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Isotope variations in a Sierra Nevada snowpack and their relation to meltwater

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Abstract

Isotopic variations in melting snow are poorly understood. We made weekly measurements at the Central Sierra Snow Laboratory, California, of snow temperature, density, water equivalent and liquid water volume to examine how physical changes within the snowpack govern meltwater δ^{18} O. Snowpack samples were extracted at 0.1 m intervals from ground level to the top of the snowpack profile between December 1991 and April 1992. Approximately 800 mm of precipitation fell during the study period with δ^{18} O values between -21.35 and -4.25%. Corresponding snowpack δ^{18} O ranged from -22.25 to -6.25%. The coefficient of variation of δ^{18} O in snowpack levels decreased from -0.37 to -0.07 from winter to spring, indicating isotopic snowpack homogenization. Meltwater δ^{18} O ranged from -15.30 to $-8.05\%_e$, with variations of up to $2.95\%_e$ observed within a single snowmelt episode, highlighting the need for frequent sampling. Early snowmelt originated in the lower snowpack with higher δ^{18} O through ground heat flux and rainfall. After the snowpack became isothermal, infiltrating snowmelt displaced the higher δ^{18} O liquid in the lower snowpack through a piston flow process. Fractionation analysis using a twocomponent mixing model on the isothermal snowpack indicated that δ^{18} O in the initial and final half of major snowmelt was 1.30% lower and 1.45% higher, respectively, than the value from simple mixing. Mean snowpack δ^{18} O on individual profiling days showed a steady increase from -15.15 to -12.05% due to removal of lower δ^{18} O snowmelt and addition of higher δ^{18} O rainfall. Results suggest that direct sampling of snowmelt and snow cores should be undertaken to quantify tracer input compositions adequately. The snowmelt sequence also suggests that regimes of early lower δ^{18} O and later higher δ^{18} O melt may be modeled and used in catchment tracing studies. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Snowmelt; Environmental isotopes; Watershed processes; Mixing; Flow paths

1. Introduction

Investigations of snow accumulation and melt processes have typically involved studies of snow meta-

morphism (Giddings and LaChapelle, 1962; de Quervain, 1963; Sommerfeld, 1983; Colbeck, 1987), movement of meltwater through snowpacks (Colbeck, 1979; Jordan, 1983; Marsh and Woo, 1984, 1985; Feng et al., 2001), quantification of energy balance components (Anderson, 1968; Price and Dunne, 1976; Male and Granger, 1981; Sauter and McDonnell, 1994; Marks and Dozier, 1992; Tarboton et al., 1995) and glacier studies (Nijampurkar and Rao, 1992; Isaksson and Karlen, 1994; Raben and Theakstone, 1994, 1998).

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During the past two decades, environmental stable isotopes have been applied to basin-scale investigations of hydrologic processes in snowmelt-dominated temperate catchments (Rodhe, 1981, 1998; Sklash, 1990; Bonell, 1993; Cooper, 1998). Early studies investigated snowpack isotopic evolution and evaluated the use of isotopes as tracers. Isotopic data have been used in snowmelt studies together with mixing models to show the predominance of pre-event water in stream runoff (Sklash and Farvolden, 1979; Rodhe, 1981; Christophersen et al., 1984; Stichler, 1987) and to assess the susceptibility of catchments to acidification during spring snowmelt (Bottomley et al., 1986; Maule and Stein, 1990). A combination of hillslope hydrometric and isotopic data has been used to examine specific flow generation mechanisms such as the groundwater ridging hypothesis (Buttle and Sami, 1992), macropore flow (McDonnell, 1990), and saturation overland flow (Wels et al., 1991). Recent hydrological studies have also shown an increase in the combined use of isotopes with chemical tracers such as silica and magnesium (Hooper and Shoemaker, 1986; Obradovic and Sklash, 1987; Maule and Stein, 1990; Wels et al., 1991).

Proper characterization of the isotopic compositions of snowmelt is essential to trace flow paths and for applications to mixing studies. Previous studies have used the isotopic compositions of melted snow cores as input values (Dinçer et al., 1970b; Rodhe, 1981; Christophersen et al., 1984; Bottomley et al., 1986; Cooper et al., 1991). Melted snow cores were found to be depleted (lower) in ¹⁸O and ²H relative to snowmelt samples (Dincer et al., 1970a,b; Meiman et al., 1972; Hooper and Shoemaker, 1986). Investigation of isotopic variation within winter snowpacks has been conducted in the Modry Dul watershed in northern Czechoslovakia (Dinçer et al., 1970b), the Rocky mountains in Colorado (Judy et al., 1970), Weissfluhjoch in Switzerland (Arnason et al., 1972), central Sierra Nevada (Krouse and Smith, 1972), the Bavarian Alps (Stichler, 1987) and the Austre Okstindbreen glacier, Norway (Raben and Theakstone, 1998). These studies indicated that, during the accumulation stage, snowpack levels reflected the distinct isotopic compositions of individual precipitation events. After the snowpacks became isothermal, a combination of snowpack metamorphism processes, snowmelt infiltration, and rainfall resulted in isotopic homogenization of the snowpack. Stichler (1987) found that the initial snowmelt was depleted in the heavier isotope due to fractionation as compared to later melt. This was attributed to the heavier isotope preferentially remaining in the condensed solid snow phase during initial melt. Consequently, the final snowmelt from the ¹⁸O enriched snowpack together with ¹⁸O enriched late spring rainfall was enriched in the heavier isotope. These temporal variations in isotopic compositions are missed when isotopic compositions of melted snow cores are used as tracer inputs in catchment studies.

Isotopic fractionation occurs during many physical, chemical and biological processes. Elements with low atomic numbers may have isotopic mass differences that are large enough to cause changes in the relative proportions of the different isotopes of the element in various compounds in response to these processes (Gat, 1981; Kendall and Caldwell, 1998). The isotopic fractionation process results in waters and solutes developing unique isotopic compositions that are related to their sources or processes forming them.

Despite the apparent importance of carefully characterizing snowmelt through the spring freshet, most published studies have not related precipitation and snowpack property measurements (such as snow water equivalent, temperature and liquid water volume) to isotopic measurements of precipitation, pack snowpack levels (height within the snowpack) and snowmelt at high temporal resolutions. A detailed analysis of the interactions between snow level measurements and snow level/snowmelt isotopic compositions is needed to better understand these processes and to assess changes in tracer composition during melt. These data could be used to predict how physical and isotopic tracer composition changes within the snowpack affect the evolving snowmelt isotopic composition. Consequently, the objectives of this study were to: (1) observe the temporal variation of snowpack level isotopic compositions during snow accumulation and melting; (2) link snowpack level isotopic variations to snowpack level measurements such as temperature, liquid water volume and snow water equivalent; (3) compare snowmelt isotopic composition to those of the snowpack levels, and the bulk snowpack; (4) evaluate the extent of intra-event variability in snowmelt isotopic compositions; and (5) quantify the fractionation and isotopic depletion of early season snowmelt.

2. Study area and methods

This study was conducted at a 0.5 ha forest clearing at the Central Sierra Snow Laboratory (CSSL) operated by the Pacific Southwest Forest and Range Experimental Station of the United States Department of Agriculture (USDA) Forest Service. The research facility is west of the crest of the Sierra Nevada, near Soda Springs, California. The study area is located at 39°22′19.5″N and 122°22′15″W at an elevation of 2100 m. Winter temperatures range typically from -20 to 15 °C (McGurk et al., 1988). Winter precipitation is often high (1000-2500 mm) due to prevailing maritime climatic conditions. The snowpack typically accumulates to 5 m depth by early April and remains to the end of May (McGurk, 1986). The comprehensive infrastructure developed to monitor snowpack processes at the Central Sierra Snow Laboratory has described elsewhere (Kattelmann, McGurk, 1986; McGurk et al., 1988).

Precipitation is measured using an Alter-shielded Belfort type gauge. Snowmelt is measured from seven $1.2 \times 2.4 \text{ m}^2$ spatially distributed collectors using tipping buckets located in an underground room within the bedrock beneath the forest clearing (Kattelmann, 1984). Hourly average snowmelt from all the seven collectors are computed to obtain spatially averaged snowmelt depths. Liquid water volume measurements are made using a Denoth meter (Boyne and Fisk, 1987; Brun, 1989). Hydrometeorological data related to snow energy balance are also recorded on an hourly basis.

In the present study, detailed monitoring of the snowpack profile was conducted during the winter of 1991–1992. At approximately weekly intervals between December 11, 1991 and April 17, 1992, a snow pit was excavated to facilitate measurements of snow temperature, density, snow water equivalent and liquid water volume at 0.1 m intervals from the bottom to the top of the pack. The snow pits were located a few feet apart. Snow water equivalent was measured using the standard LaChapelle snow density kit. Snowpack profile samples from these 0.1 m inter-

vals were collected for isotopic analysis. Isotopic samples for precipitation were collected on a snow board and for liquid rainfall a simple bucket collector was used. All snow samples were placed in polyethylene bags and melted at room temperature. Snowmelt was sampled from a single eighth collector, also located in the underground room. Melted snow and water samples were stored in bottles with Polyseal® caps. Water samples were analyzed for δ^{18} O at the United States Geological Survey (USGS) facility, Menlo Park, California. Values reported in this paper are in the standard per mil (%o) notation, relative to VSMOW (Craig, 1961); analytical precision is 0.05\%. Fresh snow densities were measured on a snow board throughout the study period. A sequential sampler consisting of fourteen 250 ml containers was used to monitor temporal variations in meltwater isotopic composition within individual snowmelt events.

Hourly precipitation water equivalent was partitioned into either rain or snow water depending on a temperature threshold to track movement of liquid water within the snowpack. Since there is no precise threshold for such a partitioning (Dingman, 1994) a range of threshold temperatures was explored. Hourly precipitation that fell when prevailing air temperature was greater than the threshold temperature was assumed to be rain; when air temperature was below the threshold temperature, precipitation was assumed to be snow.

A two component isotopic mixing analysis was conducted on the isothermal snowpack to assess the extent of snowpack fractionation. The following assumptions were made for this analysis: (1) snowmelt from the isothermal snowpack is derived from two reservoirs: precipitation input (snow and rainfall) and the snowpack, (2) isotopic composition of these two reservoirs and the snowmelt remains constant over Δt , the time step of analysis. Δt was chosen as the time between adjacent snowpack profiling days. The equations for mass and tracer balance are

$$V_{\rm b} + P - E - M = V_{\rm f} \tag{1}$$

$$V_{\rm h}\delta_{\rm h} + P\delta_{\rm P} - E\delta_{\rm E} - M\delta_{\rm M} = V_{\rm f}\delta_{\rm f} \tag{2}$$

where V_b and δ_b represent the depth of snowpack water equivalent and the mean snowpack isotopic composition, respectively, at the beginning of time

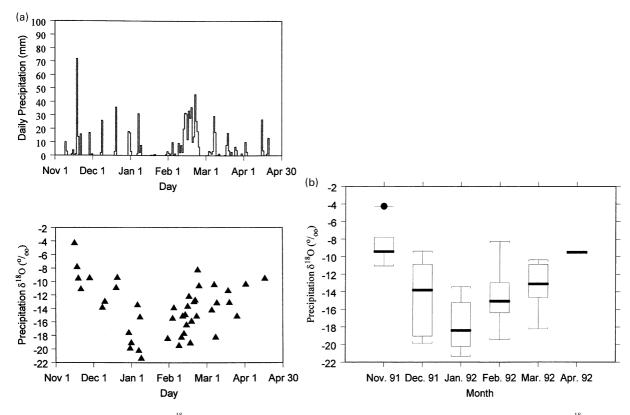


Fig. 1. (a) Daily precipitation and δ^{18} O values (December 24, 1991–April 30, 1992). (b) Monthly box plots of precipitation δ^{18} O values between November 1991 and April 1992.

interval Δt . Variables $V_{\rm f}$ and $\delta_{\rm f}$ are corresponding values at the end of Δt . Variables P, E and M denote the depths of precipitation, evaporation and snowmelt, respectively, over time interval Δt . $\delta_{\rm P}$, $\delta_{\rm E}$ and $\delta_{\rm M}$ represent the average isotopic compositions of precipitation, evaporation and snowmelt, respectively, over time interval Δt .

The various isotopic values in the above equation were obtained for each Δt as amount-weighted average values. For precipitation, individual values of precipitation during the time period Δt were multiplied by their respective isotopic compositions. These were added together and divided by the total precipitation for the time period Δt to yield $\delta_{\rm P}$. For mean isotopic compositions of the snowpack on a certain day, values of snow water equivalent of each 0.1 m snowpack layer were multiplied by the isotopic composition of that layer. These were added together over the entire snowpack profile and divided by the total snow water equivalent of the snowpack on that

day to yield δ_b (or δ_f). Values of δ_E were assumed to be equal to the isotopic composition of the uppermost snowpack layer.

The snowmelt isotopic composition from the twocomponent mixing model is:

$$\delta_{\rm M} = (V_{\rm b}\delta_{\rm b} + P\delta_{\rm P} - E\delta_{\rm E} - V_{\rm f}\delta_{\rm f})/M \tag{3}$$

The two-component mixing procedure described above does not account for fractionation processes occurring within the snowpack. Consequently, snowmelt $\delta^{18}O$ ($\delta_{\rm M}$) obtained from Eq. (3) will represent the two-component mixing output from a non-fractionated snowpack. Model-predicted $\delta^{18}O$ was compared with the observed snowmelt $\delta^{18}O$ value for the time period Δt . The observed $\delta_{\rm M}$ for a particular Δt was also obtained as an amount-weighted average value. Daily snowmelt amounts (average of all seven collectors) were multiplied by the corresponding snowmelt isotopic composition, summed over the time period Δt and divided by the total

Table 1
Monthly precipitation partitioned as rain and snow components (Central Sierra Snow Laboratory, California, November 1, 1991–April 30, 1992)

Month	Rain (mm)	Snow SWE (mm)	Total precipitation (mm)
November	36	103	139
December	0	105	105
January	2	47	49
February	23	323	346
March	25	91	116
April	28	16	44

snowmelt amount during the period. If model-predicted δ^{18} O is different from observed melt value, then 18 O fractionation has occurred during snowmelt. Differences between model-predicted and observed $\delta_{\rm M}$ values should represent the magnitude of fractionation effects.

3. Results

3.1. Precipitation data

Daily precipitation data were recorded in the initial part of the study from November to late December 1991. Measurements of hourly meteorological data commenced from December 24, 1991. Precipitation (water equivalent) of 800 mm was recorded between November 1, 1991 and April 30, 1992 (Fig. 1(a)). A

summary of monthly precipitation totals is provided in Table 1.

3.1.1. Partitioned precipitation

Precipitation was partitioned into snow and rain components using a 2 °C threshold. Several combined rain and snow events occurred during the high precipitation spring months of February and March. Rainfall amounts obtained using the partitioning scheme were similar for February, March and April 1992 (Table 1). Rain-snow partitioning was also conducted using other air temperature thresholds. Rainfall amounts decreased in total magnitude as the threshold was increased from 1 to 4 °C. However, individual rain events matched the timing of events obtained from the 2 °C partitioning threshold. A 2 °C threshold will therefore be adopted for describing liquid water movement through the snowpack.

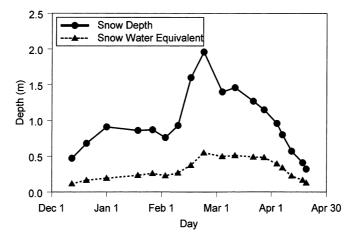


Fig. 2. Maximum snowpack height and snow water equivalent on snow pit profiling days at the Central Sierra Snow Laboratory, California (December 11, 1991–April 17, 1992).

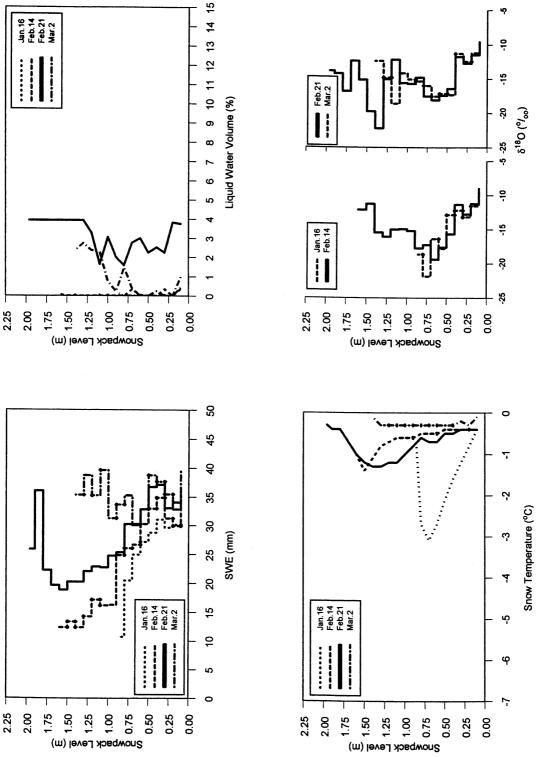


Fig. 3. Snow pit properties during winter and early spring 1992 for January 16, February 14, February 21 and March 2 showing: (a) snow level snow water equivalent (SWE) (mm), (b) snow level temperature (°C), (c) snow level liquid water volume (%) and (d) snow level (%o).

3.1.2. Precipitation $\delta^{18}O$

Precipitation δ^{18} O values ranged from -21.35 to -4.25% (Fig. 1(a)). Monthly box plots of δ^{18} O values of individual precipitation samples are shown in Fig. 1(b). The horizontal line within the box represents the median value, length of the box represents interquartile range, and whiskers at upper and lower extremities are located at 1.5 times the interquartile range. Solid circles represent outliers. November precipitation events had higher δ^{18} O values than the following months with δ^{18} O values ranging from -11.05 to -4.25% (Fig. 1(b)). Precipitation δ^{18} O values in December ranged from -19.85 to -9.35%. After a 36 mm precipitation with high $\delta^{18}O = -9.35\%$ on December 19, precipitation δ^{18} O values remained low until the end of February (Fig. 1(a)).

3.2. Snowpack processes

Snowpack reached a maximum depth of 1.96 m (550 mm SWE) on February 21 (Fig. 2). Maximum rate of snowpack accumulation (25 mm day⁻¹) occurred between February 14 and 21 when 0.175 m SWE was added to the pack. Peak snowpack depletion of 22 mm day⁻¹ SWE occurred between April 4 and 9. Snowpack depth diminished rapidly from 0.96 m on April 1 to 0.32 m on April 17, the final snowpit profiling day. Although ice layers were observed in the snowpack in this study, no detailed monitoring of ice layers was undertaken.

3.2.1. Winter and early spring snowpack processes

Snowpack properties with interesting variations in winter and early spring are shown for January 16, February 14 and 21, and March 2 in Fig. 3. Values are plotted for the individual 0.1 m levels sampled from the ground surface to the top of the snowpack. The uppermost level may be less than or equal to 0.1 m.

Snowpack SWE values of individual 0.1 m levels were mostly less than 30 mm and generally decreased from ground level to the surface on January 16 (Fig. 3(a)). SWE values on February 14 exceeded January 16 values at all levels. Snowpack SWE continued to increase from February 14 to March 2. Maximum snowpack height was 1.96 m on February 21. The SWE peak of 36 mm at the 1.9 m level on this day

resulted from precipitation. The SWE peak on February 21 appeared as multiple peaks at lower levels on March 2 (Fig. 3(a)). Translation of spikes to lower levels accompanied by decrease in snowpack height and increase in SWE in lower layers under additional precipitation inputs between February 14 and 21 suggest snowpack compaction between February 21 and March 2.

The snowpack showed cooler temperatures ranging between -1 and -3 °C at mid snowpack height on January 16. The snowpack warmed from January 16 to near-isothermal conditions on February 14 with the exception of a few upper snowpack levels that had temperatures close to -1 °C (Fig. 3(b)). The snowpack cooled from February 14 to 21 when temperatures at mid snowpack height fell below -1 °C. The snowpack again warmed after February 21, reaching isothermal conditions on March 2. Snow level temperatures showed minimum values of up to −0.4 °C even after the snowpack became isothermal. Accuracy of the temperature sensor is 0.5 °C (McGurk, 1983) and temperatures less than −0.5 °C may therefore be considered 0 °C. The lower 0.4 m was generally warmer with temperatures essentially at 0 °C.

Liquid water volumes at all snowpack levels were less than 0.43% on both January 16 and February 14 (Fig. 3(c)). The uppermost snowpack levels showed a slug of constant liquid water volume of 3.92% on February 21 as a result of precipitation. Below this slug, the snowpack had three high liquid water volume peaks ranging from 3.00 to 3.82%. On March 2, the magnitudes of liquid water volumes decreased along the profile of the isothermal snowpack. Liquid water volume at the snowpack base decreased from 3.82% on February 21 to 0.97% on March 2 indicating snowmelt removal from the pack.

 $\delta^{18}{\rm O}$ values documented snowpack compaction and infiltration of melt water into the snowpack. $\delta^{18}{\rm O}$ values in the lower snowpack levels were consistently higher than in the upper levels due to higher $\delta^{18}{\rm O}$ values in November precipitation. Before the snowpack became isothermal, $\delta^{18}{\rm O}$ values in the 0.1 and 0.2 m layers ranged from -9.65 to -6.25% and -11.55 to -9.50%, respectively. On January 16, $\delta^{18}{\rm O}$ values decreased from -9.00% at ground level to the snowpack surface with lows of -17.80% and

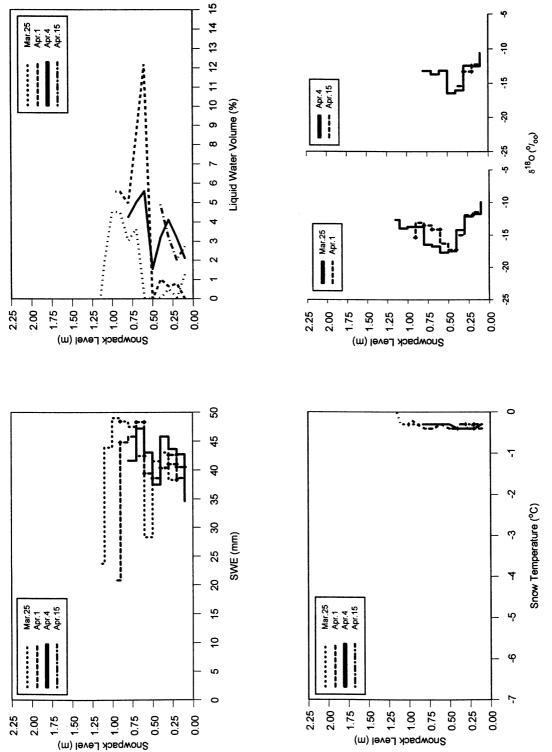


Fig. 4. Snow pit properties during late spring 1992 for March 25, April 1, April 4 and April 15 showing: (a) snow level snow water equivalent (SWE) (mm), (b) snow level temperature (${}^{\circ}$ C), (c) snow level liquid water volume (${}^{\circ}$ 5) and (d) snow level δ 18 O (${}^{\circ}$ 6).

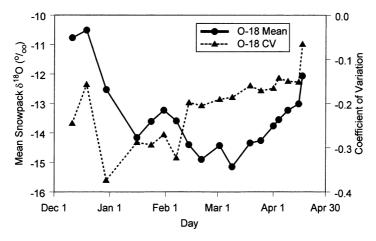


Fig. 5. Mean snow water equivalent weighted $\delta^{18}O$ of snowpack levels showing snowpack enrichment towards end of snowmelt. Reduction in the absolute value of coefficient of variation (CV) of $\delta^{18}O$ values along the snowpack profile on individual snowpit sampling days indicating snowpack isotopic homogenization.

-21.90% at mid snowpack height (Fig. 3(d)). These low δ^{18} O values correspond to the low precipitation δ^{18} O values of late December and early January. On February 14, δ^{18} O showed three peaks and one low (Fig. 3(d)). δ^{18} O peaks of February 14 were also observed on February 21 with the uppermost peak moving down from the 1.5 m level to 1.1 m level. The February 21 snowpack also had a fourth peak of -12.35% at 1.7 m as a result of precipitation. A δ^{18} O low of -22.25% that appeared at the 1.4 m level on February 21 probably resulted from fractionation February precipitation (28.0 mm, of 15 $\delta^{18}O = -19.05\%$ *o*).

The uppermost δ^{18} O peak of February 21 moved down to the 1.4 m level on March 2 without any change in isotopic value (Fig. 3(d)). Infiltrating rain (February 21 rain = 5.1 mm, δ^{18} O = -8.25%) and melt from upper layers with higher δ^{18} O increased the -22.25% low at 1.4 m to -18.60% at 1.2 m on March 2. These translations of δ^{18} O relate well to the snowpack compaction explained earlier (Fig. 3(a)). The February 21 δ^{18} O peak of -12.15% at 1.2 m decreased to -14.15% at 1.1 m on March 2. This resulted from mixing of February 21 rainfall with the previous δ^{18} O of -15.60% at this level. Some contribution may also have occurred from the melt out of uppermost layers of the isothermal snowpack.

3.2.2. Late spring snowpack processes

Snowpack properties with interesting late spring

variations are shown for March 25 and April 1, 4 and 15 (Fig. 4).

Individual levels within the isothermal snowpack showed SWE values mostly exceeding 30 mm between March 25 and April 15. The snowpack showed two SWE peaks at mid snowpack height throughout this period (Fig. 4(a)). Snowpack height decreased rapidly from 1.15 m on March 25 to 0.41 m on April 15. SWE values of lower snowpack levels both increased (when melt infiltration into a snowpack level exceeded melt rate out of it) and decreased during this period.

Temperatures profiles from March 25 to April 15 showed isothermal conditions with all levels effectively at 0 °C at the resolution of the sensor (Fig. 4(b)).

Higher liquid water volume above 0.6 m on March 25 resulted from March 22 to 23 precipitation of 10.7 mm, of which 4.7 mm was rain (Fig. 4(c)). Liquid water volume at each level above 0.1 m on April 1 was greater than that of the corresponding level on March 25 (Fig. 4(c)). The liquid water volume peak of 4.52% at the 1.0 m level on March 25 increased to 12.2% at the 0.6 m level on April 1. This resulted from infiltration of March 30–31 precipitation of 12.8 mm (of which 8.8 mm was rain) together with melt out of upper snowpack levels. Increased liquid water volume at mid-levels also corresponded to the SWE increase at 0.4–0.7 m from March 25 to April 1 (Fig. 4a). On April 4, the 12.2% peak decreased to 5.59% at the same level and

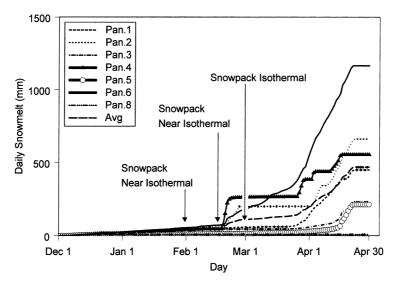


Fig. 6. Cumulative snowmelt amounts measured in the seven tipping bucket collectors between December 1, 1991 and April 30, 1992 showing the spatial and temporal heterogeneity of snowmelt rates and amounts (Central Sierra Snow Laboratory, California).

also produced a 4.11% peak at 0.3 m. The profile for April 15 showed larger liquid water volumes at the snowpack surface. This resulted from April 12–13 precipitation of 30.5 mm (of which 15.0 mm was rain) together with active melt production.

The δ^{18} O peak of -12.65% at 1.1 m on March 25 decreased to -13.05% at 0.9 m on April 1 and to -13.30% at 0.3 m on April 15. Mixing of infiltrating melt from the March 25 peak with snow along the profile level resulted in this decrease. The March 25 δ^{18} O low of -17.70% at 0.6 m increased to -16.45% at 0.5 m on April 4 (Fig. 4(d)). These changes resulted from rainfall on March 23 $(3.6 \text{ mm}, \delta^{18}\text{O} = -15.10\%)$ and on March 30 $(6.0 \text{ mm}, \delta^{18}\text{O} = -10.35\%)$, respectively. There was a trend of linearly increasing δ^{18} O values from the 0.5 m layer to the bottom of the snowpack. The 0.1 m level continued to have higher and distinct isotopic values relative to upper levels with δ^{18} O ranging from -11.22 to -11.10%. The 0.2 m level also had higher δ^{18} O between -12.70 and -9.50%.

3.2.3. Snowpack ¹⁸O enrichment and homogenization Mean isotopic composition of the snowpack was estimated on individual snowpack profiling days. δ^{18} O values of individual 0.1 m snowpack levels were weighted by SWE of the level before estimating

the mean. Mean snowpack isotopic values decreased

from -10.75% on December 11 to -15.15% on March 9 (Fig. 5), reflecting the lower precipitation δ^{18} O between December and early February. After March 9, the mean snowpack δ^{18} O showed a consistent increase to -12.05% on April 17, the final snowpack profiling day.

To investigate snowpack homogenization, the coefficient of variation of δ^{18} O values for all snowpack levels was computed on individual profiling days. Snowpack levels showed maximum coefficient of variation in δ^{18} O of -0.37 on December 30 (Fig. 5). The coefficient of variation of δ^{18} O decreased from -0.32 on February 7 to -0.20 on February 14 indicating snowpack homogenization. This resulted from infiltration of 7.6 mm of rainfall that fell in two spells of 4 mm on February 8 and 9, and 3.6 mm on February 13, with δ^{18} O values of -17.85% and -13.65%, respectively. The coefficient of variation of δ^{18} O decreased further to -0.07 during major snowmelt on April 17. This indicated additional snowpack isotopic homogenization following melt out of the upper levels and snowmelt infiltration into the snowpack (Fig. 5).

3.3. Snowmelt data

Snowmelt recorded from the heterogeneous snowpack exhibited considerable spatial and temporal

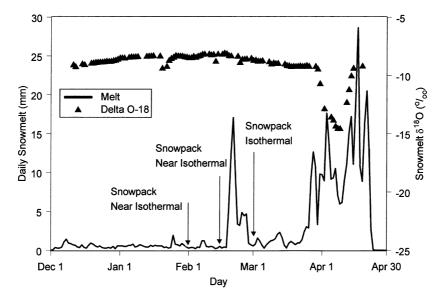


Fig. 7. Daily snowmelt and δ¹⁸O values at the Central Sierra Snow Laboratory, California (December 1, 1991–April 30, 1992).

variation. Snowmelt recorded in the seven collectors between December 1, 1991 and April 30, 1992 totaled 451, 663, 230, 556, 214, 1167 and 9 mm (Fig. 6). Early snowmelt occurred from the snowpack at fairly uniform and low rates (<1 mm day⁻¹), even before the snowpack became isothermal on March 2.

Spatially averaged snowmelt from all the collectors was 16, 19, 75, 79 and 282 mm for December, January, February, March and April, respectively (Fig. 6). A major melt episode of 65 mm occurred between February 19 and 27. Snowpack warming to near isothermal conditions on February 14 combined

Table 2 δ^{18} O ranges of intra-event spring snowmelt samples collected with the sequential sampler, and spatially averaged snowmelt amounts on corresponding days at the Central Sierra Snow Laboratory, California

Day	Minimum δ^{18} O to maximum δ^{18} O $(\%o)$	$\left \delta^{18} ext{O range } (\%e)\right $	Melt amount (mm) (number of snowmelt samples)	
March 30, 1992	−9.30 to −9.15	0.20	3.28 (7)	
March 31, 1992	-9.35 to -9.15	0.20	9.79 (3)	
April 3, 1992	-9.25 to -9.20	0.05	17.65 (4)	
April 6, 1992	-9.25 to -9.15	0.10	9.28 (5)	
April 7, 1992	-9.60 to -9.30	0.30	10.50 (3)	
April 8, 1992	-12.70 to -9.75	2.95	7.08 (8)	
April 10, 1992	-13.70 to -12.60	1.10	6.15 (10)	
April 13, 1992	-14.15 to -13.05	1.10	15.14 (10)	
April 14, 1992	-14.35 to -13.60	0.75	17.21 (9)	
April 15, 1992	-14.45 to -14.30	0.15	11.08 (10)	
April 16, 1992	-14.90 to -14.20	0.70	19.28 (10)	
April 17, 1992	-15.30 to -13.25	2.05	28.64 (30)	
April 20, 1992	-13.25 to -11.15	2.10	16.28 (9)	
April 21, 1992	-12.35 to -10.15	2.20	20.50 (10)	
April 22, 1992	-10.20 to -9.40	0.80	12.93 (6)	
April 23, 1992	-9.75 to -9.25	0.50	2.64 (7)	

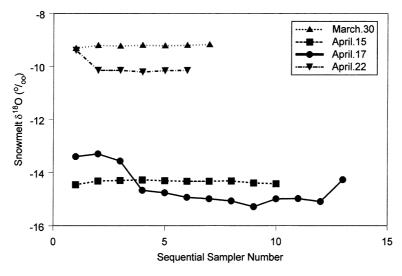


Fig. 8. Sequential sampler measurements of event snowmelt δ^{18} O on March 30 (before start of major melt), April 15 and 17 (during major melt), and April 22 (end of major melt).

with 15.2 mm of rainfall during this period prompted this melt episode. Following this late February snowmelt event, a series of five snowmelt pulses constituting 72% of total seasonal snowmelt occurred between March 24 and April 23 (Fig. 7). These pulses peaked on March 28, April 3, April 14, April 17 and April 21 with maximum snowmelt rates of 12.6, 17.6, 17.2, 28.6 and 20.5 mm day⁻¹, respectively. Snowmelt from these five pulses totaled 337 mm; 51% of the melt from these five pulses occurred in the final snowmelt days between April 12 and 22.

3.3.1. Snowmelt $\delta^{18}O$

Snowmelt δ^{18} O values are obtained from snowmelt from a single eighth collector and do not represent the composite melt signature from all the collectors. Snowmelt δ^{18} O values were high and ranged between -9.25 and -8.85%, and -9.40 and -8.30%, during December and January, respectively (Fig. 7). Snowmelt δ^{18} O values occupied a narrower range of -8.55 to -8.10% throughout February (except for a single lower value of -12.15% on February 21). A similarly high, but slightly broader range of δ^{18} O values was evident in the March snowmelt (-9.35 to -8.35%).

Snowmelt values underwent rapid decrease in δ^{18} O from -9.15% on April 6 to -11.65% on April 8 (Fig. 7). Snowmelt δ^{18} O decreased further from April 9 to 17, ranging between -15.30 and -12.60%. In the

final phase of the snowmelt between April 18 and 27, $\delta^{18}O$ increased from -14.55% on April 17 to -9.20% on April 27 (Fig. 7).

Measurements from the automatic sequential sampler indicated temporal variations of up to 2.95% in δ^{18} O values within individual daily events during snowmelt in late March and April (Table 2). Early snowmelt showed smaller ranges of melt δ^{18} O values in the sequential sampler. Melt δ^{18} O ranges increased during the isotopic decrease (April 10–17) and increase (April 20–23) phases of major snowmelt (Table 2).

Typical intra-event variations of snowmelt δ^{18} O are shown before the start of major melt (March 30), during major melt (April 15 and 17), and toward the end of major melt (April 22) in Fig. 8. Because snowmelt volumes frequently were larger than the capacity of the sequential sampler, δ^{18} O variations throughout the duration of larger melt events could not be recorded. Also, the timing of individual samples in the sequential sampler was not available. On such days, the average of the melt δ^{18} O values is shown in Fig. 7.

3.3.2. Source of early snowmelt

Cumulative snowmelt with high δ^{18} O totaling 250 mm occurred from the snowpack between December and early April; of this, 111 mm occurred

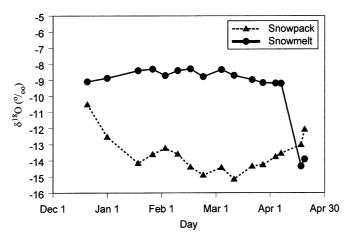


Fig. 9. Comparison of snowpack and snowmelt δ^{18} O values.

before the snowpack became isothermal on March 2. This may be accounted for as follows. Total precipitation of 139 mm fell in November. δ^{18} O values are available only for samples after November 15. Precipitation of 120 mm fell from November 17 to 27 with high δ^{18} O values ranging from -11.05 to -4.25%o. November precipitation events resulted in high δ^{18} O values in the lower snowpack layers. Precipitation of 36 mm on December 18 also had a high δ^{18} O value of -10.10%. Rainfall was practically absent during December and January (2 mm) based on the 2 °C partitioning threshold. Comparison of δ^{18} O of early snowmelt with those of the snowpack levels indicated that early snowmelt was derived from the lower portion of the snowpack with high δ^{18} O. Snowpack temperature profiles showed that the lowest 0.1 m snowpack level was essentially at 0 °C throughout the study period. Early snowmelt occurred from lower snowpack levels through ground heat flux from the underlying bedrock and from November rainfall retained in liquid form. Average daily values of ground heat flux fall in the range of 0-4.6 W m⁻² (Maidment, 1993). Ground heat flux of 1-5 W m⁻² can produce between 7.9 and 39.3 mm month⁻¹ of snowmelt. Between December and March, therefore, ground heat flux contributions from 32 to 157 mm is possible. Between mid-February and the end of March, 100 mm of precipitation fell with high δ^{18} O values resulting in increased liquid water content within the snowpack (Figs. 3(c) and 4(c)). This liquid water routed to the base of the snowpack through macropore networks (Kattelmann, 1985) together with melt out of ice layers within the snowpack may also have contributed to high snowmelt $\delta^{18}O$. Therefore, combined high $\delta^{18}O$ rainfall together with ground heat flux effects can account for the cumulative amount of early snowmelt with high $\delta^{18}O$.

3.3.3. Snowpack versus snowmelt $\delta^{18}O$

Snowmelt δ^{18} O was much higher than that of the snowpack until April 9, with maximum differences of 6.45‰ on March 9 (Fig. 9). For this comparison daily snowmelt δ^{18} O values were used on snowpack profiling days. On days with multiple snowmelt δ^{18} O values from the sequential sampler, the average melt δ^{18} O was used. During major snowmelt, melt δ^{18} O became lower than the snowpack by 1.34 and 1.85‰ on April 15 and 17, respectively.

3.4. Isotope fractionation analysis

An initial two-component analysis using average snowmelt amounts measured in the seven collectors was not successful due to the large variability in snowmelt amounts. Independent estimates of snowmelt amounts between successive profiling days were then obtained from the snowpack mass balance Eq. (1) using *M* as the unknown quantity. These snowmelt amounts were used in the two-component analysis. For estimating snowmelt amounts using Eq. (1), evaporation loss was first computed using hourly hydrometeorological data and energy balance

Table 3
Two-component mixing computed and observed amount-weighted snowmelt δ^{18} O values between adjacent profiling days in the isothermal snowpack (Central Sierra Snow Laboratory, California, March 2–April 17, 1992)

Period	Computed snowmelt δ^{18} O (%)	Observed snowmelt δ^{18} O (% $_{c}$)	
March 2–9	-3.97	-8.60	
March 9-19	-20.71	-8.80	
March 19-25	-16.85	-9.05	
March 25-April 1	-15.59	-9.20	
April 1–4	-15.02	-9.20	
April 4–9	-14.12	-9.70	
April 9–15	-12.27	-13.60	
April 15–17	-15.92	-14.45	

techniques. Details are presented elsewhere (Unnikrishna, 1996). Evaporation loss totaled 4.5 mm between January and March, and a net condensation of 1.0 mm occurred in April. Net condensation can occur with higher relative humidities and wind speeds. These values compare with those of Baldwin and Smith (1989), who obtained a total evaporation amount of 8.6 mm between January and March of 1971 and 3.3 mm in April 1971. Evaporation loss was therefore far smaller than the total precipitation of 800 mm recorded between November 1, 1991 and April 30, 1992. Although evaporation loss was minimal, spatially averaged snowmelt from the seven collectors (471 mm between December 1, 1991 and April 30, 1992) was considerably smaller than the precipitation amount, suggesting that the snowmelt collectors underestimated melt amounts.

The two-component analysis was conducted using snowmelt amounts obtained from closure of the snowpack mass balance. Snowmelt δ^{18} O obtained from this two component analysis are shown in Table 3 together with observed snowmelt δ^{18} O. Observed snowmelt δ^{18} O after March 2 and before early April was generally higher than that of computed snowmelt. This suggests that the melt was derived through pistonflow displacement of high δ^{18} O liquid water from the lower snowpack layers during this period (Fig. 4(d)). Observed snowmelt δ^{18} O was 1.30% lower than computed snowmelt between April 9 and 15. This was also the period when snowmelt rates were high and there was isotopic homogenization indicating more uniform isotopic mixing conditions within the snowpack (Fig. 5). Between the final snowpack profiling days April 15 and 17, observed snowmelt δ^{18} O was 1.45% higher than the computed snowmelt.

Therefore, the model derived estimates of initial fractionation ¹⁸O depletion and later fractionation ¹⁸O enrichment are 1.30 and 1.45%, respectively.

For this analysis, δ^{18} O of snow surface at the start of each Δt was taken as the $\delta_{\rm E}$ term in Eq. (3). To assess the effect of $\delta_{\rm E}$ on computed melt δ^{18} O, we also repeated the analysis for each of the following combinations: $\delta_{\rm E}$ as snow surface δ^{18} O at the end of each Δt ; $\delta_{\rm E}$ as average snow surface δ^{18} O at the start and end of each Δt ; and with evaporation E equal to zero. Because the magnitude of E was small relative to other mass balance terms, changes in $\delta_{\rm E}$ had virtually no effect on the magnitude of fractionation changes reported above. With E=0, 18 O depletion and enrichment changed slightly to 1.24 and 1.41‰, respectively.

Because precipitation δ^{18} O is highly variable and constitutes the single term with the most uncertainty in the two component analysis, a sensitivity analysis was performed. When precipitation δ^{18} O was varied from -6 to -12% for April 9–15, 18 O depletion decreased from 2.45 to 0.40%. Similar sensitivity analysis performed by varying precipitation δ^{18} O from -6 to -12% for April 15–17 resulted in 18 O enrichment increasing from 1.35 to 1.55%. Because summer precipitation δ^{18} O values are more likely to be higher than those at other times of the year, the magnitude of 18 O depletion within the snowpack appears to be between 1.30 and 2.45%; and the magnitude of 18 O enrichment appears to be between 1.35 and 1.45%.

Fractionation between April 17, the last snowpack profiling day and final melt out was analyzed using a simple mixing analysis. The last snowmelt δ^{18} O of -9.20% was recorded on April 27. Rainfall between

April 17 and 27 (12.5 mm) was not sampled for δ^{18} O. Using final snowpack SWE (126.5 mm) with the corresponding isotopic value (-12.06%) and assuming a rainfall δ^{18} O of -9.30%0 measured on April 12, the predicted snowmelt δ^{18} O was -11.80%0. This suggests a 2.60%0 enrichment in the final melt out. Sensitivity analysis conducted by varying precipitation δ^{18} O from -6 to -12%0 showed that 18 O enrichment increased from 2.35 to 2.85%0.

4. Discussion

Precipitation occurred as both snow and rain during the study period. Precipitation isotopic compositions were high in November, low during winter and high again in late spring as seen in other studies (Krouse and Smith, 1972; Stichler, 1987; Mast et al., 1995; Shanley et al., 1995; Nijampurkar and Rao, 1992). Box plots of monthly δ^{18} O values between January and April showed that the curve joining the median line for successive months followed the trough portion of the sinusoidal pattern normally seen in annual time series of precipitation isotopic compositions (Yurtsever and Gat, 1981; Stichler, 1987).

Temperature changes caused alternate cooling and warming of the snowpack between mid-January and March 2, when the snowpack finally became isothermal. Freeze-thaw cycles together with compaction effects and macropore networks resulted in a heterogeneous snowpack. Berg (1982) observed high density transitions within snowpacks at this site following formation of crusts on non-snowfall winter days. Kattelmann (1985) reported macropore networks with diameters between 10 and 20 mm within snowpacks in the Sierra Nevada. Flow-fingers with similar diameters transmitting water in 15-25% of the cross-sectional area have also been reported at this site by McGurk and Marsh (1995). During this process, flow-fingers may be near 0 °C while the surrounding area may be colder and have lower liquid water content. Raben and Theakstone (1998) also report the development of unstable vertical channels during the early stages of melting in the Austre Okstindbreen glacier near the Arctic Circle. Because of snowpack heterogeneity and highly variable meltwater flux, single measurements of snow level properties may involve some error and may not represent the average value of the property for that level.

Early snowmelt with high δ^{18} O values began in December before the snowpack became isothermal and continued into early April. Comparison of early snowmelt δ^{18} O with snowpack values indicated that this melt occurred from the lower snowpack layers. These snowpack layers had higher δ^{18} O values from November precipitation. Minor increase in δ^{18} O values may also have occurred through depth hoar formation resulting from fractionation during upward transport of vapor flux. Densities of some lower snowpack levels in December were less than 300 kg m⁻³, the value normally reported in snowpacks with depth hoar (Sommerfeld et al., 1991). However, maximum snowpack temperature gradients in our study of 0.12 °C cm⁻¹ were far below the 1 °C cm⁻¹ required to promote depth hoar (Friedman et al., 1991; Sommerfeld et al., 1991). Mass balance studies showed that melt out of lower snowpack layers through ground heat flux together with high δ^{18} O rainfall after mid-February contributed to early snowmelt with high δ^{18} O. Although the effect of ground heat flux is considered negligible, its cumulative effect can be significant over a season (Male and Gray, 1981; Stichler, 1987).

Maximum δ^{18} O changes were observed in the snow surface level, which was subject to the combined effects of precipitation, evaporation and condensation, and melt out. Higher snowpack levels underwent compaction following large snow precipitation events. This resulted in pure translation of some upper level δ^{18} O values into the snowpack with practically no change in value. At lower snowpack levels, δ^{18} O values changed from mixing of infiltrating rain water with local isotopic values and with compacting upper snowpack levels. When the snowpack became isothermal, isotopic values at lower levels were influenced more by mixing of local δ^{18} O with that of meltwater infiltrating from upper snowpack layers.

During the phase of early high $\delta^{18}O$ snowmelt derived from lower snowpack layers and infiltrated rainfall, snowmelt $\delta^{18}O$ was higher than the snowpack with maximum differences of 6.45‰. During major snowmelt, meltwater $\delta^{18}O$ became lower than the snowpack by 1.34 and 1.85‰ on April 15 and 17, respectively. Similar differences between snowpack

and snowmelt isotopic compositions were also observed by Hooper and Shoemaker (1986) and Shanley et al. (1995). Hooper and Shoemaker (1986) observed snowmelt δD up to 40% heavier than the snowpack.

We observed snowpack isotopic homogenization over the course of snowmelt as has been reported in earlier studies (Dinçer et al., 1970b; Arnason et al., 1972; Herrmann et al., 1981; Stichler, 1987; Raben and Theakstone, 1998). Snow temperature profiles showed near isothermal conditions on January 31 and February 14. These warming events combined with continuous moisture exchange of infiltrating rainfall and snowmelt with snowpack levels resulted in homogenization of δ^{18} O values along the snowpack profile.

After the snowpack became isothermal, high δ^{18} O values in snowmelt persisted up to early April due to piston-flow displacement of high δ^{18} O liquid water from lower levels by infiltrating snowmelt. In the two-component model analysis, therefore, modelderived δ^{18} O melt values were lower than observed melt values. Ice layer growth ceases when the snowpack is wet and isothermal (Marsh and Woo, 1985). As the melt increased in mid-April, mixing conditions within the snowpack became more uniform as indicated by the isotopic homogenization and the two-component model predicted melt δ^{18} O values became closer to observed values. Snowmelt δ^{18} O values decreased from April 6 to 17 reflecting the lower δ^{18} O values of upper snowpack layers. Similar melt out of upper layers and snowmelt infiltration into the snowpack has been documented recently using ammonium chloride in an investigation of NO₃ sources to surface waters (Bales et al., 1993; Williams et al., 1996). This phase of initial low δ^{18} O snowmelt outflow from the snowpack has also been observed in other studies (Arnason, 1981; Stichler, 1987; Maule and Stein, 1990; Shanley et al., 1995). Isotopic fractionation during initial snowmelt caused the heavier isotope to be preferentially concentrated in the condensed solid snow phase, producing ¹⁸O depleted snowmelt. Following additions of high δ^{18} O rainfall and removal of low δ^{18} O snowmelt, mean snowpack δ^{18} O values on successive profiling days showed a steady increase. Such a trend of increasing δ^{18} O and δD in snowpacks during melt has been documented (Herrmann et al., 1981; Rodhe, 1981; Stichler, 1987;

Cooper, 1998; Raben and Theakstone, 1998). During the second half of major snowmelt from April 18 to 27, meltwater had high δ^{18} O (Arnason, 1981; Stichler, 1987). Individual melt episodes showed both small and large variations in δ^{18} O values.

Two-component mixing calculations for the isothermal snowpack showed a 1.30 to 2.45% decrease in $\delta^{18}O$ in the initial half of major snowmelt through isotopic fractionation. Isotopic mixing calculations beyond the final snowpack profiling day also showed ^{18}O enrichment of 2.60% in the final melt out. The equilibrium isotopic fractionation factor for phase transition between solid (ice) and liquid water is 1.0035 at 0 °C (Gat, 1981). Consequently, the solid phase of water would be more enriched in ^{18}O than the liquid phase by 3.50%. Our values of fractionation separation compare favorably with this estimate.

Although several studies of catchment flow generation have been conducted in snowmelt dominated environments, only a few studies have used actual meltwater isotopic compositions to characterize the input (Hooper and Shoemaker, 1986; Obradovic and Sklash, 1987; Maule and Stein, 1990; Wels et al., 1991; Buttle and Sami, 1992; Ogunkoya and Jenkins, 1993; Unnikrishna, 1996). Sampling only snow cores may lead to gross errors in the characterization of basin tracer input compositions. Isotopic fractionation effects cause early snowmelt to be depleted in the heavier isotope. Also, snowpack isotopic compositions are continuously modified by late spring rainfall toward heavy isotope enrichment. Therefore, late snowmelt becomes enriched in the heavier isotope. These temporal dynamics of snowmelt isotopic compositions are not captured by sampling snow cores. The present study highlights the importance of measuring the isotopic composition of snowmelt for describing the isotope input in catchment studies. Significant temporal variations in isotopic compositions may occur during large snowmelt events. Therefore sequential sampling of snowmelt several times during such events becomes necessary. Because we sampled snowmelt in a single collector for isotopic analysis, results from this study do not specifically address spatial heterogeneity in snowmelt δ^{18} O values. Raben and Theakstone (1998) found that horizontal variations of snowpack δ^{18} O compositions were far lesser than vertical variations. However, snowpack heterogeneity suggests that variations of

melt δ^{18} O may also exist spatially. Therefore melt samples must be representative of elevation, vegetation and slope within catchments. In a recent study, Gotu-Azuma et al. (1997) showed that sites with wind scour have higher δ^{18} O values than non-scoured sites. This results from the removal of lighter δ^{18} O winter precipitation from the scoured sites. Snow accumulation amounts also have an effect on δ^{18} O values. Years with smaller snow accumulation have snowpacks with higher δ^{18} O values (Schlosser, 1999). Snowmelt dominated environments demand a more rigorous and extended sampling schedule over several months as compared to rainfall influenced regions (McDonnell, 1990). This study confirms that specific sequences of early low δ^{18} O and late high δ^{18} O snowmelt can be anticipated at most sites with deep snowpacks. These sequences should provide sufficiently distinct isotopic inputs for a useful interpretation of catchment flow processes.

5. Conclusions

Detailed monitoring of a winter snowpack in the Central Sierra Snow Laboratory, California, documented minor snowmelt between December 1991 and early April 1992 with high δ^{18} O values that matched δ^{18} O values of the lower snowpack levels. Combined isotopic and snowpack temperature profile interpretations indicated that a combination of ground heat flux from underlying bedrock and high δ^{18} O rainfall contributed to this early snowmelt. Mass balance studies verified that water equivalent depths in the lower snowpack levels together with high δ^{18} O rainfall after mid-February were sufficient to sustain snowmelt before the snowpack became isothermal. The snowpack temperature profiles indicated freezethaw cycles during peak winter. These cycles prompted crust and ice level development and contributed to snowpack heterogeneity. Measurements of liquid water volume documented preferential flow of rainwater through the pack and into the lower levels. After the snowpack became isothermal and major snowmelt began, the snowpack showed overall ¹⁸O enrichment. Also, isotopic mixing became more uniform as indicated by snowpack isotopic homogenization. Fractionation analysis using a two-component isotopic mass balance model on the isothermal

snowpack showed that snowpack ¹⁸O enrichment resulted from fractionation removal of ¹⁸O depleted snowmelt in the first half of major snowmelt in April. Melt out of the isotopically enriched snowpack together with high δ^{18} O rainfall resulted in a consistent increase in δ^{18} O in the second half of major snowmelt. This study has not addressed the spatial variability in snowmelt δ^{18} O values. However, such variability can be expected in catchments where marked differences in vegetation and topographic features can induce changes in snow depositional patterns and snowmelt rates, and contribute to differences in snowmelt δ^{18} O values. To capture the snowmelt δ^{18} O melt input values in such situations, multiple snowmelt collectors may be located in snow drift and non-drift areas, and other regions with differences in vegetation and catchment topography. Snowmelt occurring within catchments with deep snow drifts is also expected to have distinct regimes of early low δ^{18} O and late high δ^{18} O values during major melt. These snowmelt regimes should permit effective flow tracing. Large δ^{18} O variations observed within individual melt episodes highlight the need for frequent sampling of snowmelt to arrive at appropriate amount-weighted tracer input values. Where costs become prohibitive, fewer composite snowmelt samples may be collected during the melt event.

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