ELSEVIER

Chemical Geology 177 (2001) 117–131

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

www.elsevier.com/locate/chemgeo

Radiocarbon studies of plant leaves and tree rings from Mammoth Mountain, CA: a long-term record of magmatic CO_2 release

Andrea C. Cook [a,*], Laura J. Hainsworth [b,1], Michael L. Sorey [c,2], William C. Evans [c,2], John R. Southon [a,3]

[a] High Tech High School, 2861 Womble Rd. San Diego, CA 92106-6025, USA
[b] Chemistry Department, Emory and Henry College, Emory, VA 24327, USA
[c] U.S. Geological Survey, Menlo Park, CA 94025, USA

Received 13 October 1999; accepted 17 March 2000

Abstract

Evaluation of ^{14}C in tree rings provides a measure of the flux of magmatic CO_2 from Mammoth Mountain both before and after 1994 when copious diffuse emissions were first discovered and linked to tree kill. We analyzed the annual rings of trees with two main purposes: (1) to track changes in the magnitude of magmatic CO_2 emission over time, and (2) to determine the onset of magmatic CO_2 emission at numerous sites on Mammoth Mountain. The onset of CO_2 emission at different areas of tree kill was determined to be in 1990, closely following the seismic events of 1989. At Horseshoe Lake (HSL), CO_2 emission was found to have peaked in 1991 and to have subsequently declined by a factor of two through 1998. The tree-ring data also show that emissions of magmatic carbon from cold springs below the tree-kill areas occurred well before 1989. Trees located on the margins of the kill areas or otherwise away from zones of maximum gas discharge were found to be better integrators of magmatic CO_2 emission than those located in the center of tree kills. Although quantitative extrapolations from our data to a flux history will require that a relationship be established between ^{14}C depletion in tree rings and average annual magmatic CO_2 flux, the pattern of ^{14}C depletion in tree rings is likely to be the most reliable indicator of the long-term changes in the magnitude of CO_2 release from Mammoth Mountain. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mammoth Mountain; CO_2 emission; Radiocarbon; Tree rings

1. Introduction

Beginning in 1990, extensive tree mortality has been observed at eight locations (Fig. 1) on the north, south, and west flanks of Mammoth Mountain, CA (Farrar et al., 1995; Rahn et al., 1996; Sorey et al., 1998). The species-independent nature of the tree death was unprecedented and hinted at a cause other than the typical drought stress or pest

* Corresponding author. Tel.: +1-619-243-5033; fax: +1-619-243-5050.
E-mail addresses: acook@hightechhigh.org (A.C. Cook), ljhainsw@ehc.edu (L.J. Hainsworth), mlsorey@usgs.gov (M.L. Sorey), wcevans@usgs.gov (W.C. Evans), southon1@llnl.gov (J.R. Southon).
[1] Fax: +1-540-944-6934.
[2] Fax: +1-650-329-4463.
[3] Fax: +1-925-423-7884.

0009-2541/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0009-2541(00)00386-7

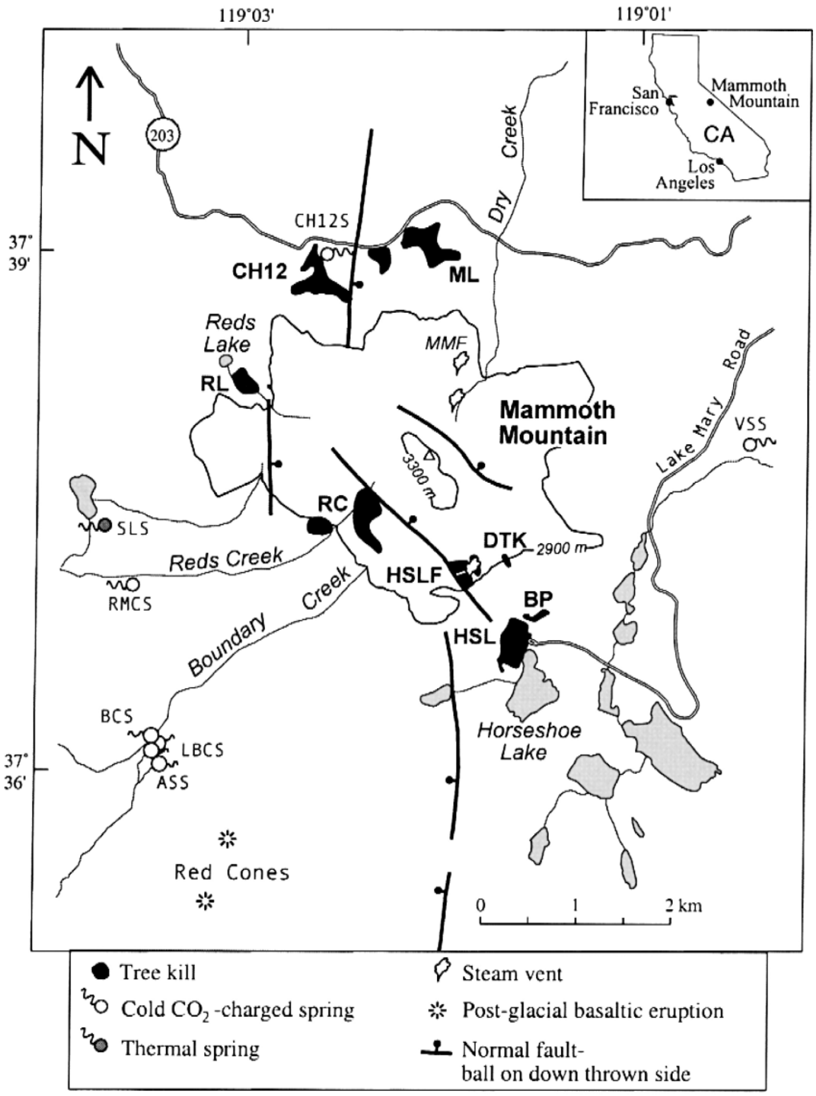

Fig. 1. Mammoth Mountain region showing tree kill areas and cold springs with significant dissolved magmatic carbon. Tree kills are abbreviated as ML (Main Lodge), CH12 (Chair 12), RL (Reds Lake), RC (Reds Creek), HSL (Horseshoe Lake), HSLF (Horseshoe Lake Fumarole), DTK (Dave's tree kill), and BP (Borrow Pit). Soda springs are abbreviated as RMCS (Reds Meadow Cold Spring), VSS (Valentine Soda Spring), CH12 S (Chair 12 Spring), ASS (Artesian Soda Spring), BCS (Boundary Creek Spring), SLS (Sotcher Lake Spring), and LBCS (Lower Boundary Creek Springs).

infestation, and in 1994 the cause of these tree kills was linked to the diffuse release of CO_2 from beneath Mammoth Mountain (Farrar et al., 1995). At that time, Farrar et al. (1995) hypothesized that the CO_2 flux to the atmosphere from the areas of tree kill might be 1200 t/day. Within the tree-kill areas, they also reported extremely high soil–gas concentrations, ranging from 30% to 90% CO_2 by volume; and proposed that the trees were dying from the buildup of magmatic CO_2 in the soil and subsequent deprivation of oxygen to the root system.

The release of gas is thought to have been triggered in 1989 by a swarm of earthquakes associated with shallow magma intrusion under Mammoth

Mountain (Hill, 1996). Based on chemical and isotopic analyses of both soil and fumarole gas, Sorey et al. (1998) proposed that most of the CO_2 is being released from a large reservoir of magmatic gas on the order of several tens of cubic kilometers in volume, rather than direct outgassing from the 1989 magmatic intrusion itself. The gas in the reservoir is estimated to be 99% CO_2 and 1% N_2, with 10–18 ppm He. The diffuse emissions are cold, and other magmatic gasses are absent, with the exception of mantle helium.

In the interest of human safety on both large (volcanic hazard) and small scales (asphyxia hazard), changes in CO_2 flux over time must be understood. Diffuse emission of carbon dioxide has been described at other volcanoes including Mt. Etna (Allard et al., 1991; Anza et al., 1993; Giammanco et al., 1995; D'Alessandro et al., 1997), Vulcano (Baubron et al., 1990, 1991) and Oldoinyo Lengai (Brantley and Koepenick, 1995). Williams (1995) noted that changes in volcanic gas output can signal increases in the level of volcanic activity long before deformation and seismicity become notable, due in part to the high mobility of the gas phase. Thus, gas flux is an important parameter to be monitored in volcanic hazard surveillance.

Accurate estimates of total CO_2 flux from accumulation chamber measurements of gas flow rates at various tree-kill areas on Mammoth Mountain have proven difficult to attain. A combination of factors complicates such determinations, including significant spatial variability in flow rates (25 to over 10,000 $g/day/m^2$) at each tree-kill area (Farrar et al., 1998; Gerlach et al., 1998a). Given this wide range in flow rates, disagreements in direct gas flux determinations made by different research groups at approximately the same time can arise from differences in techniques used to make the individual flow rate measurements and to convert such measurements to estimates of total gas flux. A large temporal variability in flow rates, on time scales of hours to days, has also been observed (Rogie et al., 1998). Such variations appear to be influenced by meteorological processes such as changes in barometric pressure, temperature, and wind speed.

In this paper, we present time series of data that outline the history of magmatic CO_2 emission from Mammoth Mountain over the past ~40 years. We use radiocarbon (^{14}C) measurements on samples of plants taken from the region to determine the extent to which vegetation in areas of high flux incorporate magmatic CO_2 into their tissues via photosynthesis. The relative quantity of magmatic CO_2 being released at a specific location is inferred from the extent of ^{14}C deficiency in the plant material from areas of high flux relative to the biomass being produced on other parts of the mountain where CO_2 concentrations are ambient. This inference is possible due to the absence of ^{14}C in magmatic CO_2, as opposed to the ^{14}C content in atmospheric CO_2, which is on the order of 110 ‰ (per mil).

Because tree rings form annually and integrate CO_2 concentrations over the course of the growing season, they have less temporal variability in their CO_2 signature. To the extent to which local (atmospheric) CO_2 concentrations reflect emission rates, each annual ring contains a record of the annual average CO_2 flux at each location on the mountain. Since no direct flux measurements were made before 1995, tree rings may provide the only quantitative way to determine mean CO_2 fluxes prior to 1995. The tree-ring data help to resolve some of the uncertainty over the timing of the onset of tree kill in each area (Rahn et al., 1996) and uncertainly over the pattern of change in average annual flux since 1995. In addition, the tree-ring data can provide information on the pattern of CO_2 release from CO_2-charged springs on the flanks of Mammoth Mountain.

2. Site descriptions

Two main tree-kill areas were selected for detailed study, Horseshoe Lake (HSL) and Reds Creek (RC). HSL rests on the southeast flank of Mammoth Mountain at an altitude of approximately 9000 ft and is a popular camping and recreational area. The HSL tree kill was the first area of tree kill noticed in 1990 and is the largest tree kill on Mammoth Mountain. It encompasses approximately 15 ha of dead coniferous forest, and is composed mostly of red fir (*Abies magnifica*) and lodgepole pine (*Pinus contorta*).

The total gas discharge from HSL was estimated to be 350 metric tonnes per day in 1995 (Sorey et al., 1999). HSL provides an ideal site for pinpointing the timing of the onset of CO_2 emissions because a USFS ranger experienced severe symptoms of asphyxia at the site during March of 1990, but not in February of 1990 (Richter, personal communication, 1996). These events help to bound the timing of the onset of cold CO_2 discharge in the area. Heavier than normal needle cast and dead trees were first noticed at HSL during the summer of 1990, but were initially attributed to drought stress and pest infestation. Tree kill was also noticed that summer at Chair 12 (CH12) and Reds Lake (RL).

Four additional areas of tree kill became apparent by 1993, at the main lodge (ML), Borrow Pit (BP), HSL fumarole (HSLF), and RC. It was uncertain whether the onset of CO_2 emission at these sites had occurred in the same year or later than at HSL, CH12 and RL.

The RC tree kill is located on the south flank of Mammoth Mountain and consists of dead and dying coniferous forest, with extensive leaf browning and species-independent tree death. It was chosen as the second intensive study site because it was the largest (10. 2 ha) in the second suite of sites and had very high CO_2 flux (estimated to be 300 metric tonnes per day in 1996) (Sorey et al., 1998). Soil CO_2 concentrations in some parts of RC exceed 80% by volume, while in other areas of RC they are relatively low, 3–10% by volume. Isotopic measurements indicate that the same magmatic gas is escaping from both HSL and RC, but it is mixed with a large volume of air in parts of RC. The source of air flow at RC has not yet been identified, but it may be associated with circulation through the granitic edifice to the north of the site (Sorey et al., 1998).

In addition to the diffuse release of gas through the soils at Mammoth Mountain, CO_2 is also emitted at fumaroles (steam vents) and dissolved in groundwater. The pCO_2 values of some springs on the flanks of the mountain are so high that the water actually contains bubbles of free gas at the point of discharge (i.e. CH12 Spring). While many of the springs did not emit bubbles, they still contain large amounts of dissolved CO_2 that is rapidly lost to the atmosphere along the outflow channels. Analyses of ^{13}C, pCO_2 and He in spring and well waters show that the CO_2 and helium dissolved in the groundwater contains a significant component of magmatic gas, essentially the same gas that is discharging in the areas of tree kill (Sorey et al., 1999). The amount of gas leaving the mountain dissolved in the groundwater system is estimated to be as much as 50–100 metric tonnes per day (Sorey et al., 1999).

3. Methods

Sample acquisition began in May of 1995, with the collection of pine needles from trees in the high flux regions, soon after the cause of tree death had been linked to the release of magmatic CO_2 from beneath Mammoth Mountain (Farrar et al., 1995). Needles were collected from the areas of tree kill to determine whether the distinct isotopic signature of the magmatic CO_2 (concentration of $^{14}C = 0$) was being incorporated into the plant material at a level high enough to be distinguishable from background (ambient) levels.

In the area of HSL, needle samples were collected from five dead trees located close to the center of the tree-kill area, and from four visibly stressed but living trees located on the margins of the tree kill. Needle samples were also collected from three dead trees located near the center of the CH12 tree-kill area. Background needle samples were also collected from healthy trees growing along Mammoth Lakes Scenic Loop Road, the Tamarack Lodge parking area, and on Route 88 West of Markleeville.

Needle samples were brought to Lawrence Livermore National Laboratory (LLNL) and chemically pretreated with acid–base–acid washes to remove surface contaminants and soluble compounds that might not have been present in the original leaf material. The pretreatment regime was as follows: 1 N HCl for 15 min, 1 N NaOH for a minimum of 45 min (until the solution no longer turned brown), and finally 1 N HCl for 15 min, all at 80°C. The samples were then washed three times with de-ionized water and dried overnight. The dried samples were weighed to yield 1 mg of C, combusted in vacuum sealed 6-mm quartz tubes with CuO for 3.5 h at 900°C, and graphitized using hydrogen reduction with a cobalt catalyst (Vogel et al., 1989). Radiocarbon was measured by accelerator mass spectrometry at LLNL (Davis et al., 1990; Southon et al., 1990). Based on replicate analyses, the overall reproducibility (extraction, graphitization, AMS analysis) is estimated to be 7 per mil.

Tree coring began in July of 1995 after needle analyses demonstrated that trees in the areas of high flux were incorporating a significant proportion of magmatic CO_2 into their tissues. Red fir trees were cored at two main sites, HSL and RC, using a 16-mm Suunto increment borer (Forestry Suppliers, USA). Only mature trees that were alive in 1989 were cored so that the onset of CO_2 emission could be determined for each site. Five trees were cored from the HSL tree-kill area: three dead trees from near the center of the tree kill (one small 5–10-m-tall tree and two larger 15–45-m-tall trees) and two live trees from the near the edge of the tree-kill area (two smaller 5–10-m-tall trees). One small dead tree (5–10 m) was also cored from the center of the RC tree kill.

Early in the summer of 1999, we returned to HSL and cored three additional trees that were growing on the margins of the HSL tree-kill area (tree #1, ~15-m lodgepole, tree #2, ~10-m hem-fir, tree # 3, ~8-m lodgepole). These trees were alive in 1999 and were thought to have been incorporating magmatic CO_2 into their tissues since the onset of the emission. These trees were cored specifically to in-

Table 1
$\Delta^{14}C$ and percent magmatic carbon values for plants overhanging CO_2-charged groundwater springs on Mammoth Mountain

Spring	Vegetation type (year collected)	$\Delta^{14}C$‰ (SE)	% Magmatic C (SE)
Reds Meadow Cold Spring (RCMS)	small herbaceous, near vent (1997)	−841.8 (1.0)	85.73 (0.13)
	needles, Cook tree (1997)	−553.6 (2.1)	59.73 (0.27)
	wood, outer ring of Cook tree (1995)	−500.9 (2.7)	54.99 (0.34)
	wood, outer ring of Hainsworth tree (1995)	−125.0 (6.4)	21.11 (0.81)
Artesian Soda Spring (ASS)	pine needles, tree # 1 (1998)	−86.2 (4.2)	17.58 (0.53)
	pine needles, tree # 2 (1998)	−253.0 (3.4)	32.63 (0.43)
	pine needles, tree # 3 (1998)	−288.1 (2.9)	35.79 (0.37)
	wood, outer ring of tree #1 (1997)	−408.8 (2.8)	46.68 (0.36)
Valentine Soda Spring (VSS)	small herbaceous, near vent (1997)	−771.2 (1.5)	79.42 (0.18)
	small herbaceous, 3 m from vent (1997)	−619.6 (2.0)	65.69 (0.25)
	small herbaceous, near tank outflow (1997)	−834.0 (1.2)	85.03 (0.15)
	small herbaceous, hillside leaching (1997)	−264.6 (3.6)	33.67 (0.46)
	needles, large pine tree near main vent (1997)	46.4 (5.1)	5.61 (0.65)
Sotcher Lake Spring (SLS)	small herbaceous (1997)	−206.6 (3.6)	28.44 (0.45)
	aspen tree leaf (1997)	92.7 (4.9)	1.44 (0.62)
Boundary Creek Spring (BCS)	small herbaceous, lupine (1997)	−355.6 (2.9)	41.88 (0.37)
	needles, lodgepole pine (1997)	−32.6 (4.4)	12.75 (0.56)
	needles, fir, downstream from vent (1997)	86.4 (6.5)	2.02 (0.82)
Lower B. Creek Spring (LBCS)	needles, lodgepole, vent w/o bubbles (1997)	48.9 (4.3)	5.40 (0.55)
Chair 12 Spring (CH12S)	grass, nearest vent to parking (1997)	−434.5 (2.8)	49.00 (0.36)
	grass, under Laura's tree (1997)	−502.6 (2.3)	55.14 (0.29)
	grass, downstream of Laura's tree (1997)	−411.4 (2.6)	46.91 (0.33)
	grass, downstream of vent, on left (1997)	−569.8 (2.9)	61.20 (0.37)
	grass, not near vent, just degassing water (1997)	−568.8 (2.0)	61.11 (0.25)
	grass, bubbling pumus vent (1997)	−457.0 (2.5)	51.03 (0.32)
	needles, 1.0 m lodgepole, yellowing (1997)	60.8 (5.0)	4.32 (0.63)
	needles, Laura's tree (1997)	42.3 (4.8)	5.99 (0.61)
	needles, Laura's second tree (1997)	65.0 (5.8)	3.95 (0.74)
	needles, 1 m from 3rd vent, on left (1997)	63.7 (5.3)	4.06 (0.67)
	needles, 1 m from 3rd vent, on right (1997)	51.7 (7.4)	5.14 (0.94)
	needles, near where 3rd vent joins main flow (1997)	−56.8 (4.2)	14.94 (0.53)
	needles, not near vent, just degassing water (1997)	−0.6 (4.5)	9.86 (0.57)
	needles, bubbling pumus vent (1997)	33.8 (4.8)	6.76 (0.61)

Note that small herbaceous vegetation always incorporates more magmatic CO_2 than trees, presumably because CO_2 concentrations are higher near the ground.

vestigate whether there have been changes in the magnitude of CO_2 flux at HSL over time (1989–1998).

All tree cores were brought back to LLNL intact and carefully dissected under a microscope. A surgical blade was used to shave 1–2 mg of C from each desired growth ring, starting with the outermost growth ring and working back 15–20 years. The shavings from each annual ring were chemically pretreated as described above. An additional bleaching/oxidation step was added in order to extract cellulose from the wood (Olsson and Possnert, 1992). Samples were digested in an acid(HCl)–bleach(NaOCl) mixture in a 60°C sonicator bath until only cellulose remained (> 1 h). The cellulose was then washed three times in de-ionized water and dried overnight. The wood samples were combusted, graphitized, and analyzed as described above.

From 1995 to 1998, leaf and needle samples were collected around numerous cold springs scattered on the flanks of Mammoth Mountain. The leaves from the plants, which were overhanging the springs were analyzed to determine the extent to which they were fixing the magmatic CO_2, which was being released from the springs. Collection sites are shown by the spring locations in Fig. 1. Trees growing near the edge of two of the larger springs, the Reds Meadow Cold Spring (RMCS) and the Artesian Soda Spring (ASS), were sampled to obtain records of the history of the CO_2 release from these springs. These trees were too small to be cored, however, so the top section of each tree trunk was removed. The trunk sections were brought back to LLNL and the annual rings were analyzed in the same manner as those from the tree cores.

The results of the analyses are shown in Table 1 and Figs. 1–6. ^{14}C activities are reported relative to an international standard known as Modern Carbon, which is defined as 95% of the ^{14}C activity in 1950 of the NBS oxalic acid 1 standard; and is equal to the ^{14}C content of the 19th century atmosphere prior to its dilution by large-scale fossil fuel CO_2 releases. The ^{14}C activities were corrected for mass-dependent isotopic fractionation to a common $\delta^{13}C$ value of −25‰ and are expressed as $\Delta^{14}C$ (Stuiver and Polach, 1977). $\Delta^{14}C$ is the difference in parts per thousand (per mil) between the $^{14}C/^{12}C$ ratio in the sample compared to that of the universal oxalic acid I standard decay corrected to 1950. We sometimes express the amount of magmatic CO_2 present in the plant leaf tissue from Mammoth Mountain as percent magmatic carbon (= [1 − (fraction modern in sam-

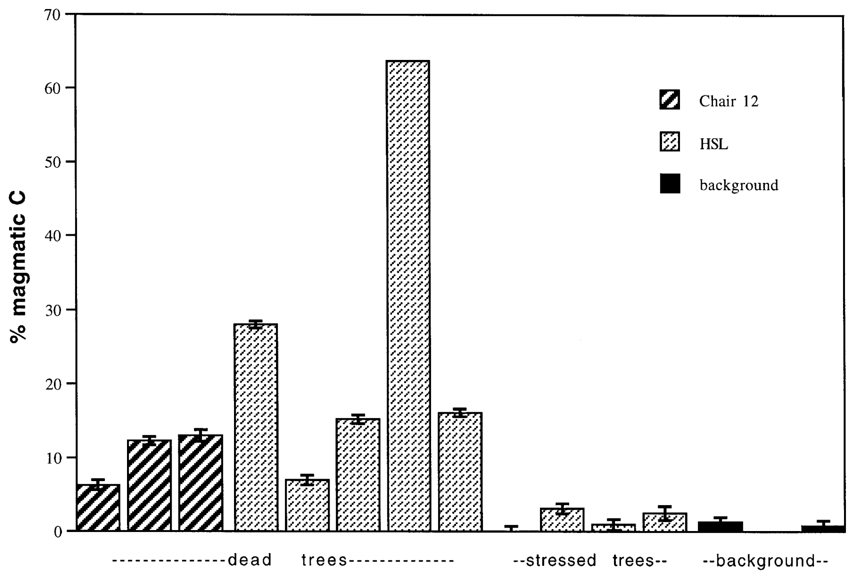

Fig. 2. Percent magmatic carbon in tree needles collected from the tree kill areas of HSL and CH12. Note that the amount of magmatic CO_2 in the needles from dead trees is clearly distinguishable from background.

ple/fraction modern in reference plant)]100) because it is often more straightforward than $\Delta^{14}C$ for non-specialists to understand. Whenever possible, both $\Delta^{14}C$ and percent magmatic carbon values are given.

The ^{14}C background, or bomb curve, shown in many of the figures is a compilation of data taken from Berger et al. (1987), Burcholadze et al. (1989), Levin et al. (1992) and two background trees col-

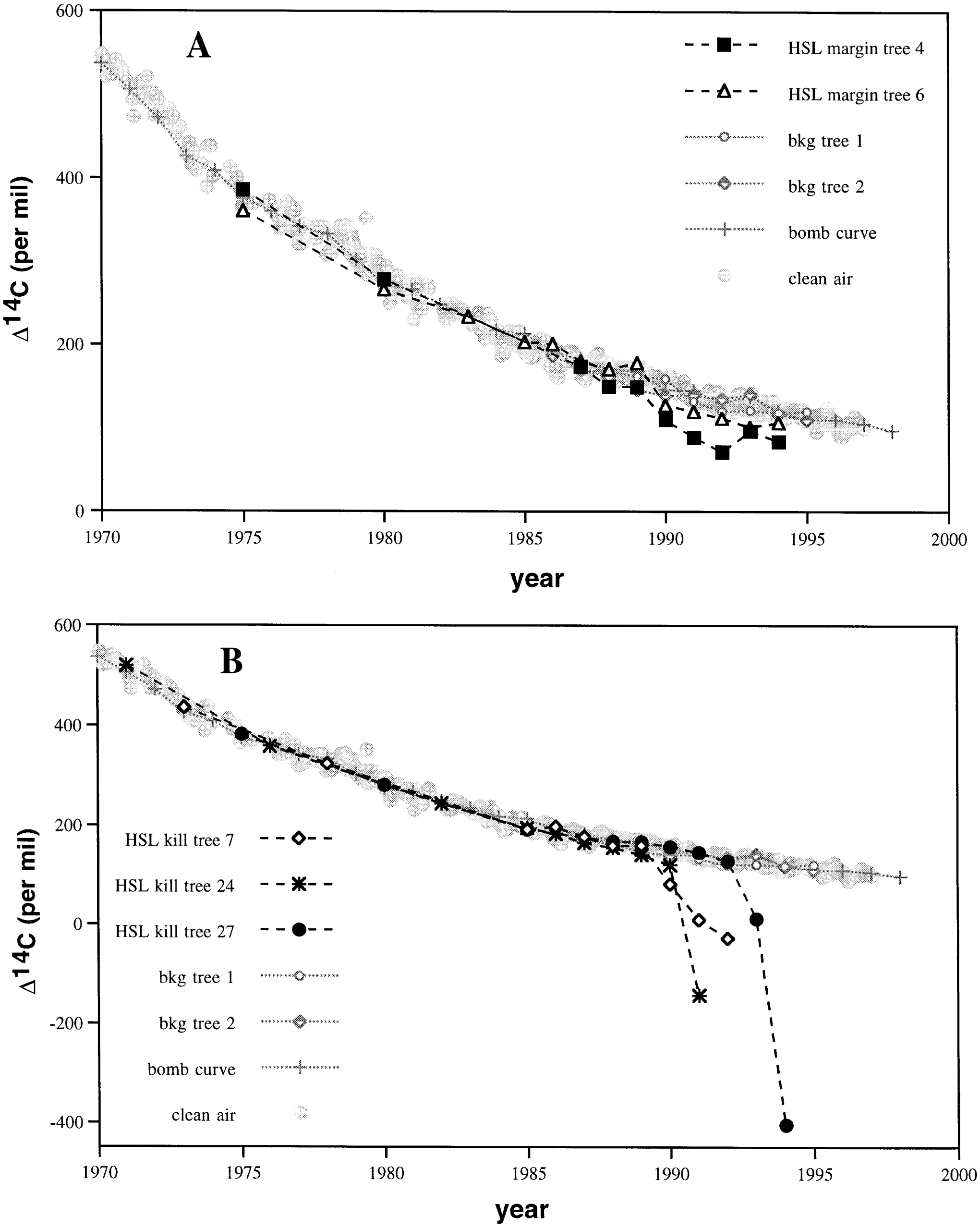

Fig. 3. $\Delta^{14}C$ in the annual rings of trees collected at HSL in 1995. The upper panel (A) represents measurements made on living trees collected on the margins of the HSL tree kill, while the lower panel (B) represents measurements made on dead trees collected near the center of the HSL tree kill. Note that magmatic CO_2 uptake began in 1990 for four of the five trees surveyed.

lected for this study from the Lake Tahoe (bkg tree #1) and Mammoth Lakes (bkg tree #2) areas. The curve shows how the atmosphere in the Northern Hemisphere was influenced by ^{14}C releases from atmospheric nuclear weapons tests in the 1950s and 1960s and how this excess radiocarbon was subsequently removed from the atmosphere by incorporation into the biosphere and the oceans. The $\Delta^{14}C$ in the atmosphere peaked in 1963 at $\approx +1000‰$, and dropped to $+110‰$ by 1997. When a plant fixes all of its carbon from the bulk atmosphere (the typical case), it has a $\Delta^{14}C$ signature that is equal to that of the atmosphere (e.g., the value of a tree ring produced in 1970 would be $+530‰$, the same value as the atmosphere in 1970). $\Delta^{14}C$ values from the Vermunt (1959–1983) (Levin et al., 1985) and Schauinsland (1978–1997) (Levin and Kromer, 1997) clean air records are plotted to show the variability inherent in the atmospheric ^{14}C record.

When the $\Delta^{14}C$ signature of a plant deviates from that predicted by the bomb curve, it suggests that some form of "contamination" has occurred. If the $\Delta^{14}C$ value is more negative than expected, it suggests that the plant is fixing carbon of ancient origin (e.g., disproportionately from fossil fuel derived sources, or in the case of Mammoth Mountain, from CO_2 emission from the magma). If a plant were to fix only magmatic CO_2 (or only fossil fuel CO_2), it would have a $\Delta^{14}C$ value of $-1000‰$. The magnitude of ^{14}C depletion (relative to the atmospheric value) corresponds directly to the proportion of the carbon being fixed from the ancient source.

4. Results

All of the needles collected in May of 1995 from the HSL and CH12 tree-kill areas showed the presence of magmatic CO_2 at levels distinguishable from background (Fig. 2). Trees growing near the center of the HSL and CH12 tree kills (labeled dead trees) incorporated more magmatic CO_2 than those grow-

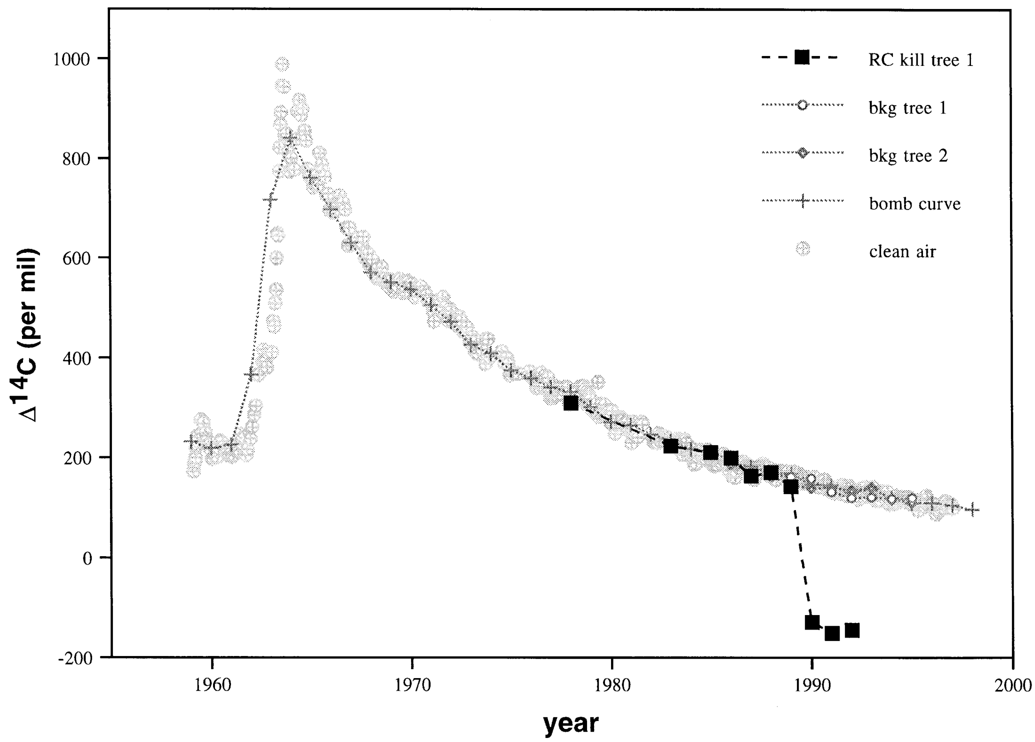

Fig. 4. $\Delta^{14}C$ in the annual rings of a single dead tree collected in the center of the RC tree kill in 1995. Note that the onset of magmatic CO_2 uptake is clearly 1990. The entire ^{14}C background, or bomb curve, is shown in this figure.

ing on the margins (labeled stressed trees). The highest level of magmatic CO_2 (65%) was observed in needles collected from a small (< 10 ft) dead lodgepole pine tree located near the center of the HSL tree-kill area. This fixation of magmatic CO_2 results in an enrichment, which would correspond to an atmospheric CO_2 concentration of approximately 990 ppm (calculated according to van Gardingen et al., 1995), about 2.7-times the current ambient atmospheric CO_2 concentration of 360 ppm.

Growth ring analyses on four of the five red fir trees cored at HSL in 1995 showed the onset of CO_2 emission to be in 1990 (Fig. 3A and B). This timing is consistent with the Forest Service report of near asphyxia in a cabin at HSL in March of 1990. Only the largest tree (HSL kill tree 27) showed the onset of CO_2 emission to be later (1993), perhaps because it was taller and photosynthesizing much further off the ground where CO_2 concentrations were lower. In all cases, the trees growing near the center of the tree-kill area (Fig. 3B) incorporated more magmatic carbon into their tissues than those growing near the margins (Fig. 3A), presumably because CO_2 concentrations were correspondingly higher. Trees sampled from the center of the HSL tree-kill area also showed a pattern of increasing magmatic CO_2 signal with time (Fig. 3B) that was not evident in the trees growing on the margins (Fig. 3A). The highest level

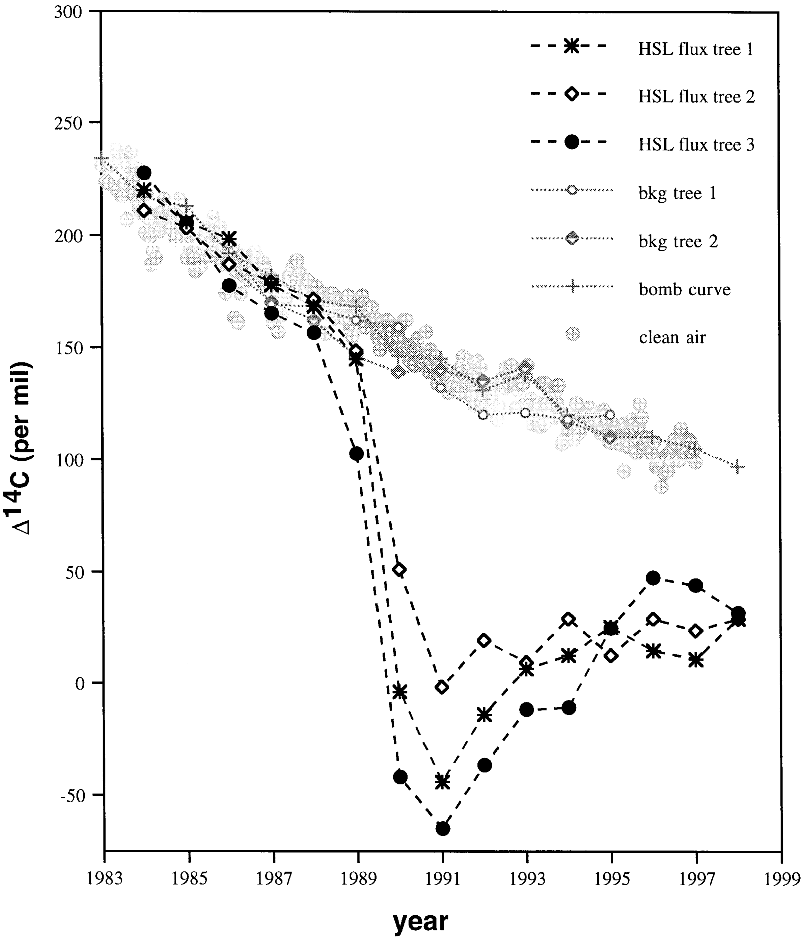

Fig. 5. $\Delta^{14}C$ in the annual rings of living trees collected on the margins of the HSL tree kill in 1999. These are the only records of magmatic CO_2 uptake from an area of tree kill that span from onset (or pre-1989) to the present. Note that the pattern of magmatic CO_2 uptake is similar in all three trees, and that magmatic CO_2 uptake peaked in 1991 and has been decreasing since then.

of CO_2 enrichment observed in the rings was 46% magmatic CO_2 (an equivalent of 670 ppm CO_2 or 1.9-times the current ambient CO_2 concentration).

Although tree kill was not recognized at the remote RC site until 1993, growth ring analyses on a small red fir tree collected in the high flux region of this site revealed a magmatic CO_2 signature beginning in 1990 (Fig. 4). The strength of the magmatic signal remained consistently high (~ 23% magmatic CO_2, 470 ppm, or 1.3-times the current ambient CO_2 concentration) from the onset of CO_2 emission in 1990 through the death of the tree during the winter of 1992.

The trees cored in 1999 on the margins of the HSL tree-kill area show how the magnitude of magmatic CO_2 uptake has changed over time: it was initiated in 1990, peaked in 1991, and has been decreasing ever since (Fig. 5). The amount of CO_2 fixed by these trees in 1998 (~ 7% magmatic CO_2 or 390 ppm) was approximately half of that fixed during peak emission in 1991(~ 13% magmatic CO_2 or 410 ppm). The pattern of ^{14}C depletion in the annual rings is remarkably consistent between all three of the trees cored, suggesting that either changes in CO_2 flux are occurring homogeneously across the entire area of the tree kill, or that trees integrate CO_2 flux very well over relatively large areas. Either way, the data suggests that tree rings provide a very good proxy for CO_2 flux. One tree (HSL flux tree #3) showed evidence of CO_2 emission in 1989, a year earlier than the other trees, suggesting that the CO_2 gas reached the surface earlier in some parts of HSL than others.

The leaf samples collected near the springs from 1995 to 1998, all showed substantial magmatic signal (Table 1). Small herbaceous plants consistently fixed more magmatic CO_2 than plants of higher stature (trees), presumably because CO_2 concentrations are higher near the ground. A ranking of the various springs near which small herbaceous plant leaf samples was taken in terms of the highest measured concentration of magmatic CO_2 (percentage) is as follows: RMCS (86% magmatic CO_2), Valentine Soda Spring (85%), CH12 Spring (61%), ASS (47%), Boundary Creek Spring (42%), Sotcher Lake Spring (28%), and Lower Boundary Creek Spring (5%).

Tree samples were taken at some of the cold spring sites. The two springs with the largest magmatic signal in trees were the RMCS (60%) and the ASS (47%). The amount of CO_2 being emitted from the other springs resulted in magmatic signals in the trees, which were much smaller: CH12 Spring (15%), Boundary Creek Spring (13%), Valentine Soda Spring (6%), Lower Boundary Creek Spring (5%), and Sotcher Lake Spring (1%).

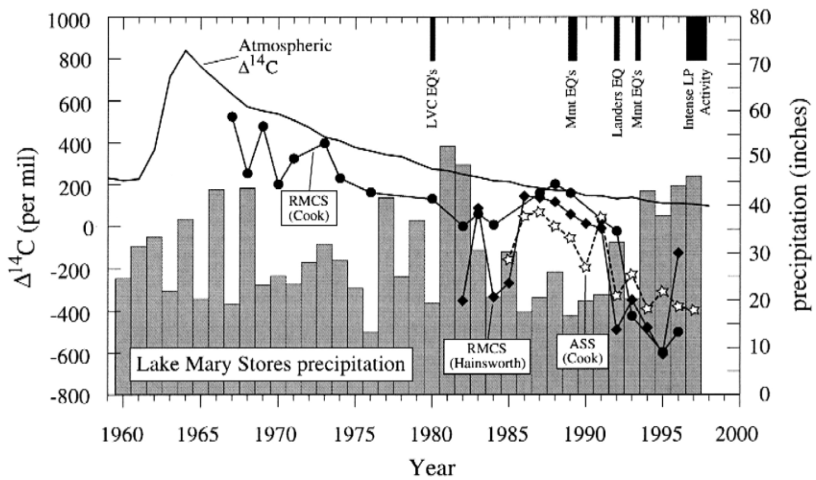

Fig. 6. Isotopic evidence for magmatic CO_2 release from cold springs prior to the seismic activity of 1989. One tree (RMCS-Cook) shows evidence of magmatic CO_2 emission going all the way back to the 1960s. Precipitation (from Lake Mary Stores) and seismic activity (denoted EQs) both show some degree of correlation with the magnitude of ^{14}C depletion over time.

The tree cores collected from the RMCS and the ASS both showed evidence of magmatic CO_2 release prior to the seismic events of 1989 (Fig. 6), with one tree (RMCS-Cook) showing magmatic CO_2 release going all the way back to 1967, the birth of the tree. The onset of CO_2 emission from the cold springs was clearly earlier than from the tree-kill areas, which supports the notion of a long-lived gas reservoir beneath Mammoth Mountain. For reasons not completely understood, the amount of CO_2 released from the groundwater system varied from year to year and from spring to spring.

5. Discussion

5.1. Onset of magmatic CO_2 emission

Growth-ring analyses clearly indicate that CO_2 emission began at both HSL and RC by 1990. There was no evidence for the release of magmatic CO_2 from any of the tree-kill areas prior to 1989 when the swarm of earthquakes hit. All trees had normal Δ^{14}Cs prior to 1989. Because HSL and RC were located on very different parts of Mammoth Mountain but shared the same timing for the onset of CO_2 emission, it is possible that CO_2 emission began in 1990 at all eight areas of tree kill.

CO_2 gas could have reached the surface anytime after the seismic activity started in May of 1989, but it did not necessarily reach the surface at exactly the same time in all locations. Only two trees (HSL flux tree 3 and HSL kill tree 27) showed the onset of magmatic CO_2 uptake to be in years other than 1990. HSL flux tree 3 first showed magmatic signal in 1989, presumably because it was the tree closest to the location within HSL where CO_2 gas first reached the surface. This tree was also the smallest of the flux trees, and was therefore the most likely to detect the earliest release of magmatic CO_2 since its leaves were closest to the ground where CO_2 concentrations were the highest. HSL kill tree 27 showed first signs of magmatic CO_2 uptake in 1993, presumably because it was the largest of the kill trees sampled and located furthest from the main area of CO_2 degassing. The magnitude and extent of the degassing at HSL could have changed over time, or meteorological conditions could have changed in such as way as to make this tree one of the latest to see high CO_2 concentrations.

Growth rings cored from trees near the RMCS and ASS provide clear isotopic evidence of CO_2 discharge from the groundwater system since at least the late 1960s, well before the seismic activity and tree kills of 1989–1990. These data provide a long-term record of magmatic CO_2 emission from Mammoth Mountain that supports the model of a large and long-lived gas reservoir beneath Mammoth Mountain (Sorey et al., 1999).

5.2. Pattern of magmatic CO_2 emission at HSL

The best record of changes in gas flux with time comes from ^{14}C depletions in three trees cored on the margins of the HSL tree-kill area in 1999. It is important to note that these trees were alive and healthy at the time of coring, and contained a record of magmatic CO_2 degassing that was complete over the entire period of interest (pre-1989 through 1998). These trees were growing close enough to the tree kill to be incorporating the magmatic CO_2 signal, yet far enough away to be buffered from the extremely high and obviously stressful CO_2 conditions that had killed trees in previous years near the center of the tree-kill area. All three trees showed a remarkably consistent pattern of ^{14}C depletion, further supporting the notion that margin trees are very good integrators of CO_2 over relatively large areas.

Using these margin tree rings, we found that magmatic CO_2 uptake was initiated by 1990, peaked in 1991, decreased through 1995, and then stayed relatively constant through 1998. From this, we infer that the rate of magmatic CO_2 emission increased drastically from 1989 to 1991, decreased quite steadily from 1991 to 1995, and seems to have leveled off through 1998. In quantitative terms, the amount of magmatic CO_2 fixed by these trees in 1998 was equal to approximately half of that fixed during the 1991 peak.

Patterns of ^{14}C depletion in dead trees cored near the center of the gas discharge areas at HSL and RC are noticeably different from those noted above for the live marginal trees cored at HSL, except for the fact that 1990 still marks the initiation of the magmatic carbon signal. Thereafter, at HSL the centrally located trees generally show a consistent trend of increasing ^{14}C depletion until the year the tree died (1991–1994). In contrast, depletions in the RC tree core were constant from 1990 to tree death in 1992. In both areas, however, the strength of the magmatic signal is greater in the centrally located dead trees than in the marginally located live trees, presumably as a result of higher gas flow rates and CO_2 concentrations in the center of the tree kills.

It is likely that the centrally located trees experienced CO_2 concentrations both above and below ground that were sufficiently stressful to affect carbon uptake, growth, and eventual death. Direct measurements show larger temporal variations in gas flow rates in regions of high average flow rate (center of tree-kill areas) than in regions of low average flow rate (margins of tree-kill areas). Also complicating the analyses of long-term patterns was the fact that for cores collected from dead trees in 1995, it was difficult to determine which calendar year corresponded to the outermost growth ring without comparing the ^{14}C signals with the bomb curve to determine the year of death.

We have no clear answer as to why the pattern of ^{14}C depletion in the tree core from the RC tree-kill area (constant values 1990–1992) differs from the pattern for the HSL centrally located tree cores (increasing ^{14}C depletion 1990–1994). Possible explanations include more stable CO_2 concentration conditions near the RC tree as a result of lower wind velocities or topographic barriers, a real difference in the temporal pattern of gas emission in the central part of each tree-kill area, or the limited data set. Collection and analyses of cores from trees located marginal to the RC tree-kill area could help to resolve this issue.

Given the differences between the carbon-isotope patterns in the centrally located trees, the relatively short periods of record before tree death, and the unknown effects of tree stress related to CO_2 toxicity, we favor the use of growth ring data from the live marginal trees at HSL for indications of long-term variations in gas flux. Such data should provide the best measure of time- and space-integrated flux.

5.3. Extrapolation to CO_2 flux

Previous studies in Italy, Iceland, and Spain have demonstrated useful relations between ^{14}C depletions and variations in average annual CO_2 concentration in vegetation adjacent to natural CO_2 springs (van Gardingen et al., 1995; Cook et al., 1996; Piñol and Terradas, 1996). For diffuse emissions of magmatic CO_2 at Mammoth Mountain, we are assuming that the strength of the magmatic carbon signal in the tree-kill areas is primarily related to CO_2 concentration in the canopy, which in turn is determined largely by the magnitude of diffuse CO_2 flux. We recognize that various factors may influence the apparent relation between ^{14}C depletion in growth rings and the magnitude of magmatic CO_2 flux, including average wind speed and direction, topographic variations, and plant height and location. However, the consistency of the pattern of long-term ^{14}C depletion in three live trees at the margin of the HSL tree-kill area argues for confidence in relating this tree-ring data to variations in CO_2 flux. We had sought to further quantify this relation using data from chamber-based determinations of gas flux at HSL.

Three different groups have made annual determinations of total flux at HSL and a few other areas; one group has also made gas-flux determinations at shorter intervals in some of these areas. Several recent publications present gas-flux data for some or all of the 1995–1998 period (Rahn et al., 1996; Farrar et al., 1998; Gerlach et al., 1998a; Sorey et al., 1999). Unfortunately, significant differences exist between published results for 1995–1996 when experimenters used different chamber sizes, distributions of grid points, and mathematical techniques. In contrast, reasonably consistent results are indicated for 5 determinations made in the late summer and fall of 1997 and 1998 for which the total measured flux averages 116 ± 22 t/day (Sorey et al., 1999), excluding the short-lived increase that began in September 1998 (Gerlach et al., 1998b).

Perhaps a more useful result from the direct measurements, although as yet unpublished, is a set of 14 determinations made during the fall of 1998 over a common grid of ~ 70 points in the HSL tree-kill area (Rogie, personal communication, 1999). The flux values range from 48 to 133 t/day, reflecting the influences of temporal variations (Rogie et al., 1998), and average 93 ± 22 t/day. If we assume that this value is representative of the average CO_2 flux over the 1998 growing season, we can use the result from our ^{14}C depletion data that the amount of magmatic CO_2 fixed during this period was approximately half of that fixed during the peak period of gas emission in 1991, to obtain an estimate of 186 t/day for the flux in 1991. This estimate, however, should be considered preliminary until the relation between ^{14}C depletion and gas flux can be strengthened with additional direct measurements of gas flux during periods of significant change in flux.

The total amount of magmatic CO_2 discharge in the groundwater system draining Mammoth Mountain was estimated to range from 50 to 100 t/day by Sorey et al. (1999). These authors also found that over the 1997–1998 period, CO_2 concentrations in the spring waters remained constant as spring flow rates varied seasonally and in response to differences in annual rainfall. We would expect the patterns of ^{14}C depletion in trees adjacent to the CO_2-charged spring vents to be influenced by the flow of each spring or group of springs, which could affect local ambient concentrations of magmatic CO_2. This, of course, complicates the use of ^{14}C depletions in growth rings as indicators of changes in gas flux from depth.

The data for trees at RMCS and ASS show little or no ^{14}C depletions in the 1986–1991 period when successive years of below normal precipitation may have resulted in lower average spring discharge (Fig. 6). Some degree of correlation is also evident between rainfall and ^{14}C depletion in 1967–1969, but at other times little correlation is seen. There are also significant differences in the magnitude of the ^{14}C depletion in the two trees near the same spring (RMCS) during the 1982–1985 period. Additional data from tree cores in such areas would perhaps help in elucidating the influence of rainfall and other external factors on ^{14}C depletion.

There is evidence that ^{14}C depletions in trees at the springs increased somewhat in 1992–1993 and thereafter, possibly indicating a delayed effect of increased upflow of magmatic gas following the 1989 unrest. This seems a reasonable inference that allows for travel times of a few years between groundwater recharge and discharge areas on the mountain. In contrast, no obvious correlations are seen between ^{14}C depletions and seismic activity and related deformation within Long Valley caldera that peaked in 1980 (Bailey and Hill, 1990).

6. Conclusions

Due to the complexities of various factors affecting magmatic CO_2 emission from Mammoth Mountain, determining total CO_2 flux from Mammoth Mountain is difficult and predicting future rates of CO_2 emission is extremely challenging. Tree-ring data have aided considerably in determining when CO_2 emission from Mammoth Mountain began, as well as in elucidating the pattern of CO_2 emission at HSL from 1990 to 1998.

At HSL, CO_2 emission began in 1990, peaked in 1991, and subsequently decreased by a factor of two through 1998. We do not yet have equivalent data from the other tree-kill sites, so we cannot say with certainty that this pattern of CO_2 emission holds for all parts of Mammoth Mountain. Tree-ring data from areas near cold springs show that CO_2 emission from the groundwater system started long before the seismic activity of 1989, and has varied substantially from year to year. In late 1998, the release of magmatic CO_2 from HSL was estimated to be 93 t/day, on the same order magnitude as that estimated to be released from the cold groundwater system.

Additional study is required before the magnitude of CO_2 emission can be accurately determined for the whole of Mammoth Mountain. Investigating ^{14}C contents in living margin trees in all the areas of tree kill is the next important step in continuing the radiocarbon study of CO_2 release from Mammoth Mountain. That information, along with continued direct measurements of CO_2 flux, should then lead to a relationship between ^{14}C depletion and flux, which will determine the extent to which past fluxes can be reconstructed from ^{14}C depletions.

Acknowledgements

We would like to acknowledge Brian Frantz, Paula Zermeno, and the others in the graphite lab at Lawrence Livermore National Laboratory for their assistance. We would also like to thank John Rogie and Derrill Kerrick for their assistance at Mammoth Lake. This work was performed under the auspices of the US Department of Energy by University of

California Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

References

Allard, P., Carbonnelle, J., Dajlevic, D., Le Bronec, J., Morel, P., Robe, M.C., Maurenas, J.M., Faivre-Pierret, R., Martin, D., Sabroux, J.C., Zettwoog, P., 1991. Eruptive and diffuse emission of CO_2 from Mount Etna. Nature 351, 387–391.

Anza, S., Badalamenti, B., Giammanco, S., Gurrieri, S., Nuccio, P.M., Valenza, M., 1993. Preliminary study on enamation of CO_2 from soils in some area of Mount Etna (Sicily). Acta Volcanologia 3, 189–193.

Bailey, R.A., Hill, D.P., 1990. Magmatic unrest at Long Valley caldera, California, 1980–1990. Geosci. Can. 17, 175–178.

Baubron, J.C., Allard, P., Toutain, J.P., 1990. Diffuse volcanic emissions of carbon dioxide from Vulcano Island, Italy. Nature 344, 51–53.

Baubron, J.C., Allard, P., Saboroux, J.C., Tedesco, D., Toutain, J.P., 1991. Soil gas emanations as precursory indicators of volcanic eruptions. J. Geol. Soc. (London) 148, 571–576.

Brantley, S.L., Koepenick, K.W., 1995. Measured carbon dioxide emissions from Oldoinyo Lengai and the skewed distribution of passive volcanic fluxes. Geology 23, 933–936.

Berger, R., Jackson, T.B., Michael, R., Suess, H.E., 1987. Radiocarbon content of tropospheric CO_2 at China Lake, California 1977–1983. Radiocarbon 29, 18–23.

Burcholadze, A.A., Chudy, M., Eristavi, I.V., Pagava, S.V., Povinec, P., Sivo, A., Togonidze, G.I., 1989. Anthropogenic ^{14}C variations in atmospheric CO_2 and wines. Radiocarbon 31, 771–776.

Cook, A.C., Oechel, W.C., Sveinbjornsson, B., 1996. Using Icelandic CO_2 springs to understand the long-term effects of elevated atmospheric CO_2. In: Raschi, A., Miglietta, F., Tognetti, R., van Gardingen, P.R. (Eds.), Plant Responses to Elevated CO_2: Evidence from Natural Springs. Cambridge Univ. Press, United Kingdom, pp. 87–102.

D'Alessandro, W., Giammanco, S., Parello, F., Valenza, M., 1997. CO_2 output and $\delta^{13}C$ (CO_2) from Mt. Etna as indicators of degassing of shallow asthenosphere. Bull. Volcanol. 58, 455–458.

Davis, J.C., Proctor, I.D., Southon, J.R., Caffee, M.W., Heikkinen, D.W., Roberts, M.L., Moore, T.L., Turtletaub, K.W., Nelson, D.E., Loyd, D.H., Vogel, J.S., 1990. LLNL/UC AMS facility and research program. Nucl. Instrum. Methods Phys. Res. 52, 269–272.

Farrar, C.D., Sorey, M.L., Evans, W.C., Howle, J.F., Kerr, B.D., Kennedy, B.M., King, C.-Y., Southon, J.R., 1995. Forest-killing diffuse CO_2 emission at Mammoth Mountain as a sign of magmatic unrest. Nature 376, 675–678.

Farrar, C.D., Howle, J.F., Neil, J.M., Sorey, M.L., Evans, W.C., 1998. Volcanic CO_2 emissions at Mammoth Mountain, CA, USA. EOS Trans., AGU 79, 45, Fall Meeting Supplement, F941 (Abstract).

Gerlach, T.M., Doukas, M.P., McGee, K.A., Kessler, R., 1998a. Three-year decline of magmatic CO_2 from soils of a Mammoth Mountain tree kill: Horseshoe Lake, CA, 1995–1997. Geophys. Res. Lett. 25, 1947–1950.

Gerlach, T.M., Doukas, M.P., Kessler, R., McGee, K.A., 1998b. Soil CO_2 efflux, emission rates, degassing trends, and degassing events at the Horseshoe Lake tree kill, Mammoth Mountain, CA, 1995–1998. EOS Trans., AGU 79, 45, Fall Meeting Supplement, F941 (Abstract).

Giammanco, S., Gurrieri, S., Valenza, M., 1995. Soil CO_2 degassing on Mt. Etna (Sicily) during the period 1989–1993: discrimination between climatic and volcanic influences. Bull. Volcanol. 57, 52–60.

Hill, D.P., 1996. Earthquakes and carbon dioxide beneath Mammoth Mountain, CA. Seismol. Res. Lett. 67, 8–15.

Levin, I., Kromer, B., 1997. Twenty years of atmospheric $^{14}CO_2$ observations at Schausinsland Station, Germany. Radiocarbon 39, 205–218.

Levin, I., Kromer, B., Schoch-Fischer, H., Bruns, M., Münnich, M., Berdau, D, Vogel, J.C., Münnich, K.O., 1985. 25 years of tropospheric ^{14}C observations in Central Europe. Radiocarbon 27, 1–19.

Levin, I., Bösinger, R., Bonani, G., Francey, R., Kromer, B., Münnich, K.O., Suter, M., Trivett, N.B.A., Wölfli, W., 1992. Radiocarbon in atmospheric carbon dioxide and methane: global distribution and trends. In: Taylor, R.E., Long, A., Kra, R.S. (Eds.), Radiocarbon after Four Decades: An Interdisciplinary Perspective. Springer, New York, pp. 503–517.

Olsson, I.U., Possnert, G., 1992. ^{14}C activity in different sections and chemical fractions of oak tree rings, AD1938-1981. Radiocarbon 34, 757–767.

Piñol, J., Terradas, J., 1996. Preliminary results on dissolved inorganic ^{13}C and ^{14}C content of a CO_2-rich mineral spring of Catalonia (NE Spain) and of plants growing in its surroundings. In: Raschi, A., Miglietta, F., Tognetti, R., van Gardingen, P.R. (Eds.), Plant Responses to Elevated CO_2: Evidence from Natural Springs. Cambridge Univ. Press, United Kingdom, pp. 165–173.

Rahn, T.A., Fessenden, J.E., Wahlen, M., 1996. Flux chamber measurements of anomalous CO_2 emission from the flanks of Mammoth Mountain, CA. Geophys. Res. Lett. 23, 1861–1864.

Rogie, J.D., Kerrick, D.M., Chiodini, G., Sorey, M.L., Virgili, G., 1998. Continuous monitoring of diffuse CO_2 degassing, Horseshoe Lake, Mammoth Mountain, CA. EOS Trans., AGU 79, 45, Fall Meeting Supplement, F942 (Abstract).

Sorey, M.L., Evans, W.C., Kennedy, B.M., Farrar, C.D., Hainsworth, L.J., Hausback, B., 1998. Carbon dioxide and helium emissions from a reservoir of magmatic gas beneath Mammoth Mountain, CA. J. Geophys. Res. 103, 15303–15323.

Sorey, M., Evans, B., Kennedy, M., Rogie, J., Cook, A., 1999. Magmatic gas emissions from Mammoth Mountain, Mono County, CA. Calif. Geol. 52 (5), 4–16.

Southon, J.R., Caffee, M.W., Davis, J.C., Moore, T.L., Proctor, I.D., Schumacher, B., Vogel, J.S., 1990. The new LLNL AMS spectrometer. Nucl. Instrum. Methods Phys. Res. 52, 301–305.

Stuiver, M., Polach, H.A., 1977. Discussion: reporting of ^{14}C data. Radiocarbon 19, 355–363.

van Gardingen, P.R., Grace, J., Harkness, D.D., Miglietta, F., Raschi, A., 1995. Carbon dioxide emissions at an Italian mineral spring: measurements of average CO_2 concentration and air temperature. Agric. For. Meteorol. 73, 17–27.

Vogel, J.S., Nelson, D.E., Southon, J.R., 1989. Accuracy and precision in dating microgram carbon samples. Radiocarbon 31, 145–149.

Williams, S.N., 1995. Dead trees tell tales. Nature 376, 644.