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# Old groundwater influence on stream hydrochemistry and catchment response times in a small Sierra Nevada catchment: Sagehen Creek, California

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[1] The relationship between the chemical and isotopic composition of groundwater and residence times was used to understand the temporal variability in stream hydrochemistry in Sagehen basin, California. On the basis of the relationship between groundwater age and  $[Ca^{2+}]$ , the mean residence time of groundwater feeding Sagehen Creek during base flow is approximately 28 years.  $[Cl^-]:[Ca^{2+}]$  ratios in Sagehen Creek can be used to distinguish between two important processes: changes in the apparent age of groundwater discharging into the creek and dilution with snowmelt. The mean residence time of groundwater discharging into the creek is approximately 15 years during snowmelt periods. The results from this study have implications for hydrograph separation studies as groundwater is not a single, well-mixed chemical component but rather is a variable parameter that predictably depends on groundwater residence time. Most current models of catchment hydrochemistry do not account for chemical and isotopic variability found within the groundwater reservoir. In addition, this study provides valuable insight into the long-term hydrochemical response of a catchment to perturbations as catchment-flushing times are related to the mean residence time of water in a basin.

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## 1. Introduction

[2] Residence time (or travel time) of water in a catchment plays a fundamental role in the intensity and flushing times of soluble contaminants [Kirchner *et al.*, 2000, 2001]. There is a direct relationship between the residence time of water in a catchment and the timescale of a catchment's long-term geochemical response and recovery to inputs and perturbations. Therefore an understanding of water residence times is essential when developing effective predictive models of the transport and fate of contaminants, as well as their downstream consequences [Kirchner *et al.*, 2001]. Quantifying catchment hydrochemical response times is difficult because water follows numerous pathways between initial precipitation and the stream channel, all with unique residence times. Groundwater flow, shallow subsurface (soil flow), overland flow, and direct precipitation into stream channels all contribute to stream flow, but these pathways potentially have residence times that range from hours to hundreds of years. The chemical composition of water flowing through each pathway depends upon the

geologic, hydrologic, vegetative, and climatic conditions and can vary seasonally and/or annually [Church, 1997]. Water entering a stream from each contributing flow path is chemically and isotopically unique due to varying water-mineral interactions and residence times within the catchment. Therefore the mixture of chemically distinct waters discharging from contributing flow paths controls the chemical composition of streams. The relative amounts of water from each of these flow paths and the residence time of water in these pathways controls catchment recovery rates from perturbations, such as contaminant inputs or changes in precipitation, climate, or biologic activity.

[3] Flow paths play an essential role in assessing susceptibility [Bottomley *et al.*, 1986; Peters and Driscoll, 1987] and hydrochemical response times determines contaminant transport rates. However, the mechanisms controlling the mobilization of water in a catchment and the variable geochemistry of this response are still poorly quantified [Kirchner, 2003]. Initial attempts to determine short-term catchment response times were based on net solute fluxes out of a catchment. Streams integrate water over an entire catchment. Therefore by examining only the stream chemistry one loses much of the information regarding processes and timescales in a catchment. Recently, short-term catchment response times to events (such as precipitation or snowmelt) were estimated using various techniques, including geochemical hydrograph separations [e.g., Sklash and Farvolden, 1979; Hinton *et al.*, 1994] and spectral analysis [Kirchner *et al.*, 2000]. Hydrograph separation studies use mixing models to determine the influence of end-member components (i.e., event water and pre-event water) that are

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defined by chemical and stable isotope compositions ( $\delta^{18}\text{O}$ ,  $\text{Na}^+$ ,  $\text{Si}$ ). The relative contributions of these event and preevent waters depend on the physical setting, climate, antecedent weather (soil moisture), and human influences [Generaux and Hooper, 1998]. In cases where two component models are insufficient to explain the complex variability in stream water chemical composition, three end-member mixing models are employed [e.g., Dewalle et al., 1988; Christophersen et al., 1990; Hinton et al., 1994; Burns et al., 2001]. Three end-member models divide preevent water into two components (i.e., soil and groundwater) based on stable isotope signatures ( $\delta^{18}\text{O}$ ) and chemical composition (often dissolved silica).

[4] Hydrograph separations require that the chemistry of end-member components is defined for each contributing flow pathway. These hydrograph separation studies often assume the chemical and isotopic composition of components is constant and that reservoirs are well mixed. While this assumption may be valid for deep groundwater, it is seldom correct for shallow subsurface flow [Rademacher et al., 2001; Scanlon et al., 2001]. Campbell et al. [1995] suggest that the chemical composition of preevent waters in catchments dominated by snowmelt processes with small groundwater reservoirs varies in response to snowmelt pulses. In addition, Rose [1996] proposes that variability in chemistry and isotope composition of a creek in the Georgia piedmont during base flow suggests that dynamic mixtures, rather than homogeneous reservoirs, are discharging into the creek. Spatial and temporal variability in chemical and isotope compositions in various flow paths, particularly in groundwater flow paths, was recently observed in a study of groundwater springs in the Sierra Nevada of California [Rademacher et al., 2001, 2002], as well as in the Georgia Piedmont [Burns et al., 2003].

[5] The chemical and isotope variability of component flow paths in a catchment often complicates hydrograph separations and inhibits the interpretation of relationships with the long-term hydrochemical sensitivity of a catchment. In particular, the groundwater component often comprises a spectrum of ages [Michel, 1992; McDonnell et al., 1999; Kirchner et al., 2000; Rademacher et al., 2001; Burns et al., 2003]. For this reason, valuable information regarding water residence times and the subsequent response time to perturbations in a catchment is lost when uniform chemical and isotope compositions are assumed for groundwater and other active flow paths.

[6] Recent studies attempted to determine the residence time of waters within a catchment using various tracer techniques, including  $\delta^{18}\text{O}$  and tritium [Michel, 1992; Dewalle et al., 1997; Herrmann et al., 1999; McDonnell et al., 1999]. However, these studies assume that each of the reservoirs supplying water to the stream is well mixed. Studies of groundwater springs in the Sierra Nevada show that the chemical and isotopic composition of groundwater is strongly correlated to its residence time [Rademacher et al., 2001, 2002]. These results indicate that assuming that the groundwater component in a catchment is a single, well-mixed end-member may lead to errors in end-member contribution estimates.

[7] Most current geochemical techniques focus on understanding event-scale processes. However, these methods are often inadequate for determining changes in annual cycles,

estimating long-term mean conditions, and quantifying the long-term hydrochemical response of catchments. The chemical composition of stream waters changes through time in response to factors that include changes in climate patterns, water sources, and residence time within a catchment. Developing accurate predictive models of how a catchment responds to changes in these variables requires a clear definition of the complex spatial and temporal variability inherent in the contributing components to stream water chemistry.

[8] This contribution examines the age of groundwater contributing to stream discharge, the linkage between chemical and isotopic variability of groundwater and the long-term mean conditions of the catchment, and the potential hydrochemical response times of Sagehen basin in California.

## 2. Study Area

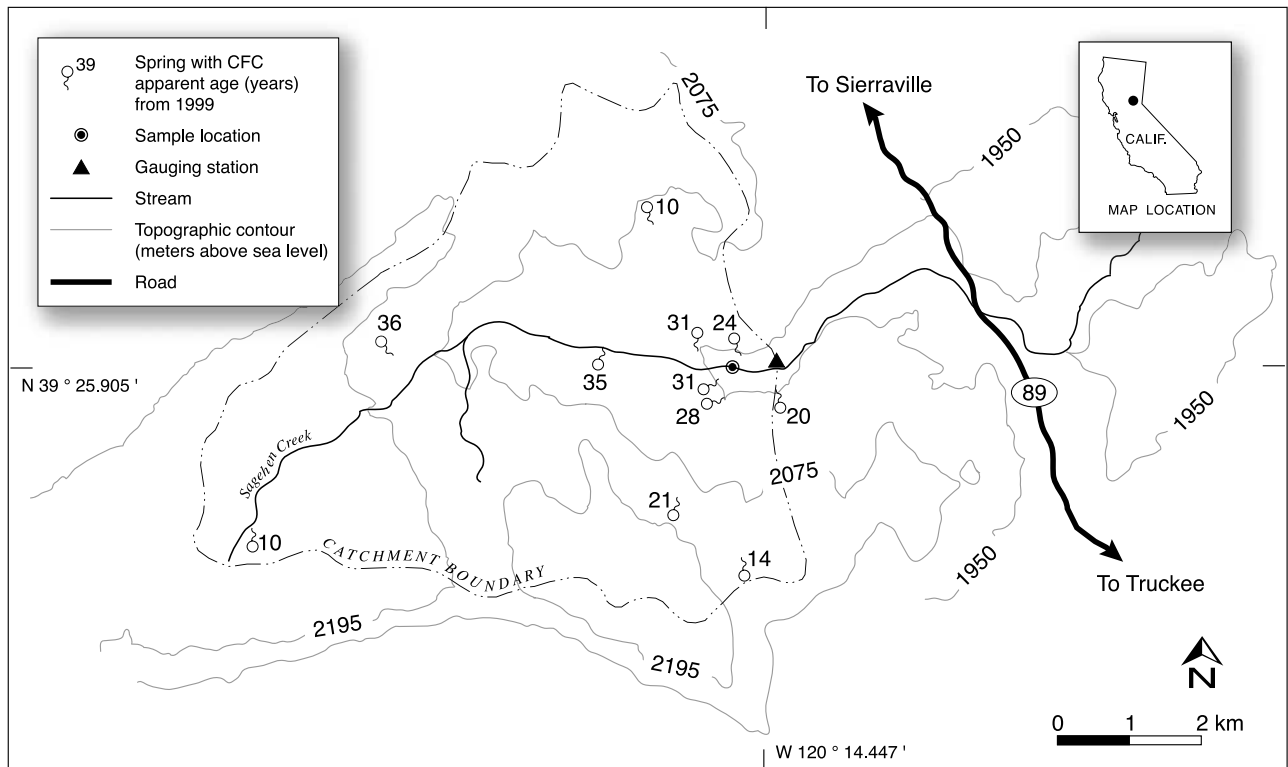
[9] Sagehen basin lies on the eastern, or lee side of the northern Sierra Nevada of California, near the crest of the Sierran divide. The Sagehen Creek drainage basin is approximately 27 km<sup>2</sup> and elevation ranges from approximately 1900 to 2600 m above sea level (Figure 1). Bedrock in Sagehen basin is largely granodiorite, which is overlain by andesitic volcanics (B. Wanner and D. Zell, unpublished data, 2000). Outcrops of bedrock are sparse and occur primarily at higher elevations throughout the basin. Alluvium and glacial till of variable thickness consists of granodioritic and andesitic clastic material overlies the bedrock at lower elevations, especially near the stream channel.

[10] Temperature and precipitation are highly variable in Sagehen basin and correlate with elevation. Mean annual temperature from 1979 to 1996 was approximately 5.9°C at 1950 m (data from the National Climatic Data Center (NCDC)). Mean annual precipitation from 1954 to 1996 was 89 cm per year (NCDC). Approximately 80% of precipitation in Sagehen basin is deposited during the winter months (November–April) primarily as snow [Andrews and Erman, 1986]. Water is typically stored in the snowpack until it is released during the spring melt season. Summers are commonly dry with only occasional precipitation.

[11] Fourteen perennial groundwater springs are known in Sagehen basin. Most of these springs continue to flow even after extended periods of drought [Erman and Erman, 1995]. A United States Geological Survey (USGS) gauging station in the basin near the Sagehen Creek Field Station at 1926 m provides a nearly continuous record of stream flow for Sagehen Creek from October 1953. A meteorological station in Sagehen basin was operational for only a portion of the study period.

## 3. Prior Results From Sagehen Basin

[12] Approximately 11 groundwater springs in Sagehen basin were sampled during August 1997, November 1999, June 2000, September 2001, and July 2003. Samples were examined for O, H, and He isotope, tritium, chlorofluorocarbon (CFC-11 and CFC-12), and general chemical analyses. The results of the 1997 and 1999 surveys [Rademacher et al., 2001, 2002] are summarized here and integrated with new data collected during 2000, 2001, and 2003.



**Figure 1.** Location of Sagehen basin and 11 groundwater springs. Chlorofluorocarbon (CFC) apparent ages are based on CFC-11 data from 1999 [Rademacher et al., 2001]. The U.S. Geological Survey (USGS) gauging station, Sagehen Creek sampling station, and the catchment boundary are also shown for reference.

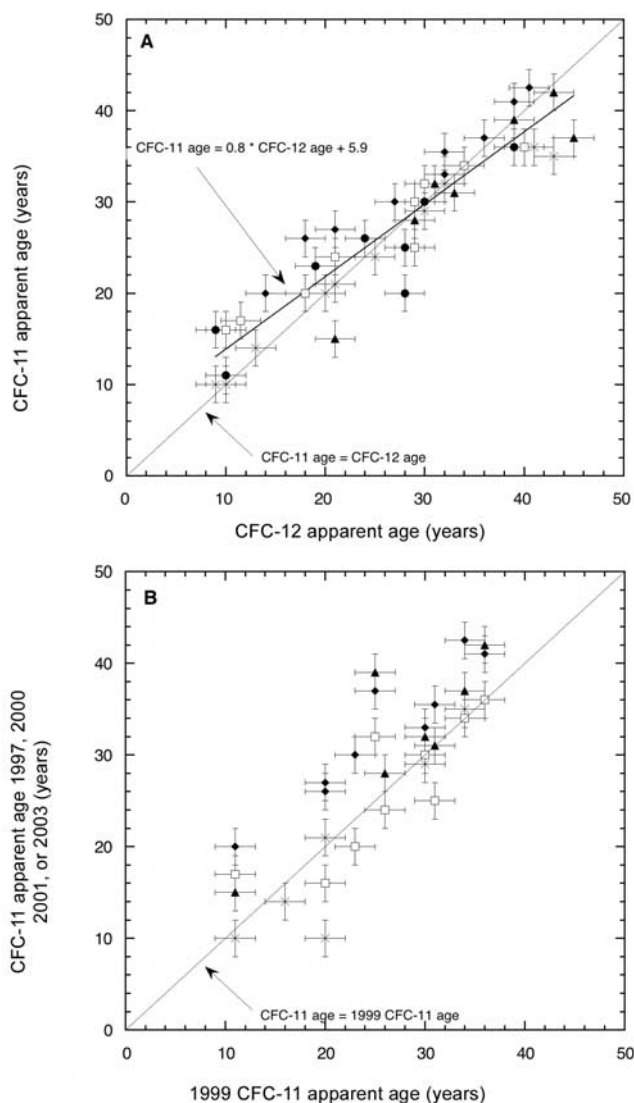
Water for all analyses was collected only from springs with discharge rates high enough to provide mud-free samples. The flow rate at low discharge springs is generally insufficient to completely flush the sampling line. As a result, mud is drawn into the sampling line and sample collection tube. Samples containing sediment are problematic during CFC analysis, as they potentially clog the extraction line and destroy the sample. Analyses of spring water chemical composition and chlorofluorocarbon (CFC) concentrations were performed at the University of California – Santa Barbara (UCSB) and measurements of O, H, He isotope compositions and tritium were made at Lawrence Livermore National Laboratory (LLNL).

[13] The primary focus of Rademacher et al. [2001, 2002] is to relate groundwater chemistry and isotope composition to residence times. Measurements of CFC and tritium/<sup>3</sup>He concentrations in groundwater provides a means for determining the residence time or “apparent age” of the groundwater [e.g., Ekwurzel et al., 1994; Plummer and Busenberg, 2000; Solomon and Cook, 2000]. CFC and tritium/<sup>3</sup>He tracer systems are based on different principles (CFC apparent ages depend on a Henry’s Law solubility relationship with atmospheric gases and tritium/<sup>3</sup>He apparent ages depend on a radioactive decay relationship). These age dating techniques are used in tandem as a check to further resolve residence times [e.g., Ekwurzel et al., 1994; Szabo et al., 1996], as well as provide valuable insight into recharge processes.

[14] Apparent ages (residence times) of spring waters discharging in Sagehen basin were calculated based on

CFC-11 (CCl<sub>3</sub>F) and CFC-12 (CCl<sub>2</sub>F<sub>2</sub>) concentrations and range from approximately 10 to 45 years (1997 and 1999 data from Rademacher et al. [2001]). These data suggest that older spring waters typically discharge at lower elevations near the creek bed (Figure 1). CFC-11 and CFC-12 apparent ages correlate well (Figure 2a), suggesting CFCs are not altered by processes such as microbial degradation in Sagehen basin [Oster et al., 1996]. The relationship between CFC-12 and CFC-11 apparent ages follows a trend slightly different than the 1:1 line (equation for linear best fit of all CFC data: CFC-11 = 0.8 \* CFC-12 + 6), which is likely the result of gas exchange in the spring pool prior to sampling [Rademacher et al., 2001]. In addition, CFC apparent ages from the Sagehen springs are consistent for individual springs from one sampling period to the next, even when collected under very different hydrologic conditions (e.g., spring snowmelt and summer drought) (Figure 2b).

[15] The residence times of Sagehen springs were also calculated in 1997 and 1999 based on tritium/<sup>3</sup>He concentrations [Rademacher et al., 2001]. Spring water apparent ages calculated based on the tritium/<sup>3</sup>He method range from approximately 1 to 40 years and correlate well with CFC apparent ages [Rademacher et al., 2001]. However, tritium/<sup>3</sup>He ages are consistently younger than CFC apparent ages, which is likely due to poor He confinement due to low recharge rates or gas exchange processes in the spring pool. These mechanisms would result in a loss of the accumulated daughter product (<sup>3</sup>He) and produce the effect of tritium/<sup>3</sup>He apparent ages appearing younger than CFC



**Figure 2.** (a) Relationship between CFC-11 and CFC-12 apparent ages in Sagehen spring groundwaters during August 1997 (crosses), November 1999 (circles), June 2000 (squares), September 2001 (triangles), and July 2003 (diamonds) sampling times. A linear curve fit through all of the data points follows the line  $\text{CFC-11} = 0.8 * \text{CFC-12} + 5.9$  ( $R^2 = 0.9$ ). The 1:1 line is shown for reference. (b) Relationship between 1999 apparent CFC-11 age and CFC-11 apparent ages during August 1997 (crosses), June 2000 (squares), September 2001 (triangles), and July 2003 (diamonds) in Sagehen spring groundwaters. The 1:1 line is shown for reference. Very few young ages were measured from the 2001 samples because the extremely dry conditions caused discharge rates in many of the springs with younger water to drop below the level at which samples can be collected. (All 1997 and 1999 data are from Rademacher *et al.* [2001].)

apparent ages. Tritium/ $^3\text{He}$  are more susceptible to the effects of poor confinement because the diffusion coefficient for He in water is much faster than for it is CFCs [Rademacher *et al.*, 2001]. Rademacher *et al.* [2001] conclude that there is little mixing of different flow paths

within the spring flow paths. CFC ages were used in discussions of groundwater residence times and hydrochemical evolution because they are less affected by poor confinement than tritium/ $^3\text{He}$  ages [Rademacher *et al.*, 2001].

[16] The good agreement between the spring water apparent ages from the five different sampling events spread over six years indicates that the Sagehen springs are fed by a very stable groundwater flow system. While the apparent ages remained relatively constant, the CFC concentration and recharge year varied during the six years. The CFC concentrations increased at rates predicted by the atmospheric record. One of the sampling events occurred at the end of snowmelt in June 2000. The other four sampling events took place during base flow conditions in the late summer and early fall (1997, 1999, 2001, 2003). The CFC apparent ages determined from the June 2000 sampling agree well with the other sampling events indicating that little recent snowmelt is discharged from the springs.

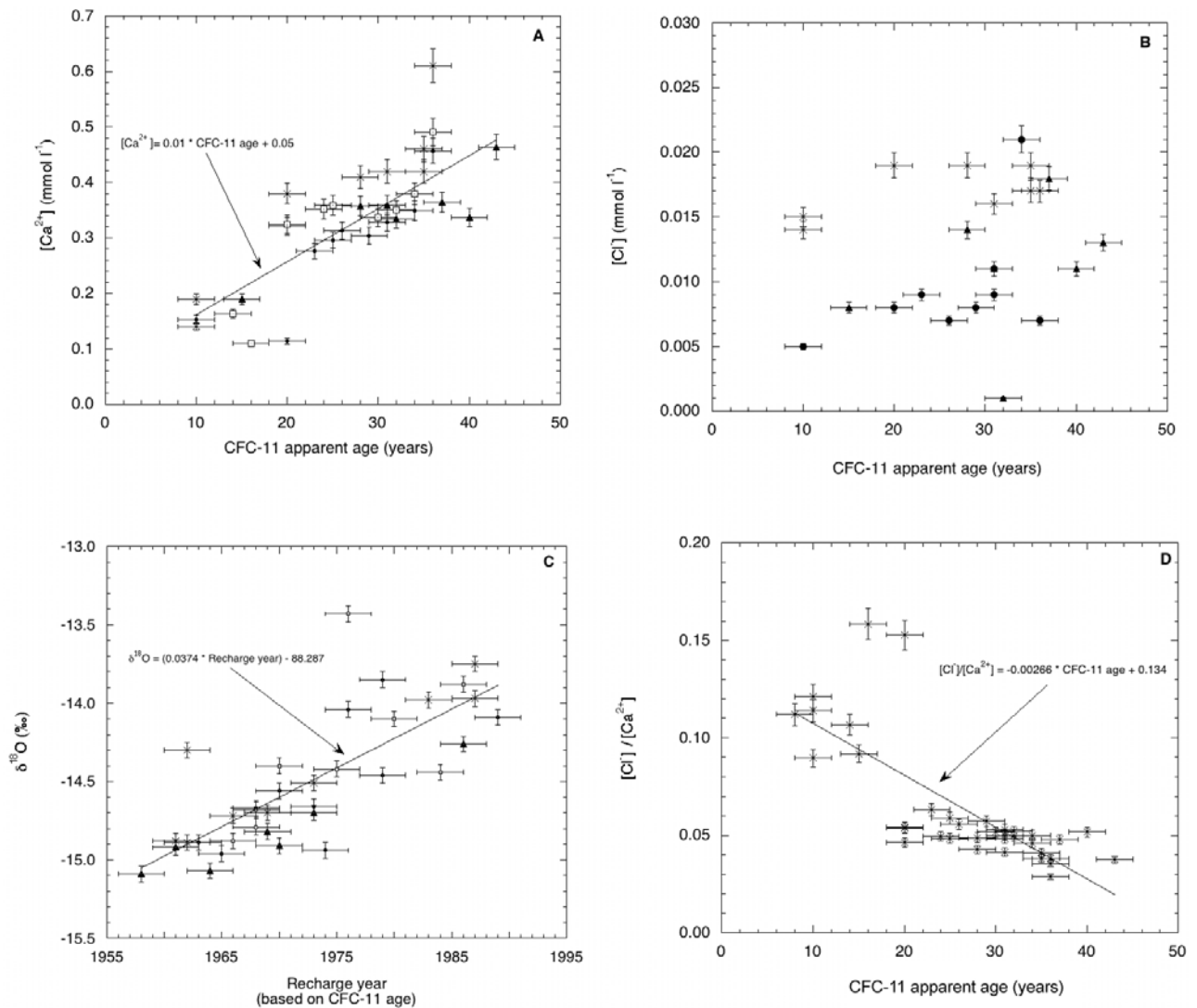
[17] Mineral weathering was identified as the primary process controlling the chemical composition of groundwater based on chemical analyses of Sagehen spring waters and mass balance calculations [Rademacher *et al.*, 2001]. The chemical compositions of the spring waters are positively correlated to groundwater residence times for solutes resulting from the weathering of minerals containing  $[\text{Ca}^{2+}]$ ,  $[\text{Mg}^{2+}]$ , and  $[\text{Na}^+]$ , such that older spring waters are more concentrated than younger spring waters (Figure 3a) [Rademacher *et al.*, 2001]. Similarly, the pH of the spring waters also increases with increasing residence time. Solutes, such as  $[\text{Cl}^-]$ , which do not have a mineral source in Sagehen basin and are likely introduced by precipitation only, show no clear correlation with residence time (Figure 3b).

[18] Stable isotope compositions ( $\delta^{18}\text{O}$ ) of the Sagehen spring waters were also found to correlate with spring water ages in Sagehen basin such that younger spring waters are isotopically heavier than older spring waters (Figure 3c) [Rademacher *et al.*, 2002]. The relationship between  $\delta^{18}\text{O}$  and spring water age is consistent for all sampling periods. Rademacher *et al.* [2002] suggest the relationship between  $\delta^{18}\text{O}$  and spring water residence time is the result of basin-wide changes in climatic parameters (e.g., temperature and atmospheric circulation patterns) but could also reflect changes in the snow hydrology (e.g., dynamics within the snowpack, such as changes in the timing and number of rain on snow events or melt events) and/or the temporal and spatial distribution of snow cover in the basin during the period of record.

[19] Data collected from groundwater springs in Sagehen basin clearly show a relationship between the chemical and stable isotope composition and the apparent age (or residence time) of spring waters (Figure 3). The chemical evolution of groundwater proceeds as a result of mineral weathering. The relationship between spring water age and chemical composition suggests that groundwater is not a single, well-mixed chemical component, but rather is a variable parameter that predictably depends on residence time.

#### 4. Methods

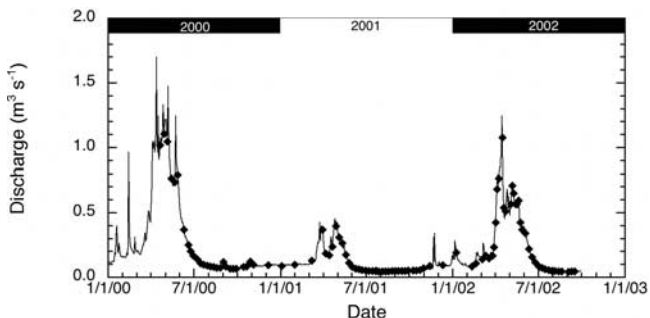
[20] Water samples were collected weekly during snowmelt and summer periods and monthly during the winter



**Figure 3.** (a) Relationship between CFC-11 apparent age and  $[\text{Ca}^{2+}]$  concentration (a solute derived from mineral weathering) for Sagehen spring waters in 1997 (crosses), 1999 (circles), 2000 (squares), and 2001 (triangles). A linear curve fit through all of the data points follows the line  $[\text{Ca}^{2+}] = 0.01 * \text{CFC-11} + 0.05$  ( $R^2 = 0.7$ ). (b) Relationship between CFC-11 apparent age and  $[\text{Cl}^-]$  (a solute not derived from mineral weathering) in Sagehen spring waters in 1997 (crosses), 1999 (circles), and 2001 (triangles) (data collected in 2000 omitted due to analytical uncertainties). A change in analytical methods resulted in an offset between  $[\text{Cl}^-]$  results from 1997 and 1999. No clear relationship exists between CFC-11 apparent age and  $[\text{Cl}^-]$  in Sagehen groundwaters. (c) Relationship between CFC-11 apparent age and  $\delta^{18}\text{O}$  for Sagehen spring waters in 1997 (crosses), 1999 (circles), 2000 (squares), and 2001 (triangles). A linear curve fit through all of the data points follows the line  $\delta^{18}\text{O} = 0.0374 * \text{CFC-11 recharge year} - 88.287$  ( $R^2 = 0.6$ ). (d) Relationship between CFC-11 apparent age and  $[\text{Cl}^-]:[\text{Ca}^{2+}]$  ratios in Sagehen spring waters in 1997, 1999, 2000, 2001. All years are represented with crosses. A linear curve fit through all of the data points follows the line  $[\text{Cl}^-]:[\text{Ca}^{2+}] = -0.00266 * \text{CFC-11 age} + 0.134$ . (All 1997 and 1999 data are from Rademacher et al. [2001].)

months (deep snowpacks limit access during these times) from Sagehen Creek (Figure 4). The creek sampling location is located approximately 200 m upstream from the USGS gauging station and immediately upstream of a weir (Figure 1). Samples were analyzed for general chemical and stable isotope compositions. Samples collected from April 2000 to March 2002 were analyzed at UCSB using standard atomic adsorption and ion chromatographic techniques. Samples collected from October 2000 to the present were

analyzed at the USGS National Water Quality Laboratory in Denver. During periods of overlap, sample splits were sent to the UCSB and USGS laboratories so an interlaboratory comparison could be evaluated. Values from both laboratories were within the expected errors for the analyses, with very few exceptions. However, initial values of  $[\text{K}^+]$  measured at UCSB (prior to USGS-led sampling) are suspect due to analytical difficulties and are excluded from further analysis. UCSB data are used until October 2000 when the



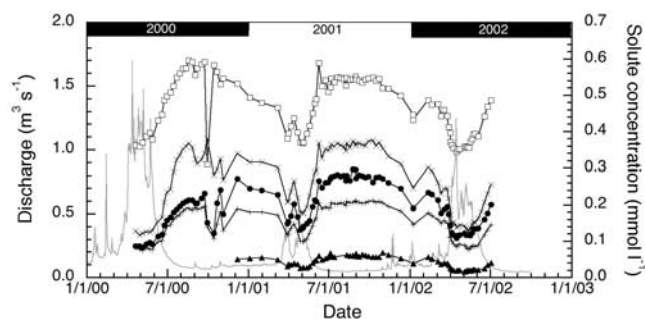
**Figure 4.** Discharge in Sagehen Creek during the study period. Points represent days when creek samples were collected.

USGS sampling began. USGS data are used in analyses for the remainder of the study period, as their sample collection is ongoing. Measurements of  $\delta^{18}\text{O}$  in Sagehen Creek were made using standard mass spectrometric techniques at LLNL.

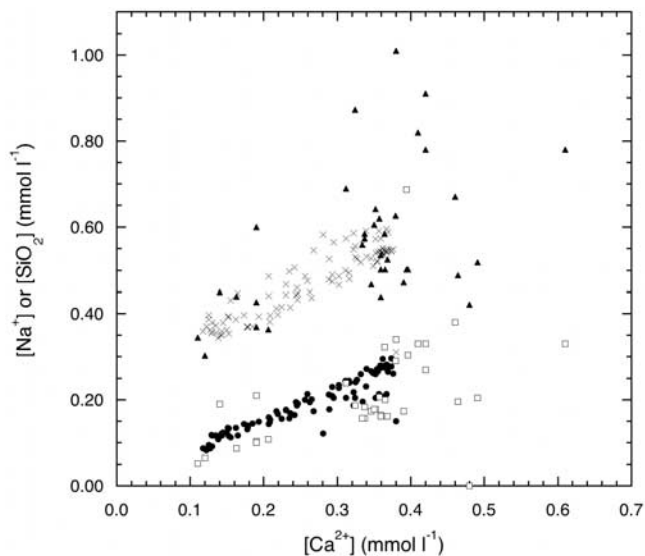
## 5. Results

[21] Discharge in Sagehen Creek has substantial seasonal variability (Figure 4). The hydrograph for Sagehen Creek exhibits complex behavior (rapid increases and decreases in flow) in the weeks leading up to the major snowmelt pulse. This complex behavior could result from rain on snow events or initial sporadic warming. Subsequent spring snowmelt periods lead to consistently higher discharge levels in Sagehen Creek ( $0.2\text{--}1.7\text{ m}^3\text{ s}^{-1}$  during the study period). The late summer, fall, and winter months are characterized by base flow conditions of a nearly constant discharge of less than  $0.11\text{ m}^3\text{ s}^{-1}$ .

[22] The chemical composition of Sagehen Creek varies throughout the year, as well as from year to year (Figure 5). Solute concentrations in Sagehen Creek are consistently lower during periods of high discharge and higher during base flow periods (Figure 5). The  $[\text{Na}^+]:[\text{Ca}^{2+}]$  ratios ( $\sim 0.7$ , standard deviation 0.1; all ratios expressed in molar units) and  $[\text{SiO}_2]:[\text{Ca}^{2+}]$  ratios ( $\sim 1.9$ , standard deviation 0.5) for



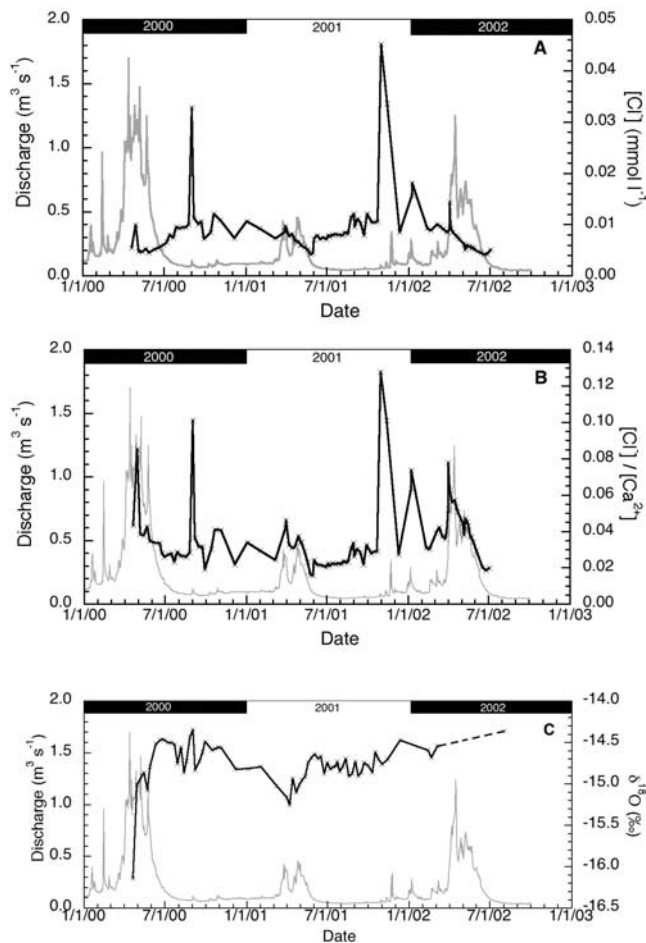
**Figure 5.** Major cation and silica concentrations in Sagehen Creek measured in grab samples collected during the study period ( $[\text{Ca}^{2+}]$ , crosses;  $[\text{Mg}^{2+}]$ , plusses;  $[\text{K}^+]$ , triangles;  $[\text{Na}^+]$ , circles;  $[\text{Si}]$ , squares). Sagehen Creek discharge is shown in light gray for reference. Chemical analyses have uncertainties of approximately 5%.



**Figure 6.** Relationship between  $[\text{Ca}^{2+}]$  and  $[\text{Na}^+]$  or  $[\text{SiO}_2]$  in the Sagehen springs (1997, 1999, 2000, 2001) and in Sagehen Creek (Sagehen Creek  $[\text{Na}^+]$ , circles; Sagehen Creek  $[\text{SiO}_2]$ , crosses; Sagehen spring  $[\text{Na}^+]$ , squares; Sagehen spring  $[\text{SiO}_2]$ , triangles). Chemical analyses have uncertainties of approximately 5%.

Sagehen Creek waters are consistent throughout the study period and are similar to the  $[\text{Na}^+]:[\text{Ca}^{2+}]$  ratios (0.7, standard deviation 0.3) and  $[\text{SiO}_2]:[\text{Ca}^{2+}]$  ratios (1.8, standard deviation 0.6) of the groundwater springs in Sagehen basin (Figure 6), suggesting similar solute sources from mineral weathering.  $[\text{Cl}^-]$  ion concentrations are also generally dilute during periods of snowmelt and concentrated during low-flow periods (Figure 7a). However, increases in  $[\text{Cl}^-]$  occur episodically throughout the study period. Some  $[\text{Cl}^-]$  spikes coincide with the onset of snowmelt. Other increases in  $[\text{Cl}^-]$  occur during the dry season and are often tied rainfall events and subtle concomitant increases in discharge. The primary source of  $[\text{Cl}^-]$  in Sagehen Creek is atmospheric deposition. The chloride ion is subsequently concentrated in the soil by evapotranspiration. Interestingly,  $[\text{Cl}^-]$  appears to be very sensitive to changes in discharge, particularly during low-flow periods. The  $[\text{Cl}^-]:[\text{Ca}^{2+}]$  ratios calculated for Sagehen Creek waters vary throughout the year (Figure 7b). Peaks in  $[\text{Cl}^-]:[\text{Ca}^{2+}]$  occur at or near the onset of the snowmelt periods, as well as occasionally in response to rainfall during base flow periods.

[23] Similar to  $[\text{Cl}^-]$  ion, the  $\delta^{18}\text{O}$  of Sagehen Creek water is derived from precipitation. The stable isotope composition of Sagehen Creek also varies throughout the record (Figure 7c). Generally, periods of low flow are characterized by heavier  $\delta^{18}\text{O}$  values ( $-14.2\text{‰}$  to  $-15\text{‰}$ ), whereas periods of high flow are isotopically lighter ( $-15\text{‰}$  to  $-16.2\text{‰}$ ). An extreme excursion in  $\delta^{18}\text{O}$  is observed at the onset of the snowmelt period during 2000 and to a lesser extent in 2001. The excursion is notably missing in 2002; however, it is possible that the sampling resolution was not adequate to detect this rapid event (low-resolution period indicated with a dashed line in Figure 7b). The incomplete creek  $\delta^{18}\text{O}$  record limits interpretation of



**Figure 7.** (a)  $[\text{Cl}^-]$  in Sagehen Creek during the study period. Crosses indicate when samples were collected. Sagehen Creek discharge is shown in light gray for reference. (b)  $[\text{Cl}^-]/[\text{Ca}^{2+}]$  ratios in Sagehen Creek during the study period. Crosses indicate when samples were collected. Sagehen Creek discharge is shown in light gray for reference. (c)  $\delta^{18}\text{O}$  in Sagehen Creek during the study period. Crosses indicate when samples were collected. The dashed line indicates an extended interval between samples. Sagehen Creek discharge is shown in light gray for reference.

the rapid and changing snowmelt influence based on  $\delta^{18}\text{O}$  alone.

## 6. Discussion

[24] Determining the mean residence time of groundwater that feeds Sagehen Creek is more complicated than calculating apparent ages in spring waters. Mean residence time of water in a stream cannot be directly calculated from CFC content due to the CFC loss that occurs via gas exchange at the air-water interface. Tritium/ $^3\text{He}$  ages are also affected by gas exchange at the air-water interface, which leads to He loss. Without detailed precipitation records, tritium cannot be used alone to determine mean residence times of stream water. Therefore a novel approach for calculating the mean residence time of stream water using the relationship between CFC age and chemical composition in groundwater is developed herein.

[25] The relationship between  $[\text{Ca}^{2+}]$  and CFC-11 age established by Rademacher *et al.* [2001] and shown in Figure 3a provides a method for directly relating the water chemistry of Sagehen Creek to groundwater mean residence times. For example, the  $[\text{Ca}^{2+}]$  composition of Sagehen Creek water during base flow conditions ( $Q < 0.11 \text{ m}^3 \text{ s}^{-1}$ ) is approximately  $0.34 \text{ mmol L}^{-1}$ . The equation  $[\text{Ca}^{2+}] = 0.01 * \text{CFC-11 age} + 0.05$  is generated when a linear best fit is applied to the relationship between  $[\text{Ca}^{2+}]$  and CFC-11 age shown in Figure 3a. The mean residence time of stream water during base flow calculated using this relationship is approximately 28 years (Table 1).  $[\text{Ca}^{2+}]$  in Sagehen Creek during base flow varies over the study period ( $\pm 0.06 \text{ mmol L}^{-1}$ ). This range in  $[\text{Ca}^{2+}]$  was used to estimate how the mean residence time of groundwater feeding Sagehen Creek varies throughout the study period ( $\pm 7$  years).

[26] It is important to note some uncertainties associated with these estimates of mean residence time for Sagehen Creek water when using the relationship between groundwater age and chemistry. First, scatter exists in the relationship between  $[\text{Ca}^{2+}]$  and CFC-11 age in Sagehen groundwaters (Figure 3a,  $R^2 = 0.6$ ). In most cases, this scatter produces an uncertainty in the estimated mean residence times of approximately  $\pm 5$  years. Second, the approach assumes that the relationship between residence time and chemistry in groundwater also applies to waters discharging into Sagehen Creek. Recall that according to the accepted model for stream discharge, water in a stream during base flow consists primarily of groundwater [Fetter, 1994]. In fact, the age versus solute concentration and age versus  $\delta^{18}\text{O}$  relationships suggest that Sagehen Creek base flow is dominated by an old component of groundwater (apparent ages between 26 and 33 years) in the basin (Table 1). Interestingly, groundwaters discharging in springs near the creek bed also have residence times of approximately 25–30 years (Figure 1), suggesting that these older groundwaters are also discharging into the creek and controlling stream water chemistry.

[27] The  $[\text{Ca}^{2+}]$  concentration of Sagehen Creek during spring snowmelt is much more dilute than during base flow. A mixture of 45% old groundwater (represented by base flow with  $[\text{Ca}^{2+}] \sim 0.34 \text{ mmol L}^{-1}$ ) with 55% dilute snowmelt ( $[\text{Ca}^{2+}] < 0.01 \text{ mmol/L}$ ) is required to obtain the average stream  $[\text{Ca}^{2+}]$  concentration in May of

**Table 1.** Mean Concentration of Solutes During Base Flow Conditions and the Corresponding Mean Residence Times for Sagehen Creek Water<sup>a</sup>

Solute	Mean Base Flow Concentration, $\text{mmol L}^{-1}$	$\pm$ , $\text{mmol L}^{-1}$	Corresponding Spring Water Age, years	$R^2$
Ca	0.34	0.06	28	0.6
Mg	0.19	0.05	26	0.6
K	0.06	0.01	33	0.6
Na	0.24	0.09	33	0.3
$\delta^{18}\text{O}$	-14.72	0.24	33	0.6

<sup>a</sup>Base flow conditions in Sagehen Creek exist when discharge is less than  $0.11 \text{ m}^3 \text{ s}^{-1}$ . Range in solute concentration during base flow is represented by  $\pm$  values. Mean residence times are based on the linear best fit for the relationship between age and solute concentrations of Sagehen spring waters (e.g., Figure 3a).  $R^2$  values are given for relationships between solute concentration and groundwater age.



0.16 mmol L<sup>-1</sup>. This relationship suggests that the old groundwater component could contribute significantly to the chemical signal of the creek, even during the highest flow periods in Sagehen Creek. However, a larger fraction of more dilute younger groundwater could also explain the [Ca<sup>2+</sup>] concentration.

[28] [Cl<sup>-</sup>] in Sagehen Creek also varies with discharge such that low-flow periods are generally characterized by higher [Cl<sup>-</sup>] than those during high-flow periods. Although the primary source of chloride ion in Sagehen basin is precipitation, concentration of chloride occurs as a result of evapotranspiration in the soil and groundwater zones. Therefore low [Cl<sup>-</sup>] that generally coincide with high-flow periods are likely a result of dilution of a relatively concentrated soil and/or groundwater reservoir by dilute snowmelt.

[29] However, numerous notable exceptions to the general inverse relationship between [Cl<sup>-</sup>] and discharge were observed during the study period. Abrupt increases in [Cl<sup>-</sup>] often occur at the onset of snowmelt and during rainfall events. The springtime increases in [Cl<sup>-</sup>] may be related to ionic pulses from melting snow, which are initially more concentrated in solutes than the mean snowpack as a result of the preferential release of soluble impurities [e.g., Colbeck, 1981; Bales *et al.*, 1990]. Alternatively, Cl may be flushed from the soil during the onset of snowmelt or during summer/fall rainfall events.

[30] It is challenging to separate the effects of dilution from changes in the age of the dominant groundwater component because of the complex hydrochemical nature of Sagehen Creek. The [Cl<sup>-</sup>]:[Ca<sup>2+</sup>] ratios can help distinguish between these two effects. Seasonal changes in [Cl<sup>-</sup>] and [Ca<sup>2+</sup>] are strongly affected by dilution of groundwater with dilute snowmelt. However, while [Ca<sup>2+</sup>] is correlated with groundwater age, [Cl<sup>-</sup>] is not. For these reasons, it is expected that the [Cl<sup>-</sup>]:[Ca<sup>2+</sup>] changes primarily in response to the age of groundwater discharging to the stream, and not does not change substantially due to dilution by snowmelt.

[31] It should be noted that previous studies [e.g., Bales *et al.*, 1990] observed a small preferential release of [Cl<sup>-</sup>] compared to [Ca<sup>2+</sup>] in the solute pulses, although results varied widely. Therefore care should be exercised when applying the [Cl<sup>-</sup>]:[Ca<sup>2+</sup>] relationship during the period of ionic pulse release from the snowpack. Ionic pulses tend to be short-lived (e.g., <10 days in a Wyoming snowpack [Bales *et al.*, 1990]) and should have a limited effect on the record.

[32] Sagehen Creek [Cl<sup>-</sup>]:[Ca<sup>2+</sup>] ratios show an interesting pattern during periods of snowmelt; an initial increase in [Cl<sup>-</sup>]:[Ca<sup>2+</sup>] ratios is followed by a gradual decrease back to base flow levels (Figure 7b). This pattern indicates that water of a younger age, either very shallow groundwater or soil water, is contributing to stream water chemistry during initial snowmelt periods. Mean residence times of groundwaters discharging to Sagehen Creek during these snowmelt periods, based on the relationship between groundwater age and [Cl<sup>-</sup>]:[Ca<sup>2+</sup>] ratios (Figure 3d), is approximately 15 (±5) years. Groundwater of this age is expected to have a [Ca<sup>2+</sup>] approximately equal to 0.2 mmol L<sup>-1</sup>. Sagehen Creek water has a [Ca<sup>2+</sup>] of approximately 0.14 mmol L<sup>-1</sup>, thus, the creek is discharging a mixture of about 70%

young groundwater and 30% dilute meltwater. It is probable that during peak discharge the influence of young groundwater (~15 years) may increase as a result of elevated hydraulic head as the melting snowpack produces a pressure response in the subsurface and raises the water table. This process leads to an increase in stream flow resulting from groundwater discharge into the streambed [Sklash and Farvolden, 1979; Phillips, 2001]. The additional consideration of soil water mobilization during snowmelt would decrease the apparent influence of shallow groundwater, although in the case of Sagehen basin, no direct measurements of soil water composition exist.

[33] [Cl<sup>-</sup>]:[Ca<sup>2+</sup>] reaches a minimum of approximately 0.03 during base flow periods, which is the minimum value measured in Sagehen spring waters (Figure 3d). This low [Cl<sup>-</sup>]:[Ca<sup>2+</sup>] ratio end-member corresponds to groundwater with an apparent age of approximately 35 years discharging directly into the creek and agrees well with the ages determined using [Ca<sup>2+</sup>] and δ<sup>18</sup>O. In addition to the general base flow and snowmelt patterns, excursions in [Cl<sup>-</sup>]:[Ca<sup>2+</sup>] ratios also occur during the low-flow periods. These excursions in [Cl<sup>-</sup>]:[Ca<sup>2+</sup>] ratios are likely the result of rapid mobilization of very young water during occasional summer discharge events or brief melting events during unusually warm periods in the early winter months. The [Cl<sup>-</sup>]:[Ca<sup>2+</sup>] ratios during these excursions indicate an apparent ages of approximately 10 years.

[34] The relationship between groundwater residence time and chemistry provides a basis for separating the influence of dilution and changing mean residence times of groundwater discharging into Sagehen Creek and suggests that groundwater (in some cases apparent ages >30 years) plays a primary role in controlling stream chemistry. Ratios of solutes derived from primary weathering reactions in Sagehen Creek reflect those measured in the groundwater springs. Sagehen Creek water has fairly consistent [Ca<sup>2+</sup>]:[Na<sup>+</sup>] and [Ca<sup>2+</sup>]:[Si] ratios even during times of high creek flow when many studies have indicated the strong influence of components other than groundwater to stream chemistry (Figure 6). The relationships between solutes and discharge indicate that even during snowmelt periods, discharging groundwaters are still controlling the chemical composition of the creek, with lesser influences from changes in water sources.

[35] The δ<sup>18</sup>O of Sagehen Creek during base flow periods reflects groundwater ages of approximately 33 years based on a linear best fit of the δ<sup>18</sup>O and groundwater age relationship (Table 1). The stable isotope composition of Sagehen Creek water is strongly influenced by the isotopic evolution of the snowpack during the melt season. Previous studies observed that initial meltwaters released from a snowpack are isotopically lighter than the mean composition of the snowpack [Taylor *et al.*, 2001, 2002]. In addition, these snowmelt values become progressively enriched in δ<sup>18</sup>O during continued melting [Taylor *et al.*, 2001, 2002]. Isotopically light meltwater was observed in Sagehen Creek during the onset of snowmelt in 2000, and to a lesser extent in 2001. The sample population collected during the 2002 melt period was insufficient to record the light meltwater pulse. It is difficult to separate the groundwater age influencing Sagehen Creek using stable isotopes during melt periods because the initial pulse of meltwater is significantly

lighter than Sagehen groundwaters and obscures the temporal trend in  $\delta^{18}\text{O}$ .

## 7. Summary and Implications

[36] The relationship between residence time and chemistry of groundwater provides a basis for determining the apparent age of groundwater discharging into Sagehen creek and the effects of dilution of solutes with snowmelt throughout the hydrograph cycle. On the basis of an established relationship between spring water chemistry and apparent groundwater age [Rademacher *et al.*, 2001], the mean residence time of water in Sagehen basin was determined to be  $30 \pm 5$  years (average based on all solutes studied) during base flow, suggesting that Sagehen Creek is dominated by a surprisingly old groundwater component. During periods of high discharge resulting from snowmelt, the groundwater component remains the dominant control on the chemical composition of Sagehen Creek water, although the mean residence time of the groundwater feeding the creek decreases.

[37] Numerous previous studies utilized geochemical hydrograph separations to understand dilution processes and changes in flow paths during hydrologic events (such as snowmelt in high-elevation catchments). These studies assume the old component (or groundwater component) is constant. The relationship between spring water age and chemical composition observed in this study suggests that groundwater is not a single, well-mixed chemical component, but rather is a variable parameter that predictably depends on residence time. The relationship between geochemical age tracer data and solute and isotopic variability in groundwater contributes to a greater understanding of catchment processes. By assuming a constant chemical composition (and therefore, constant age) for the groundwater component in hydrograph separations, valuable information on how a stream and a catchment respond to changes throughout the year are lost.

[38] In addition, understanding the discharge patterns into a stream enables further development of a conceptual model for hydrochemical responses to perturbations within catchments. If the mean residence time of water discharging in a stream reflects the mean residence time of water in a catchment, then the timescale of catchment response to disturbance can be calculated. For example, if the mean residence time of water in Sagehen basin is approximately 30 years, it is likely that the long-term flushing rate of the catchment is on the order of 30 years. This suggests that although some initial flushing of contaminants (such as those resulting from atmospheric deposition) might occur during large discharge events, it will take approximately 30 years to return to the predisturbance condition in the basin, assuming the contaminant is conservative.

[39] The variability of groundwater and surface chemistry (and the relationship between the two) in Sagehen basin presents challenges for understanding catchment hydrochemical evolution and long-term responses to disturbances based on traditional techniques. The addition of the techniques presented here will support an increasingly detailed understanding of flow paths and how the residence time of water flowing through these pathways contributes to catchment stability and response. Through this understanding of contributing flow paths and mean residence times, better

predictions of long-term catchment responses to perturbations, whether natural or anthropogenic, are possible.

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