

Using Rare Earth Elements as Chemical Tracers in Snow Studies

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ABSTRACT

We used rare earth element (REE) tracers to study snowpack dynamics at the Sleepers River Research Watershed, Vermont. REEs are ideal tracers for snow because they have very low natural abundances in snow, are soluble in natural precipitation, and can be detected at part-per-trillion concentrations. There are 14 different REEs available to mark snow layers. These elements have not previously been used as tracers in snow, and our preliminary observations confirmed their usefulness.

Fresh snow was sampled after each major storm during the winter of 1997–1998, and chemical analyses of five REEs (Ce, Dy, Pr, Tm, and La) show that their natural background ranges from 1 to 10 ppt (ng/L). After each storm, spike solutions of these REEs were sprayed onto the snowpack overlying a lysimeter and an adjacent test area. Snow cores were taken from the test area before the main melt event. The distributions of REEs in the snow cores clearly mark the snow layers on which the tracers were applied. Some fraction of each tracer was lost from the snowpack before the main melt, but there was no sign of bleeding throughout the snowpack. The tracers near the top of the pack are eluted out earlier than tracers near the base, and refreezing of meltwater, as it moves through subzero sections of the snowpack, may cause some of the high tracer concentrations we observe at low melt rates. This work is part of a larger study aimed at understanding stable isotopic variability and snow solute chemistry in snowpacks and in snowmelt.

Key Words: Rare earth elements, tracers, snowmelt, snowpack.

INTRODUCTION

Snowmelt is an important component of spring runoff, and understanding its isotopic variability is essential for separating the spring hydrograph using the isotope mass balance approach (Rodhe 1981; Hooper and Shoemaker, 1986; Kendall et al., 1995; Unnikrishna, 1996). Experimental studies have shown that the isotopic composition of snowmelt can be significantly different from that of the original snow (Hooper and Shoemaker, 1986; Herrmann et al. 1981), because isotopic fractionation may occur during the melting process. Studies of snowmelt chemistry show that solute concentrations vary diurnally (Davis, 1991; Bales et al., 1993), and that the concentration in the meltwater diminishes as the melting of the pack proceeds. For example, the initial 20% of meltwater may contain up to 80% of the total solutes in the original snow (Johannessen and Henriksen, 1978; Colbeck, 1981; Bales et al., 1989).

The behaviors of isotopic and chemical tracers differ in several ways, but both are affected by physical processes occurring within a snowpack (such as snow metamorphism), by the melt history, and by the hydrological properties of the snow (such as its permeability and the presence of flow channels or ice layers). However, the relationship between the melting conditions and the chemical and isotopic composition of snowmelt has not been determined (Shanley et al., 1995a; Smith, 1997).

We are using both chemical and isotopic tracers to study water and solute movement and redistribution within a snowpack. During the winter of 1997–1998, we used rare earth elements as chemical tracers and collected samples of fresh snow, snow pit and snow core samples, and snowmelt at two field sites, Sleep-

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ers River Research Watershed (SRRW) in Vermont and Central Sierra Snow Laboratory (CSSL) in California. In this paper we present our preliminary results from Sleepers River Research Watershed and discuss the usefulness of REEs for studying snow dynamics.

METHODS

REE tracers

We use the term rare earth elements (REEs) to refer to Lanthanum (^{57}La) and the Lanthanide elements ($Z=58-71$). These elements have several attributes that make them particularly useful for snowmelt studies. First, REEs have very low natural abundances (typically several parts per trillion). Other researchers have used major ions found in snow, such as Na^+ , NO_3^- , SO_4^{2-} , and Cl^- , to study solute fluxes from melting snow (Cragin et al., 1996; Bales et al., 1993; Shanley et al., 1995a). Some of these ions are responsible for the ionic pulse entering streams in the early spring and can adversely impact environmental systems (Johannessen and Henriksen, 1978). However, these ions are already abundant in natural snow and to use them as tracers, one needs to understand their distribution in the snowpack or, if applying them, use concentrations significantly higher than their concentrations in clean snow. High concentrations, however, depress the freezing point of water and may change the melting conditions of the snow. With REEs, it is possible to prepare a tracer solution that has an ionic strength similar to that of clean snow, yet has tracer concentrations four to five orders of magnitude greater than their background concentration in clean snow. We can, therefore, achieve high signal-to-noise ratios without altering the properties of the snow itself.

Second, the 14 available REEs have very similar chemical properties; they can, therefore, be expected to behave similarly in snow. The large number of elements allows us to mark many different snow layers. Experimental work has shown that elution efficiency from a snowpack is different for different chemical species, often following the order of $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ for anions (Tranter et al., 1986) and $\text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$ for cations (Brimblecombe et al., 1987). For elements to be useful as tracers for individual snow layers, their chemical properties (e.g., solubility, ionic radius, and valence) should be sufficiently similar that the order of elution is caused not by chemical differentiation among the elements, but rather by the position of the tracer in the pack and the processes related to snow metamorphism and melting.

Third, due to their electronic configuration and oxidation state (III^+) all REEs show similar solubil-

ity in aqueous systems. The REE chlorides, nitrates, and sulfates are all readily soluble. In the pH range of natural snow (pH 4 to 6), REEs do not precipitate as hydroxides or as carbonates for the spike solution concentrations we used (25 ppm, Spahiu and Bruno, 1996). In the absence of other strong ligands, the REEs exist in the form of their aquo-complexes.

Fourth, REEs can be analyzed efficiently by inductively coupled plasma mass spectrometry (ICP-MS), with detection limits below 1 part per trillion and a working range of up to eight orders of magnitude. All 14 REE elements can be analyzed simultaneously in about four minutes per sample. The high sample throughput is necessary to accommodate the large number of samples collected for each experiment.

Field site

Sleepers River Research Watershed, located in Danville, Vermont, is a 111-km² subbasin of the Passumpsic River Basin (Fig. 1). Meteorological data have been collected at our field site, the Snow Research Station, since 1968. SRRW is one of five WEBB (Water, Energy and Biogeochemical Budgets) sites being studied by the USGS in collaboration with universities, CRREL (Cold Regions Research Engineering Laboratory), and other federal agencies. As such, SRRW is instrumented to measure a variety of weather parameters essential for interpreting our data. These include temperature, precipitation, wind speed, humidity, incoming and outgoing shortwave radiation and outgoing longwave radiation.

The Snow Research Station is at an elevation of 552 m and receives about 100–200 cm of snow each season, corresponding to a snow water equivalent of about 30–50 cm. Snow starts accumulating in late November and has usually melted by late April. Snowpack studies conducted at Sleepers River show that the pack is highly layered (Albert and Hardy, 1993).

Two lysimeters, each about 3 m in diameter, are used to measure meltwater volume and flow rate at SRRW. The meltwater travels from the melt pan via PVC pipe to a hut where the melt rate is measured by tipping buckets. Each bucket has a volume of 175 mL and the buckets are instrumented so that each tip is counted, timed, and the data are recorded on a datalogger. Based on recorded snow water equivalent data and assuming about 1 m of snow at peak accumulation, we expected about 2,200 L from the west lysimeter that we used for our experiment. The volume measured this year was 2666 L.

Field work

We collected samples of every large snow and rain event to obtain background concentrations of

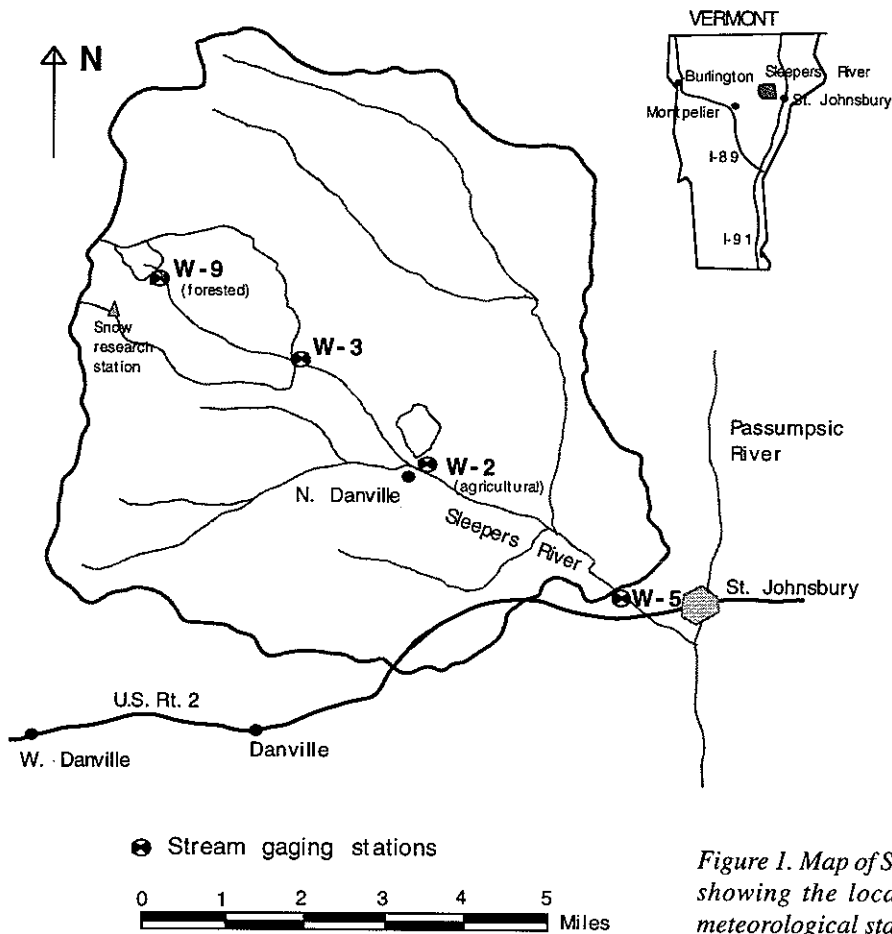


Figure 1. Map of Sleepers River Research Watershed showing the location of streamflow gaging and meteorological stations (from Shanley et al. 1995b).

REEs and we dug a snow pit during each visit to the Snow Research Station to determine where ice lenses were located and to see how the snowpack was compacting. Figure 2 is a schematic that shows the growth and decay of the pack at SRRW.

After each major snowstorm, an aqueous solution of a rare earth element (at approximately 25 ppm, with chloride as the anion) was sprayed on the snow surface over the west lysimeter. This was done using a compressed air sprayer fitted with a fine spray nozzle. We evenly and lightly sprayed the entire snow surface over the lysimeter. The concentration and amount of each spike solution sprayed is listed in Table 1. Dysprosium (Dy) was applied on 16 December, thulium (Tm) on 21 January, cerium (Ce) on 18 March and praseodymium (Pr) on 25 March (Fig. 2 and see Table 1 for additional information). Lanthanum (La) was used as a common tracer in each of the REE spike solutions. By using a common tracer, we can test whether

chemical differentiation (precipitation, absorption, etc.) occurs among the different REEs. If chemical differentiation does not occur, the total amount of La in each melt sample should equal the sum of all the

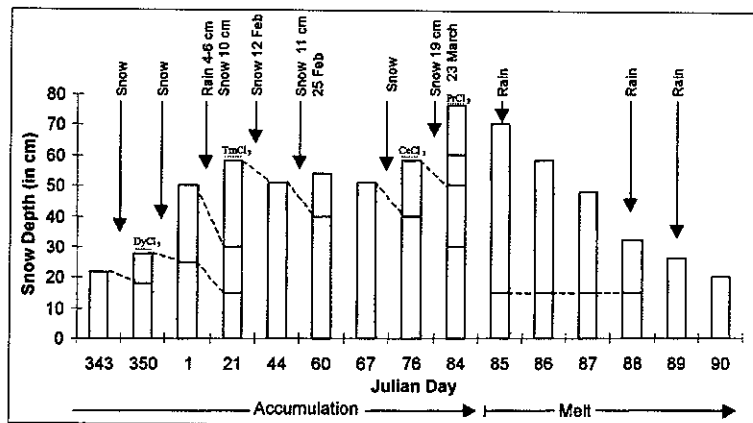


Figure 2. Sketch of the growth and decay of the snowpack and the dates when the tracers were applied at Sleepers River Research Watershed. Solid lines through the column indicate ice layers. Dashed lines between columns indicate the location of the former surface layer.

Table 1. Information about the amount and concentration of REEs used.

Tracers applied	Date applied	Julian date	Concentration (ng/L)	Volume applied (L)	Snow depth (cm)
Lanthanum	common	common	9.9×10^7	3.72	
Praseodymium	25 Mar 1998	84	4.0×10^7	0.35	75
Cerium	18 Mar 1998	77	2.1×10^7	0.82	58
Thulium	21 Jan 1998	21	2.8×10^7	0.80	57
Dysprosium	16 Dec 1997		2.3×10^7	1.75	28

other REE tracers. We also sprayed the same tracer solutions on a 0.5-m² area away from the lysimeter. After two tracers were applied, snow cores were taken from this area to study how the tracers

migrated within the snowpack before the onset of the main melt.

Snowmelt was collected at the outflow port of the lysimeter. Our goal was to collect every fiftieth tipping bucket sample from the early melt and every hundredth from the high flow main melt period. Unfortunately, the earliest events were considerably undersampled (Fig. 3a and b). For example, during the January thaw, water flow was measured for 13 consecutive days (from 3 to 15 January), yet we only have a sample from 8 January. We intensively sampled the meltwater during the main melt event, which lasted less than a week; it began on March 27 (Julian day 86) and most of the snow cover was gone by 1 April (Julian day 91). A small amount of snow remained in the lysimeter until 3 April but most of the flow measured at the lysimeter after 1 April (Fig. 3a) was due to new precipitation.

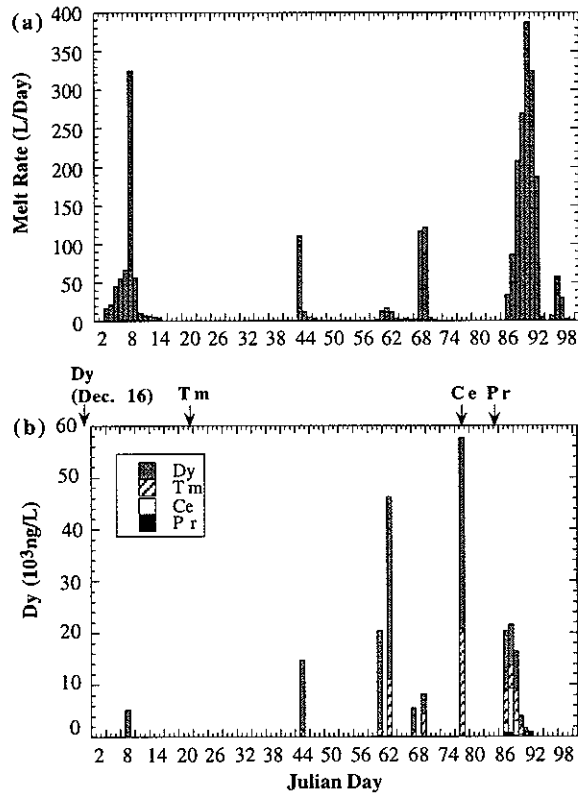


Figure 3. The melt rate for the west lysimeter (a), in liters per day, and Dy, Tm, Ce, and Pr concentration in melt samples (b) as a function of Julian day. The melting rate data were obtained from the instrumented tipping buckets. The dates when the tracers were applied are marked in (b). The data show that the tracer was detected in the meltwater soon after it was applied. Each bar in (b) indicates that at least one sample was collected. By comparing (b) with (a) it is evident that the January thaw was considerably undersampled. There are also several days when water was collected from the lysimeter but the flow rate was too low to be visible in (a).

Sample handling and analysis

Before use, all sample bottles were ultrasonically cleaned in a solution of Citranox (acid solution and detergent) and then rinsed with distilled water. Sampling or cutting tools used to collect the core samples were rinsed with distilled water between samples to avoid cross contamination. For REE analyses, a 5- to 30-mL aliquot from each sample was acidified to a 1 wt% HNO₃ solution using Seastar® HNO₃ acid. The acidified solutions were analyzed for REE concentrations using a High Resolution ICP-MS (Vandecasteele and Block, 1993). The analytical accuracy was better than 5% in all cases.

RESULTS AND DISCUSSION

Natural background concentrations of rare earth elements in snow

The natural background levels of the REEs were examined by analyzing samples of new snow. The results of these analyses are listed in Table 2. For the five REEs sprayed at SRRW, the mean concentrations in the clean snow were 1 to 10 parts per trillion (ng/L). The REE concentrations of the spiked solu-

tions were about 20 to 40 ppm (mg/L), which allows the tracer to be diluted 10^5 to 10^6 times and still have a concentration well above the natural background. This dilution factor was more than sufficient for 1 L of tracer solution to be diluted with the total amount of snow accumulated above the lysimeter in a typical winter at SRRW (30–50 cm of water equivalent or

Table 2. Average “background” REE concentration of eight fresh snow samples collected at Sleepers River Research Watershed (ng/L = parts per trillion).

REE	Average, $n=8$ (ng/L)	Std dev (ng/L)
La	10	17
Ce	10	15
Pr	1	1
Dy	9	17
Tm	1	0

specifically for 1997–98, 1 L diluted by the 2666 L measured by the west lysimeter).

Tracers in snow cores

Two snow cores were collected on 3 March (Julian day 62). Two of the four tracers, Dy and Tm, had been applied when these cores were collected. REE data from one of the cores are shown in Figure 4. The peaks in La, Dy, and Tm concentration occurred at discrete horizons in the pack, suggesting that the tracers were retaining their original position in the snowpack; slight dispersion, both above and below where the tracer was applied, is also evident. The tracers, however, were also mobile, as indicated

by their presence in the meltwater (Fig. 3b). Tracers may have moved to the base in melt fingers that were not intersected by the snow cores or they may have moved as a wetting front through the pack without refreezing before reaching the base.

Figure 4 also shows that the ratios of the peak La/Dy and La/Tm in the core samples are 0.82 and 0.83, respectively. These ratios are identical, within analytical error, to the ratio of La/Dy (0.79) and La/Tm (0.87) in the spike solution. This indicates that chemical differentiation did not occur between La (the common tracer) and Dy and Tm.

Tracers in meltwater

Tracer concentrations in the melt samples are shown in Figure 3b. Although sampling was not frequent before the beginning of the main melt, it is clear that tracers were leached out into the meltwater soon after they were applied.

Figure 5 shows the melt rate data and the fraction of each of the REE tracers released per day for the main melt period (27 March to 1 April). For each day, we calculated the amount of the tracer release by multiplying the average concentration of the tracer in the samples collected on that day by the daily melt rate. This value, which has units of ng/day, was then divided by the total amount (nanograms) of the tracer applied (concentration of tracer multiplied by the volume of the solution applied) to obtain the fraction of the tracer released for the given day. By normalizing the data this way, we avoid variations introduced by having sprayed different amounts of each tracer.

We make three observations from Figure 5. First, the tracers that were applied later, and thus higher in

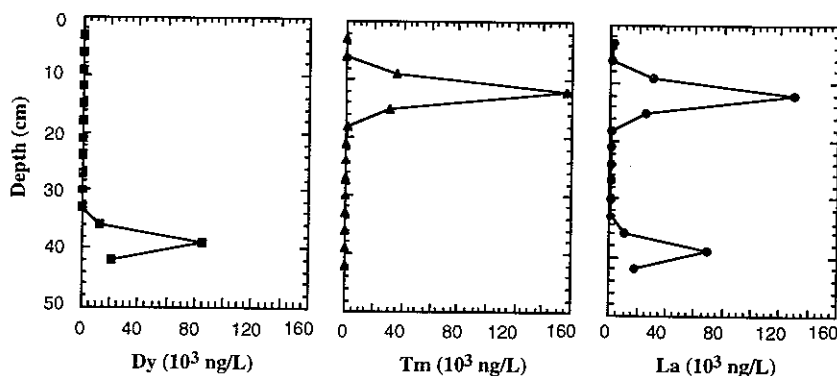


Figure 4. Concentration of Dy, Tm and La (the common tracer) vs. depth in a SRRW snow core obtained on 3 March. Dysprosium was applied on 16 December and Tm on 21 January. The ratio of La to Dy in the Dy spike was 0.79 and ratio of La to Tm in the Tm spike was 0.87.

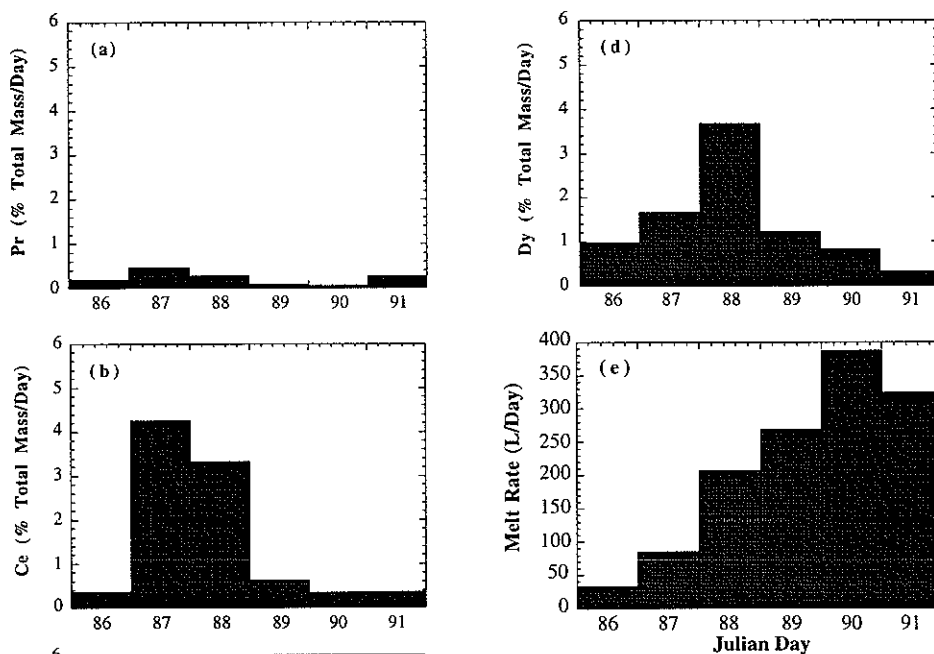


Figure 5. Comparison of the melt rate in L/day with the percent of tracer released at each day for the main melt period of 27 March to 1 April at Sleepers River Research Watershed: (a) Pr; (b) Ce; (c) Tm; (d) Dy and (e) melting rate. The order of application of the REE tracers from the base of the pack upward is Dy, Tm, Ce and Pr. The horizontal axis for all the plots is Julian day.

the pack, were flushed from the pack earlier. The earliest applied tracers, Tm and Dy, had peaks on their elution curves on 29 March (Julian day 88) (Fig. 5c and d), while Pr and Ce, the two tracers closest to the top of the pack, had their peaks a day earlier on 28 March (Julian day 87, Fig. 5a and b). This is consistent with the understanding that a snowpack melts from the top down. Second, there is significant overlap among the elution curves, suggesting the percolating meltwater entrained tracers from layers below the surface. Third, REE tracers were more concentrated in the earlier melt samples than in the later ones. Figure 5e shows that the melt rate peaked on 31 March (Julian day 90), well after the peaks of all of the tracers. This behavior is similar to that of major ions (Cl^- , Na^+ , NO_3^- , Na^+ , etc.) in snow (Bales et al. 1993), which suggests that similar chemical processes govern the elution of both major elements and REEs from snow.

Tracers recovered

It is difficult to quantify the total amount of tracers recovered from the melt due to incomplete sam-

pling during early melt events. We can, nevertheless, obtain useful information from the available data. The percentage recovered from the main melt event is 9% for Dy, 12% for Tm, 9% for Ce, and 1% for Pr. These values do not correlate with the sequence in which the tracers were applied. For example, Praseodymium has the lowest recovery rate, although it was the last tracer applied and we sampled most of the melt water after its application (i.e., there were no missing melt events).

The low recovery of Pr suggests that the tracer moved laterally in the pack, missing the lysimeter almost completely. Pr was applied on 25 March; the snow pit dug on the same date showed two well-developed ice layers below the surface (Fig. 2). On the next day (26 March), the area received rain, but not enough to percolate through the snowpack, as evidenced by the tipping record. The rainwater might have flowed laterally above the low-permeability ice layers, dispersing the tracer into a large area. Clearly, the behavior of the tracer and its subsequent distribution in the snowpack depend on the snow structure and weather conditions during and immediately after

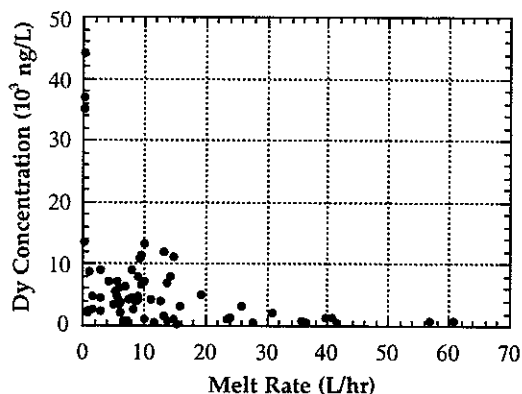


Figure 6. Concentration (ng/L) vs. melt rate (L/hour) for Dy in individual meltwater samples from Sleeper River Research Watershed.

tracer application. However, water samples taken from the tipping bucket of the adjacent lysimeter (2 m to the east of the lysimeter we used) on subsequent days have background REE levels, suggesting that if lateral flow occurred it did not transport the REE tracer toward this lysimeter.

Tracer concentration vs. melt rate

The concentration of Dy is plotted against the melt rate in Figure 6. Dysprosium was the first tracer we applied and the Dy layer is near the bottom of the snowpack. All samples plotted in this figure were collected when the surface of the snowpack was above the Dy layer. In other words, Dy was leached into solution long before the layer containing the spike was melted. Figure 6 shows that the concentration is quite variable when the melt rate is low. Specifically, three samples have concentrations that are higher than the remaining samples by a factor of two or more. These samples were collected before the snowpack became isothermal and when snowpack temperatures were less than 0°C. We suspect that refreezing of the meltwater, caused Dy to be concentrated in the pore water. We will test this by studying the oxygen isotope composition of the meltwater. If refreezing did occur, the $\delta^{18}\text{O}$ value of the water should be low, because isotopic fractionation results in ^{18}O enrichment of the condensed phase.

CONCLUSION

In winter 1997–1998, we studied snowpack accumulation and melt dynamics using rare earth elements as tracers. We made the following observations.

1. The background concentrations of REEs were on average about 1 to 10 ng/L. This low natural concentration makes REEs ideal tracers for studying snow, since tracer solutions can be at least four orders of magnitude above the natural background and yet have ionic strengths similar to that of clean snow.
2. The tracers began to leach from the snowpack soon after they were applied, but prior to the main melt period the tracers remaining in the pack sharply marked the position of the snow surface on which they were sprayed. Thus we can use REE tracers as markers within the snowpack.
3. The tracers applied early in the season came out later than those applied later in the season, indicating that the snowpack melts from the top down (as has been found by others) and that these tracers track the melting process.
4. The tracers were more concentrated in the first meltwaters; this is similar to the behavior of major chemical components in snow. Therefore, detailed studies using REEs may provide new insight to the chemical evolution of snowpacks.
5. Tracer concentrations are highly variable at low melt rates. Part of this variability may result from refreezing of meltwater within the snowpack, leading to high tracer concentrations in the pore water. Our subsequent stable isotope study should be able to determine if this process is occurring.

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