Groundwater, Chemical Weathering and Stable Isotopes of the Sierra Nevada’s Kern River and its Drainage Basins

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Abstract

The Kern River cuts through the southern region of the Sierra Nevada batholith. Beginning from the head waters near Mt. Whitney, the river flows south towards Kernville where it discharges into Lake Isabella before continuing to Bakersfield. Along the way, creeks from various drainage basins contribute to the river. River and tributary water samples as well as ground water samples were taken from various locations and analyzed for hydrogen and oxygen isotopes, radium isotopes, major cations and temperature. The snow melt precipitation is a mix of isotopically light northern drainage runoff from high elevations and heavier runoff from various western drainage basins. Potassium and calcium enriched granodiorite of the northern head water regions grade to sodium and calcium enriched rocks of the more southerly regions. River water chemistry reflects this bedrock change as increases in sodium and calcium concentrations are observed down river. Radium isotopes indicate possible residence times of water in head water lakes of 20 to 60 days. More studies and measurements are needed for radioisotopes, however due to the lack of time for ingrowth of 228Ra.
INTRODUCTION

Kern County is a large county in central California and is comprised of the southern area of the San Joaquin Valley as well as surrounding mountain ranges. As a large farming county, water is readily needed to maintain the hundreds of thousands of farm acres. The Kern River, flowing from the Sierra Nevada mountain range, supplies water for the valley’s farming as well as the community of Bakersfield and surrounding towns such as Arvin and Wasco. The Kern River begins at the headwaters near Mt. Whitney and travels south through the southern Sierra Nevada Mountain Range to the foothills east of Bakersfield where it is then terminated for human needs.

Few documented studies of the Kern River are available or have been conducted (Hill and Rai, 1984). Studies which have been conducted are constrained to areas surrounding Lake Isabella (800m) and further south. Documentation of major cations, silica, chloride, temperature, δD, δ18O, and radioisotopes are not only limited, but are non-existent for the river north of the Kernville area.

The objective of this introductory study is to survey the isotopic compositions, the source of solutes during weathering, and ground water influences of the upper Kern River and several of its drainage sub-basins. By collecting samples beginning near its headwaters and ending at its termination, these geologic influences can be examined. More emphasis is given to the portion of the river above Forks of the Kern, as the majority of the water is from the drainage basins in the high Sierra Nevada.

Figure 1 shows the major tributaries of the upper Kern River. Not every tributary was sampled. Access and time permitted sampling of only the largest western tributaries. The lower Kern River has limited input as most of the snow melt comes from the northern Upper Kern. Little Kern River was not sampled, however, and would be a good sample point for any future studies as it is a major contributor to the Kern River.

METHODS

Collection Points:

Samples in the upper Kern River between KR_HS_up and KR_LC were taken at larger tributaries. (Fig. 1). To isolate tributary and hot spring contributions to the river, samples were taken approximately 50m above the inflows, directly out of the inflows, and approximately 200m down river of the inflows. KR_KL was taken at the top end of an approximately 7km section of a shallow and slow section of the river, and KR_LCup was taken just after the end of this section. The goal of taking these samples was to attempt to understand the hyporheic exchange of radium/radon. At most sites, one sample was taken for radium (20L) and a second (60ml) for stable isotopes and solutes. The ground water samples were difficult to take due to the subsurface layers beneath the shallow soil. The piezometer was not able to penetrate more than a few centimeters without being damaged.

Radium Collection:

Twenty liters of water was pulled from each river and creek sampling location using a collapsible plastic bucket. Then the water was poured into and measured using a calibrated water bag. The twenty liters were gravity fed from the bag through an eight inch PVC cartridge packed with acrylic fiber impregnated with MnO₂ to absorb radium (Moore, 1976). The used fiber was labeled and stored for lab processing. Only one liter of the Sandbar ground water was passed through the cartridge. Samples were not filtered but did not have obvious turbidity.
Solute/ Stable Isotopes/ Radon:

Using a 60cc plastic syringe and 25mm sterile Acrodisc 45µM filters, 30cc-60cc of water were collected from each sampling site and stored in 30cc nalgene HDPE bottles for lab testing. 50ml of ground water samples were collected using a ground piezometer and filtered into Tedlar bags for radon analysis. Care was taken to avoid air contact before injecting it into the bag. 40ml of ground water sample taken from KR_RCgr was removed from the Tedlar bag and slowly pushed through 0.23g of Mn fiber to extract radium.

Analytical Techniques:

Ca, K, Mg and Na concentrations were measured using a Metrohm 850 Professional ion chromatograph fitted with a C2 cation column. Four mixed standards were prepared using MgSO₄·7H₂O, CaCO₃, NaCl and KCl, each at concentrations from zero to about 1mM. Each salt was dried at 105°C overnight. The hydrated MgSO₄ lost its water of hydration during drying and was weighed quickly to avoid adsorption of atmospheric water. The Ion Chromatograph measured each standard and sample in order and then proceeded to measure them twice more in order to produce triplicate results and to correct for drift. No significant drift was observed. Calibration curves were mainly linear but were fit with quadratic equations. Precision for each element was 1-3% based on replicates (Table 1).

δO18 and dD were measured using a Picarro L1102-i water isotope analyzer. Each sample was measured six times with the first three measurements rejected. Every measurement takes 10 readings for a total of 30 readings per sample. The precision based on replicate runs was typically 0.02‰ for δO18 and 0.1‰ for δD.

Cl⁻ was measured using an Aminco-Cotlove coulometric chloride titrator. Two measurements were taken per sample with blanks and standards taken throughout to correct for drift in the titrator and to decrease the standard deviation. Each sample required 4ml of sample. Only two measurements were run per sample to conserve the limited resources of sample water. The precision for sample runs was about 2%.

Radium 223 and Radium 224 were measured using Radec (Moore and Arnold, 1996). Each sample was run three times to allow correction for supported activity from ²²⁸Th and ²²⁷Ac. These parent activities were determined by repeating analyses 30 to 50 days after collection. Due to the limited time available it is not possible to determine if supported activity comes from dissolved parents, grandparent (²²⁸Ra in particular) or particulates trapped in the fiber. Three measurements allow for the necessary data points to calculate and account for Thorium 228’s background levels. A lab standard prepared from solutions of dissolved uraninite and monazite of known activity (Colbert, 2004) was used, and should be accurate within 5% for ²²⁴Ra and 10% for ²²³Ra. ²²⁶Ra was measured by sealing cartridges to allow ²²²Rn ingrowths and extracting ²²²Rn as described by Mathieu et al (1988). A few samples were passed through a second cartridge to test the efficiency of Ra extraction. These results (Appendix A) were not definitive but indicate adsorption efficiency is near 90%. Due to the uncertainty in these, no correction has been made.

²²²Rn on one groundwater sample was run by injecting 60cc air into the Tedlar bag, equilibrating gas and air phases, and using a 40cc aliquot of gas injected into a Lucas counting cell.
Fig. 1 Map of the Kern River. Johnsondale Bridge and further south will be considered lower Kern River. Leggett Creek and further north will be considered upper Kern River. The inset shows an enlarged portion of the upper Kern River.
Fig. 2  Photo showing major drainage basins of the upper Kern River. Western Range area shows the vast mountain range west of the western and eastern drainage basins. The unmarked area points out the peaks west of Rattlesnake Creek. Samples points are shown with a line pointing into the canyon for reference (Google Earth).

Table 1. Major ions (µM) and Isotopic Composition (% vs vsmow)

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<th>Sample_date</th>
<th>Location**</th>
<th>Elev (m)</th>
<th>T (ºC)</th>
<th>Cl</th>
<th>Na</th>
<th>Na†</th>
<th>Ca</th>
<th>K</th>
<th>K‡</th>
<th>Mg</th>
<th>Si</th>
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<td>-13.46</td>
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*Near tributary or hot spring input. May not be well mixed.
**gr indicates ground water, numbers indicate sample dates
†Na sample value minus aerosal input using chloride
‡K sample value minus biotite input using magnesium

| _mean | 2 | 2 | 3 | 1 | 2 | 1 | 0.02 | 0.1 |
Results and Discussion

Isotopic Composition

$\delta^{18}O$ and $\delta D$ isotopes vary significantly between tributaries, Kern Hot Spring and the Kern River. In general, the river water becomes more enriched with these isotopes as elevation decreases, and east flowing tributaries are added to the water. A major factor controlling isotopic concentrations in precipitation is altitude. Along the west side of the Sierra Nevada divide, $\delta D$ decreases by 40‰ for every 1000m of elevation (Friedman et al. 1970). Fig. 3a indicates that the uppermost river is lighter in $\delta^{18}O$ and $\delta D$ while the Arroyo Creek and Rattlesnake Creek have significantly heavier compositions. Fig. 3b shows the $\delta D$ versus $\delta^{18}O$ Hot Spring samples as compared with the meteoric water line (Craig, 1961). The sample points fall very closely to the meteoric water line, suggesting that the water has not been modified significantly, other than heating, and therefore may not have reacted with silicate rocks.

A linear regression was fit to the data (Fig. 3a). The regression line is very close to the meteoric water line (Craig, 1961). KR_END and KR_LI were not included because they were samples taken below Lake Isabella. The relatively long residence time of Lake Isabella (about one year based on data in Hill and Rai, 1984) allows for 1) time for evaporation of lighter water which results in a greater concentration in $\delta^{18}O$ and $\delta D$ and 2) a mix of multiple seasons of snow and precipitation runoff. The rightward shift from the meteoric water line and decreased slope are likely caused by the greater evaporation rate of $\delta D$ compared to the heavier $\delta^{18}O$ (Faure, pg. 435). Because the lighter deuterium evaporates at a higher rate than $\delta^{18}O$, the data points are skewed to the right of the regression, which is similar to the meteoric water line.

The eastern portion of the Sierra Nevada region near Mount Whitney and Mount Muir will have relatively lighter snow melt compared to the western side. Even then, the western drainage basin side of the Kern River directly west of the Mount Whitney area will have relatively light snow due to the abundant high peaks west of the drainage basin (see Fig 2). The high altitude path of storms will have likely rained out heavier compositions before reaching the Kern River’s western drainage basin. Alta Peak is approximately 12km west from the nearest western drainage basin peak, giving ample storm time and travel distance for heavier precipitation before reaching the Kern River drainage basin. With the western drainage basin being relatively light and the eastern drainage basin being even lighter, the majority of the Kern River’s volume is low in $\delta^{18}O$ and $\delta D$.

Arroyo Creek lies to the east of a relatively low altitude portion of the Sierra Nevada mountain range, making it the first major elevation gain leading to preferential precipitation of deuterium and $\delta^{18}O$. South of the Arroyo Creek drainage basin (and sharing a peak ridgeline) lies the Rattlesnake Creek drainage basin. East of Rattlesnake Creek is a significantly high ridgeline that peaks at 3,600m which likely protects the Rattlesnake’s drainage basin from $\delta^{18}O$ and $\delta D$. 
KR_LC is a sample taken from a small creek originating from Leggett Creek. Leggett Creek is mostly fed from Angora Mountain. Angora Mountain peaks at 3100m which is significantly lower than the peaks surrounding Big Arroyo Creek, Rattlesnake Creek and the Kern River’s headwaters. Therefore, the low altitude of Angora Mountain would collect relatively heavier precipitation. A lack of high peaks west of Angora Mountain decreases the chances of δ¹⁸O and δD to precipitate out of storms before passing over Angora Mountain. Also, the low altitude would have been melting older snow as compared to the peaks further north, producing heavier snow melt runoff. These two observations are the probable causes for the higher δ¹⁸O and δD concentration found in the KR_LC samples.

Ground water sample KR_RCgr, taken out of the sand at the edge of the river just upstream from Rattlesnake Creek, shows a significant increase of δ¹⁸O and δD. KR_LCgr was taken in the same manner from the same creek as KR_LC but these two have similar compositions. I cannot account for the behaviors of these two ground water samples.

![Fig. 3a dD vs. d18O for samples from the Kern Basin. The long solid line is a least squares fit. Samples KR_END and KR_LI (short solid line, taken below Lake Isabella) were not included due to the residence time of the water in the lake. Extension of this trend may represent an evaporation trend that would intersect the meteoric line near the cluster of points for the main Kern River. The dashed line indicates KR_RCup and KR_RCgr, samples from the same location but KR_RCgr is a groundwater sample. Analytical uncertainty is about the size of the data points.](image)

![Fig. 3b dD vs. d18O for the Hot Spring samples. The solid line is the meteoric water line (Craig, 1961) which the samples fall very close to. The water has not been modified, indicating that the water may not have reacted with silicate rocks.](image)
Fig. 4. Kern River Geologic Formations. Thick line represents the Kern River. (adapted from Geologic Map of California, CA Dir. of Mines).
Fig. 5. Co-variation of major cations and Si. These lines were fitted to the samples taken from the Kern River to show the changing trends of the river water. These figures do not include KR_HSdwn, KR_ACdwn or KR_RCdwn because they do not show well mixed river waters. Sodium values have been corrected for expected aerosol contributions by assuming all chloride comes from marine aerosols. Corrections for other cations are negligible. Analytical precision is about the size of data points.
Fig. 6 The Sierra Nevada batholith is represented by dotted region. Dark shaded areas represent metamorphosed rock. Rectangle area represents Fig. 7 (Moore, 2000)

Fig. 7 Mt. Whitney’s Granodiorite has higher concentrations of potassium feldspar and is part of the Kern River’s north western drainage basin. (Moore, 200)
Chemical Composition and Weathering
The ratio of plagioclase to orthoclase is greater than 50% and therefore the Sierra Nevada batholith is granodiorite; not the familiar name of granite that it is often associated with the mountain range (Moore, 2000).

Although granodiorite is the main rock formation of the Sierra Nevada mountains, the composition within the granodiorite varies slightly as granitic intrusions of the batholith occurred spatially at varying times. The geologic map (see Fig. 6 and 11, Moore, 2000) shows three different granitic features. Mt. Whitney granodiorite contains greater amounts of potassium feldspars than bordering areas.

The river water chemistry should reflect weathering of the rocks in the drainage basin and its sub-basins. A portion of the cations in the Kern waters should come from deposition of marine aerosols. The measured chloride was used to adjust data presented in Figure 5, leaving the remaining weathering component. The sodium used in the plots equaled the total sodium minus 80% of the chloride value. Likely weathering reactions for several common minerals are given in Figure 8.

The sodium and calcium relationships observed in River waters, after adjusting for marine aerosols, are seen in Fig. 5a and 5b. The upper Kern River has a y-intercept at 57 µM indicating a possible surplus of calcium over sodium at the headwaters of the Kern River (Fig. 5a). This trend indicates that the weathering process for these two elements might not be explained by dissolution of only feldspar with a single composition. Big Arroyo has a greater Ca/Na ratio than the river as indicated by a line from the origin to the data point. Rattlesnake Creek and Leggett Creek are progressively more alkali in comparison and may indicate a difference in the geology of their drainage basins.

As for the plagioclase constituents, Rademacher et al., 2001, found the northern granodiorite near Lake Tahoe to be 45% anorthite and 55% albite. Even though a few hundred kilometers span the gap between Lake Tahoe and the Kern River, this ratio will be used as a guide in understanding the water chemistry of the river water. If the cations weathered congruently, the expected Ca/Na would be 0.8. Observed ratios are greater than this, indicating that either weathering is not congruent, or another mineral contributes Ca, perhaps calcite which is found in some places in the drainage basin. Some of the changes in the Ca/Na ratio observed in tributary streams may be because the northern drainage basin’s suspected anorthite rich granodiorite is therefore postulated to give way to albite as the plagioclase end member. The Big Arroyo drainage basin is postulated to have similar calcium rich granodiorite as its neighboring northern drainage basin, or it contains a higher proportion of other Ca-bearing minerals that are weathered, while Rattlesnake Creek and Leggett Creek contain fewer Ca-rich minerals or an increasing ratio of albite to anorthite.

Johnsondale Bridge and south show a similar story. Both Ca and Na increase down river, with a slope of about 1.4 (Fig. 5b). Evaporation may play some role in this increase, but probably not for samples above Lake Isabella, because the stable isotopes for this region of the river are still on a meteoric water line. The increase is probably due to weathering in ground waters or small tributaries that contribute some flow below Forks of the Kern. Important geological changes are the gabbro intrusion in the sub-basin of the Little Kern River which flows into the Kern River below Leggett Creek. The samples points taken in May above Lake Isabella as well as below are calcium rich. KR_BCH sampling point, taken one month later is equal in calcium and sodium.

Temporal variations are the probable cause of differences between KR_JB, KR_KV and KR_BCH. KR_BCH, taken eight days after
Leggett Creek, shows similar calcium to sodium ratios. Fig.7 further helps to explain the mineralogy of the granodiorite. As mentioned earlier, Whitney Granodiorite is relatively rich in potassium feldspar. It also contains some biotite, which should release both K and Mg. If the slope of the K vs. Mg relations (Figs. 5c,d) indicate contributions of biotite, the intercept should indicate the contribution of K from orthoclase weathering. The intercept of potassium on the graph points to an initial surplus of potassium input. This is due to the K-feldspar’s weathering contribution.

Magnesium increases at a fairly constant rate in relation to potassium. Biotite is the only mineral in granodiorite that would contain sufficient amounts of magnesium to show any significant concentrations as well as show a dependence upon potassium. Biotite contributes about 3% volume of granodiorite (Klein et al. 582). Fig. 5d shows a much larger contribution of magnesium as a constituent. Biotite below Leggett Creek must be influencing the magnesium input. The Little Kern River that drains a more mafic area may also influence these sample points.

Fig. 5e plots sodium plus potassium to silica in order to see if the theoretical ratio is maintained in the river and creeks. The tributary samples are close to the theoretical ratio of 1:2 between cations and silica (based on weathering reactions in Fig. 8) but the river samples trajectory is instead a 1:1 ratio. There is a small initial deficit in silica among the tributaries. The Kern River, however is very depleted in silica. One possible explanation is biological uptake of silica. This theory can even be supported by the difference in temporal difference among the KR_JB, KR_KV and KR_BCH samples. Perhaps the large difference in silica between these points is related to the time of season. KR_BCH, taken one month after the other others has less Si, indicating a greater amount of biological activity as a result of increased water temperature and a possible growth of fresh water diatoms. If biological uptake is the reason for silica depletion then increased activity should deplete the water even more.

**Fig. 8. Weathering reactions of common granodiorite minerals**

Anorthite- $\text{CaAl}_2\text{Si}_2\text{O}_8 + 2H^+ + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

Orthoclase- $2\text{KAlSi}_3\text{O}_8 + 2H^+ + 9\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+ + 4\text{Si(OH)}_4$

Albite- $2\text{NaAlSi}_3\text{O}_8 + 2H^+ + 9\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Na}^+ + 4\text{Si(OH)}_4$

Biotite- $2\text{K(Mg , Fe)}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + 14\text{H}^+ + \text{H}_2\text{O} \rightarrow 2\text{K}^+ + \text{Mg}^{2+} + 5\text{Fe}^{2+} + 2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{H}_4\text{SiO}_4$
Using the Kern Hot Spring’s water concentrations (this sample comes from ground water less than a few seconds before collection and is assumed to have the same activity as the ground water), concentrations compared to the river water just north of it we can estimate the time the water has been out of contact with ground water. Radium 223 has an eleven day half life which means that to get from an activity of 117 dpm/m$^3$ to 2.4 dpm/m$^3$, 60 days would be required. The river water at that point has therefore been out of contact with subsurface soil for 60 days. Likewise we can use the same method with radium 224. The measured values were 35 dpm/m$^3$ for the river sample and 2262dpm/m$^3$ for the hot spring water. With a half life of 3.6 days we can calculate approximately 22 days from the last contact with subsurface water. These ages are lower limits because surface water may also receive continuous input, so the closed system model may not be the best description of the system.

Three possibilities may account for the long residence time out of the ground water. River flow rates are great enough that within
a couple of days the river water should have covered the distance of the river. Also, creek flow rates are high enough that 20 to 60 days will not have passed between the time samples were collected and the water’s last contact with subsurface soils. The first possibility is that the drainage basin’s many small lakes have seasonal residence times between 20 and 60 days. As water leaves contact with the active soils, they would enter the lake for 20 to 60 days and then continue to flow down the river. Another possibility is that as the rivers and creeks flow downstream the water interacts with subsurface ground waters. This hyporheic exchange would introduce more radioisotope activity and makes the calculated residence time a lower limit. Finally, if the residence time in groundwater is too short to permit equilibration, or if a significant fraction of the runoff is not passing through the subsurface, these numbers may not be reliable estimates.

More samples are needed to fully understand the ground water influences on the drainage basins, tributaries and the Kern River. Filtering the water to remove particles may also help in the precision of the measurements. A more quantitative analysis would then be a possibility. Ground water samples were hard to acquire because of the rocky subsurface but these samples are imperative for analysis. Samples of the lakes in the drainage basins could aid in dating the water. Finally, analysis of 228Ra could not be completed within the time available for this study, as it requires about 6 months for sufficient ingrowth of its progeny, 228Th and 224Ra. This analysis may provide further insight.

Conclusions

δ18O and δD have larger concentrations of in the precipitation of the western drainage basin. Mountain ridges and ranges have great effects on precipitation’s isotopic composition. The chemical weathering of the drainage basins reflect the granodiorite make up of the batholith, although the possible contributions of Ca from more than one mineral make quantitative evaluation of the sources difficult. Potassium is a large end member component in the upper and eastern Sierra Nevada range, and further south more sodium replaces the potassium input. Magnesium increases in river composition indicating an increase in biotite dissolution. Silica has a major deficit and it is not clear why the silica is at such a deficit. The radio isotopes indicate possible 20-60 day residence times in the lakes of the drainage basins. More samples are needed for the radioisotope data.

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