061	-.456
29 Mar 90	-.980	-1.850	-1.358	-.043	-5.896
Miller well (23S/14E-27)					
29 Mar 90	-.885	-1.162	-.769	-.145	-3.676
Kerr Spring (25S/15E-9)					
3 May 88	-.586	-1.213	-1.115	-.006	-3.632
13 Jun 88	-.605	-1.253	-1.137	-.011	-3.689

Table 3. Chemical analyses of deep waters issuing from springs near known faults. Constituents ara in mg/L, conductivity is in µS and isotopic values are in per mil from mean seawater.

	Coalinga[1] Mineral Spring 20S/13E-34	GTA-1[1] well 23S/14E-35	unnamed[1] nr El Pajaro 12S/8E-10	Alum Rock Park[2] Spring #4[a] 6S/2E-19	 Spring #11[b]
Date	10Jun89	29Mar90	29Mar90	26Apr90	26Apr90
Temp	34	23.7	21.4	28.3	28.2
f pH	8.8	--	--	6.8	6.8
l pH	6.61	7.05	6.82	6.78	7.00
SiO_2	58.2	37.3	36.2	43.4	25.2
Fe	--	4.28	.07	.16	.25
Mn	--	.09	.03	.27	.41
Ca	.67	13.1	2.05	102	50.3
Mg	.04	24	97.1	69	22.3
Na	130	256	50.7	739	586
K	1.28	4.52	5.45	17.6	15.5
Li	.023	.045	.072	.57	.40
NH_4	--	--	--	15	13.5
HCO_3	188	612	793	1780	1710
SO_4	4	63	400	38	196
Cl	67.9	124	62.5	165	458
F	4.5	.20	.83	2.0	1.9
B	7.1	2.7	.73	8.5	27.6
H_2S	--	1.8	68.7	3.7	6.3
Conduct.	603	1278	793	2780	3870
δD	-62.	-55	-39	-55	-45
$\delta^{18}O$	-7.7	-7.9	-5.8	-7.4	-5.2

[1] collected by J. M. Thompson

[2] collected by D. S. Basler

[a] Matches chemistry for White Sulphur Spring in Berkstresser (1968).

[b] Matches chemistry of Sulphur Tunnel No. 3 in Berkstresser (1968).

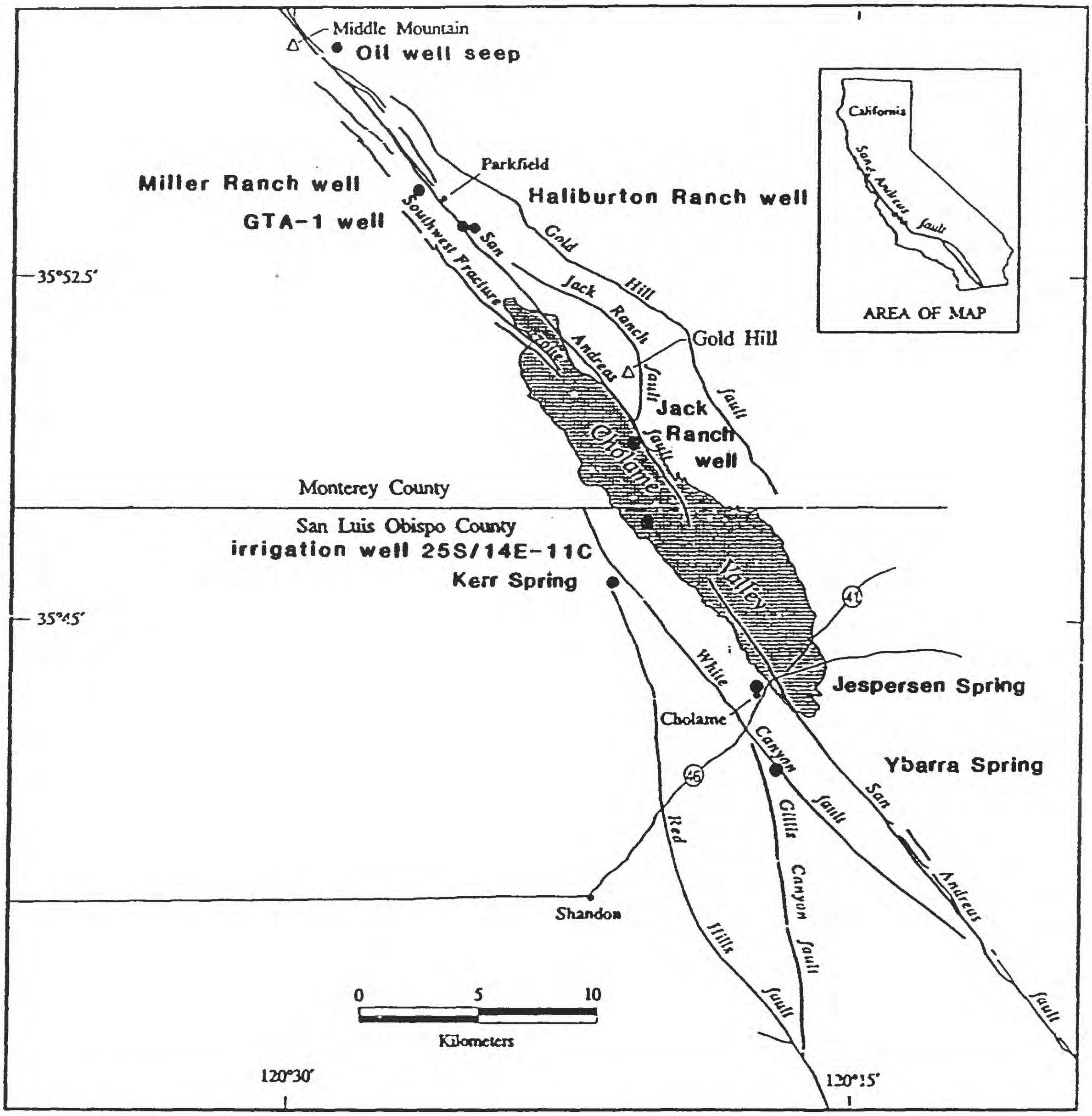

Figure 1. Locations map of water sampling sites in this study. Map courtesy of J. D. Sims and J. C. Hamilton, Geologic Map of the Cholame Quadrangle, San Luis Obispo County, in press.

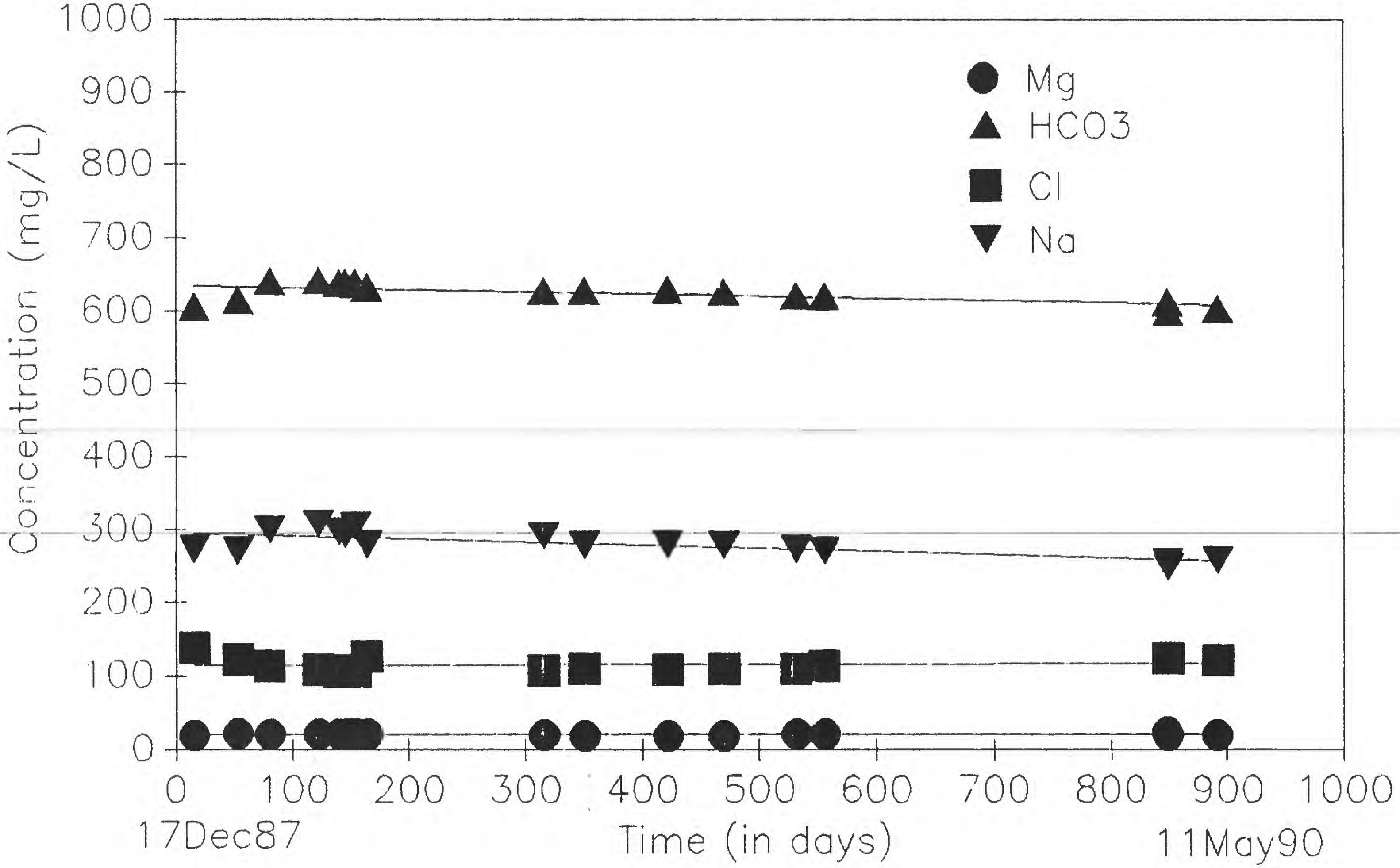

Figure 2a. A constituent - time (in days) plot for Mg, HCO_3, Cl and Na in the GTA-1 well (23S/14E-35, NE 1/4 section) in Monterey County, California. Lines through data points are calculated first order regression.

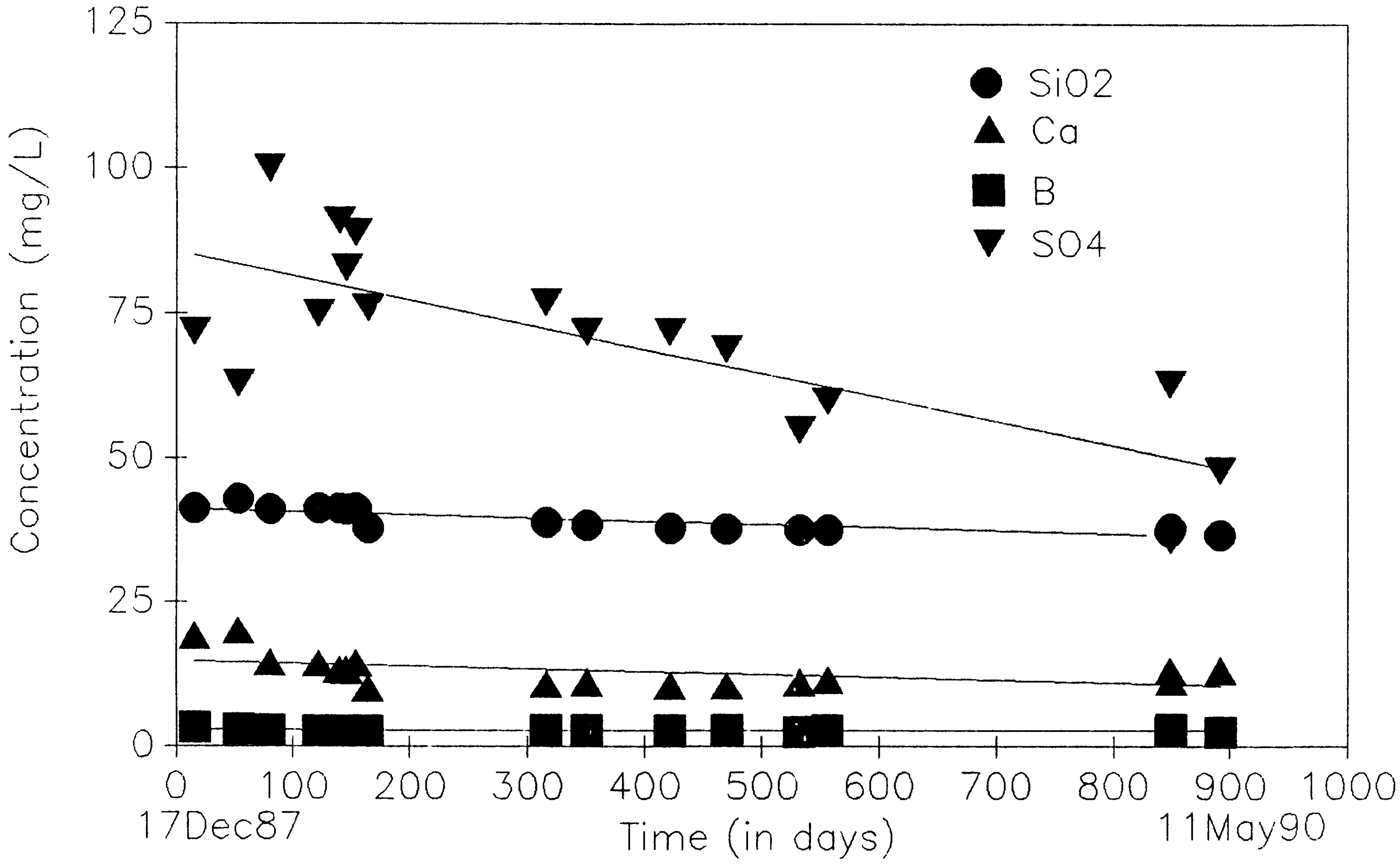

Figure 2b. A constituent - time (in days) plot for SiO_2, Ca, B and SO_4 in the GTA-1 well (23S/14E-35, NE 1/4 section) in Monterey County, California. Lines through data points are calculated first order regression.

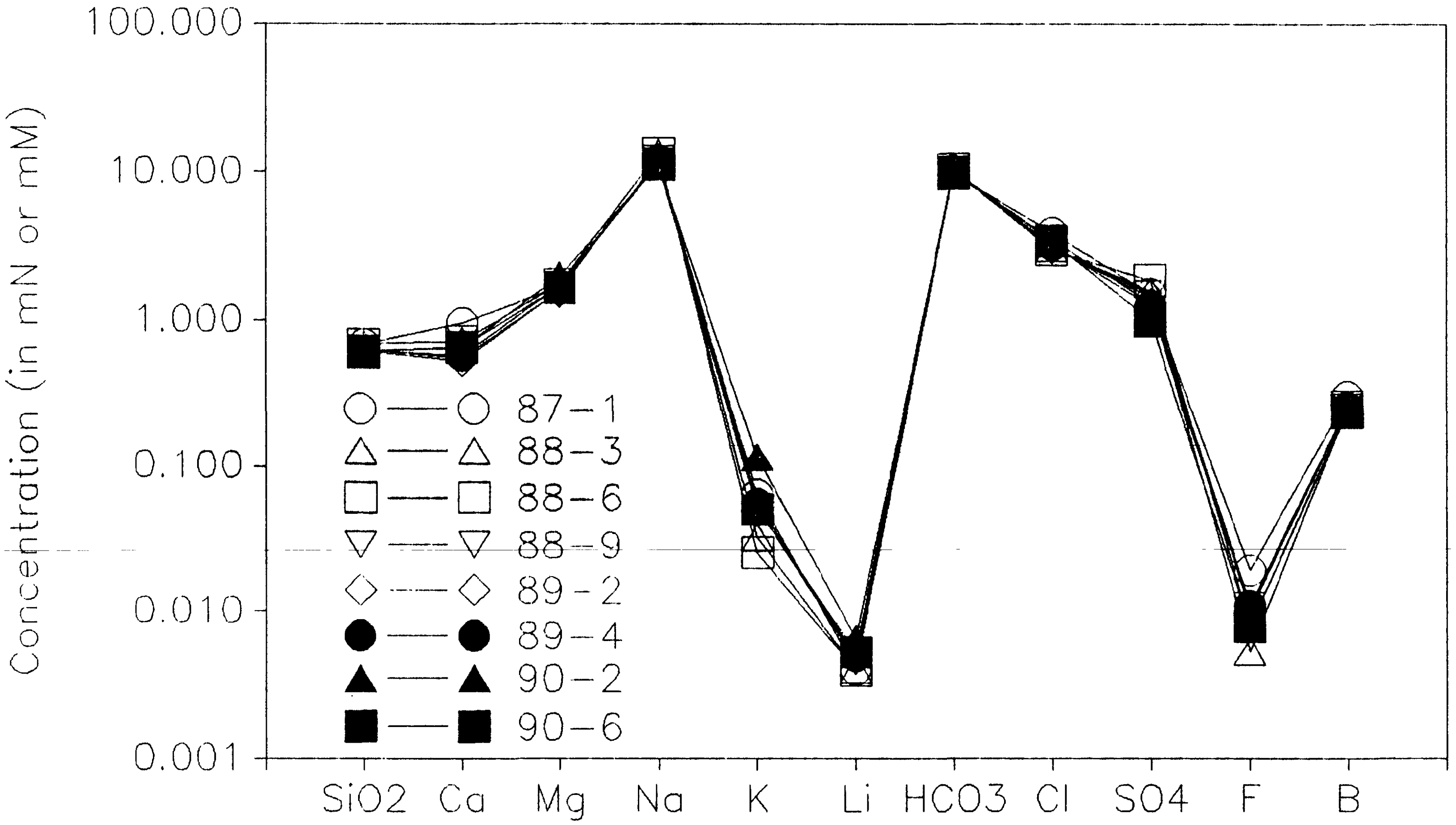

Figure 3. Schoeller Diagram for the GTA-1 well water.

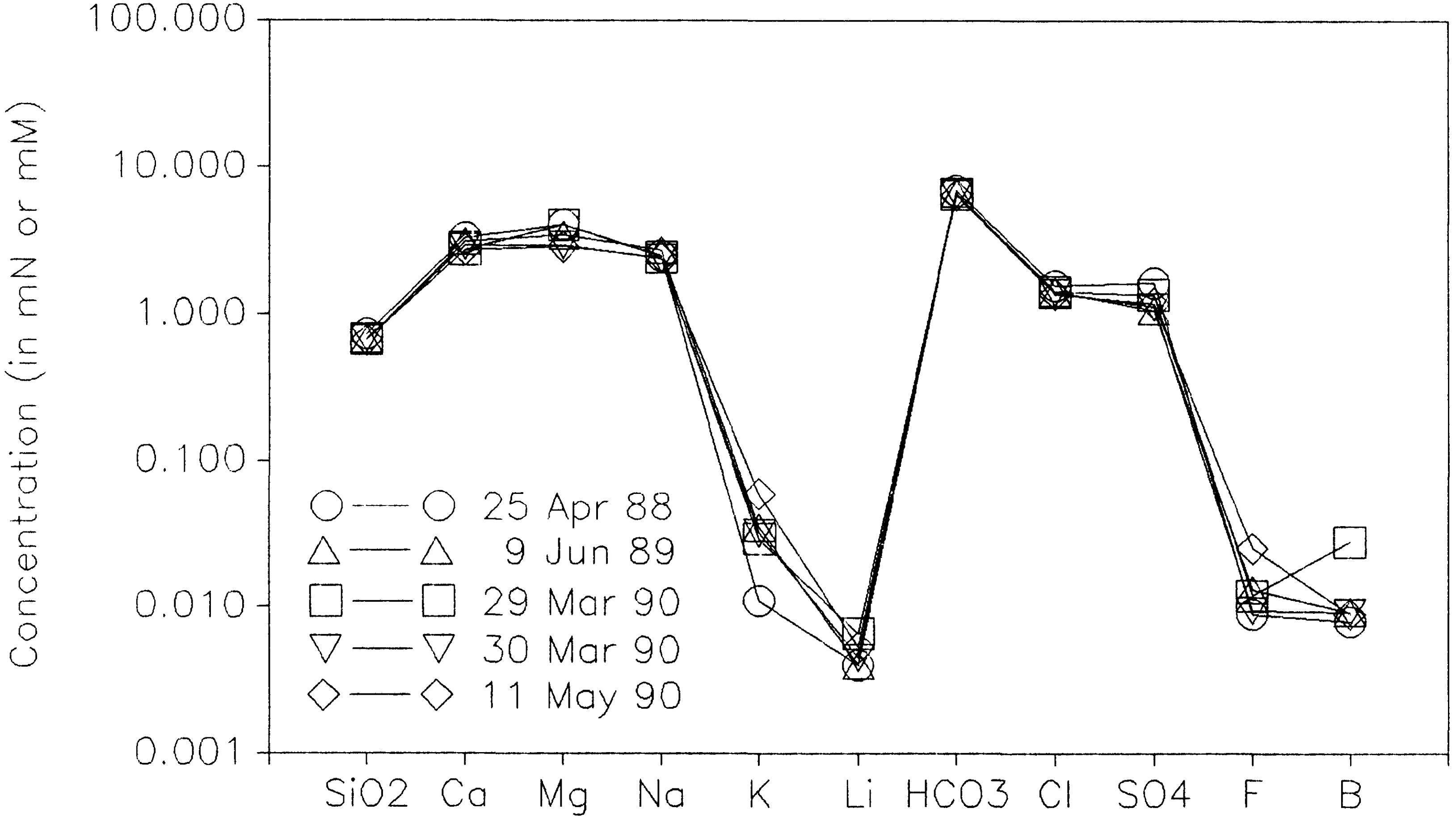

Figure 4. Schoeller Diagram for the Haliburton well water.

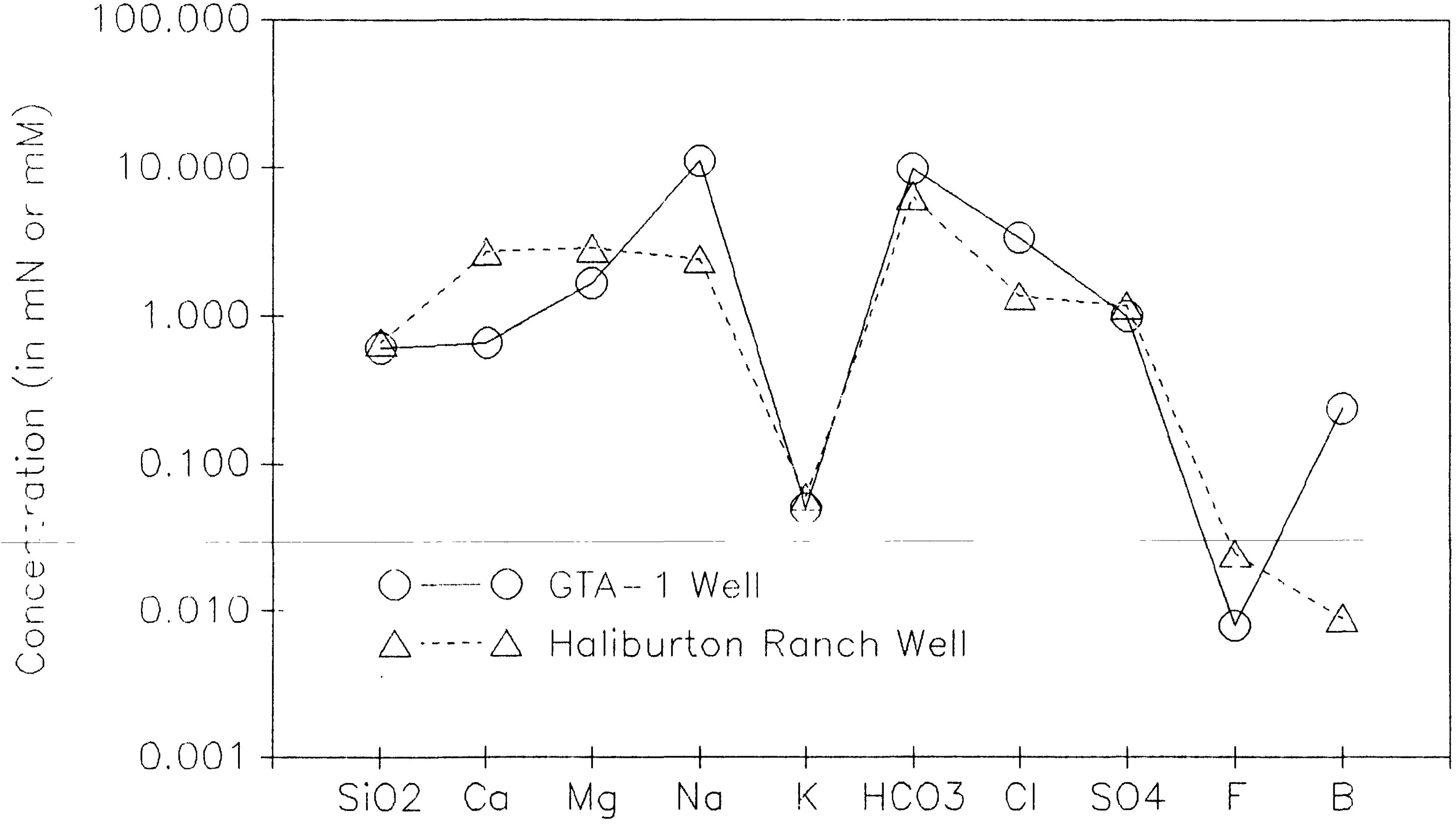

Figure 5. Schoeller Diagram comparing GTA-1 well water to the Haliburton Ranch well water on 11 May 1990.

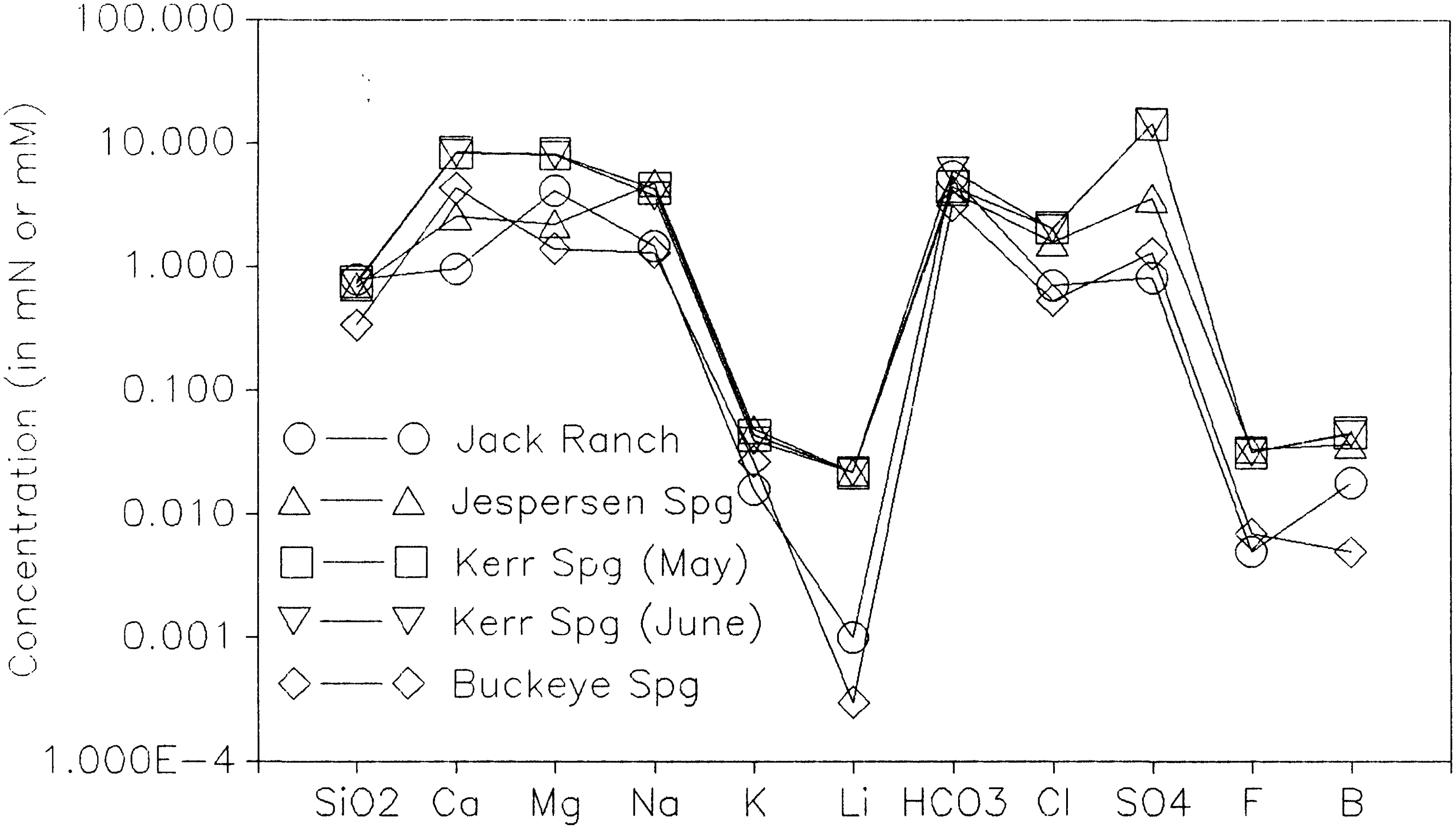

Figure 6. Schoeller diagrams for cold springs in the Cholame Valley and vicinity.

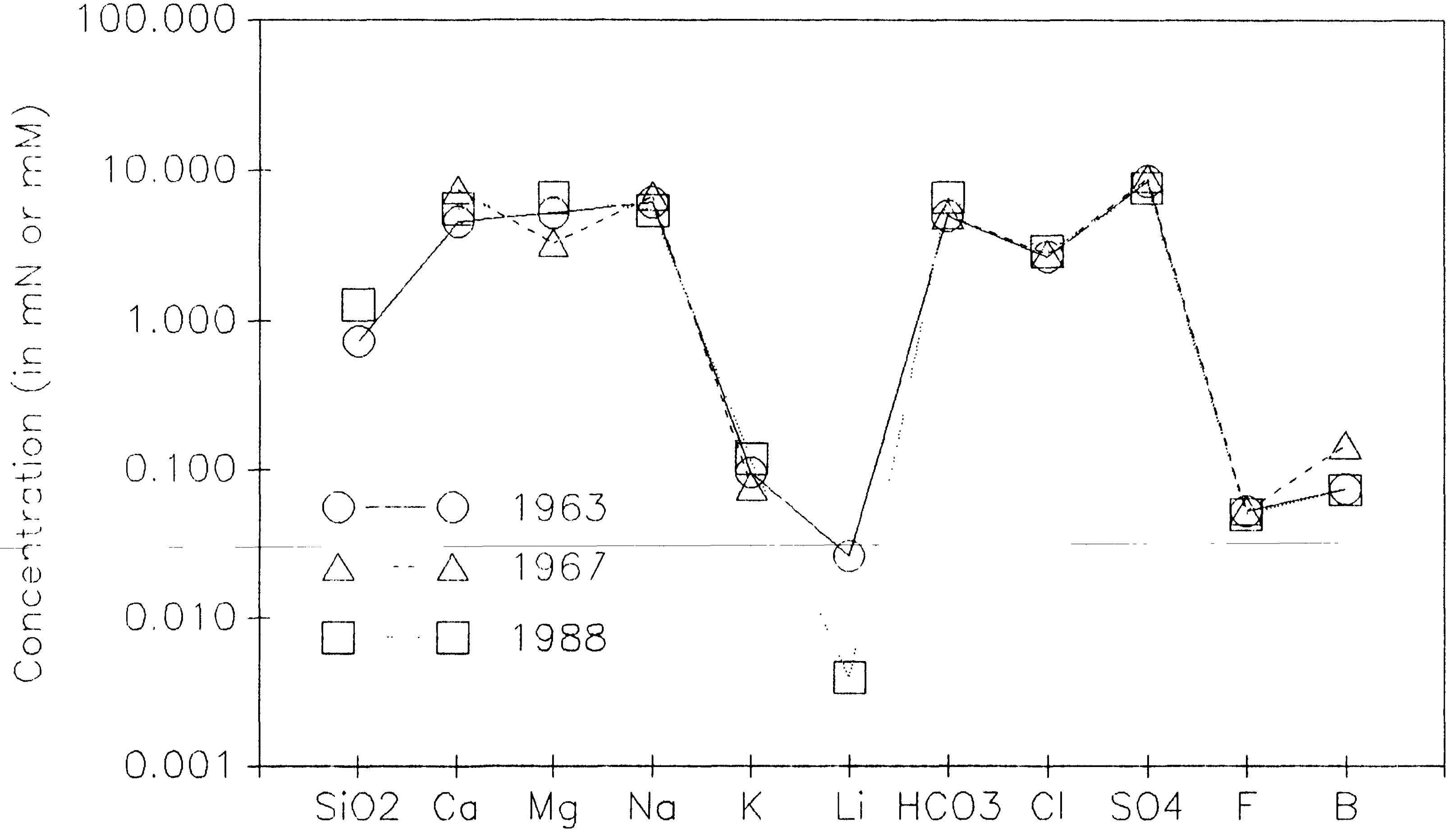

Figure 7. Schoeller diagrams for Ybarra Spring.

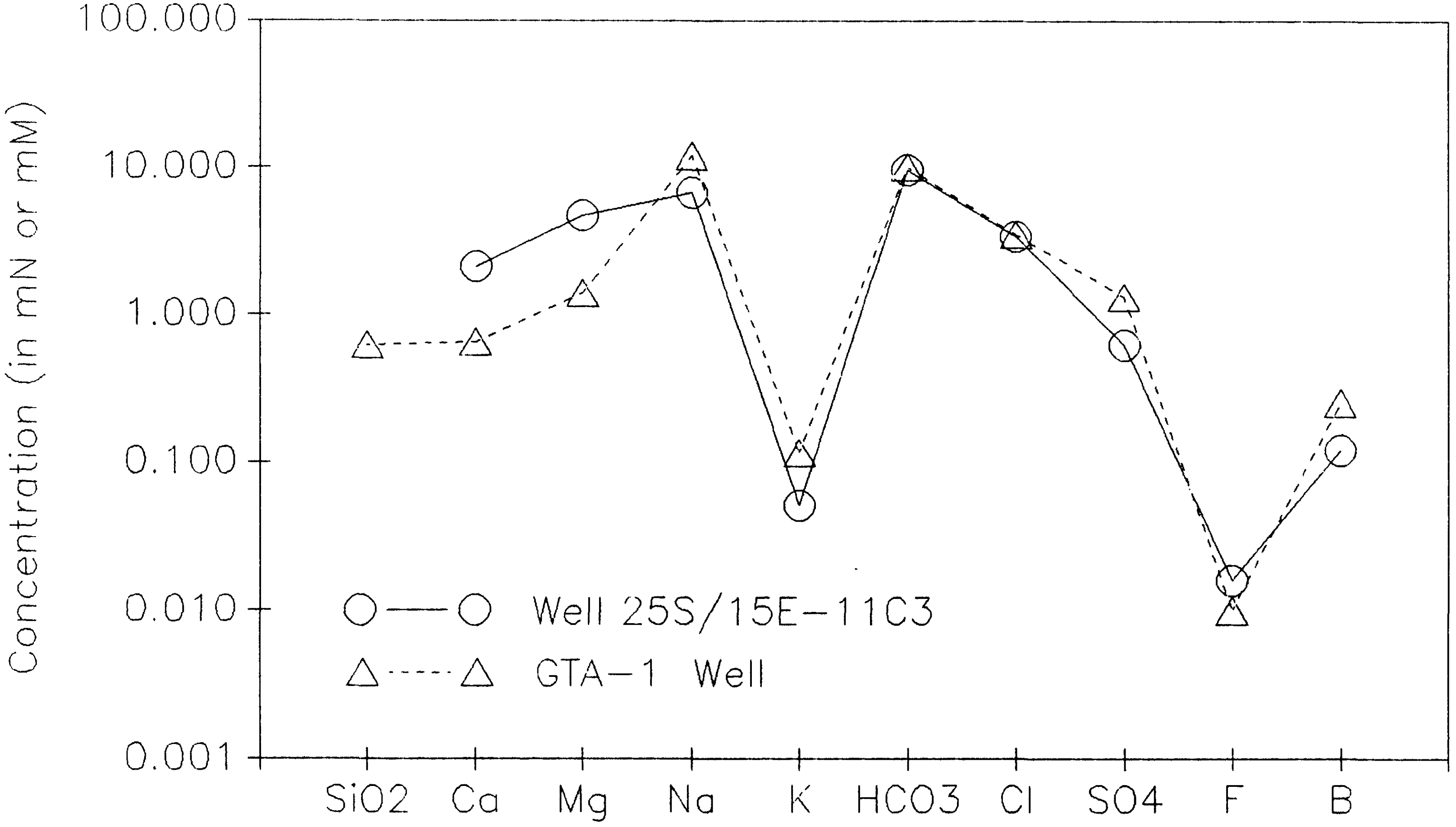

Figure 8. A comparison using Schoeller diagrams between GTA-1 well water and irrigation water at 25S/15E-11, NE 1/4 section.

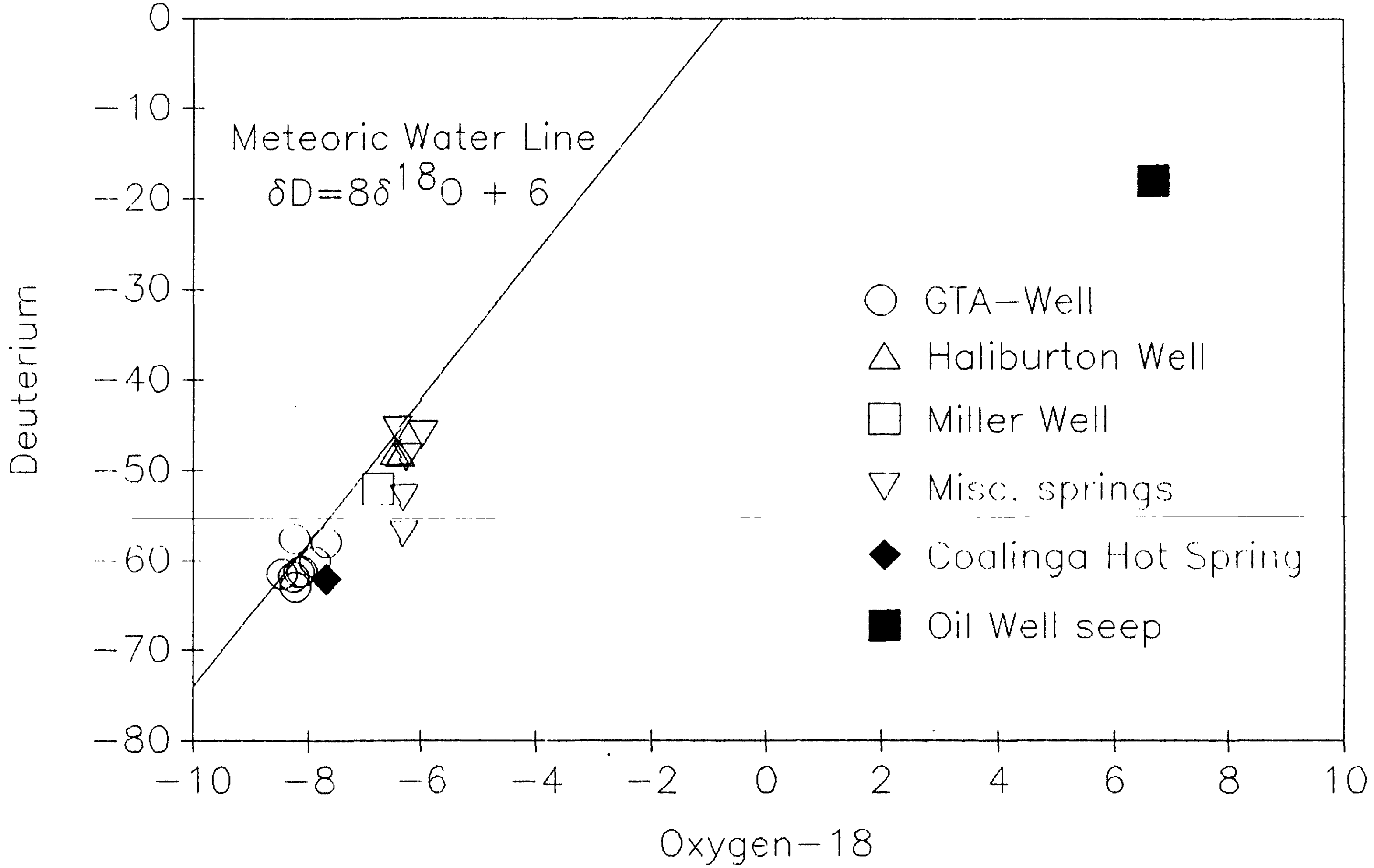

Figure 9. Relation between deuterium and oxygen-18 for waters from springs and wells near Parkfield and in the Cholame Valley and vicinity, California.

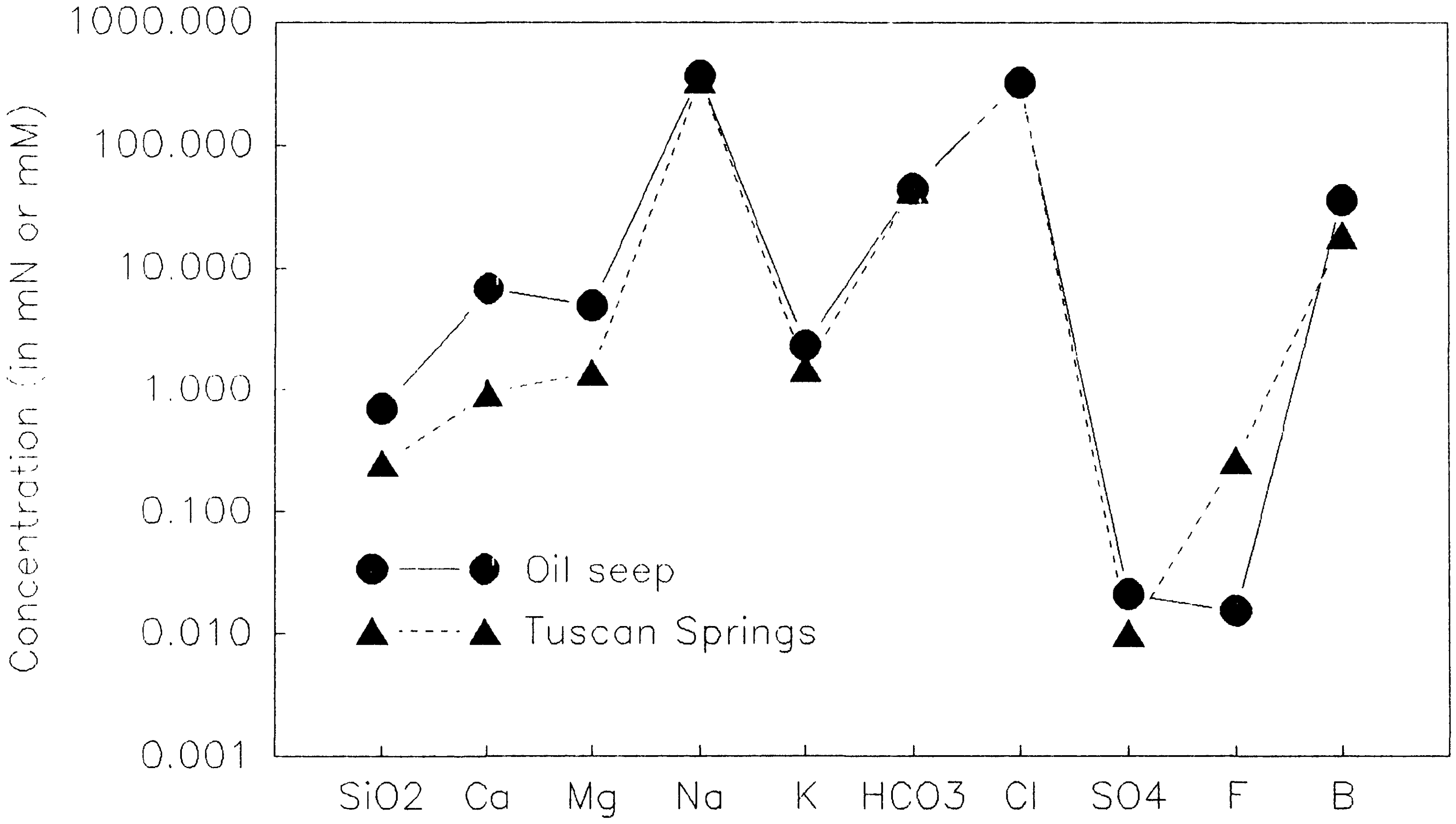

Figure 10. A comparison using Schoeller diagrams between the oil well seep and Tuscan Springs (see text for discussion).