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### Permalink

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### Journal

Chemical Geology, 179(1-4)

### ISSN

0167-6695

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### Publication Date

2001-09-01

### DOI

10.1016/s0009-2541(01)00314-x

Peer reviewed

## Chemical evolution of shallow groundwater as recorded by springs, Sagehen basin; Nevada County, California

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### Abstract

Springs in Sagehen basin, California, were used to document the effect of chemical weathering on the chemical evolution and composition of groundwater in a high elevation catchment. Geochemical tracer ages were determined with chlorofluorocarbons (CFCs) and tritium/<sup>3</sup>He dating techniques. The spring water ages range from less than 5 years to almost 40 years. Mass balance calculations performed by NETPATH were combined with spring water ages to calculate chemical weathering rates observed throughout the basin, which range from 0.0116 to 0.0018 and from 0.0036 to 0.0006 mmol l<sup>-1</sup> year<sup>-1</sup>, for plagioclase and hornblende, respectively. Major cation concentrations, pH, and spring water conductivity were found to correlate positively ( $R^2 = 0.7$ ) with spring water age. This suggests that shallow groundwater, as represented by the springs, is a chemically evolving system. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Weathering; Groundwater tracers; Catchment hydrodynamics; Sierra Nevada-CA

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### 1. Introduction

The dynamics of catchment hydrochemistry are the subject of intense study due to their complex nature and multi-disciplinary applications. Many variables affect the solute content of surface waters, including variations in atmospheric deposition, biological activity, local geology, sediment transport, and chemical weathering. Studies of chemical weathering and the chemical evolution of shallow ground-

water are often impeded by the slow rates of these reactions and the difficulties associated with determining flow paths, mineral contact times, and mineralogy of the aquifer.

Field-based studies of chemical weathering often rely on monitoring the chemical composition of stream water (e.g., Paces, 1983; Stallard and Edmond, 1983; Velbel, 1985; Drever and Zobrist, 1992; Williams and Melack, 1997a; Furman et al., 1998). Using this approach, weathering rates are calculated from the total flux of solutes out of a catchment. Streams, however, are integrative systems which incorporate waters from many different flow paths, including overland, soil, and shallow groundwater flow (Church, 1997). The lengths of these pathways

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vary significantly, and thus have different water–rock interaction times. Recent studies in catchments have attempted to isolate the soil component of flow and quantify its contribution to catchment hydrochemistry (e.g. Mulder et al., 1990, 1991; Hinton et al., 1994). Different soil end-members, however, cannot completely explain the hydrochemistry of catchments and suggests that another major contributing component, such as groundwater, is necessary to explain the variability in catchment hydrochemistry (Christophersen et al., 1990; Hooper et al., 1990).

Springs provide a natural surficial access point to groundwater systems. By studying spring waters with different travel times (i.e. geochemical ages), it is possible to study the chemical evolution of groundwater. In this study, we use spring waters of differing ages to investigate water rock interactions and how they affect the chemical evolution of shallow groundwater in a small, high elevation catchment located in the Sierra Nevada of California.

The chemical evolution of groundwater in both shallow aquifer systems and catchments has been studied through the use of geochemical analyses (eg. Salama et al., 1993) and age tracers (eg. Böhlke and Denver, 1995; Katz et al., 1995). Previous studies on springs in the Sierra Nevada examined the chemical evolution of water (Feth et al., 1964; Garrels, 1967; Garrels and Mackenzie, 1967; Erman and Erman, 1995). Primary weathering reactions were determined using mass balance calculations and an understanding of the local geology. These studies concluded that a strong correlation exists between the permanence of spring flow, conductivity, and water chemistry. The authors were unable to link these variations to groundwater residence times because geochemical dating techniques for shallow groundwater were not yet developed. Thus, they were unable to calculate chemical weathering rates.

We present a method for evaluating chemical weathering rates and understanding the chemical evolution of shallow groundwater by incorporating the mass balance approach developed by Garrels and Mackenzie (1967) with groundwater dating techniques. The mass balance calculations are performed using the geochemical model NETPATH (Plummer et al., 1994). By assuming that the groundwater residence time is the same as the mineral interaction time, we provide a means of using springs to study

groundwater evolution and its contribution to catchment hydrochemistry.

## 2. Geochemical tracer ages

Geochemical tracers, including CFCs, tritium/<sup>3</sup>He, and <sup>4</sup>He, are now used to determine the residence time of shallow groundwaters (e.g., Schlosser et al., 1988; Busenberg and Plummer, 1992; Solomon et al., 1996; Ekwurzel et al., 1994; Cook and Solomon, 1997). The CFC and tritium/<sup>3</sup>He methods record the time it takes groundwater to flow from the recharge area to the discharge location, typically with an uncertainty better than  $\pm 2$  years. Previous shallow groundwater studies have demonstrated good agreement between the CFC and tritium/<sup>3</sup>He tracer methods in some areas (Ekwurzel et al., 1994; Szabo et al., 1996). A less commonly used method relies on the ingrowth of <sup>4</sup>He. <sup>4</sup>He concentrations in groundwater increase with time as a result of alpha decay of U and Th series nuclides (e.g., Bottomley et al., 1984; Torgersen and Clark, 1985; Solomon et al., 1996). The rate of this increase differs between aquifers, and therefore it can be difficult to calculate absolute ages from the <sup>4</sup>He concentration. Nevertheless, this method can be used to determine relative ages of groundwater and the influence of an older groundwater component.

Atmospheric concentrations of CFCs increased nearly exponentially since their introduction in the 1930s to the mid-1990s. Thereafter, concentrations remained almost constant or decreased slightly. The atmospheric record is transferred to groundwater at the water table through a temperature, salinity, and elevation dependent solubility relationship (Warner and Weiss, 1985). Once groundwater is isolated from the soil air, the CFC signal becomes fixed and is carried by the flow system. The year in which the water recharged is determined by comparing the amount of CFCs dissolved in the groundwater and atmospheric growth curve using the solubility relationship. CFCs are conservative in aerobic systems but can be consumed by microbes under anaerobic conditions (Lovley and Woodward, 1992; Oster et al., 1996). In some areas, CFCs can also be added to groundwater through point-source contamination (eg.

Schultz et al., 1976; Busenberg and Plummer, 1992; Clark et al., 1995).

The tritium/ $^3\text{He}$  method of groundwater dating is based on the decay relationship between tritium, the parent isotope ( $t_{1/2} = 12.43$  years), and  $^3\text{He}$ , the daughter isotope. Although tritium is naturally produced in the upper atmosphere by cosmic rays, most of the tritium in the environment was produced during the above ground nuclear bombs tests in the late 1950s and early 1960s. At the time of its maximum in the mid-1960s, tritium concentrations in precipitation were 2 to 3 orders of magnitude greater than the background concentration. Because of other sources of  $^3\text{He}$  to the groundwater, a helium mass balance must be employed to isolate the amount  $^3\text{He}$  derived from the decay of tritium, the  $^3\text{He}_{\text{tritogenic}}$  (Schlosser et al., 1989).

### 3. Study area

The Sagehen springs are located in a small, high-elevation basin (mean elevation = 2100 m) in the eastern Sierra Nevada, about 30 km north of Lake Tahoe (Fig. 1). At the University of California, Berkeley research station (1932 m), the mean annual temperature and precipitation is 5.2°C and 89 cm/year, respectively. Sagehen basin is covered by extensive glacial till deposits derived from a combination of andesite and granodiorite basement rocks. Granodiorite fragments at the surface are commonly found only in close proximity to outcrops of granodiorite, which lie in the northwestern portion of the basin. Andesite outcrops exist around the edges of the basin at the higher elevations and in a few locations along Sagehen Road, just north of Sagehen Creek. The granodiorite consists primarily of plagioclase (40%), quartz (30%), hornblende (20%), and biotite (10%), and the andesite consists primarily of plagioclase (45%) with varying amounts of hornblende (5–25%) and augite (1–25%) and a small amount of glassy groundmass.

All springs sampled during this study flowed continuously between 1997 and 1999 (Fig. 1). Two springs within the basin, S12 (not included in this study) and S10, dried temporarily at the end of the late 1980s and early 1990s droughts; however, the range in spring discharge prior to the drought was

from < 1 l/s to over 8 l/s (Erman and Erman, 1995). The size of the discharge zone varies from spring to spring. Most springs have a small primary discharge pool in which most of the flow is captured. Some springs, however, have multiple discharge locations with multiple pools.

## 4. Methodology

### 4.1. Sampling procedures

Samples were collected from 11 springs in Sagehen basin in August of 1997 and November of 1999 following several months of little to no precipitation. Precautions were taken to ensure that samples were taken directly from the springs' uppermost discharge zone. A copper tube sampling line was positioned in the pool at the sediment–water interface, and all samples were collected from its outlet. Field measurements of pH, conductivity, temperature, and dissolved oxygen were made at each spring (Table 1). Samples collected for cation and anion analyses in 1999 were filtered in the field using 0.4- $\mu\text{m}$  polycarbonate filters, stored in polyethylene bottles, and refrigerated until analysis in the laboratory (1997 samples were not filtered in the field, and thus these data are not presented here). Samples for analysis were collected in two bottles, one of which was acidified with a few drops of concentrated hydrochloric acid. Samples for measurement of dissolved inorganic carbon (DIC) were collected in septa sealed amber glass bottles and were poisoned with  $\text{HgCl}_2$ .

Samples were also collected for analysis of CFC-11 ( $\text{CCl}_3\text{F}$ ), CFC-12 ( $\text{CCl}_2\text{F}_2$ ), tritium, helium isotopes, neon (1997 only), and argon. Samples for He isotopic, argon, and neon analyses were collected in 10-ml copper tubes sealed with stainless steel pinch-off clamps. Samples for tritium analysis were stored in glass bottles. In 1997, samples for CFC analysis were extracted from the copper tube sampling line with glass syringes and immediately transferred to borosilicate ampoules (Busenberg and Plummer, 1992). The ampoules were subsequently flame-sealed in the field leaving a  $\text{N}_2$  headspace, and stored refrigerated until analysis. In 1999, CFC samples were collected in 10-ml copper tubes and sealed with

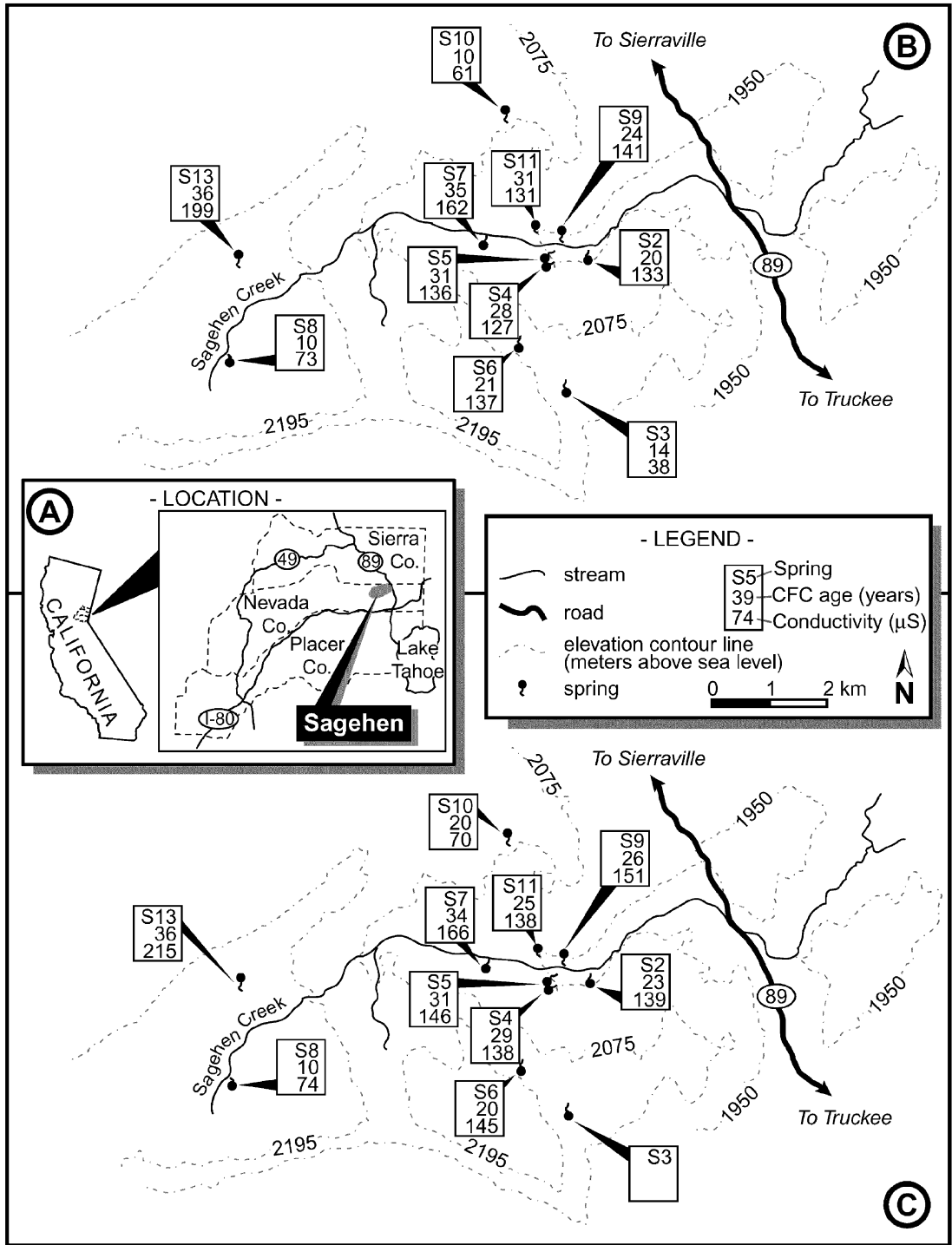


Fig. 1. Map showing location of Sagehen basin in the Sierra Nevada (A) and spring locations with their corresponding CFC-11 age and conductivity for 1997 (B) and 1999 (C). Figure adapted from Erman and Erman (1995).

Table 1  
Sagehen spring chemical data from November 1999

Sagehen number	Sample date	Temperature (°C)	pH	Conductivity (μS)	DO (mmol/l) <sup>a</sup>	DIC (mmol/l-C)	Ca <sup>2+</sup> (μmol/l)	Na <sup>+</sup> (μmol/l)	Mg <sup>2+</sup> (μmol/l)	K <sup>+</sup> (μmol/l)	Si (μmol/l)	Cl <sup>-</sup> (μmol/l)	NO <sub>3</sub> <sup>-</sup> (μmol/l)	SO <sub>4</sub> <sup>-</sup> (μmol/l)	Charge balance error (%) <sup>b</sup>
S2	11/1999	4.9	6.8	139	0.2	1.75	312	239	165	39	689	12.8	9.0	0.9	+2
S4	11/1999	4.7	7.0	138	0.4	1.41	390	174	201	43	472	6.8	21.1	0.8	+12
S5	11/1999	5.1	7.3	146	0.4	1.47	359	165	193	47	438	9.2	14.2	1.6	+1
S6	11/1999	3.9	6.3	145	0.4	1.97	367	161	214	21	525	8.0	4.3	2.4	+25
S7	11/1999	8.8	7.7	165	0.3	1.62	396	304	206	69	501	15.0	4.1	2.7	+2
S8	11/1999	3.0	6.3	74	0.4	0.87	190	104	77	19	369	4.8	0.7	1.0	+34
S9	11/1999	6.7	6.8	151	0.3	1.78	365	200	246	42	502	10.8	2.2	8.7	+8
S10	11/1999	8.3	6.2	70	0.1	1.69	120	65	108	3	303	8.6	< 0.1	1.0	-9
S11	11/1999	6.0	7.2	138	0.5	1.43	346	174	178	45	467	6.6	12.4	1.3	+2
S13	11/1999	6.2	8.0	215	0.3	2.07	480	191	350	45	421	7.6	6.0	1.4	-4
Precipitation <sup>c</sup>		-	5.4	-	-	-	1.2	3.7	0.6	0.3	-	3.9	8.1	2.9	

<sup>a</sup>DO was measured in Sept. 1999.

<sup>b</sup>Charge balance error was calculated using WATEQFP.

<sup>c</sup>Only ion concentrations used in the cyclic salt correction were reported in the precipitation data.

stainless steel pinch off clamps. These samples were also stored refrigerated until analysis.

#### 4.2. Analyses

Measurements were made of the major cations using standard inductively coupled plasma atomic emissions spectrometric (ICP–AES) and atomic absorption spectrometric (AA) techniques. The anions were measured using ion chromatographic techniques. Both acidified and unacidified samples were analyzed for cation content and no difference was detected. The ICP–AES has an analytical precision of  $\pm 4\%$ . Samples for cation analysis were run multiple times, and the values reported in Table 1 are averages.

DIC was measured on a flow injection analyzer (FIA, Lachat Zelweiger, Milwaukee, WI) and is the sum of  $(\text{CO}_2)_{\text{aq}}$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ . The method involved acidifying the sample stream, then diffusing gaseous  $\text{CO}_2$  across a membrane into a phenol red solution (25 mg/l), which is a pH indicator. The acidic peaks were measured at 440 nm (Doyle and Schimel, submitted). DIC measurements have an error of  $\pm 0.2$  mmol/l. CFCs were measured using a method adapted from the procedure developed by Smethie et al. (1988) using a Shimadzu gas chromatograph equipped with an electron capture detector. A  $^3\text{He}$  accumulation method was employed for measurement of tritium (Surano et al., 1992).

The copper tube sample collected for He, Ne, and Ar analyses was attached to a sample manifold using a flare compression fitting. The water sample (10 g) was released into a 250 cm<sup>3</sup> evacuated volume by removing the bottom pinch-off clamp. The receiving volume was heated with a hot air gun to boil the sample for approximately 1 min to completely degas the sample. The water was then frozen with liquid nitrogen (77 K) leaving the noncondensable gases in the headspace volume. This gas was then expanded into the processing manifold and exposed to a Ti-alloy getter at 400°C for 5 min to remove  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , and other gases. Argon, Kr and Xe were then collected on activated charcoal at 77 K. The remaining He and Ne were collected on a separate activated charcoal trap at 15 K. The charcoal trap is then warmed to 35 K releasing the He, which was then expanded into the mass spectrometer (VG-5400) for

isotopic analysis. The Ne was then released at approximately 90°K and was analyzed in the same mass spectrometer after the He sample had finished. The trap was warmed to 150°C and the released gases were re-exposed to the Ti-alloy getter. The total pressure (virtually all due to Ar) was measured with a capacitive manometer (1 Torr full scale).

#### 4.3. Chemical weathering rates

Chemical weathering rates were estimated for each of the springs sampled in Sagehen basin by dividing the amount of minerals weathered (determined using mass balance calculations) by the groundwater age (determined with geochemical tracers). NETPATH, a geochemical mass balance model developed by the USGS (Plummer et al., 1994), was used to estimate the total amount of reacted minerals. The initial pre-weathering chemical composition of the spring waters was assumed to be that of precipitation. Precipitation chemistry was determined from the nearest high Sierra NADP precipitation station (Yosemite), which is located approximately 190 km south of Sagehen basin at an elevation of 1408 m. The chemistry of the discharging water at the springs was used as the final post-weathering composition of the groundwater (Table 1). A cyclic salt calculation was used to correct for evapotranspiration and is based on  $\text{Cl}^-$  concentrations (Garrels and Mackenzie, 1967; Stallard and Edmond, 1983). The cyclic salt correction was small (less than 10%) for the major cations in almost all cases. All other variations in the chemical composition of the spring waters were assumed to result only from chemical weathering processes occurring along a flow path. In this manner, the chemical evolution of the spring water from precipitation through the soil and groundwater zones is modeled.

NETPATH requires user input of the mineral phases and their solid solution chemistry. For the Sagehen springs, which are primarily flowing from granodioritic and andesitic glacial till, the primary phases include  $\text{CO}_2$  gas (generated by plants and microbes in the soil zone), quartz, biotite, hornblende, plagioclase ( $\text{An}_{45}$  composition based on microprobe analysis of granodiorite), kaolinite, Ca–montmorillonite (the phase NETPATH refers to as Ca–montmorillonite is equivalent to Ca–beidellite),

and calcite (similar to Garrels and Mackenzie, 1967). NETPATH calculates all possible combinations of these phases based upon solutions to mass balance equations and the concentrations of constraining ions given for the system. When more than one mineral phase is dominated by a shared cation, NETPATH is often unable to produce unique solutions (e.g. Plummer et al., 1994; O'Brian et al., 1997; Furman et al., 1998). Therefore, the user is required to assess the validity of each model based on mineralogy of the study area, solubility calculations, and spring chemistry.

Geochemical tracer ages of spring waters are used to determine the amount of time over which these weathering reactions occurred and solutes were released. The CFC and tritium/<sup>3</sup>He techniques begin recording time when groundwater flows across the water table during recharge. This definition of recharge begins after infiltration and transport through the soil zone where mineral dissolution begins. Thus, there is an offset between the geochemical clocks and the beginning of the chemical weathering. Residence times of water in the soil zone,

however, are likely to be less than the uncertainty of the estimated tracer ages ( $\pm 2$  years), and this offset will introduce a very small error in the calculated weathering rates.

## 5. Results

### 5.1. Groundwater residence time and its relationship to water chemistry

Groundwater residence times for the Sagehen springs calculated from CFCs range from 10 to nearly 40 years (Table 2). Good agreement exists between CFC ages estimated by CFC-11 and CFC-12, indicating that CFCs were not decomposed within the aquifer or subjected to point-source contamination (Fig. 2). Additionally, springs sampled in both 1997 and 1999 record similar spring water CFC ages (Table 2, Fig. 3). Tritium/<sup>3</sup>He ages of spring waters range from 0 to 36 years (Table 2) and increase with the increasing CFC age (Fig. 4). However, there is an offset between the age estimations of these two

Table 2

CFC, tritium, and helium data for the Sagehen springs and corresponding tracer ages.

CFC ages in years were calculated for a recharge temperature of 3°C and 2300-m elevation.

Sagehen number	Sampling date	CFC-11 (pmol/l)	CFC-12 (pmol/l)	CFC-11 (age)	CFC-12 (age)	tritium (TU)	<sup>3</sup> He <sub>tritogenic</sub> (TU)	tritium/ <sup>3</sup> He (age)	δ <sup>3</sup> He (ccSTP/g)	<sup>4</sup> He (×10 <sup>8</sup> ccSTP/g)
S2	08/1997	3.47	1.47	20	20	–	–	–	–	–
S2	11/1999	2.98	1.76	23	20	14.1	5.5	6	21	4.25e – 08
S3	08/1997	4.76	2.26	14	12	7.0	3.1	7	14	3.679e – 08
S4	08/1997	1.10	0.46	28	30	9.9	18.9	20	70	4.750e – 08
S4	11/1999	1.25	0.51	29	31	11.2	–	–	–	–
S5	08/1997	0.70	0.24	31	35	–	–	–	–	–
S5	11/1999	0.97	0.17	31	39	9.3	17.1	18	53	5.44e – 08
S6	08/1997	3.12	1.36	21	21	13.1	10.1	11	46	3.820e – 08
S6	11/1999	3.85	1.58	20	21	12.9	12.3	12	49	4.16e – 08
S7	08/1997	0.36	0.09	35	42	0.9	1.3	17	4	4.392e – 08
S7	11/1999	0.60	0.35	31	34	1.3	1.3	12	4	4.92e – 08
S8	08/1997	5.60	2.49	10	10	–	–	–	–	–
S8	11/1999	6.11	2.71	10	10	10.3	8.9	12	42	4.26e – 08
S9	08/1997	2.12	0.86	24	25	–	–	–	–	–
S9	11/1999	2.16	1.25	26	23	2.8	1.6	8	5	4.06e – 08
S10	08/1997	5.62	2.61	10	9	6.0	–0.1	1	–1	9.020e – 08
S10	11/1999	3.75	1.25	20	23	6.7	–	–	–	–
S11	08/1997	0.71	0.37	31	32	6.1	9.3	18	14	1.147e – 07
S11	11/1999	2.28	0.70	25	29	6.6	11.9	18	40	4.87e – 08
S13	08/1997	0.28	0.11	36	40	1.3	5.6	30	20	4.641e – 08
S13	11/1999	0.39	0.20	36	38	0.7	4.9	36	16	4.91e – 08



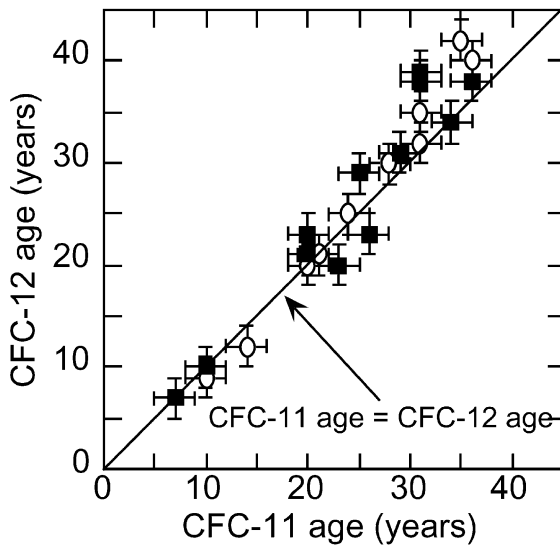


Fig. 2. CFC-11 and CFC-12 ages for 1997 (open circles) and 1999 (solid squares). Line represents CFC-11 age equal to CFC-12 age.

tracer methods. Tritium/<sup>3</sup>He ages are consistently 10–15 years younger than the CFC ages.

Older spring waters (> 20 years) are consistently found at lower elevations (Fig. 1). The higher elevation springs have shorter residence times in the groundwater system and shorter flow paths. There-

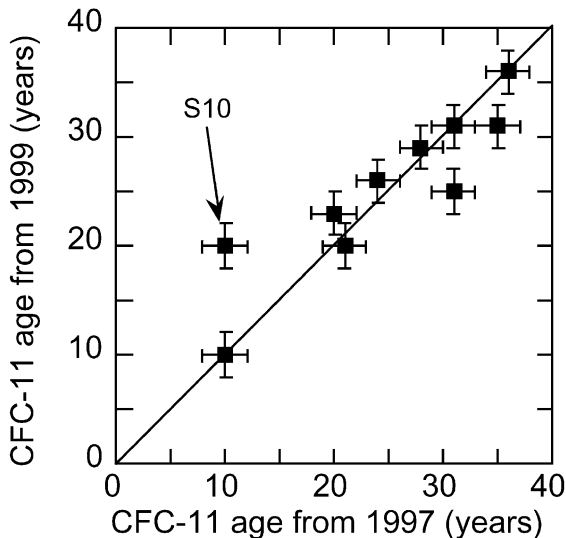


Fig. 3. CFC-11 age in 1997 and 1999 for the Sagehen springs. Line represents 1997 age equal to 1999 age.

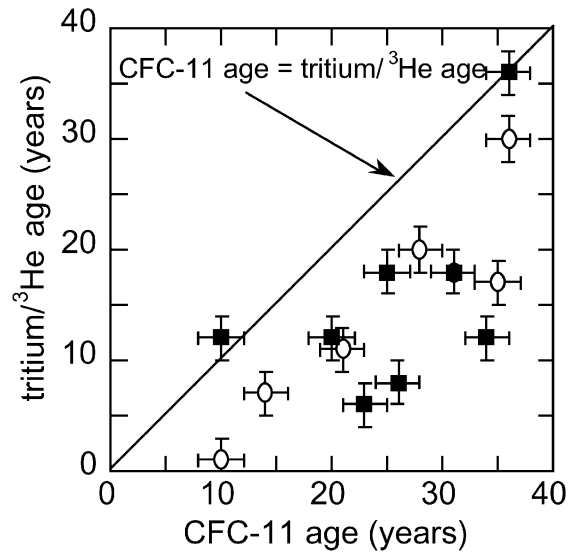


Fig. 4. CFC-11 and tritium/<sup>3</sup>He ages from 1997 (open circles) and 1999 (solid squares) for the Sagehen springs. Line represents CFC-11 age equal to tritium/<sup>3</sup>He.

fore, these spring waters will have less time to interact with the surrounding rocks. One exception to this trend is S13, which has a CFC age of 36 years and is found above younger spring water.

Charge balance errors calculated for the sampled springs are all less than 12% with only two exceptions (S6 and S8). Because these waters are extremely dilute, the measurements of some cations approached the detection limit. The two springs which exceed the 12% charge balance error have excess positive charge. Possible explanations for this excess positive charge include degassing of the DIC sample or a poor pH reading. It is likely that degassing of CO<sub>2</sub> has occurred in these two samples with low pH.

The age of spring waters correlates well with a number of water quality measurements including conductivity, pH, and concentrations of Ca<sup>2+</sup> and Na<sup>+</sup> (Fig. 5), and poorly for other constituents such as DIC and Cl<sup>-</sup> concentrations. After accounting for the likely loss of CO<sub>2</sub> from the two samples with low pH, no systematic relationship exists between DIC and spring water age. This lack of a systematic relationship between DIC and spring water age, combined with the large increase in pH with age, implies that the carbonate speciation is changing. As the

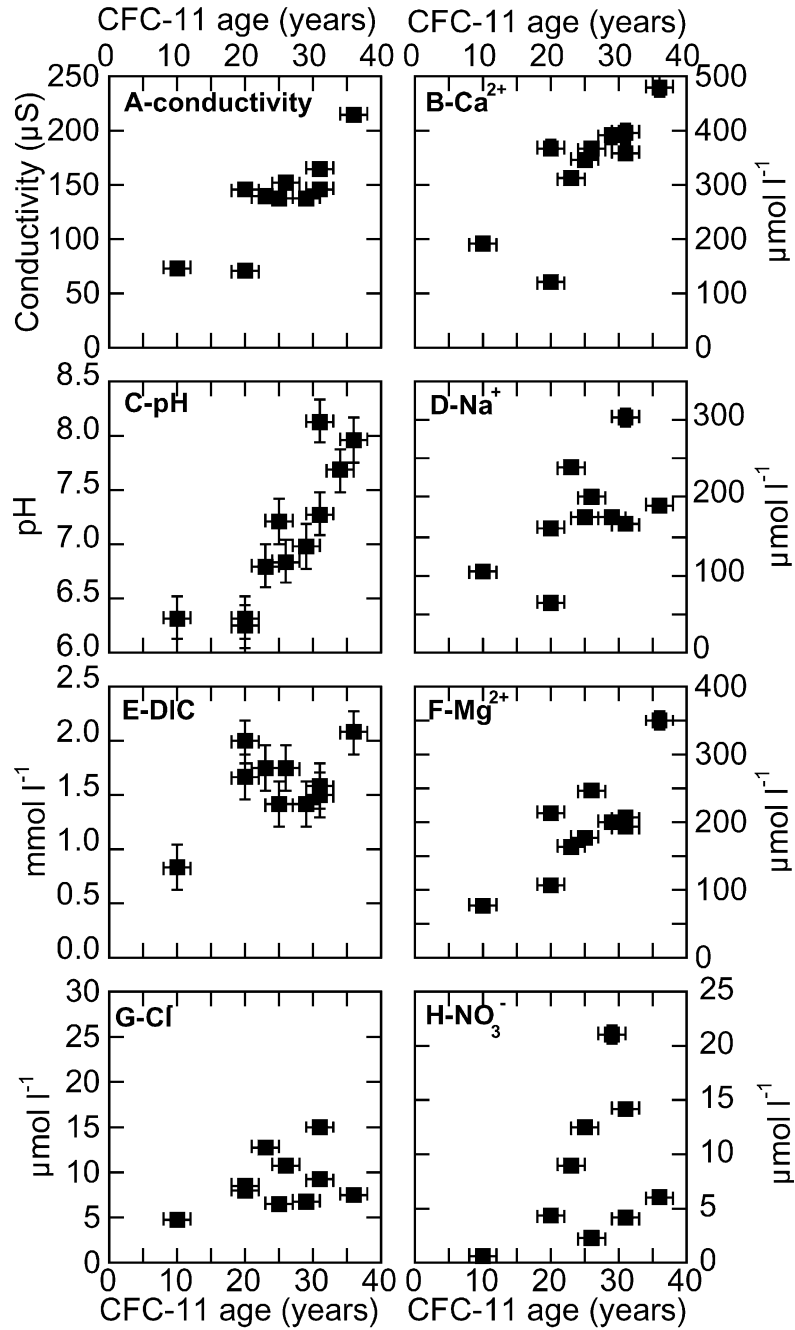


Fig. 5. CFC-11 age and (A) conductivity, (B) Ca<sup>2+</sup> concentration, (C) pH, (D) Na<sup>+</sup> concentration, (E) DIC concentration, (F) Mg<sup>2+</sup> concentration, (G) Cl<sup>-</sup> concentration, (H) NO<sub>3</sub><sup>-</sup> concentration. In all cases, only 1999 data were shown for simplicity.

water ages,  $(\text{CO}_2)_{\text{aq}}$  is lost and  $\text{HCO}_3^-$  is gained. Spring waters with longer residence times have higher conductivity, greater concentrations of  $\text{Ca}^{2+}$  and  $\text{Na}^+$ , and higher pH. This suggests that the age of the spring water (i.e. the mineral interaction times) and weathering reactions at least partially control the chemical composition of the water. The release of cations, specifically  $\text{Ca}^{2+}$  and  $\text{Na}^+$ , is consistent with what is expected for the dissolution of plagioclase, one of the primary minerals found in Sagehen basin, as  $\text{Ca}^{2+}$  and  $\text{Na}^+$  are released in a reasonably consistent ratio.

Nitrate concentration in the Sagehen springs shows a nonlinear relationship to spring water age (Fig. 5). Very young spring waters contain little or no nitrate while older spring waters have significantly higher nitrate levels. The peak in nitrate concentration, 21  $\mu\text{mol/l}$ , is found in approximately 30-year-old water. Denitrification does not appear to be the cause of the low nitrate concentration in the young springs because they have the highest dissolved oxygen concentrations and because good agreement was found between the CFC-11 and CFC-12 ages. Earlier studies in Sierra Nevada streams and lakes show that nitrate concentrations rarely exceed 10  $\mu\text{mol/l}$  (Sickman and Melack, 1998). Nitrate concentrations in stream water greater than 10  $\mu\text{mol/l}$  are found only following major fires (e.g. Chorover et al., 1994; Johnson and Susfalk, 1997; Riggan et al., 1994; Williams and Melack, 1997b). Extensive fires in Sagehen basin and the surrounding area are documented in 1960 and 1969 and may explain the high concentrations observed in the spring waters.

### 5.2. Chemical weathering rates

NETPATH was used to solve the weathering-water chemistry mass balance equations. The simulations produced multiple solutions for each spring. From these possible solutions, many models such as those which had primary minerals, such as biotite, precipitating or secondary minerals weathering were immediately eliminated. The remaining models are thought to be reasonable under the specified geologic conditions. Although the solutions differed, a number of patterns emerge from the results. All reasonable solutions for each spring consistently calculated the same amount of plagioclase, hornblende, and

biotite weathering. Errors associated with using NETPATH to calculate chemical weathering rates result from variability in the mineralogy of the area, as well as errors in the measurement of ion chemistry.

Chemical weathering rates calculated from CFC ages and solutions to the mass balance equations produced by NETPATH for two common minerals found in Sagehen basin, plagioclase and hornblende, were approximately 0.0116–0.0018 and 0.0036–0.0006  $\text{mmol l}^{-1} \text{ year}^{-1}$ , respectively (Fig. 6). In addition, small amounts of calcite were found to be dissolving in the Sagehen springs, however, the carbon resulting from the dissolution of calcite accounts for less than 15% of the total DIC. Because precipitation chemistry is used as the initial condition of the

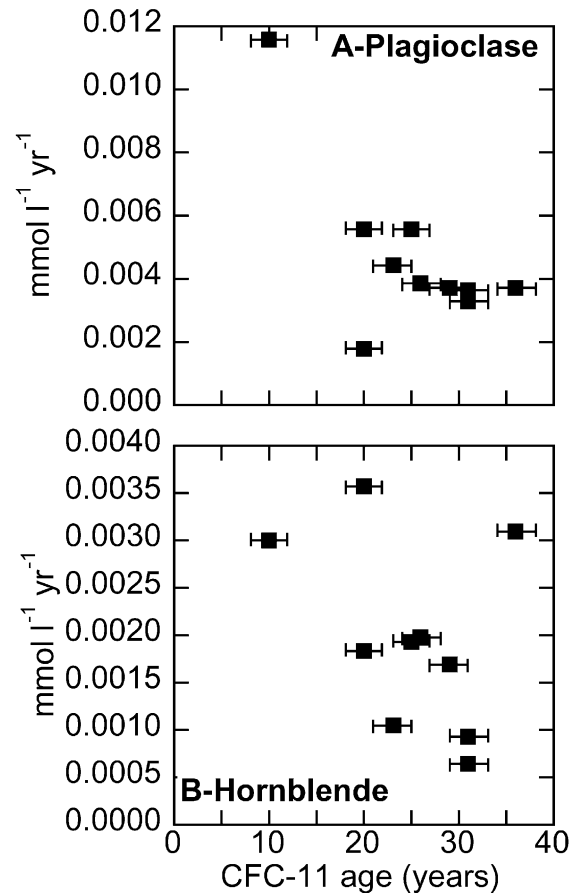


Fig. 6. CFC-11 age and chemical weathering rates for (A) plagioclase and (B) hornblende in 1999.

water, these weathering rates reflect mineral reactions occurring in the soil and groundwater zones. The combination of these two zones controls the chemical evolution of the spring waters by providing both a source of acid and fresh mineral surfaces. There is no clear correlation of weathering rate with tracer age.

## 6. Discussion

A common explanation for the discrepancy between tracer ages based on two methods is mixing of flowpaths. However, since CFCs and tritium/<sup>3</sup>He are independent tracers and have significantly different input functions, a collection of analyses can be performed with the data to determine the degree of mixing in the system. CFC and tritium/<sup>3</sup>He ages do not mix linearly. Tritium/<sup>3</sup>He ages of a water mixture are always biased towards the water mass with the higher tritium content (Schlosser, 1992). Therefore, a mixture of waters which are all younger than 40 years will lead to an older apparent tritium/<sup>3</sup>He age. Mixing of CFC ages produces a different effect. CFC concentrations in the atmosphere have increased nearly exponentially with time, therefore mixing of groundwaters of different ages, which are younger than 40 years, will lead to younger apparent CFC ages. The Sagehen springs consistently have tritium/<sup>3</sup>He ages that are younger than the CFC ages. This is contrary to what is expected for mixtures of less than 40-year-old waters.

If the springs were mixing water that is less than 40 years old with water much older, the observed difference between CFC and tritium/<sup>3</sup>He ages could be explained. In this case, tritium/<sup>3</sup>He ages would shift towards the water with the higher tritium content (the water with a less than 40-year age) and younger ages, which in some cases would be younger than the mixed CFC age. The excess <sup>4</sup>He data can be used to test this mixing scenario because more deeply circulated groundwaters with residence times greater than 50 years should contain detectable excess <sup>4</sup>He (e.g., Solomon et al., 1996). After correcting for excess air using neon and argon in 1997 and only argon in 1999, little to no excess <sup>4</sup>He was detected in the Sagehen spring waters, suggesting that a deeply circulating groundwater component is at most a very

small fraction of these spring waters (Fig. 7). S7 is the only spring appearing to have some <sup>4</sup>He excess.

Time series measurements of tracer ages can also be used to assess the degree of mixing and stability in a groundwater system. If spring waters were fed by a number of flow paths which vary in lengths and travel times, tracer ages would not be consistent from one sampling time to another, unless the fraction from each flow path remained constant with time. Spring waters in Sagehen basin sampled in 1997 and 1999 show reasonable agreement in CFC measurements (Fig. 3), as well as tritium/<sup>3</sup>He measurements (Fig. 4) following water years with varying amounts of precipitation. This suggests that there is little variation in the flow paths feeding the springs.

Correlation of conductivity, Ca<sup>2+</sup>, and Na<sup>+</sup> with spring water age provides another basis for assessing the degree of mixing in the system. Springs within the basin with similar conductivities also have similar spring water ages, yet their geographic locations within the basin can vary significantly (Fig. 1). If mixing of deep and shallow groundwater was occurring in this system, this geographic correlation would

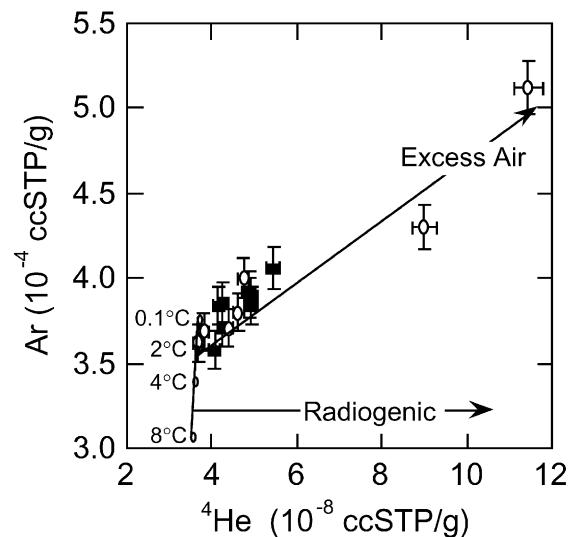


Fig. 7. Sagehen springs <sup>4</sup>He and Ar concentrations in 1997 (open circles) and 1999 (solid squares). Atmospheric equilibrium values are given for 0.1°C, 2°C, 4°C, and 8°C calculated at 2300 m. Line marked Radiogenic represents the trend data should follow if there is a large radiogenic <sup>4</sup>He influence on spring waters. Line marked Excess air represents the trend data would follow if excess air was the reason for variability in <sup>4</sup>He and Ar data.

be unlikely because it would require that springs of similar age and conductivity would be mixing old and young groundwater in similar proportions. This explanation is highly unlikely given the size of the basin and geographic distance separating the springs.

Finally, the sum of tritium and  $^3\text{He}_{\text{tritiogenic}}$ , which is equal to the initial tritium concentration of the recharged water, can be tested against the record of tritium concentration in local precipitation. If a spring contained a significant component of groundwater recharged prior to the nuclear bomb tests, the amount of tritium plus  $^3\text{He}_{\text{tritiogenic}}$  would be too low to reproduce the tritium input function. With only two exceptions (S7 and S13), the Sagehen springs reproduce the tritium input function relatively well (Fig. 8).

The sum of this evidence suggests that the Sagehen springs are lacking a significant deeply circulated groundwater component mixing with the shallow groundwater. The evidence provided by the tracer data, however, does not conclusively rule out mixing of groundwater of similar ages within a spring discharge zone as well as mixing caused by dispersion within the groundwater system. The possibility of mixing of groundwater of similar ages ( $\pm 2\text{--}3$  years) does not significantly alter the inter-

pretation of the chemical data and evolution of the spring waters. The low tritium +  $^3\text{He}_{\text{tritiogenic}}$  in S7 and S13 suggests that these two springs may be candidates for having a deeply circulated component mixing with the shallow groundwater. Additionally, these two springs have the highest conductivities in the basin, also suggesting a component with long mineral interactions times.

Working under the assumption that mixing between very young and very old groundwaters is minimal in most of the Sagehen springs, there are two possible explanations for the observed offset between the CFC and tritium/ $^3\text{He}$  ages. The first is a thick unsaturated zone. A basic assumption of the CFC method is that the concentration of CFCs in soil air at the water table is approximately equal to the concentration of CFCs in the atmosphere at the time of recharge. In the case of a thick unsaturated zone, CFC ages are overestimated because the CFC concentration in soil air at the water table lags the CFC concentration of the atmosphere (Cook and Solomon, 1995; Cook et al., 1998; Plummer et al., 2000). This apparent lag depends on gas solubility, the gas diffusion coefficient, the thickness of the unsaturated zone, and soil water content (Cook and Solomon, 1995). For water tables less than 10 m deep, the difference between the soil air at the water table and the atmosphere is small, and the CFC age of the groundwater is very close to the true age. If the depth of the water table is increased to 30 m, however, this difference is significant and the CFC age of the groundwater is between 8 and 15 years older than the true age (Cook and Solomon, 1995).

The second possible explanation occurs in areas with low recharge rates, where  $^3\text{He}_{\text{tritiogenic}}$  is poorly confined at the water table and is able to escape into the soil atmosphere.  $^3\text{He}_{\text{tritiogenic}}$  confinement increases with increasing recharge rates and decreasing dispersion coefficient (Schlosser et al., 1989). If  $^3\text{He}_{\text{tritiogenic}}$  escapes, the tritium/ $^3\text{He}$  age will be younger than the true age. He confinement is nearly 100% where recharge rates exceed 0.25 (low dispersion) to 0.5 (high dispersion) m/year (Schlosser et al., 1989).

The present data set cannot distinguish between these two hypotheses. However, the peak of nitrate concentration was found in approximately 30-year-old water (which would represent a recharge year of

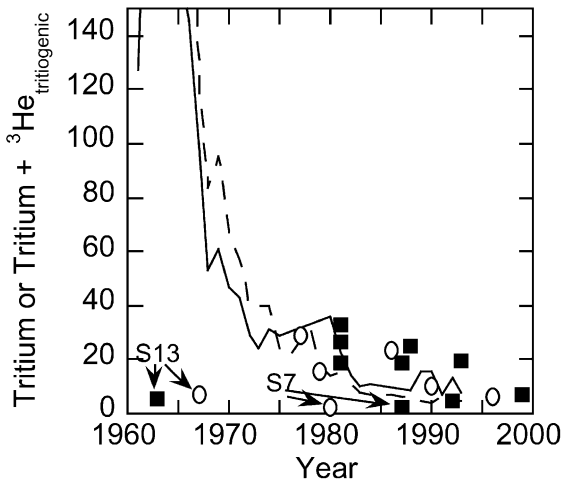


Fig. 8. Observed tritium in precipitation for Portland, OR (dashed line) and Menlo Park, CA (solid line) and Sagehen spring water concentrations of tritium +  $^3\text{He}_{\text{tritiogenic}}$  from 1997 (open circles) and 1999 (solid squares) plotted versus either year of precipitation (for input function values) or estimated recharge year of spring water (based on tritium/ $^3\text{He}$  ages).

1969) with known fires in the basin and this may provide evidence to support the CFC ages, assuming the recharging nitrate pulse was preserved in the groundwater system after departure from the water table. Furthermore, 100%  $^3\text{He}_{\text{tritogenic}}$  confinement would require that on average more than 30% of precipitation must recharge the aquifer. Based on the hydrograph base flow recession method for estimating recharge, it is unlikely that sufficient recharge is occurring in Sagehen basin during most years for 100%  $^3\text{He}$  confinement. In addition, the low values of tritium +  $^3\text{He}_{\text{tritogenic}}$  for S13 and S7 and their inability to reproduce the input function (Fig. 8) suggest that these two springs are good candidates for  $^3\text{He}_{\text{tritogenic}}$  loss.

The positive correlation between tracer age and conductivity, as well as major cations derived from mineral weathering reactions ( $R^2$  of approximately 0.7 based on linear fit, with the exception of Na), suggests that groundwaters in Sagehen basin are chemically evolving through time. The relationship between spring water age and chloride concentration (Fig. 5) suggests that these changes are not a result of changes in evapotranspiration in the basin. Spring waters of older ages have longer residence times in the host material and a greater opportunity to weather primary minerals and release solutes to the water. The spring waters are recording a complex history of water–rock interactions, initially in the soil, and then progressing in the groundwater.

Although using NETPATH to solve the mass balance equations does not provide unique solutions to possible weathering scenarios, the program can be used to examine possible reaction paths and establish important trends. The possible solutions help provide an understanding of the complexity of groundwater and weathering systems. In addition, patterns established with these solutions, such as formation of varying amounts of secondary minerals, provide more focused questions for future direction of these studies. Uncertainty as to which secondary minerals are forming in Sagehen, however, limits the interpretation of some of these patterns.

The combination of spring water chemical data, mass balance calculations, and geochemical age data provides a unique opportunity to study how shallow groundwaters evolve chemically through time. This method is an excellent means for determining the

chemical evolution of groundwater in a small, high-elevation catchment, and may provide a basis for quantifying the contribution of groundwater to the hydrochemistry of streams.

## 7. Conclusions

The chemical composition of spring water varies significantly throughout Sagehen basin and correlates well with spring water ages. This suggests that water discharging in the Sagehen springs is recording a complex history of rock weathering and changes in the recharge conditions. By sampling springs, the groundwater component was separated from the other flow components contributing to the chemical composition of a stream. This isolation provides a means of directly studying the chemical evolution of shallow groundwaters and the influence of chemical weathering rates and potential land use changes on their chemical composition and contribution to catchment hydrochemistry.

Springs provide access to water discharging from a discrete range of flow paths in Sagehen basin. Because there is a range of residence times for the Sagehen spring waters, the effects of varying amounts of chemical weathering can be evaluated. Much of the chemical composition of the groundwater is already present by the time these waters have been within the system for 10 years. This trend in chemical composition is evidence for initial weathering activity in the soil, which contributes a finite amount of acid at the water table. Once these shallow groundwaters move away from the water table, there is no systematic change in the weathering rates. The groundwater zone appears to be largely closed to the soil zone, and it is likely that acid can no longer be replenished. Our method of calculating chemical weathering rates using mass balance calculations and geochemical tracer ages in spring waters successfully explains differences in spring water chemistry.

## Acknowledgements

We thank B.G. Katz, C.M. Wicks, and J.I. Drever for their conscientious handling and editing of this paper and special volume; J.R. Boles, O.A. Chad-

wick, J.M. Melack, A. F. White, and two anonymous reviewers for critical reviews; Brett Wanner and David Zell for producing a geologic map of Sagehen basin; Frank Setaro and Robert Petty for anion and cation measurements, respectively; Dave Pierce for assistance with the microprobe; Jeff Gamlin for assistance in the field and laboratory; Jason Stormo and Laurent Meillier for assistance in the field; the managers of the Sagehen Field Station (Warren Schifini and Joanne Marie Pomeroy Schifini). This work was performed under the auspices of the US Department of Energy by University of California Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48. Funding was provided by the University Collaborative Research Program at Lawrence Livermore National Laboratory.

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