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Carbon sources and signals through time in an Alpine groundwater Basin, Sagehen California

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ABSTRACT

In 2003, chlorofluorocarbon (CFC) apparent ages, major ion chemistry and C isotopes were determined in nine springs from Sagehen Basin, a high elevation watershed in the eastern Sierra Nevada. Springs with similar apparent ages, which ranged between 15 and 45 a, had very similar chemistry despite being found in different areas of the watershed. In agreement with earlier studies, concentrations of rock-derived cations (Ca^{2+} and Na^+), conductivity, temperature and pH increase with apparent age, documenting the chemical evolution of this groundwater system. In contrast with the cation data, $\delta^{13}\text{C}$ and ΣCO_2 show no correlation with apparent age. $\delta^{13}\text{C}$ displays a strong linear relationship with $1/\Sigma\text{CO}_2$ ($R^2 = 0.91$). This is consistent with results from a previously developed soil respiration/diffusion model. Spring radiocarbon content ranged between 85 and 110 pmc and varied with apparent age, whereby the youngest groundwater has the highest radiocarbon values. The spring radiocarbon is set by the soil $p\text{CO}_2$ and its trend can be best described assuming the soil CO_2 is composed of a mixture of 50–66% fast- (15–25 a) and 33–50% slow- (4 ka) cycling components. These results are consistent with previous soil C studies. The C isotope data indicate that in Sagehen Basin the groundwater ΣCO_2 is inherited from the soil zone with little, if any, contribution from the dissolution of disseminated calcite.

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1. Introduction

Field-based weathering rates are often estimated by catchment studies that focus on the variations of the chemical composition of streams (Stallard and Edmond, 1983; Paces, 1983; Velbel, 1985; Mast et al., 1990; Williams and Melack, 1997; Furman et al., 1998). Streams are surface waters, which integrate direct precipitation, overland flow, flow through soils and groundwater discharge (Church, 1997), and therefore their chemical compositions reflect this multi-source integration (e.g., Hinton et al., 1994; Burns et al., 2001). Which of these flowpaths proportionately dominates the solute flux out of a catchment depends

on the local climate, geomorphology, soil development, bedrock structure and permeability.

Groundwater is a fundamental hydrologic component in many watersheds, feeding streams and rivers via baseflow long after the cessation of snowmelt or storm events. The residence time of groundwater is relatively long compared with other water sources to streams. For instance, Vitvar and Balderer (1997), Burns et al. (2003), Rademacher et al. (2005) and Rose (2007) demonstrated using geochemical tracer techniques that the apparent ages of groundwater feeding baseflow in mountain catchments range from years to decades.

Recently, Rademacher et al. (2001) and Burns et al. (2003) developed a method for evaluating chemical weathering rates in catchment groundwater by combining the mass balance approach of Garrels and Mackenzie (1967) with groundwater dating techniques. Both groups employed the geochemical model NETPATH (Plummer et al.,

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1994) to facilitate the mass balance calculations and showed groundwater chemistry evolves on the time scale of years, demonstrating chemical weathering extends beyond the soil zone into the aquifer. Furthermore, they were able to estimate weathering rates and thus identify which minerals contribute to the flux of each cation.

Disseminated calcite can play a key role in determining the rate and style of chemical weathering in granitoid catchments where accessory calcite often occurs as replacement of cores in plagioclase and as disseminated grains within the silicate matrix (White et al., 1999). The dissolution of accessory calcite opens vast secondary permeability, exposing more primary minerals and advancing the plagioclase weathering front through granitoid bedrock (White et al., 2001). Its high solubility compared with silicates and common occurrence in crustal environments make calcite potentially the dominant source of Ca^{2+} to groundwater and a primary buffer to acidity derived from soil water. Furthermore, calcite weathering significantly imprints the dissolved inorganic C (ΣCO_2) pool by altering its isotope composition and increasing its concentration.

The prevalence of calcite as a source of Ca^{2+} and ΣCO_2 to groundwater can vary temporarily as well as spatially (Telmer and Veizer, 1999). White et al. (1999) suggested that calcite weathering may dominate the Ca flux and C chemistry in groundwater following periods of glaciation or tectonism, which can expose abundant fresh mineral surfaces. In older, more stable environments, they concluded that the weathering of accessory calcite is less important because after a flow path is active for a sufficient duration, the highly soluble but limited calcite will have been removed by chemical weathering. In these cases, Ca

fluxes are dominated by weathering of silicates such as plagioclase and amphibole and the ΣCO_2 reflects other sources.

In this study, the concentration and isotope composition of ΣCO_2 from nine springs in Sagehen Basin, CA, are examined to determine the relative influences of calcite and soil CO_2 as C sources, and to explore temporal and isotopic variations in the spring C chemistry for what they can reveal about the soil processes affecting groundwater chemistry.

2. Study area

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 drainage basin is approximately 27 km² and ranges from approximately 1900 to 2600 m in elevation (Fig. 1). Fourteen groundwater springs are known to emerge from the Sagehen groundwater system on the north and south sides of Sagehen Creek and exist in the alluvium and glacial till, which overlie the bedrock. The bedrock in the basin is predominantly granodiorite overlain locally by andesite; outcrops are sparse and occur primarily at higher elevations throughout the basin (Rademacher et al., 2001).

Precipitation and temperature in Sagehen Basin are variable and correlate with elevation. The 35-a mean annual air temperature and precipitation at 1950 m are, respectively, 5.9 °C and 89 cm/a (National Climatic Data Center). Approximately 80% of the annual precipitation in the basin occurs during the winter months (November through April) primarily as snow. Water is stored in the snowpack

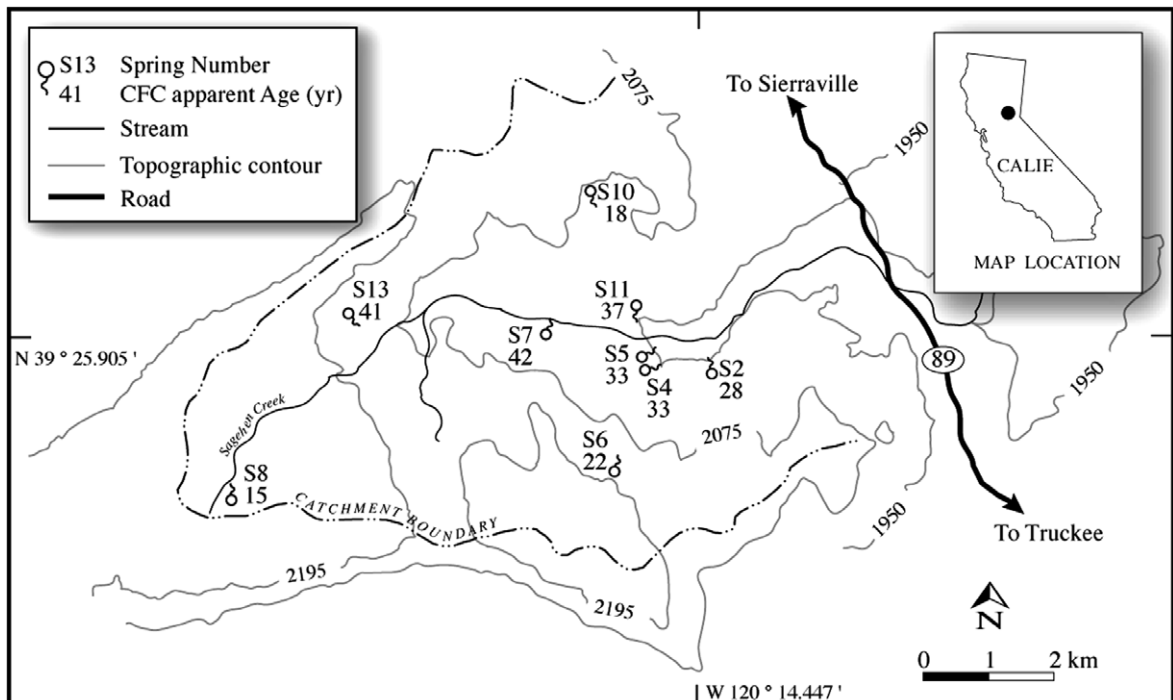


Fig. 1. Map of Sagehen Basin showing the location of the sampled springs. The CFC apparent age and ID numbers are listed beside each spring.

until it is released during the spring melt season, and either leaves the basin via surface flow or recharges the surficial aquifer. Groundwater discharge occurs throughout the year at most of the springs and via baseflow into the Sagehen creek, even during extended periods of drought (Erman and Erman, 1995; Rademacher et al., 2001, 2005).

Rademacher et al. (2001, 2002, 2005) related groundwater chemistry and isotope composition to apparent age or residence time, which were determined using CFC and $^3\text{H}/^3\text{He}$ concentrations (e.g., Schlosser et al., 1988; Busenberg and Plummer, 1992; Plummer and Busenberg, 2000; Solomon and Cook, 2000). The apparent age of spring water discharging in Sagehen Basin, calculated using CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) concentrations, ranges from approximately 10 to 45 a. Older spring water discharges lower in the basin near the creek. CFC-11 and CFC-12 apparent ages correlate well with each other (Fig. 2), suggesting CFCs are not altered by processes such as microbial degradation in the Sagehen groundwater system (Oster et al., 1996; Plummer and Busenberg, 2000) or impacted by wastewater sources (e.g., Clark et al., 1995; Plummer and Busenberg, 2000).

The $^3\text{H}/^3\text{He}$ apparent ages correlate positively with the independently determined CFC apparent ages, although the $^3\text{H}/^3\text{He}$ ages are consistently 10–15 a younger than CFC apparent ages (Rademacher et al., 2001, 2005). This is likely the result of poor He confinement associated with low recharge rates or gas exchange effects as bubbles were observed within many of the spring pools. Both mechanisms would drive the loss of the accumulated daughter product (^3He), producing the effect of $^3\text{H}/^3\text{He}$ apparent ages appearing younger than CFC apparent ages.

There is good agreement among CFC apparent ages of the Sagehen springs from samples collected in July-97, November-99, June-00, September-01 and July 2003, despite collection during variable hydrologic conditions (Fig. 3). For instance, the June 2000 sampling event oc-

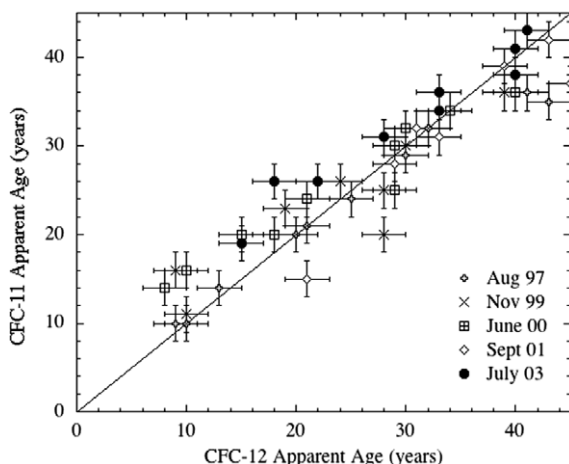


Fig. 2. CFC-11 apparent ages are plotted against CFC-12 apparent ages, with a one-to-one line, from the 2003 and four earlier sampling events (Rademacher et al., 2001, 2005). The good agreement between the CFC-11 and CFC-12 ages suggests their concentrations have not been altered by microbial degradation (Rademacher et al., 2001).

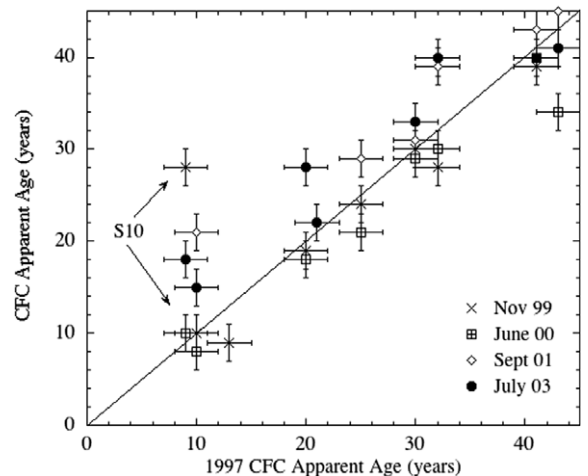


Fig. 3. CFC-12 apparent age of each spring from the 1999, 2000, 2001 and 2003 sampling events plotted against the initial 1997 apparent age.

curred at the end of that year's snowmelt when the creek discharge was 484 L/s, while the other sampling events took place during baseflow conditions in the late Summer or early Fall when the creek discharge ranged between 75 and 115 L/s. Nevertheless, CFC apparent ages from the June 2000 sampling agree well with those collected during baseflow indicating that little recent snowmelt discharges from the springs (Rademacher et al., 2005) and the springs are fed by a stable groundwater flow system.

Rademacher et al. (2001) identified mineral weathering as the primary process controlling groundwater chemistry in Sagehen Basin. Concentrations of the mineral-derived cations (e.g., Ca^{2+} and Na^+), conductivity and pH increase with apparent age (Fig. 4A–C). For each year's data, the correlation coefficients, R^2 , ranged between 0.71 and 0.78 for Ca^{2+} , 0.57–0.63 for Na^+ (excluding 2001), and 0.62–0.87 for pH. Non-lithogenic solutes, such as Cl^- ($R^2 < 0.1$), which is introduced via precipitation and concentrated within the soil by evapotranspiration, do not show any clear correlation with groundwater residence time (Fig. 4D). Using mass balance calculations performed with NETPATH (Plummer et al., 1994) and the geochemical ages, Rademacher et al. (2001) estimated weathering rates for two common minerals found in the glacial till of Sagehen Basin: 1.8–11.6 and 0.6–3.6 $\mu\text{mol l}^{-1} \text{a}^{-1}$ for plagioclase and hornblende, respectively. These rates are remarkably similar to values Burns et al. (2003) determined in Panola Mountain Research Forest, GA, using the same approach.

4. Methods

In late July 2003, nine springs in Sagehen Basin were sampled for general chemistry, stable isotopes, CFCs, and C isotope analyses. These springs had been sampled previously on four occasions: July-97, November-99, June-00, and September-01. All of the groundwater samples were extracted directly from springs using a Cu tube sampling line placed in the pool at the sediment–water interface to avoid atmospheric contamination, following protocols

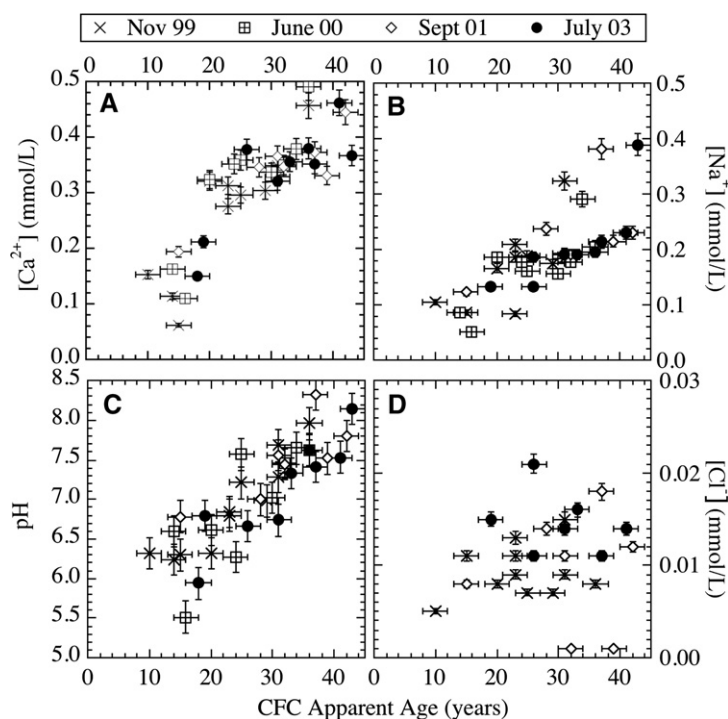


Fig. 4. Spring chemistry plotted as a function of CFC apparent age. Strong positive trends are observed in the chemical parameters found in weathering reactions (A–C), while there is no apparent age trend in the chloride data (D). Data are from this study and Rademacher et al. (2001, 2005).

established during earlier studies. CFC samples were collected in 10 mL Cu tubes sealed with stainless steel pinch-off clamps. Samples collected for major ion analyses were filtered in the field using 0.4 μm polycarbonate filters and stored in 125 mL polyethylene bottles. Cation samples were acidified with about 0.2 mL of 6 N HCl. Carbon chemistry samples (ΣCO_2 , $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$) were poisoned in the field with HgCl_2 and stored in 500 mL glass bottles.

CFC samples were analyzed on a gas chromatograph equipped with an electron capture detector, following the procedure outlined by Smethie et al. (1988) and Rademacher et al. (2001). Conductivity, pH, and temperature were measured directly at the spring with hand-held devices. Major ion chemistries were measured using standard ICP-AES and AA techniques.

Carbon dioxide from the C isotope samples was isolated on a vacuum line. The first step in the procedure was degassing about 30 mL of 1 N HCl. A known volume of spring water (~ 80 mL) was then mixed with the acid for about 30 min and the released CO_2 was cryogenically trapped using liquid N_2 . Between the liquid N_2 trap and reaction vessel was a dry ice-alcohol trap for water. The trapped CO_2 was expanded into a calibrated volume. After the calibrated volume had thermally equilibrated, the total CO_2 pressure was recorded and the concentration of ΣCO_2 was determined. The extracted CO_2 was then split and flame sealed in two glass tubes, with one for $^{13}\text{C}/^{12}\text{C}$ ratio analysis on a conventional mass spectrometer at the University of California, Davis and the other for ^{14}C analyses using standard AMS techniques at the University of Arizona.

5. Results

Major ion chemistry and CFC dating results from the 2003 sampling campaign agree well with the earlier results of Rademacher et al. (2001, 2005). Conductivity, pH, and cations derived from weathering reactions correlated with apparent age (Fig. 4). Similar to Cl, neither spring water $\delta^{13}\text{C}$, which ranges between -19 and -17‰ , nor ΣCO_2 show a clear correlation with spring water apparent age (Table 1, Figs. 4 and 5), indicating that the process dominating the spring C signal is not dependent on the residence time of groundwater and, therefore, mineral weathering. Temporally progressive calcite dissolution in groundwater, for example, should produce heavier $\delta^{13}\text{C}$ values and greater ΣCO_2 concentrations in groundwater of increasing apparent ages.

Spring radiocarbon abundance varies systematically with groundwater apparent age (Fig. 6), decreasing from 110 pmc for 15-a-old spring water to 85 pmc for 42-a-old spring water (Table 1). It is important to recognize that the direction of this strong ^{14}C -age trend is consistent with progressive calcite dissolution, which would add 'dead' C (^{14}C of ~ 0 pmc) to the groundwater. The range in spring ^{14}C values, however, argues against this. The temporal spring radiocarbon trend climbs to conspicuously elevated values, with four of the nine springs sampled for ^{14}C having values >100 pmc. This high ^{14}C range indicates the incorporation of radiocarbon derived from nuclear arms testing of the 1950s and 1960s.

$\delta^{13}\text{C}$ and ΣCO_2 , which do not correlate with spring apparent age (Fig. 5), also do not correlate with spring

Table 1
CFC apparent age, Ca and C chemistry data from the July 2003 sampling event

Spring ID	CFC-12 age (a)	CFC-11 age (a)	pH	Ca (mmol/L)	ΣCO_2 (mmol/L)	$\delta^{13}\text{C}$ (‰)	^{14}C (pmc)
S2	28	31	6.7	0.32	1.30	-18.3	105.0
S4	33	36	7.3	0.36	1.44	-18.6	99.4
S5	33	33	7.6	0.38	1.47	-18.5	95.3
S6	22	26	6.7	0.38	2.06	-19.0	104.5
S7	42	43	8.1	0.37	1.09	-18.3	84.6
S8	15	19	6.8	0.21	0.90	-17.6	109.3
S10	18	26	5.9	0.15	1.85	-18.9	109.9
S11	37	37	7.4	0.35	1.42	-18.3	94.9
S13	40	41	7.5	0.46	1.98	-16.9	87.6

See Fig. 1 for the locations of the springs.

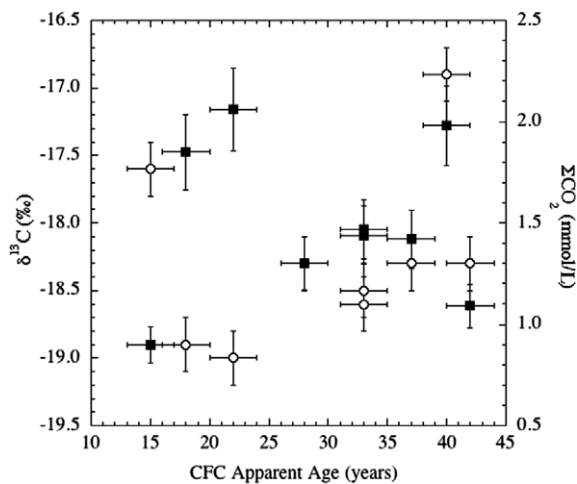


Fig. 5. Apparent age trend of ΣCO_2 and its stable isotope ratio ($\delta^{13}\text{C}$). Open circles = $\delta^{13}\text{C}$ and filled squares = ΣCO_2 .

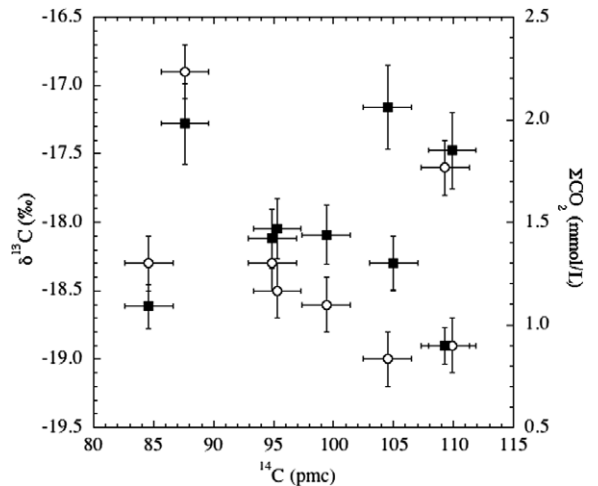


Fig. 7. $\delta^{13}\text{C}$ (filled squares) and ΣCO_2 (open circles) do not correlate well with spring radiocarbon content.

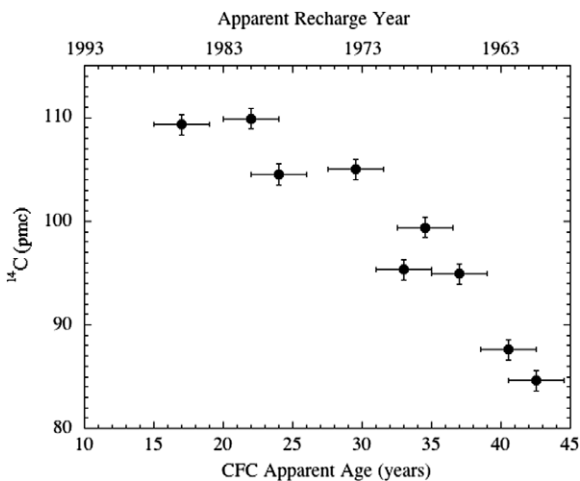


Fig. 6. Spring radiocarbon abundance plotted as a function of apparent age. Note that the apparent recharge year is displayed along the top axis in the reverse direction.

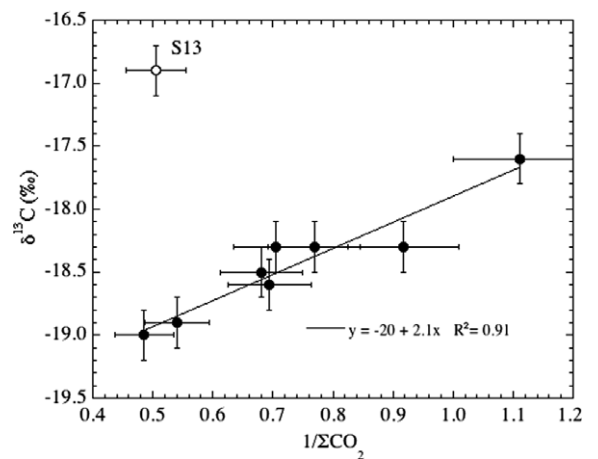


Fig. 8. The spring C chemistry shows a strong linear correlation between $\delta^{13}\text{C}$ and $1/\Sigma\text{CO}_2$ ($R^2 = 0.91$), a result predicted by the soil respiration/diffusion model of Cerling (1984), and consistent with observed isotopic variation in soil CO_2 (Cerling et al., 1991; Amundson et al., 1998).

^{14}C content (Fig. 7). If calcite dissolution were a dominant C source to the groundwater, then correlations among these three parameters ($\delta^{13}\text{C}$, ΣCO_2 and ^{14}C) would be pro-

nounced and internally consistent. Additionally, if calcite were a dominant Ca and C source to the Sagehen groundwater system, isotopically heavier spring $\delta^{13}\text{C}$ values

would correlate with increasing Ca^+ and ΣCO_2 concentrations. Instead, there are no clear correlations indicating that a process other than progressive calcite weathering is controlling the spring C chemistry.

With the exception of one spring (S13), a very strong correlation ($R^2 = 0.91$) exists between $\delta^{13}\text{C}$ and $1/\Sigma\text{CO}_2$ (Fig. 8). The spring C exhibits systematically lighter $\delta^{13}\text{C}$ values with increasing ΣCO_2 concentrations. This linear correlation between $\delta^{13}\text{C}$ and $1/\Sigma\text{CO}_2$ in spring water is consistent with predictions of the soil CO_2 respiration/diffusion model of Cerling (1984) and Cerling et al. (1991) assuming that the ΣCO_2 concentration is set by the soil $p\text{CO}_2$.

6. Discussion

Cerling (1984) and Cerling et al. (1991) examined controls on the stable isotope composition of soil CO_2 , a gas occupying the pore space, and soil-respired CO_2 , a flux of gas through a horizontal plane within the soil profile. They found a consistent offset between the isotopic compositions of soil CO_2 versus soil-respired CO_2 , whereby the $\delta^{13}\text{C}$ of soil CO_2 was $\sim 4.4\%$ heavier. Although other workers had shown that soil CO_2 was isotopically enriched compared to soil-respired CO_2 (Dörr and Munnich, 1980), Cerling et al. (1991) were first to show that this enrichment could be explained by molecular diffusion. Their model predicts a linear relationship between the $\delta^{13}\text{C}$ of soil CO_2 and $1/p\text{CO}_2$ and that $\delta^{13}\text{C}$ of soil CO_2 is a function of depth and total soil respiration rates. Field data from the Wasatch Mountains of Utah and the Sierra Nevada of California agreed well with model predictions (Cerling et al., 1991; Amundson et al., 1998).

According to Cerling's diffusion model results, the observed range in $\delta^{13}\text{C}$ of ~ -17 to -19% in the spring data is consistent with a soil respiration rate of approximately $0.5 \text{ mmol/m}^2/\text{h}$. The linear $\delta^{13}\text{C}$ - $1/\Sigma\text{CO}_2$ relationship in the spring C data, with lighter C isotope compositions corresponding with higher dissolved inorganic C concentrations, is opposite in sense to the $\delta^{13}\text{C}$ - $1/\Sigma\text{CO}_2$ relationship expected from progressive calcite weathering, whereby heavier C isotope compositions correspond with greater dissolved inorganic C concentrations.

The $\delta^{13}\text{C}$ value of spring 13 is the isotopically heaviest data point and deviates substantially from the otherwise linear relationship of $\delta^{13}\text{C}$ to $1/\Sigma\text{CO}_2$. This isotopically heavy excursion reflects the sensitivity of spring $\delta^{13}\text{C}$ values to pedogenic versus lithogenic C sources, and may reflect C sourced from calcite dissolution.

The $\delta^{13}\text{C}$ - $1/\Sigma\text{CO}_2$ linear relationship points to soil respiration rather than calcite weathering as the dominant process controlling the C chemistry in the Sagehen groundwater system. Therefore, the spring ^{14}C temporal trend (Fig. 6) can be interpreted as the movement of the anthropogenic (i.e., nuclear weapon tests) radiocarbon through the soil zone and into the groundwater. This is compelling because the range of the radiocarbon trend in Sagehen spring water is similar to values determined for soil organic material (SOM) (e.g., Trumbore et al., 1989, 1990; Harrison and Broecker, 1993; Milton and Kramer, 1998; Gaudinski et al., 2000). As a result of the above-ground nu-

clear weapon testing of the 1950s and 60s, the ^{14}C content of atmospheric CO_2 doubled (Burchuladze et al., 1989; Levin and Kromer, 2004). This short term variation, as well as its moderately long half life, has allowed detailed studies of soil C turnover rates, τ , using the atmospheric radiocarbon trend as the input function of ^{14}C to the soil C reservoir (Trumbore et al., 1989, 1990; Harrison and Broecker, 1993; Milton and Kramer, 1998; Gaudinski et al., 2000).

A box model, similar to those used in pedologic soil C modeling (Trumbore et al., 1989, 1990; Harrison and Broecker, 1993; Milton and Kramer, 1998; Gaudinski et al., 2000; Michalzik et al., 2003), was employed to quantify the temporal variation in ^{14}C content as a function of turnover time. The model results show that greater C residence times produce trends that increasingly lag behind the atmospheric record, and that radioactive decay significantly lowers the ^{14}C content when the turnover time exceeds a few hundred years (Fig. 9A). The radiocarbon trend for the C pool having a 4-ka residence time, for example, is substantially decayed and lies flat with a radiocarbon value of less than 70 pmc.

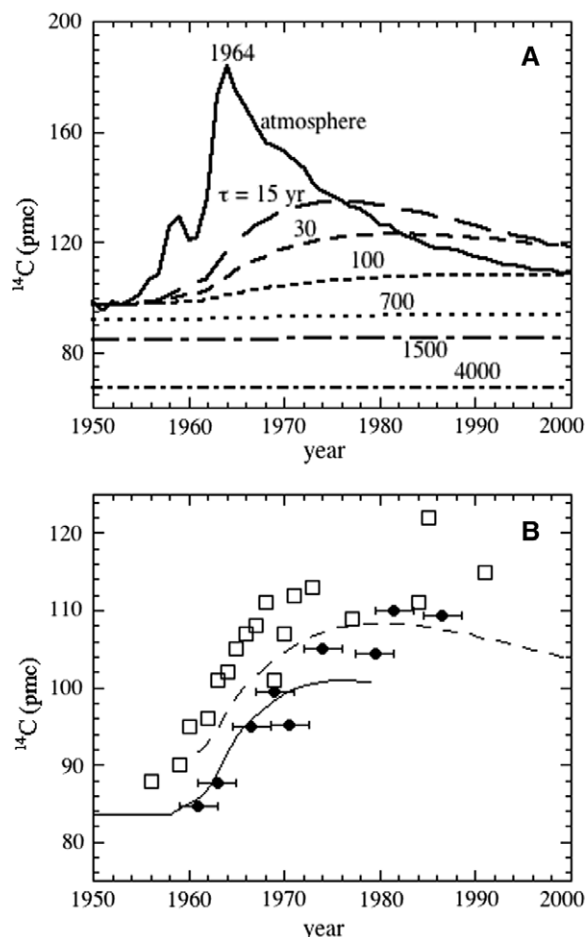


Fig. 9. (A) The temporal ^{14}C trend modeled for soil C with varying turnover times, τ . (B) The spring radiocarbon trend lies below soil data compiled by Harrison and Broecker (1993) and is bracketed by model trends that mix fast- and slow-cycling soil C components (see text). Atmospheric ^{14}C trend is based on data from Levin and Kromer (2004).

Fierer et al. (2005) examined CO₂ production, SOM and dissolved organic C (DOC) in soil profiles of annual grassland in coastal southern California. The radiocarbon content of the SOM in their study area diminished sharply with profile depth, with ¹⁴C values from as high as 112 pmc near the surface, to as low as 40 pmc at ~2.5 m depth. The ¹⁴C of soil pCO₂, in contrast, was relatively constant through the soil profile, exhibiting an entirely modern (post-bomb) ¹⁴C range of 109–111 pmc. In light of these data, these workers proposed that the bulk of the pCO₂ is derived from the microbial mineralization of 'young' (less than 40-a-old) DOC that has been transported by water through the soil profile.

The results of Fierer et al. (2005) demonstrate the strong influence that the age fractions of the oxidized SOM have on the ultimate radiocarbon content of soil pCO₂. The highest pCO₂ are observed near the base of the vadose zone at or near the water table (Amundson and Davidson, 1990; Bacon and Keller, 1998; Fierer et al., 2005) where recharging waters are expected to equilibrate with soil gas (Stute and Schlosser, 2000). As discussed above, in the absence of additional C from another source, such as calcite dissolution, the groundwater C chemistry should preserve this soil C signature.

In the context of SOM residence times and with the soil established as the dominant C source to the Sagehen groundwater system, the spring radiocarbon trend can be used to estimate soil C turnover rates in this Sierran catchment. Spring waters recharging in ~1960 were tagged with a soil CO₂ signal having a radiocarbon content of ~85 pmc, leading through the intervening years to the youngest spring water, recharged in ~1990, which carries a soil CO₂ radiocarbon signal of ~110 pmc.

Although soils are composed of numerous organic reservoirs that have a variety of turnover times, it is common to treat soils as being composed of only two reservoirs (e.g., Trumbore et al., 1989, 1990; Harrison and Broecker, 1993; Gaudinski et al., 2000): a fast-cycling or active pool, with turnover rates of months to decades and a slow-cycling or passive pool, with turnover rates of centuries to millennia. The spring radiocarbon data lie between model trends of $\tau = 15\text{--}25$ a and $\tau = 4$ ka, representing fast- and slow-cycling soil C components, respectively. It was not possible to fit the 30-a spring data trend using a single two-component model (Fig. 9B). The best fit was achieved by assuming a 50:50 mix of young and old reservoir sources for the early part of the record and a 33:67 mix for the later portion. This change in mixing ratio implies the soil reservoirs are spatially variable in this catchment. The residence time estimates for the fast and slow soil C components are consistent with previous pedologic soil C modeling, which typically compresses the range of soil C residence times indicated above into 75% fast- and 25% slow-cycling pools (Harrison and Broecker, 1993; Gaudinski et al., 2000).

Considered as a combined data set, the spring data form the bottom of the soil radiocarbon envelope as compiled by Harrison and Broecker (1993). It is important to note that the soil ¹⁴C data are from samples taken from the upper 30 cm of various soils from North America and northern Europe. The slightly lower spring trend may reflect where soil CO₂ equilibrates with groundwater, which occurs deep

in the soil profile at or near the water table (Stute and Schlosser, 2000). The systematically lower ¹⁴C values of the spring data indicate the greater incorporation of the older, slower cycling soil reservoir presumably from this deeper zone. The offset between spring and soil radiocarbon trends could also be explained by uncertainty in the CFC-based spring chronology. For instance, the spring data would blend well with the soil data were the spring radiocarbon trend moved back about 5 a.

There is remarkable agreement between the hydrochemical and pedologic soil C modeling results. They both indicate a wide range in soil C turnover rates, with the fast-cycling pool dominating the radiocarbon signal. It is worth recalling that the soil radiocarbon values are from samples collected during the years between the mid 1950s and early 1990s, whereas the spring radiocarbon values are from a single sampling event in 2003. Application of the groundwater archive to investigate soil C cycling will be limited to catchments where calcite weathering is negligible.

The results also have implications for the radiocarbon dating of fossil groundwater. Most dating models assume the ¹⁴C content of the soil end member is 100 pmc. The present results indicate this is too high. The respiration of partially decayed soil organic C dilutes the atmospheric ¹⁴C signal prior to recharge, reducing the initial content below 100 pmc.

6. Summary

Sagehen spring data show a clear relationship between chemical composition and the apparent age of spring waters. This chemical evolution of groundwater is the result of progressive mineral weathering and indicates that groundwater is not a single, well-mixed component, but rather its composition is variable and depends on age. Absent from the weathering trend is calcite dissolution indicating (1) silicate weathering dominates in this catchment and (2) spring C chemistry preserves chemical and isotopic signals inherited from the soil. The linear correlation between $\delta^{13}\text{C}$ and $1/\Sigma\text{CO}_2$ is consistent with predictions of a soil respiration/diffusion model of Cerling et al. (1991). The observed range in $\delta^{13}\text{C}$ of ~-17 to -19‰ in the spring data is consistent with a soil respiration rate of approximately 0.5 mmol/m²/h. The spring radiocarbon trend is not a function of ΣCO_2 or $\delta^{13}\text{C}$, and, because the spring C chemistry is dominated by soil C, provides a hydrochemical basis for modeling soil C turnover rates. The results of a simple box model bracket the combined soil-spring radiocarbon trend – by 67% 25-a – and 33% 4-ka – cycling components for the more recent portion of the record, and by 50% 15-a – and 50% 4-ka – cycling components for the earlier portion – a result consistent with pedologic C studies.

Thus, the conclusions enumerated above based on the spring C data represent an intersection between disparate efforts to explain the isotopic and temporal nature of the soil C chemistry: the modeling of the diffusion and isotope systematics of the soil gas phase, and the modeling of soil C cycling of the soil solid phase. The spring C chemistry in

the Sagehen groundwater system provides a more complete understanding of how the isotopic and temporal nature of soil process impacts catchment hydrochemistry.

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