

MEMORANDUM

To: Randy Henkle
Joel Ronne
Cayley Geothermal

Date: 19 August 2006

From: Chris Klein

Pages: 10 + tables, figures

Subject: Fluids chemistry of the thermal waters and playa brines at the Silver Peak (Clayton Valley) geothermal prospect, Nevada

Attachments

Table 1 Caley Geothermal - Western Geothermal Partners, Silver Peak Project, Ground Water Quality data

Figure 1 Legend and maps of sample information

Figure 1b Temperature information

Figure 2 Stable isotope compositions of Silver Peak NV thermal waters and associated brines

Figure 3 δ -D and δ -¹⁸O vs. Cl, with data from Owens Lake

Figure 4 T°F vs. Cl, SiO₂ vs. T°F and Na vs. K

Figure 5 Li, Mg, SO₄ and HCO₃ vs. Cl

Figure 6 Mg vs. Cl (detail), B vs. Cl, SO₄ vs. Cl (detail) and SO₄ vs. Ca (detail)

Figure 7 Na, K and Ca vs. Cl

Figure 8 SiO₂ vs. Cl

Table 1 is a version of Randy's compilation, expanded with the new data from Desert Research Institute (duplicates of NHS well and Foote Minerals brines) and IGNS (isotopes), with the chemical geothermometers, and reformatted to facilitate generating the Figures.

Figures 1 and 1b include information from temperature gradient holes originally drilled by Phillips and now available in USGS Open-File Report 99-425.

Comments on the Analyses

In this memo the concentration units "mg/l" and "ppm-wt" (same as mg/kg) are used informally and interchangeably. For a more formal presentation a single units system (ppm-wt) should be used throughout. Converting mg/l to ppm-wt requires dividing by density (or specific gravity). Dole (1912) reported mg/kg and also reported specific gravity, which here is linear with respect to Cl: $SpGr = 1 + 1.31 \times 10^{-6} \times (\text{Cl in ppm-wt})$.

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We don't have complete information on the concentration units for all of the other data in Table 1, but the USGS data (Davis, 1979; Davis and others, 1989; and Mariner, 1976) are probably all in ppm-wt.

Great Basin Labs (GBL) reported "ppm" but this term gets used casually at some commercial labs and it has not been verified with GBL. Desert Research Institute (DRI) is the only party to report "mg/l" (also not verified). The adjustment to ppm-wt reduces the DRI concentrations by 3% in their most dilute sample, to 6% in their most saline sample. These corrections (not made herein) are small enough that there is no significant impact on the graphs and conclusions of this memo.

The analyses of NHS Well (1 June 06) and the Foote Minerals brines (FM- samples 19 June 06) by DRI show much better ion balances than the GBL analyses, and higher DRI numbers for Cl and bicarbonate alkalinity (HCO_3) are sufficient to explain most of the difference.

As Randy has pointed out, the GBL numbers for alkalinity appear to suffer from a decimal point error, and there are other systematic differences between the two lab's results: higher B (GBL), higher SiO_2 (DRI), higher K (DRI), higher Li (GBL), slightly higher Mg (GBL), and slightly lower SO_4 (GBL). In general, DRI appears to agree more closely than GBL with previous playa brine analyses by other parties (see Figures), except that there are insufficient older data for B.

Randy has also pointed out that data from GBL indicate that the SiO_2 -splits of NHS Well sample (1 June 06) and FM-wells samples (19 June 06) were field-diluted by an average factor 1:7.87 and not the previously assumed 1:10. The DRI data for SiO_2 in Table 1 and Figure 4 incorporate the 7.87 correction factor, and the resulting SiO_2 values are in good agreement with previous analyses of the playa brines and NHS Well. We assume that the GBL numbers for SiO_2 used the correct dilution factor, and that the low values reported are due to some other error.

IGNS reports that their stable isotope analyses have uncertainties of ± 1.0 o/oo for $\delta\text{-D}$ and ± 0.1 o/oo for $\delta\text{-}^{18}\text{O}$. These are standard uncertainty values for these isotopes, and the U.S.G.S isotope sample (Bath House SPk HS standpipe Feb-76) should have similar precision. In contrast, Davis and others (1986; USGS Bulletin 1622) report values for deuterium (but no data for oxygen) that appear to be much too low when compared with Cl in the same samples. This is discussed further below.

Because the "west side" (NHS Well (1 June 06) and Bath House standpipe (Feb-76)) thermal water samples have been bailed from stagnant wells, it is possible that they have been affected by some evaporation. We assume that this evaporation has not been significant, because our

experience is that “stagnant” thermal wells tend to be mixed by slow convection, and because hot spring water from the NE side (Pearl H.S.) has a very similar composition.

Comments on the Fluids Chemistry

- 1) The following comments consider the fluids chemistry in terms of two fundamental issues:
(a) the genetic and possible flow path relationships between the thermal waters of the area and the playa brines, and (b) in light of the first point, the possible thermal reservoir temperatures.
- 2) Genetic Relationships:
 - a) Stable isotopes of oxygen and deuterium in the “west side” thermal waters (NHS Well (1 June 06) and Bath House standpipe (Feb-76)) are similar to other Nevada thermal waters (see Figure 2). The deuterium content of these waters essentially matches contemporary precipitation within central Nevada, where typical δ -D is -110 to -130 o/oo.
 - b) Compared to the meteoric water line (world average and slight regional variations examples of which are shown on Figure 2), the isotopes of oxygen in the west side thermal water show a shift of about +2 o/oo. This shift, caused by water-rock exchange at elevated temperature, compares with shifts of 0 to +3.5 o/oo that are observed in a selection of other Nevada thermal waters (Figure 2).
 - c) We do not have isotope data from Pearl H.S. at the NE edge of the Playa (about 8.5 miles from the west side). However, Pearl H.S. is extremely similar in dissolved ion composition to the west side thermal water, and there is little reason to expect that the isotopes of Pearl H.S. will be different from those on the west side.
 - d) The extreme similarity between the west side and NE side (Pearl) thermal waters is remarkable and suggests some common source at depth. (There is some evidence, below, that the water at Pearl H.S. is diluted by a cool component.)
 - e) In relation to the similarity between west side and Pearl thermal waters, we have mentioned previously that these appear to be the most highly saline thermal waters known in Nevada, where it is rare to find geothermal Cl above about 2,000 to (rarely) 4,000 mg/l. One exception is at the Alum prospect, further N in Clayton Valley, where 4,600 mg/l Cl was found in $\geq 221^{\circ}\text{F}$ water produced from Paleozoic rocks at a depth of 775 ft (see the PIER geothermal database at GeothermEx’s web site.)

- f) Stable isotopes in the playa brines and thermal waters show a general distribution from lighter to heavier isotopes (more negative to less negative δ values of both isotopes on Figure 2) and also show a strong correlation between progressively heavier isotopes and the concentration of chloride (see the two uppermost graphs on Figure 3).
- g) The isotope trend on Figure 2 is characteristic of low-temperature evaporation (from a water surface or shallow groundwater table) starting from the thermal water composition. (The thermal water itself could be a point along the evaporation trend, not the dilute end-member.) Evaporation preferentially releases lighter isotopes and concentrates the heavier isotopes along with Cl and other salts in the residual brines. Because evaporation is controlled by such factors as humidity, solution chemistry and salinity, and temperature, the exact slopes of evaporation trends depend upon local conditions and may vary over time. However, the Clayton Valley waters all fall within the expected range (see slopes of evaporation trends on Figure 2).
- h) The correlations between isotopes and Cl (two uppermost graphs on Figure 3) may be due to evaporation. However, data from evaporation studies at Owens Lake, CA (pointed out by Davis and others, 1986 and reproduced in part within the two lowermost graphs on Figure 3) suggest that the deuterium isotope shift should be much larger, to values that approach $\delta\text{-D} = 0$ o/oo.
 - i) [Aside - Two measurements of deuterium presented by Davis and others (1986) are lower than deuterium at similar Cl in the newer IGNS data set (see Figure 3, $\delta\text{-D}$ versus Cl). The slope of a line connecting the Davis values is the same as the slope of the new data, but the intercept value of $\delta\text{-D}$ at low Cl seems unreasonable, and we suspect that the Davis deuterium values are incorrect.]
- i) Therefore, it appears likely that the isotope and isotope-Cl trends among the playa well brines are created by mixing between the thermal water and a saline playa brine end-member which has evolved through some combination of:
 - i) evaporation of the thermal water itself (providing the salt content and certain characteristic ion ratios),
 - ii) mixing with dilute meteoric water (keeping the isotopes lighter than they would be if evaporation were the only process), and
 - iii) re-dissolving of salts in the playa sediments by thermal water, dilute groundwater and mixtures thereof (also keeping the isotopes lighter).

Multiple saline end-members with slightly different compositions are probably involved, but the "parent" source of the playa salts (dissolved and solid) appears to be the hydrothermal system(s) on both sides of the Valley (see more below). Process (iii) along

with precipitation of the salts during historic periods of extreme desiccation would be responsible for some skewing of certain ion ratios with respect to values in the thermal water source. (Davis and others (1986) emphasized production of the playa brines by dissolution of halite (process (iii)), but they did not have the isotope data now available which indicate that some fraction of the brine water has isotopes shifted by evaporation.)

- j) Li (lithium) typically does not precipitate from evaporating Na-Cl salt solutions, and NaCl itself only precipitates at extreme concentrations (a saturated cool NaCl solution contains about 142,000 ppm Cl). With some scatter, Li/Cl is the mostly same (about 0.0025) in the thermal water and the playa brine samples (Figure 5). In contrast, Li/Cl in the cool, dilute Waterworks spring (one sample in Table 1) is only 40% of this ratio. Other cold springs in the area, documented by Davis and others (1986), contain even lower Li/Cl, although there is a cold spring with 2,020 mg/l Cl at Fish Lake Valley, to the west, where Li is 5.6 mg/l and Li/Cl is 0.0028 (USGS Open-File Report 77-54). Overall, it appears that extreme evaporation of Clayton Valley cool spring waters is not a likely earlier source for the salt content of the thermal waters and playa brines. (See more on the Li source below.)
- k) Pearl H.S. shows a slightly greater affinity with most playa brines than does west side thermal water: lower Ca/Cl (Figure 7) and higher SO₄/Cl (Figure 6). This suggests that thermal water from the NE is more significant than thermal water from the west as a playa brine component (both as the early source of salts, and as later mixing component). This is not surprising given: (a) the significant thermal temperature gradient anomaly which extends W from Pearl H.S. (Figure 1b), and (b) the Goat Island horst, which lies between most of the W side and the main playa.
- l) A few playa brines are somewhat more dilute than the thermal waters, and some components in the thermal water show evidence of a dilution trend (B vs. Cl, Mg vs. Cl). This is further evidence that a dilute mixing component is present in the system. This component is probably a small composition range of meteoric waters best represented by the Waterworks spring (well). We note also the comments in U.S.G.S. Prof. Paper 42 (Spurr, 1905) regarding an apparent seasonal variation of the temperature at Bath House spring, and the record in Dole (1911) that the cold springs at Silver Peak then flowed at about 240 gpm.
- m) Mg plotted vs. Cl shows evidence of a bimodal distribution (Figure 5), with the lower concentration group comprising west side and NE side thermal waters and also some (not all) of the playa brines in the NE (Figure 1).
- n) Data for Mg vs. Cl at the NHS Well (Figure 6) suggest that a thermal component with about 5000 mg/l Cl could be present, because Mg would approach zero at that value.

(Waters at temperatures above 125~150°C rarely contain measurable Mg if Cl is this low, but the same waters can re-gain Mg rapidly during cooling.) Most other thermal water samples lie close to the same trend. Other evidence for a more dilute thermal component at NHS Well includes the fact that SiO₂ increases as Mg and Cl decrease (Figure 8). The existence of this more dilute thermal component remains uncertain. There are only four samples, the range of values is small, and silica in waters that mix in the aquifer tends to re-equilibrate. However, the data do establish 5,000 mg/l Cl as a probable lower limit, and about 180 mg/l SiO₂ as an upper limit, in the hypothesized component.

- o) The B - Cl relationship shows some evidence of a bimodal distribution (higher and lower levels of B). Possible causes of this are different thermal water sources (different aquifer rocks), capture of B into clays, and/or mobilization of B into steam during an earlier and hotter period of thermal activity.
- p) In the dataset as a whole, and especially among the thermal waters, there is an inverse relationship between SO₄ and Ca (Figure 6). This suggests that the concentrations of these two ions are at least in part controlled by the solubility of anhydrite ((CaSO₄), which becomes decreasingly soluble as temperature increases. Anhydrite solubility temperatures (calculated using GeothermEx's proprietary version of the WATCH code) are considered below. Some playa brines show the dilution effects suggested above, on both Ca and SO₄ (Figure 6).
- q) Possible initial lithic sources of the hot spring and playa brine Li are discussed by Papke (1976; N.B.M.G Bulletin 87), Davis and Vine (1979; RMAG-UGA - 1979 Basin and Range Symposium) and Davis and others (1986; USGS Bulletin 1622). These include Tertiary volcanic rocks (and related hydrothermal activity) with somewhat high Li that are found E and SE of the valley. High levels of Li are also found in Na-Cl playa brines of Fish Lake Valley and Columbus Salt Marsh. These have been assigned to a similar source in Tertiary volcanic rocks, without intervening thermal activity (USGS Open-File Report 77-54), but overall the ratio Li/Cl in those areas is only one-half of the ratio in Clayton Valley.

Whatever its lithic source, the ~35 mg/l Li in the Silver Peak hot springs is more than found at most hot springs world-wide, but similar geothermal Li and Li/Cl are matched elsewhere. Examples include: springs at El Tatio in Chile (30 to 45 mg/l Li at 4,000 to 8,000 mg/l Cl); a well at Salton Sea geothermal field (215 mg/kg Li at 155,000 mg/kg Cl); a well at Wairakei geothermal field in New Zealand (14 mg/kg Li at 2200 mg/kg Cl); and Tokaanu Hot Springs in New Zealand (22 mg/kg Li at 3,060 mg/kg Cl).

3) Thermal Reservoir Temperatures (all rounded to nearest 5°)

Table 1 includes one form of the silica geothermometer (chalcedony) and four forms of cation geothermometers that are of principal interest: Na/K (as the Fournier variant under heading **Na/Kf**), Na-K-Ca (under column heading **NKC**), Na-K-Ca-Mg (under heading **Cmg**), and K-Mg (as Fournier variant under heading **KMgf**). These may be summarized as follows.

Source	Temperature, °F (°C)					
	Chalcedony	Na/K	Na-K-Ca	Na-K-Ca-Mg	K-Mg	Anhydrite
NHS Well	260° (125°C) 300°(150°C)?	390° (200°C)	420° (215°C)	310° (155°C)	330° (165°C)	295° (145°C)
Bath House Standpipe	235° (114°C)	385° (195°C)	410° (210°C)	285° (140°C)	320° (160°C)	300° (150°C)
Pearl H.S.	150° (65°C)	420° (215°C)	445° (230°C)	340° (170°C)	345° (175°C)	310° (155°C)

- a) At sample collection temperatures the concentrations of silica (SiO_2) in the thermal waters and playa brines fall in-between the solubility curves for amorphous silica and chalcedony (Figure 4). (Quartz is less soluble than chalcedony and not likely to control SiO_2 at the low temperatures of this dataset.) Silica in the playa brines is probably set by low-temperature silicate-water reactions, although the observed levels could be due to non-equilibrium conditions which even involve some silica deposits associated with salt deposits in the playa sediments. Silica in the NHS Well is more likely set by chalcedony, with over-saturation being a result of cooling. We therefore regard the chalcedony temperature of the NHS Well water as a reasonable first estimate of higher temperatures at deeper levels.

If the waters sampled from NHS Well are mixtures between a more dilute thermal component and more saline cooler brine (see above), then the chalcedony temperature of the thermal component (180 ppm SiO_2) becomes about 300°F (150°C)

- i) The much lower chalcedony temperature at Pearl H.S. is puzzling in light of the much higher cation temperatures and high temperature gradients in that area. Because Pearl H.S. has been analyzed twice, the silica data (especially 46 ppm reported by Davis, 1979) are presumed to be accurate. The cold spring near Pearl H.S. is equivalent

water, but Cl, SiO₂ and most other ions are diluted by about 1/3, Mg is somewhat higher, and Na/K is somewhat lower. The dilution at this cold spring indicates that Pearl H.S. itself could be diluted during upflow, which would have lowered the SiO₂ and chalcedony temperature. Other possible explanations for the low SiO₂ concentration are solubility control by quartz and/or very slow cooling with precipitation of silica. The quartz temperature would be 210°F (100°C), which is still fairly low. Precipitation seems unlikely because most of the playa brines have SiO₂ at higher levels, the most notable example being very close to Pearl H.S. itself: 86 ppm in 96.8°F water with 21,000 ppm Cl from 795 ft in hole CV-4; this has a chalcedony temperature of 210°F (100°C). It therefore seems likely that the water at Pearl H.S. becomes diluted during upflow. Mg in Pearl H.S. and the adjacent cold spring constrains the amount of dilution, limiting the hot component to about 80 ppm SiO₂ and 20,000 ppm Cl, at which Mg would be 0 ppm (very unlikely). This constraint and the other limitations on conditions at Pearl H.S. are very approximate, and the matter requires further resolution.

- b) Na/K temperature is a function of the ion ratio, which tends to decrease as temperature increases in a system of chemical reactions between water and rock silicates (specifically, feldspars).

A caveat concerning the Na/K temperature in this case is that saline cool groundwaters can have anomalously high Na/K temperatures. For example, the Na/K temperature of seawater is 145°C (295°F). Figure 4 (lower right graph) shows Na and K in the Clayton Valley waters in relation to seawater, several other saline and cool water sources in the western US, and the hypersaline and very hot Salton Sea geothermal field.

Not shown on Figure 4 are data from Owens Lake, CA (the samples shown on the bottom of Figure 3), which like seawater would plot at an Na/K ratio higher than in Great Salt Lake.

Also not shown on Figure 4 are data from the cool brines in Fish Lake Valley and Columbus Salt Marsh which have somewhat elevated Li (see above). USGS Open-File Report 77-54 reports only Li, K, Ca, Mg and Cl from these brines, so the Na level is uncertain. (Na could be calculated from the other components, but only by assuming that Cl is the only significant anion.) A plot of K vs. Cl in more than 40 samples of these brines (not reproduced herein) virtually overlaps the data distribution on the Figure 7 plot of K vs. Cl, and this means that these cool waters (which also might have thermal parentage???) could well have Na/K values that match the ratios in Clayton Valley.

We conclude that depressed Na/K ratios in the Clayton Valley thermal waters are likely to have been set by high-temperature water-rock reactions, but it remains possible that

low temperature processes have been involved. The Na/K geothermometer is relatively insensitive to cooling, and so it may be a fair representation of the highest temperatures deep in the hydrothermal system. Temperatures at commercially drillable depths may be significantly lower.

Another caveat concerning the Na/K temperatures is that precipitation (and re-dissolution) of NaCl and/or KCl can affect the ion ratio. The levels of K in the playa brines are sufficiently low that KCl should not be of concern here, but the halite deposits in playa sediments are probably responsible for at least some of the scatter of Na/K ratios among the brines. It appears that this scatter has developed after the thermal water has set an initial ion ratio, but if the thermal waters themselves have been affected by an earlier history of evaporation and precipitation processes, then the Na/K ratio (and other cation geothermometers) could be inaccurate. It seems to be more probable that the thermal Na/K has been set by elevated temperatures.

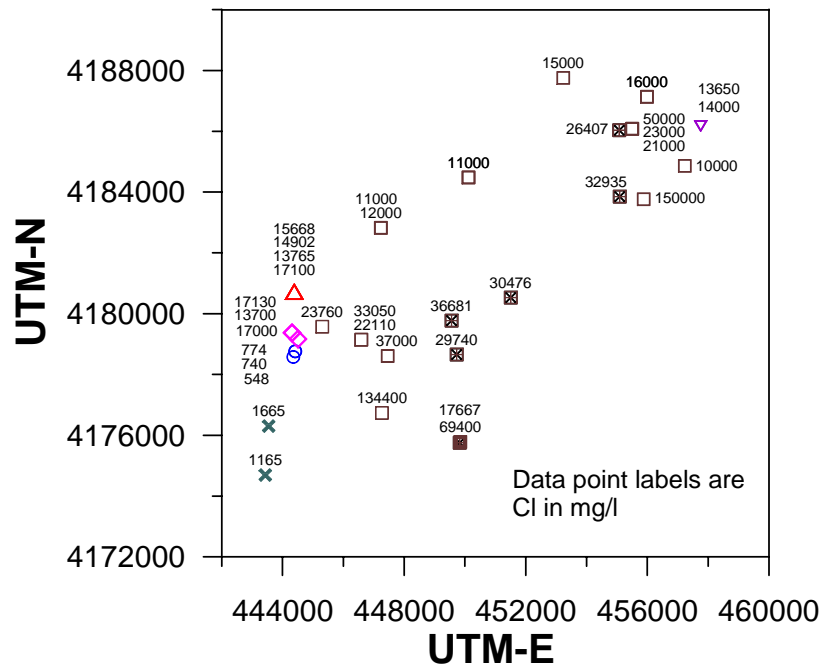
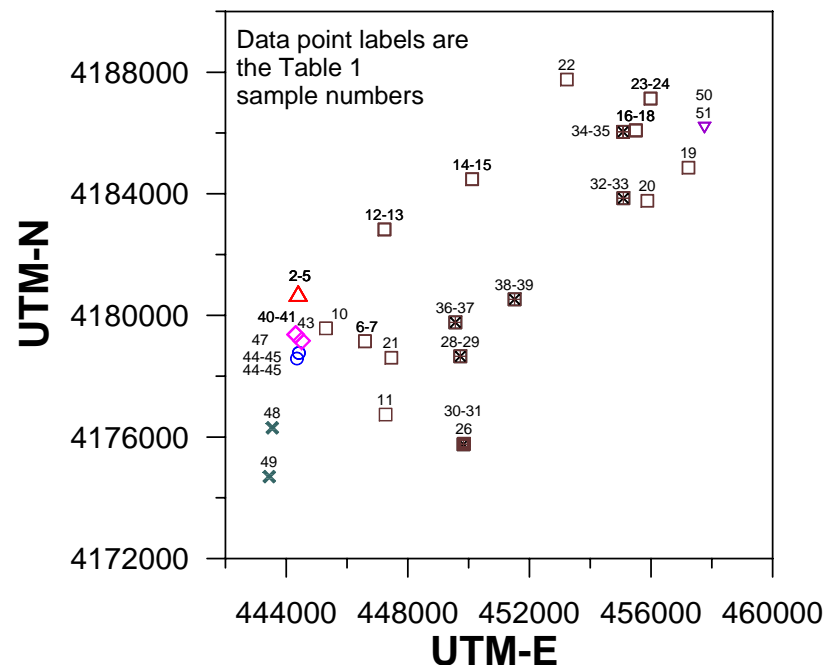
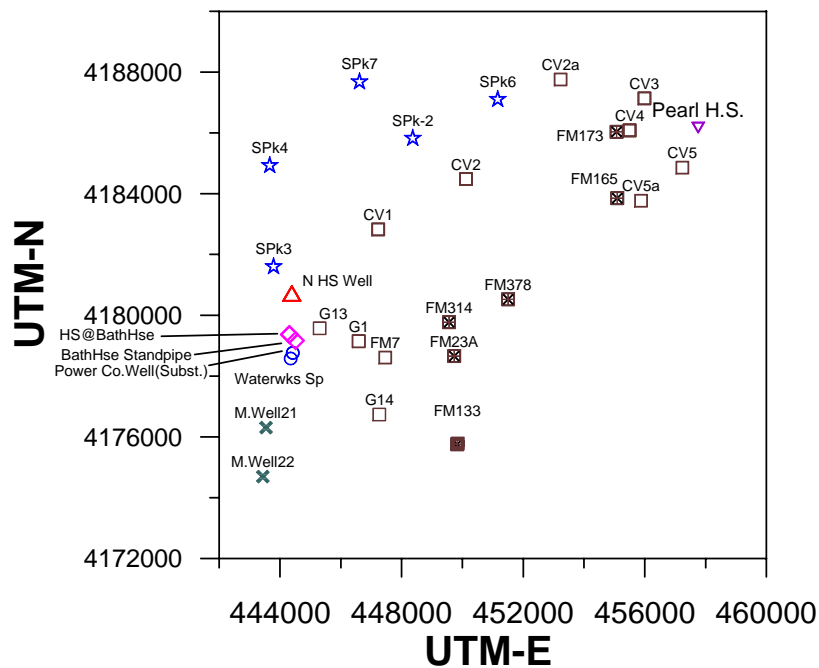
- c) In some thermal waters, Na-K-Ca temperatures show temperature adjustments during cooling that are not shown by Na/K. In this case the results are somewhat higher than Na/K temperatures, but the differences between Na-K-Ca and Na/K values are within the margins of error of these methods.
- d) Temperatures in the shallowest and coolest part of a hydrothermal system are usually best given by the two cation forms that include Mg, because Mg responds quickly to cooling. Theoretically, at least, the Mg forms (especially Na-K-Ca-Mg) are also accurate for waters with Na/K that has been depressed by low-temperature processes, giving Na/K temperatures that are otherwise too high.
- e) As discussed above, there is reason to believe that Ca and SO₄ in the thermal waters are being controlled by anhydrite, the solubility of which decreases with temperature. Accordingly, we have calculated anhydrite solubility temperatures, using GeothermEx's proprietary version of the WATCH code for chemical thermodynamics, with results as shown in the table.

4) Summary

The balance of chemical and isotopic data from Clayton Valley indicate that the brines produced from Li mining wells and other exploration holes drilled in the playa have evolved from the hydrothermal water that issues on the west side and on the NE side at Pearl H.S. Processes of evaporation, dilution caused by mixing with meteoric water, and solution of salt deposits (themselves originating from thermal water) all appear to be involved. Overall, the playa brines show somewhat greater affinity to Pearl H.S. than to the thermal water on the west side.

The water at Pearl H.S. may be somewhat diluted by a cool meteoric component, and thermal water on the west side shows evidence of mixing as well (although perhaps between a more dilute thermal component and a more saline playa brine). Nevertheless, there is a very striking similarity between the thermal waters on the two sides of the Valley, which supports the idea of a common source at depth. There is a fairly large temperature gradient anomaly in the valley around Pearl H.S. (Figure 1b gradients of 7 to 20°F/100ft), and temperatures on at least the far west side are anomalous, but gradients in the west-central part of the Valley (along a line between the west side and Pearl) are low (1.6 to 4.0°F/100ft). Therefore, it may be that hot water does not underlie the entire Valley. This matter requires further investigation. One possibility seems to be that hot water migrates into each area (west and NE) from a common source to the N.

The chalcedony geothermometer provides fairly reliable evidence that temperatures at shallow depths on the west side should reach 260°F and may reach 300°F. Cation geothermometers involving Mg provide good but somewhat less confident evidence that temperatures on the west side and on the NE side reach 300~340°F at commercially drillable depths. The other cation geothermometers (Na/K and Na-K-Ca) suggest that the deepest levels of the hydrothermal system reach 400~440°F, but this evidence is still fairly tentative, due to the complexities of the hydrochemical system and uncertainties about the deeper origins and history of these relatively saline thermal waters. It may be notable that cation temperatures in the shallow, 221°F, Na-Cl thermal water at the Alum prospect to the north (see above), also in Paleozoic rocks, are similar to those at Silver Peak: Na/K and Na-K-Ca are 450°F and Na-K-Ca-Mg and K-Mg are 305°F.



- △ NHS Well
- ◇ Bath House Sprs
- Playa Brines 1912
- Playa Brines 1979
- Playa Brines 1986
- Playa Brines (Foote Min.)
- ▣ Playa Brines - 2006 GB Lab
- ⊠ Playa Brines - 2006 DRI Lab
- ▽ NE Playa (Pearl H.S.)
- Waterworks
- × Meinzer

★ Gradient holes from
USGS Open-File Report 99-425

Figure 1:
Legend and maps
of sample information,
Cayley Geothermal -
Western Geothermal Partners
Silver Peak Project, NV

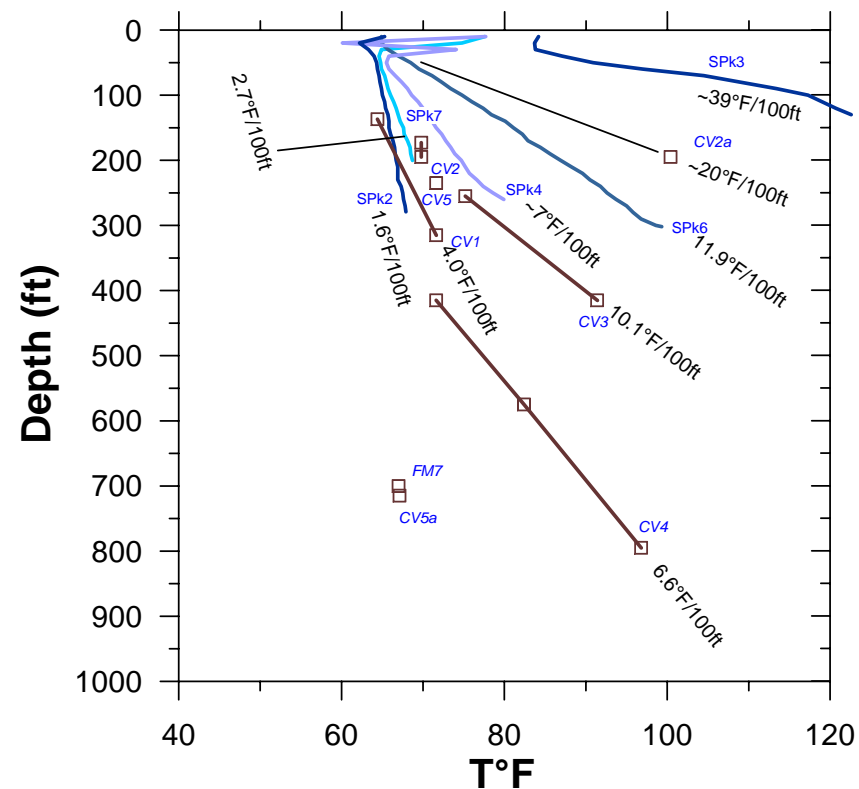
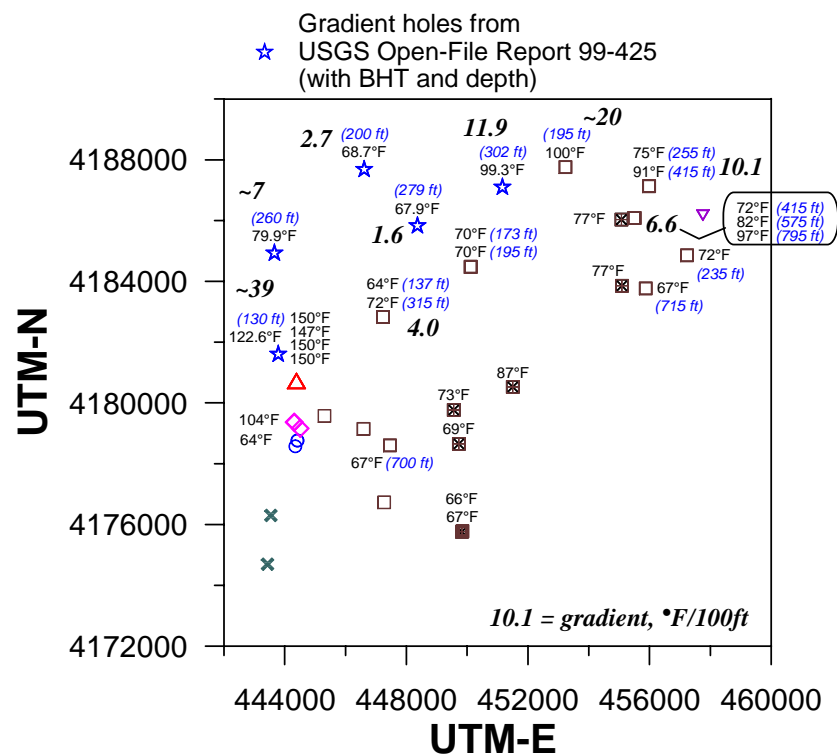


Figure 1b: Temperature information

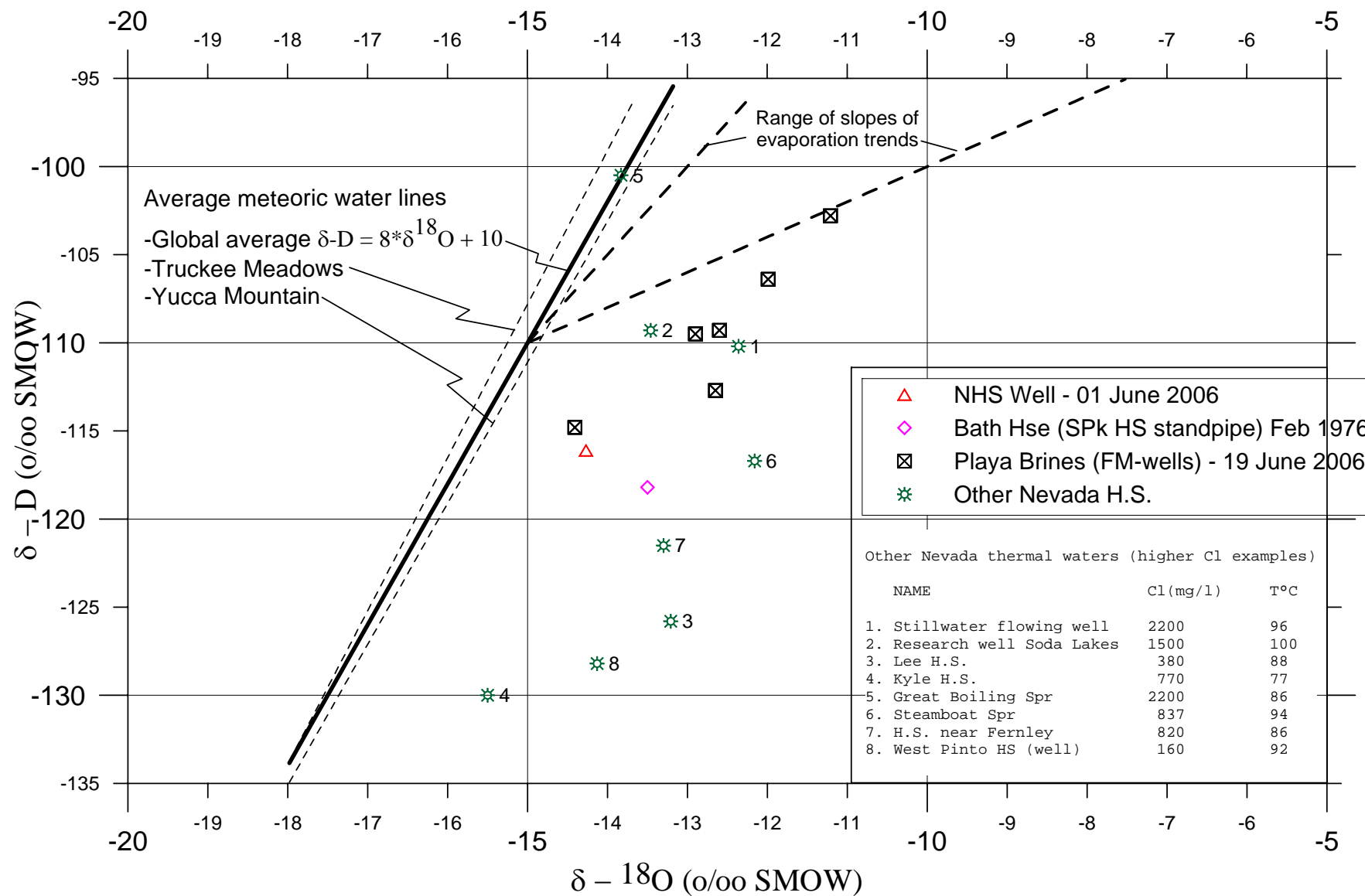


Figure 2: Stable isotope compositions of Silver Peak NV thermal waters and associated brines

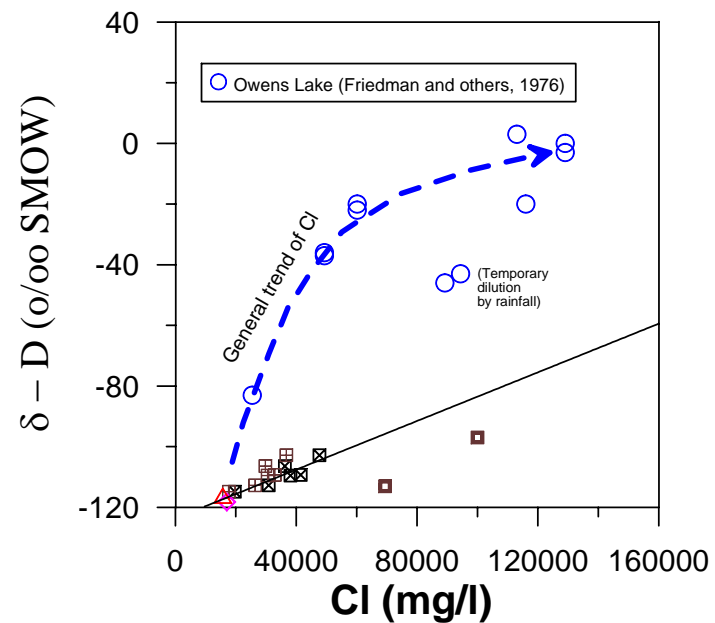
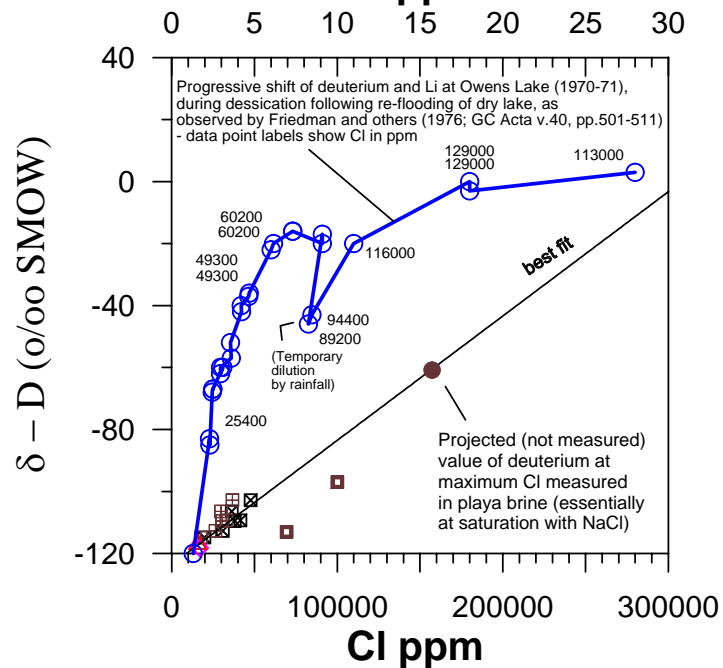
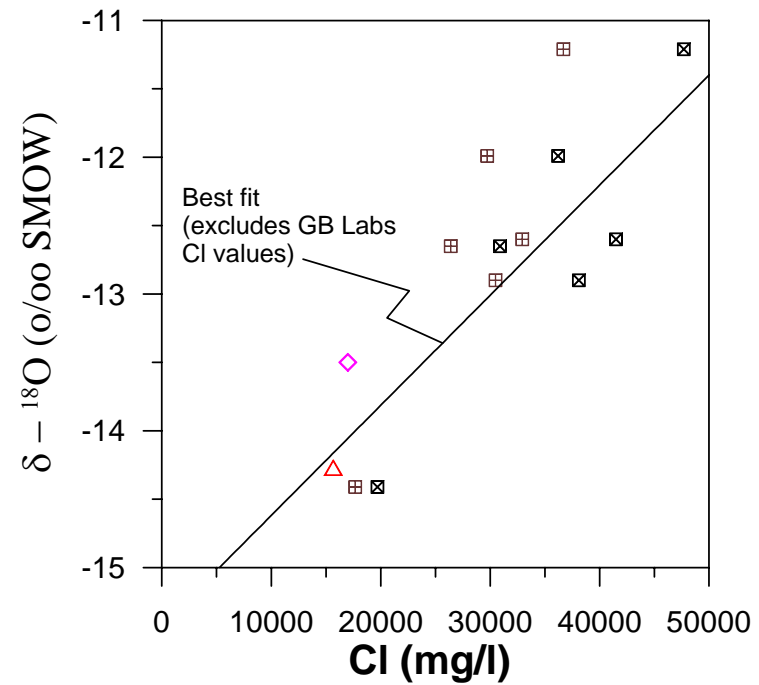
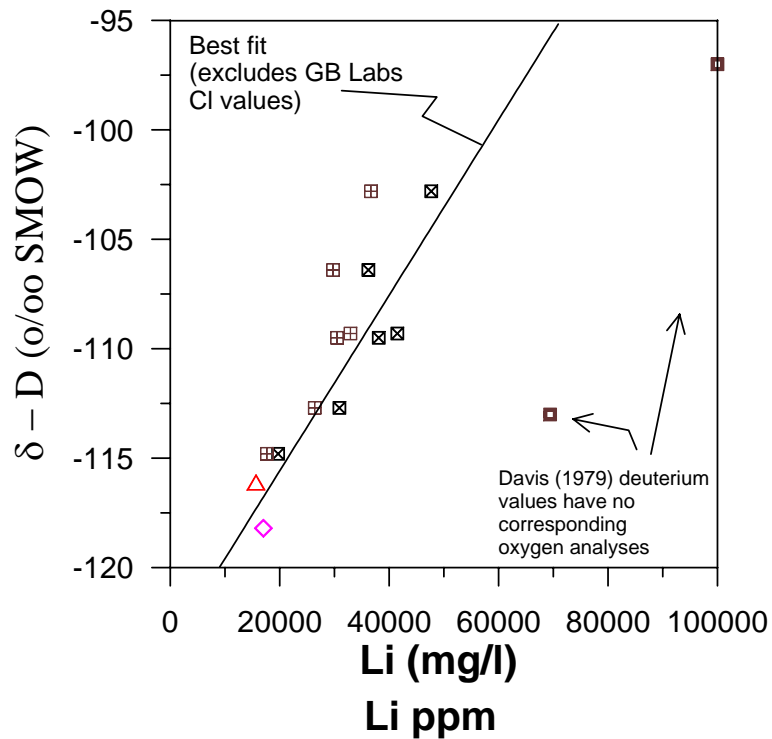


Figure 3

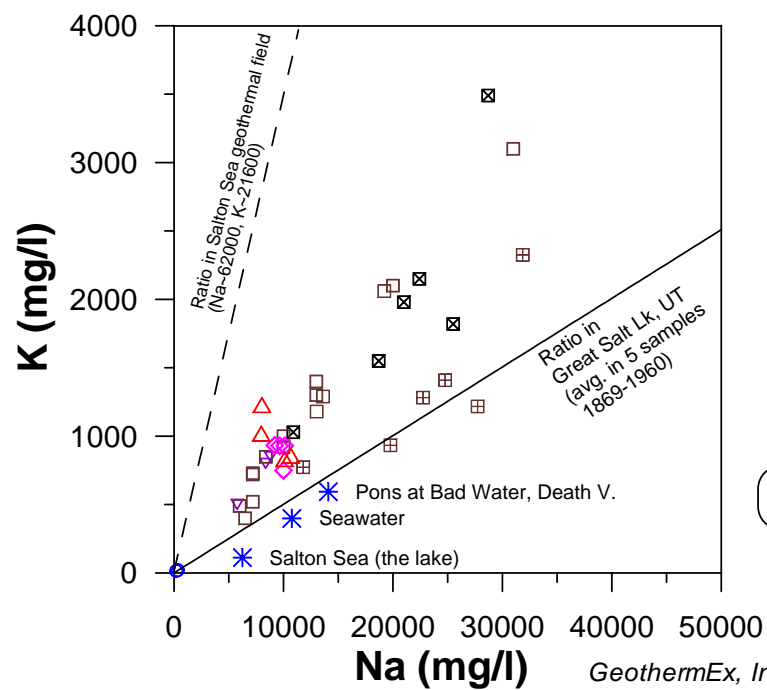
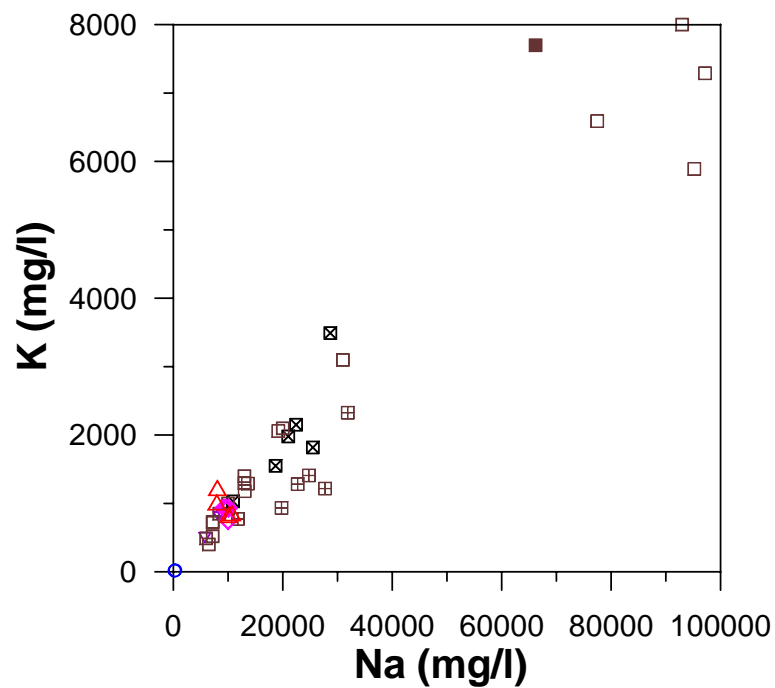
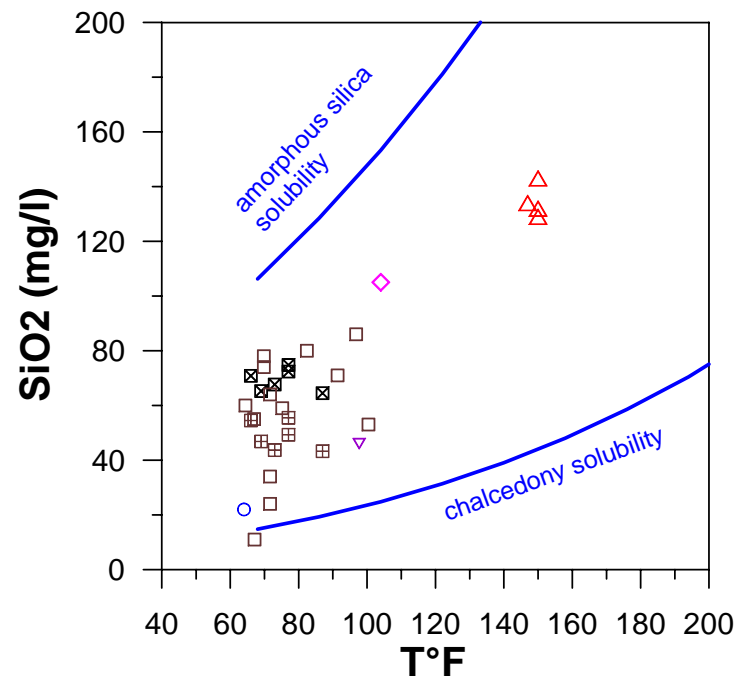
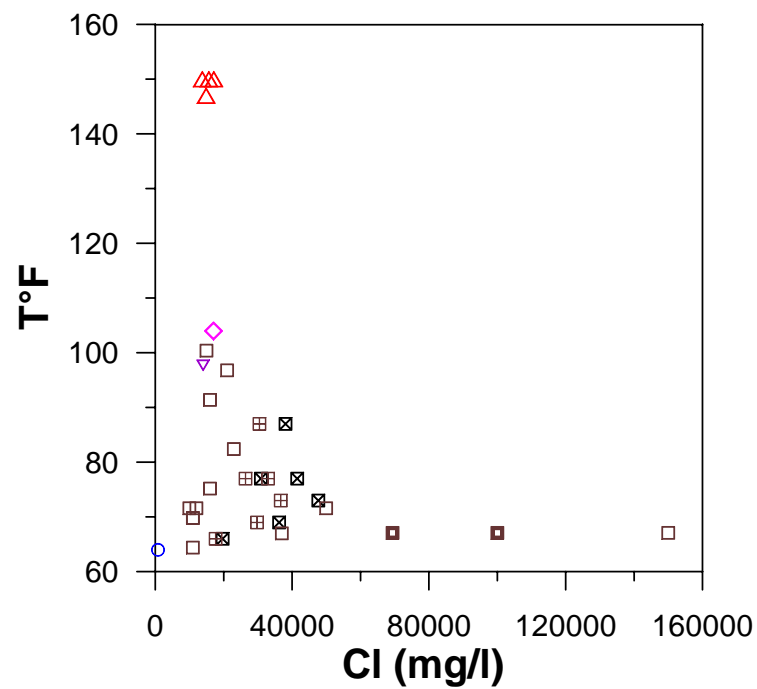


Figure 4

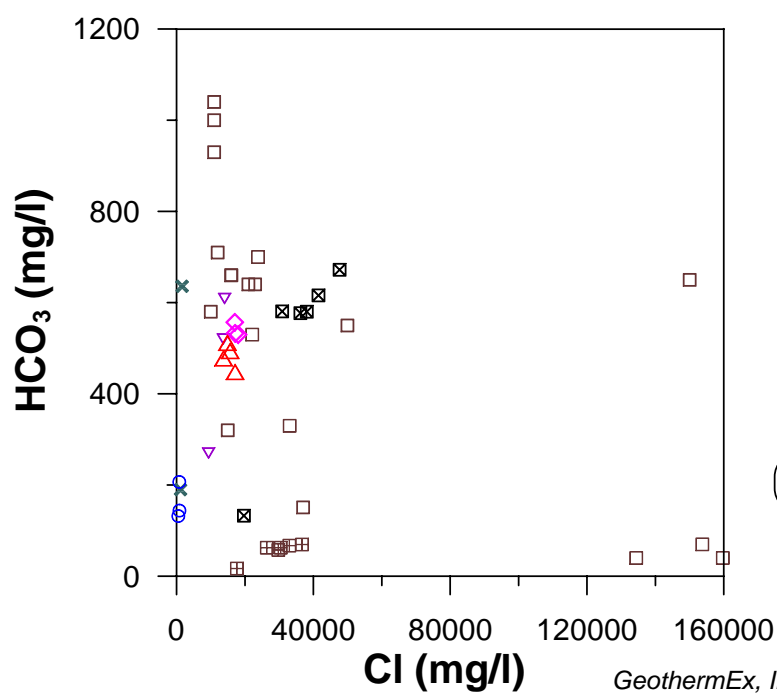
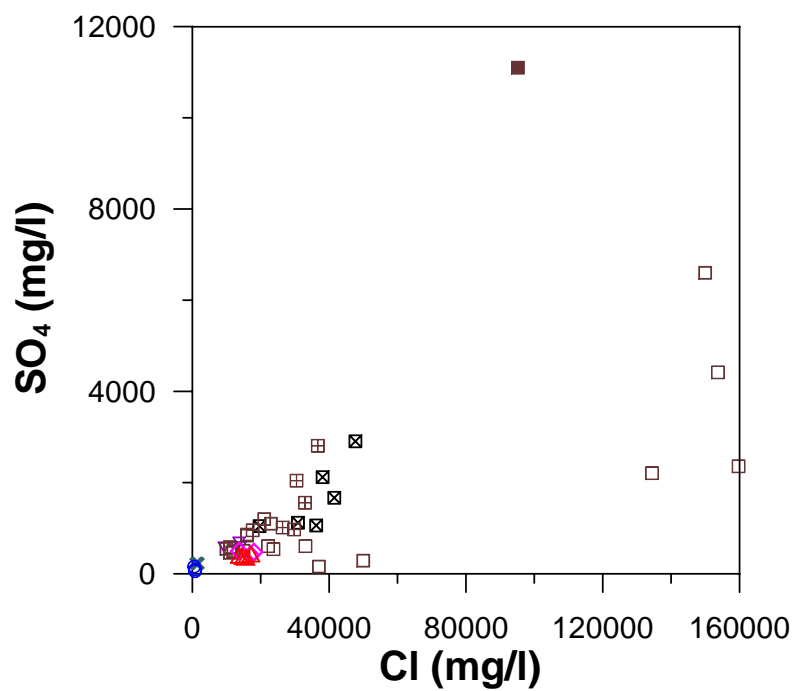
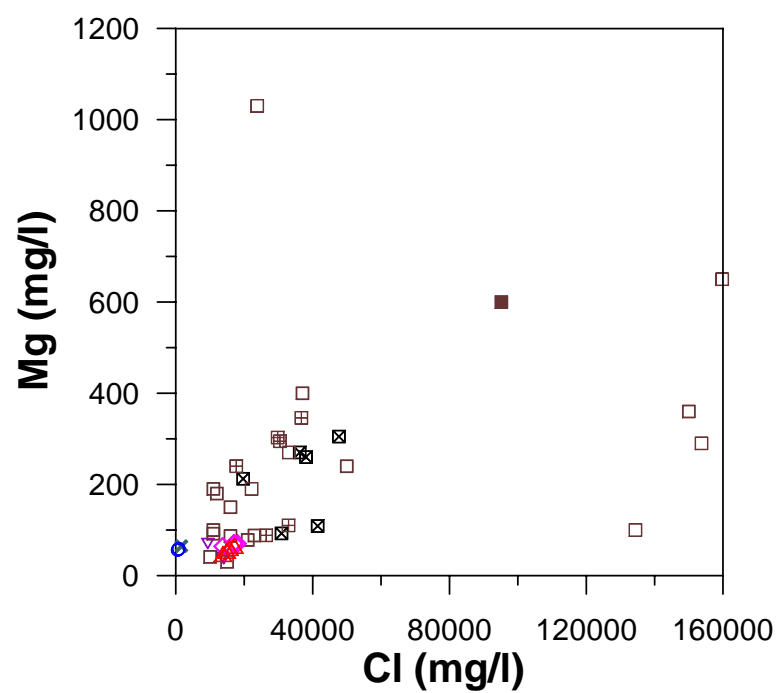
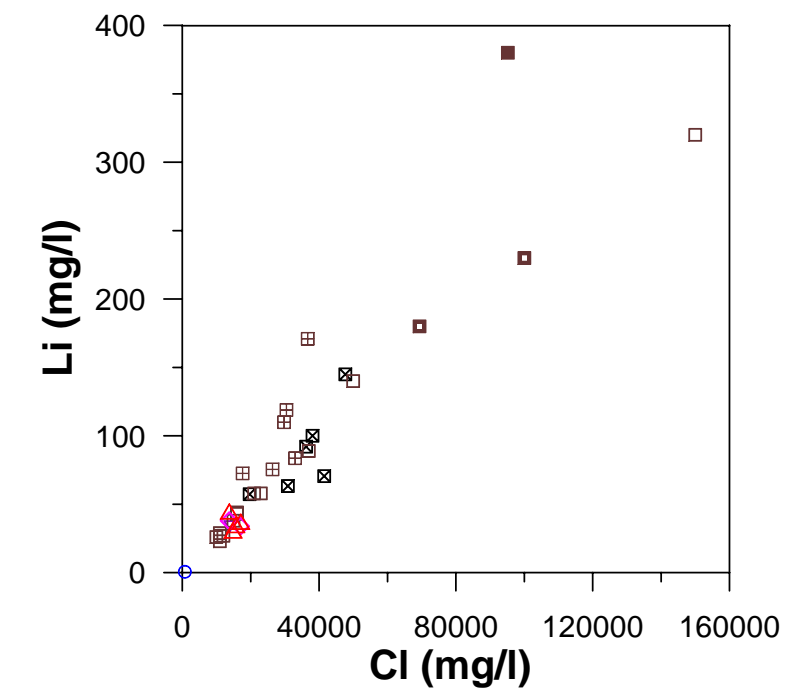


Figure 5

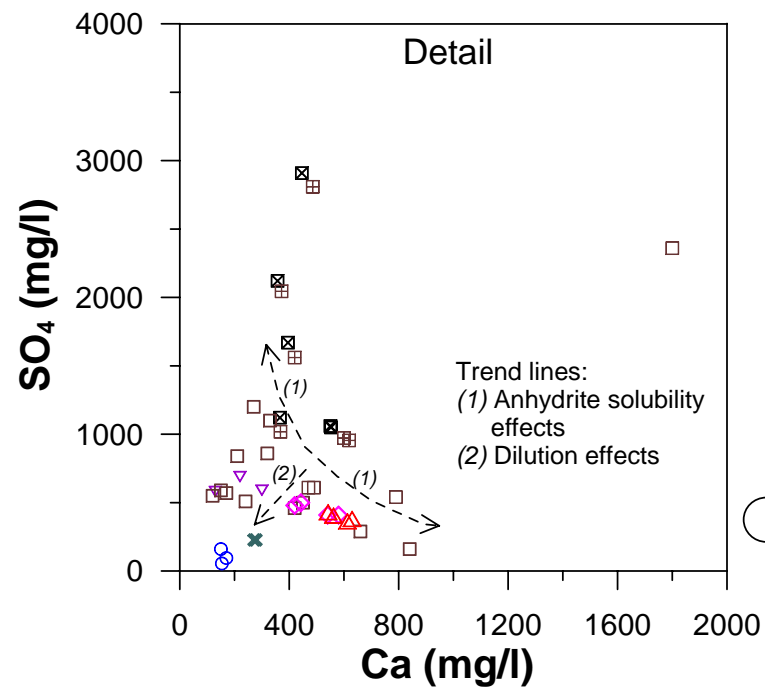
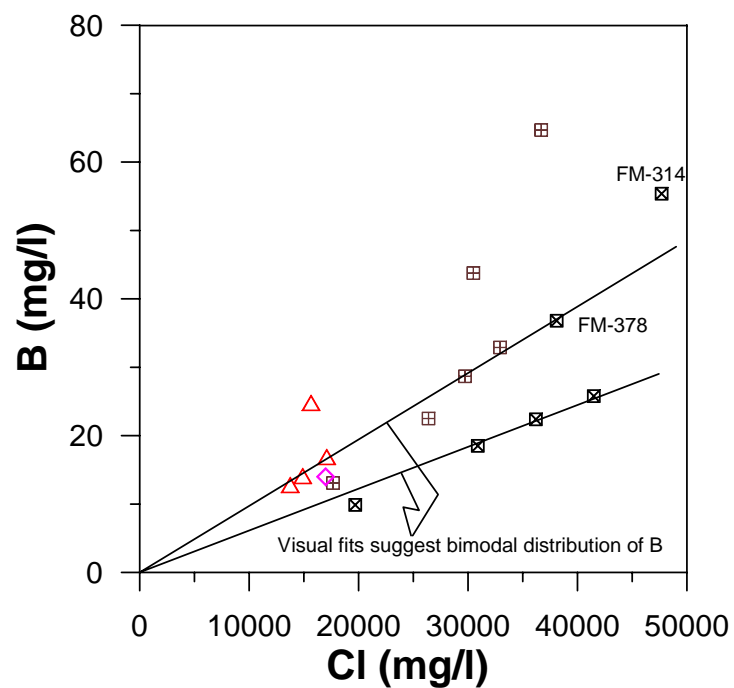
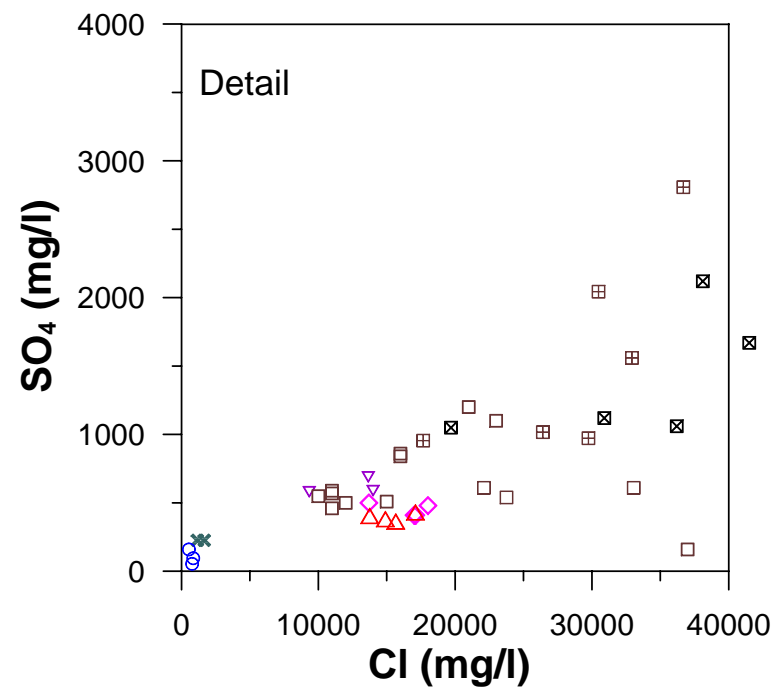
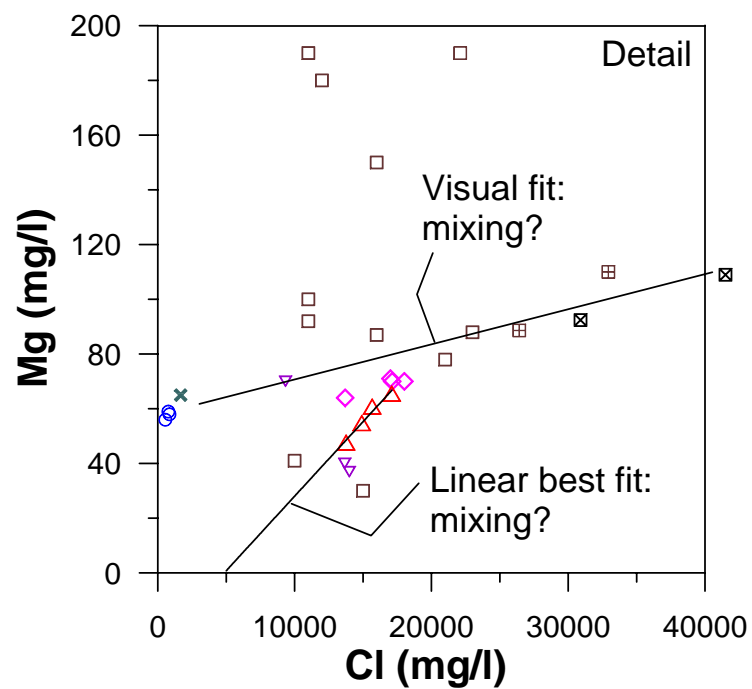


Figure 6

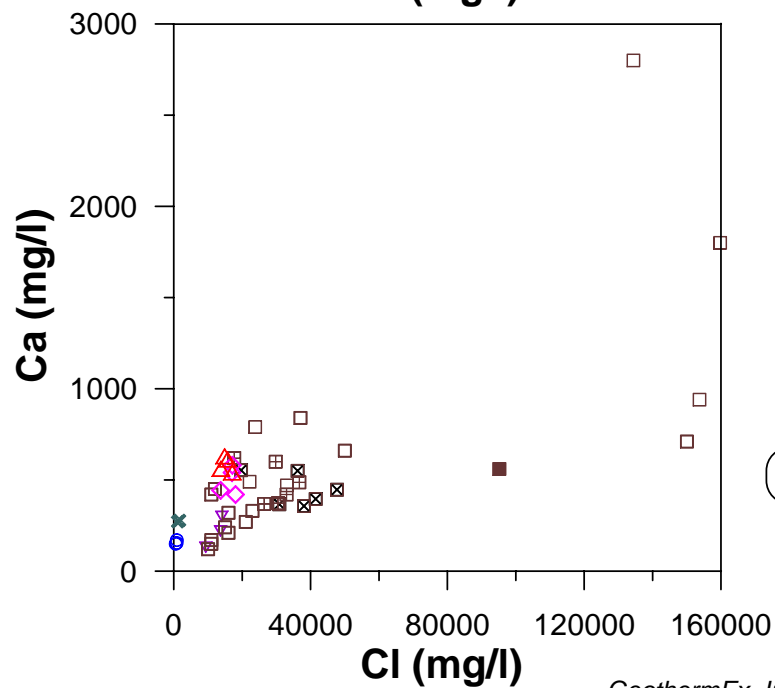
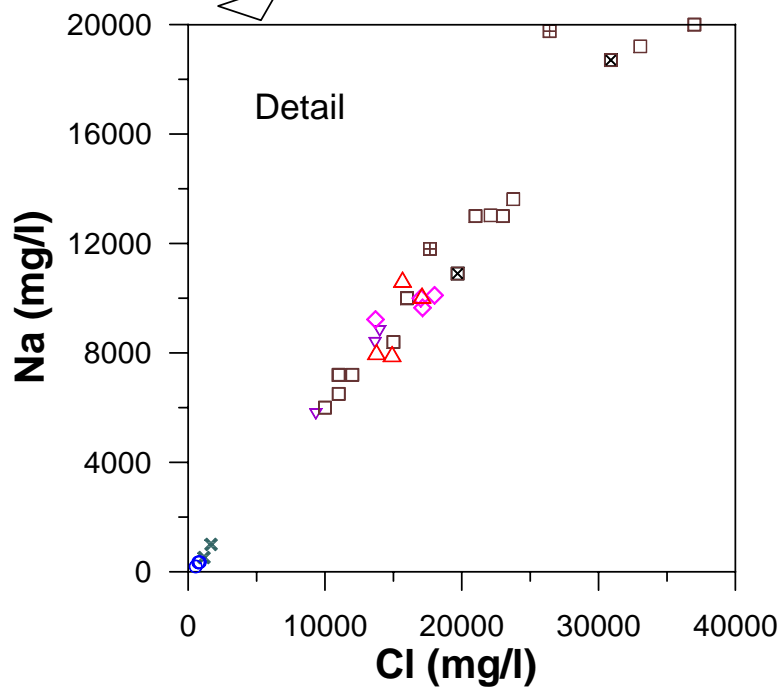
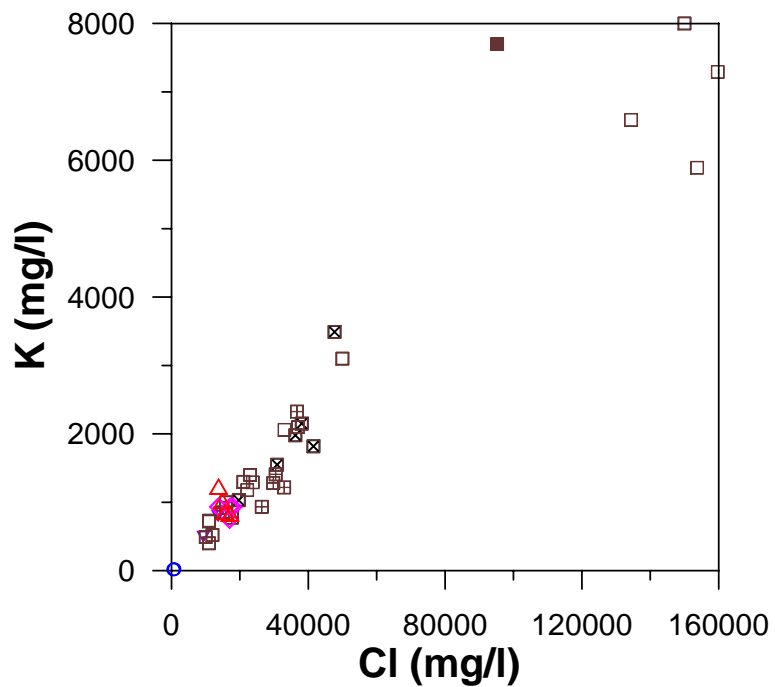
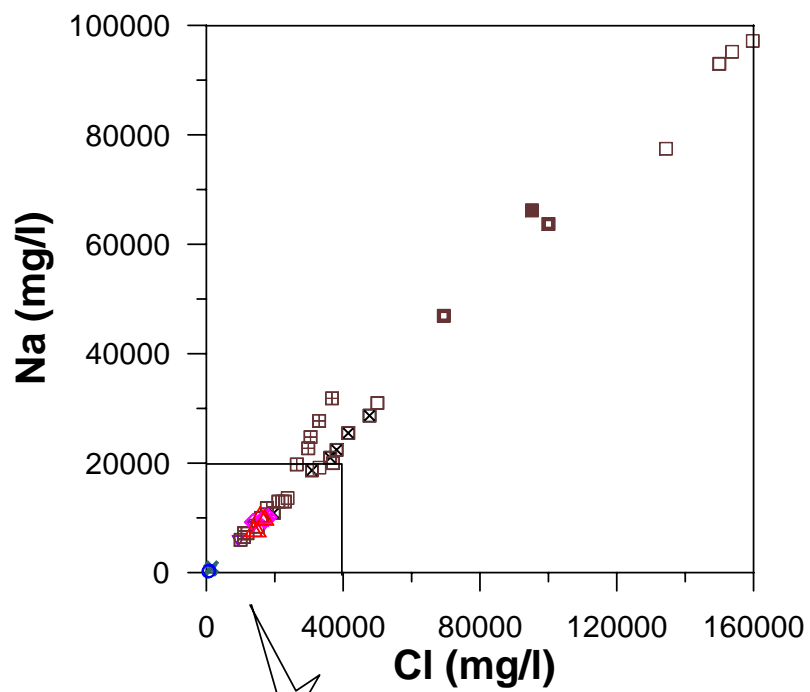


Figure 7

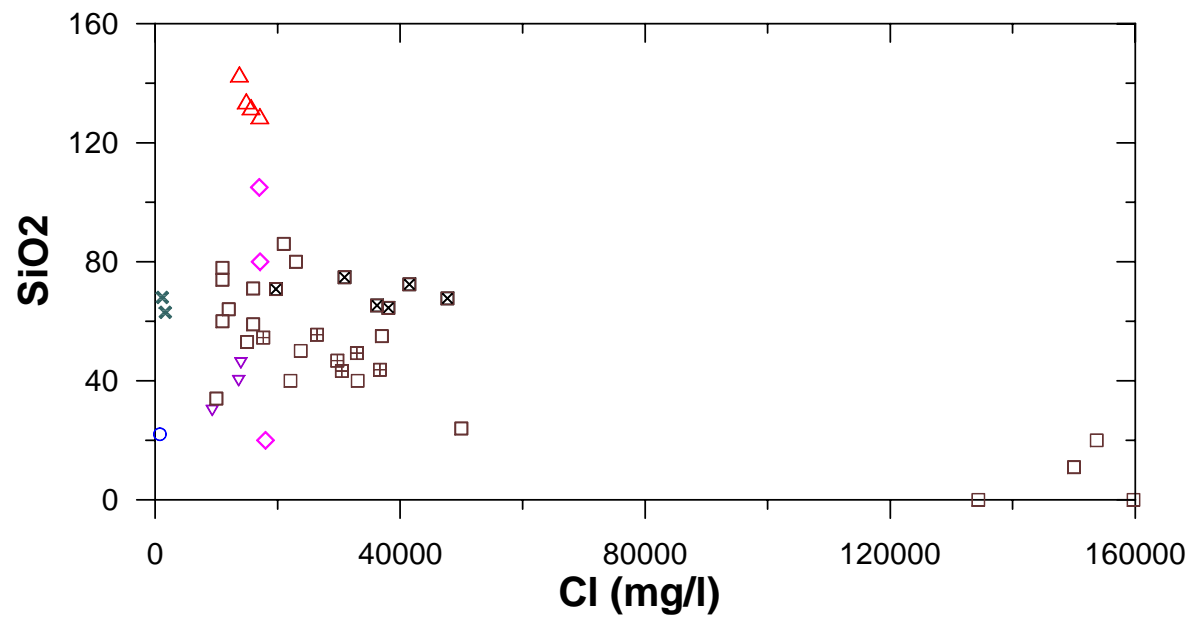
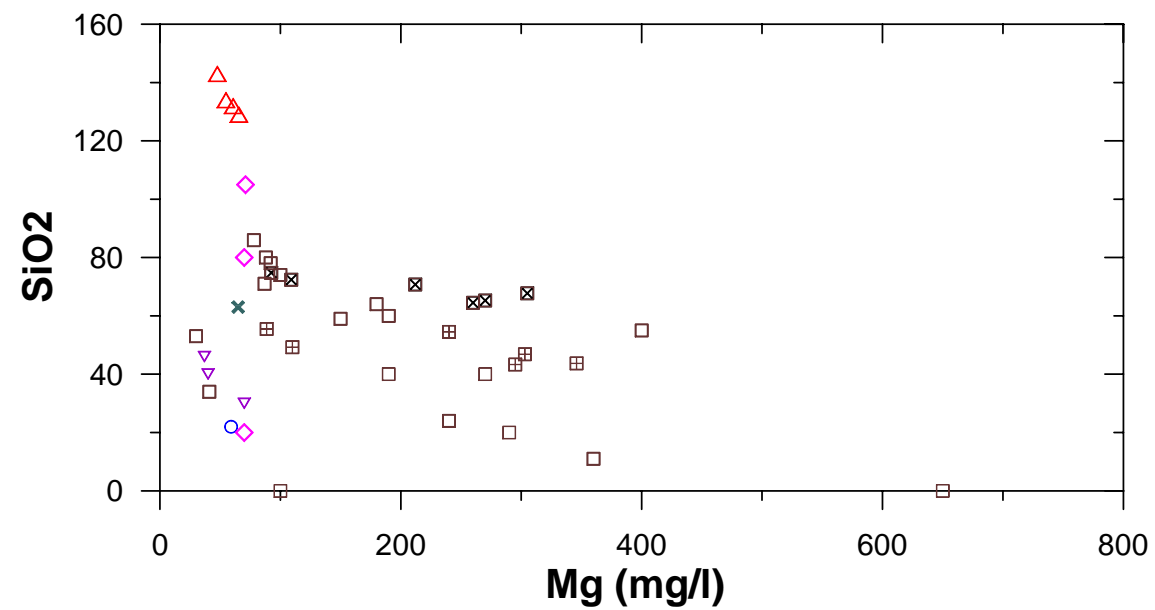


Figure 8