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Carbon isotopes in aquatic plants, Long Valley caldera, California as records of past hydrothermal and magmatic activity

John B. Reid, Jr.[1], Jesse L. Reynolds[2], Nathan T. Connolly, Shari L. Getz, Pratigya J. Polissar[3], and Lawrence J. Winship

School of Natural Science, Hampshire College, Amherst, Massachusetts

Laura J. Hainsworth[4]

Lawrence Livermore National Laboratories, Livermore, California

Abstract. Hot and cold springs contribute "dead" (^{14}C free) dissolved inorganic carbon (DIC) to the Owens River and Hot Creek. Headwaters aquatic plants have modern ^{14}C, but live plants downstream of the intracaldera springs are depleted in ^{14}C, (as low as 19% modern, with apparent ages up to 13.3 kyrs). In an abandoned meander of the upper Owens River, preserved streambed plants are buried by 600 year old Inyo Craters pumice. Apparent ^{14}C ages of these plants exceed true ages by ~ 1100 years indicating that they also incorporated dead DIC as they grew. The preserved plants are downstream of Big Springs, whose elevated dead DIC may represent magmatic `CO_2. The buried plants incorporated ~10% dead carbon, although modern plants here have ~50% dead carbon, suggesting that more magmatic CO_2 is now entering the upper Owens River than at the time of the Inyo Craters eruptions 600 years ago.

Introduction

Long Valley caldera (Fig. 1), a 17 x 32 km depression on the eastern boundary of the Sierra Nevada, California, formed about 760 kyr ago (Bailey, 1989). Magmatic activity since then has produced a 500 m high resurgent dome in the west-central caldera floor. The most recent caldera-related volcanism was the Inyo Crater eruptions, ~600 years ago, and phreatic explosions on Mammoth Mountain, ~700 years ago (M.L. Sorey, pers. comm, 1997). Since 1980, there have been several indications of renewed magmatic unrest. Seismic activity and changes in fumarole composition may indicate shallow magmatic intrusion (Hill et al., 1990; Sorey et al., 1993). Leveling surveys along U.S. Highway 395 have shown ~60 cm of inflation of the dome between 1979 and 1984 (Castle et al., 1984). Diffuse emissions of magmatic CO_2 near Mammoth Mountain followed a swarm of seismic activity in 1989 (Farrar et al., 1995). Magmatic CO_2 may also be entering the surface waters of Long Valley and taken up by aquatic plants. In this report, we use the anomalous ^{14}C content of streambed plants as indicators of present and past magmatic CO_2 emissions into the caldera's surface waters.

The use of aquatic plants for this purpose came about accidentally. Where the Owens River skirts the northeast flank of the caldera's resurgent dome, its course has alternated between two parallel meander belts, apparently in response to tilting of its floodplain. One possible cause of the tilting is the alternating inflation and deflation of the dome (Reid, 1992). We hoped to date the river's occupation of these meander belts by radiocarbon-dating the remains of ancient plants buried in abandoned channels of both meander belts. For control, we also dated modern plants in the Owens River and Hot Creek. Modern plants throughout the caldera - and for at least 65 km further downstream - have anomalous ^{14}C ages (up to 13,000 years), particularly near the hot and cold springs. While this finding meant that buried plants could not be used for dating the hypothetical past behavior of the dome, it suggested that they might be useful in assessing modern and past emissions of dead CO_2 into the caldera's river system. Other investigators have seen ^{14}C deficiencies in modern plants due to magmatic activity (e.g.: Sveinbjörnsdóttir et al., 1992; Srdoc et al., 1986); As discussed below, Long Valley provides the additional opportunity of comparing past and present releases of magmatic CO_2 to surface waters in a volcanic setting.

"Dead" (^{14}C free) dissolved inorganic carbon (DIC) in hydrothermal and volcanic areas has been attributed to magmatic inputs (e.g., Shevenell and Goff, 1993; Giggenbach, 1995; Rose and Davisson, 1996). While dissolution of carbonate minerals at depth is a possibility, and the deep reservoir of the Long Valley hydrothermal system may reside in metamorphic marine sediments (Sorey et al., 1991), CO_2-rich gas with magmatic He and C isotopic character has been entering the caldera as diffuse emissions (~1200 T CO_2/day) at Mammoth Mountain since 1990 (Farrar et al., 1995; Sorey et al., 1996). The isotopic character of DIC in wells and springs near Mammoth Mountain shows that the groundwater is dissolving magmatic CO_2 (Sorey et al., 1996). Hilton (1996) examined He and C isotopes of hydrothermal gases and concluded that the primary source of CO_2 is magmatic gas, although a small input from thermal decarbonization of marine carbonates could not be excluded. Taylor and Gerlach (1984) found that volcanic rocks are not a source of hydrothermal CO_2. In addition, we can rule out decay of atmospheric ^{14}C in the groundwater system as the main reason for diminished ^{14}C activity since residence time is estimated at ~1200 years (small compared with the half life of ^{14}C) in the hydrothermal reservoir (White et al., 1990).

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[1] to whom correspondence should be sent

[2] Now at Department of Environmental Science, Policy and Management, University of California, Berkeley, CA 94701

[3] Now at Department of Geosciences, University of Massachusetts, Amherst, MA 01003

[4] Now at Chemistry Department, Emory and Henry College, Emory, VA 24327

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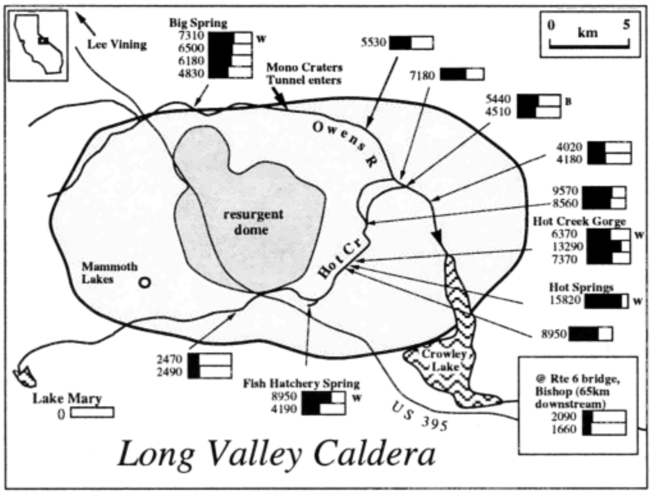

Figure 1. Map of Long Valley caldera (after Bailey, 1989) showing apparent ages (numbers in years) and percent "dead" C (solid portions of horizontal bars) for streambed plants, waters (W) and an aquatic insect casing sample (B) in the Owens River and Hot Creek.

Here, we report the results of carbon isotopic studies of the aquatic plants and spring waters of Long Valley as measures of present and past magmatic CO_2 release in the caldera. Hainsworth et al. (1995) used tree rings at a fumarole near Mammoth Mountain to document local variations in the emissions of magmatic CO_2 over the past decade. In this report, we suggest that apparent radiocarbon ages of preserved aquatic plants may provide clues to magmatic CO_2 during the Inyo Craters eruptions 600 years ago, provided the plants can be dated by other means.

Methods

Surface waters and aquatic and terrestrial plants were collected in June of 1994 and 1996. We measured pH and alkalinity for every site in 1996; stream discharge was measured at selected sites near stream and spring junctions. We precipitated DIC samples as $SrCO_3$ using strontium chloride and ammonium hydroxide. Liquid scintillation spectrometry (Beta Analytic, Miami, Florida) was used to measure ^{14}C of all plant samples and all DIC precipitates but one. It, the conifer charcoals and the buried plant remains were analyzed by accelerator mass spectrometry (AMS) (Lawrence Livermore National Laboratory). Fractionation in ^{14}C was corrected using measured $\delta^{13}C$. We performed ^{13}C analyses on additional plants by combustion and mass spectrometry at the University of Vermont Stable Isotope Laboratory. Inductively coupled plasma-atomic emission spectroscopy (Thermal Jarrell Ash ICAP 61) at Middlebury College and inductively coupled plasma-mass spectrometry (Perkin Elmer Elan 6000) at Hampshire College were used for dissolved cation analyses of the 1994 and 1996 water collections, respectively.

Results

The results of the elemental analyses show that the caldera surface water chemistry is controlled by the hot and cold springs (Fig. 2a). Most conservative elements enter the stream in pronounced, discrete inputs at the major springs and have essentially constant concentrations between these inputs. This results in stepwise increases in concentration, such as those shown for arsenic in Fig. 2a. The highest inputs of most of the analyzed elements occur at the major hot springs (especially As, Na, Rb, Cs, W); cold springs contribute the bulk of a few elements (eg: Mg, Ca, P, Mo, Zn). Sr, K and Si are added from both spring types about equally. These data are available upon request.

Carbon isotopic data for Long Valley plants and water samples are shown in Figs. 2b, 2c and 3. On a plot showing ^{14}C and ^{13}C variation together (Fig. 3), ^{14}C ranges widely from 0% modern in magmatic CO_2 to 113% in atmospheric CO_2, and thus mixing is the main cause of ^{14}C variation. $\delta^{13}C$ varies much more narrowly, mainly due to fractionation accompanying photosynthesis. CO_2 samples from waters appear to be mixtures of atmospheric, magmatic and soil gas (shaded triangle in Fig. 3). Plants show typical depletion in $\delta^{13}C$ by about 20-25 per mil relative to their host waters (Hoefs, 1997), with plants near Big Springs containing the most negative $d^{13}C$, and thus the highest proportions of soil gas. Variation in ^{14}C and ^{13}C with distance down each drainage are shown in Figs. 2b and 2c. An aquatic plant sample from Lake Mary (headwaters of Hot Creek) has a full complement of ^{14}C (113 % modern ^{14}C (pmC)), but all other streambed plants we have sampled are depleted in ^{14}C. Where data for both exist, plants and their waters are similar in pmC, with mismatches due probably to incomplete mixing of water types, photosynthesis-induced fractionation and possibly the fact

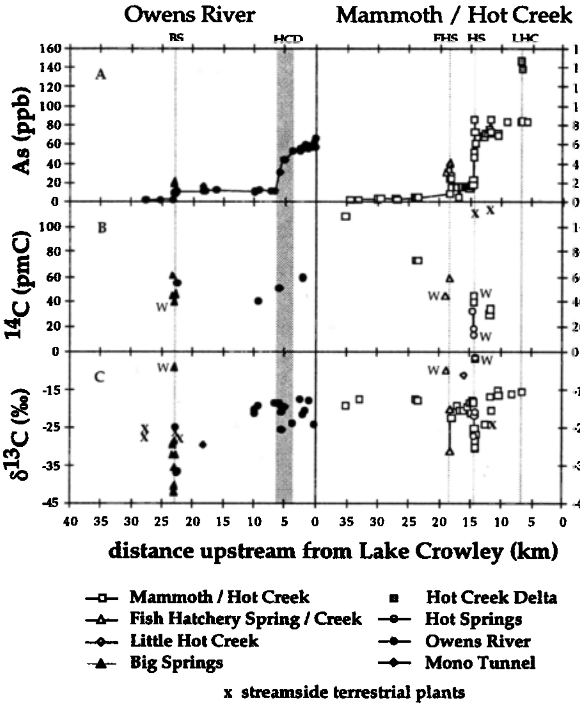

Figure 2. (A) Arsenic concentrations in spring and surface waters; this stepped pattern is typical of most analysed elements. Little Hot Creek = 248 ppb and Hot Springs = 191 ppb (off scale). (B) ^{14}C content of plants and DIC. (C) ^{13}C of plants and DIC. All plants are aquatic except (x) which are terrestrial grasses immediately adjacent to the stream. "W" next to a point signifies DIC. The grey vertical lines represent input from Big Springs (BS), the Hot Creek delta (HCD), Fish Hatchery Springs (FHS), Hot Springs in Hot Creek gorge (HS), and Little Hot Creek (LHC).

that plants integrate over the growing season, while water samples are instantaneous. Fractionation of $^{14}C/^{12}C$ during photosynthesis, ~45 ‰ (Fritz et al., 1989), is small compared to the range of values among plant samples (19 to 113 pmC). The large amounts of dead DIC at Big Spring and Fish Hatchery Spring, the two major cold springs, indicate that they receive dead carbon from magmatic gases, the hydrothermal system, or contact with carbonate minerals.

Total dead DIC leaving the caldera can be estimated from simultaneous measurement of stream discharge, alkalinity, and ^{14}C content (estimated from plant isotopes). In June, 1996, ~15 T/day total DIC and ~6 T/day dead DIC were discharging from the Owens River into Lake Crowley. These values are probably slight underestimates since by the time the water reached the lower Owens River some dead DIC may have been lost through photosynthesis and atmospheric mixing. The maximum dead DIC fluxes of the Owens River and Hot Creek were 4.6 and 5.7 T/day, respectively, giving an estimate of ~10 T/day dead DIC entering the surface waters of the caldera.

Although the waters of Mammoth Creek (upper Hot Creek) at US 395 chemically resemble those of the headwaters with very low cation concentrations, the ^{14}C contents of two aquatic plants there are depleted (74 pmC). $\delta^{13}C$ values (-17.5 ± 0.2‰) of these samples are normal for aquatic plants (Deines, 1980). There are no major springs upstream from this point, and contributions from carbonates is excluded by the low and nearly constant calcium and magnesium concentrations from Lake Mary to US 395. This ^{14}C anomaly is likely produced by fumarolic activity in a small valley ~1.5 km northwest of the sampling site, where CO_2 from hydrothermal fluids boiling at depth is entering the shallow groundwater.

Unlike ^{14}C, the ^{13}C contents of aquatic plants are not useful as indicators of past stream carbon isotopic character. The $\delta^{13}C$ of all analyzed terrestrial plants (~-26‰) and aquatic plants above the major springs (~-18‰) are typical (Deines, 1980). Two major springs, Big Spring and Fish Hatchery Springs contribute lighter carbon (lower $\delta^{13}C$) to plants immediately downstream (Fig. 2c). The lighter carbon stems mainly from biogenic soil CO_2. As one progresses on downstream, the low $\delta^{13}C$ of the plants returns quickly to the "baseline" value of -18‰. ^{14}C excursions are considerably larger, and persist for much greater distances downstream.

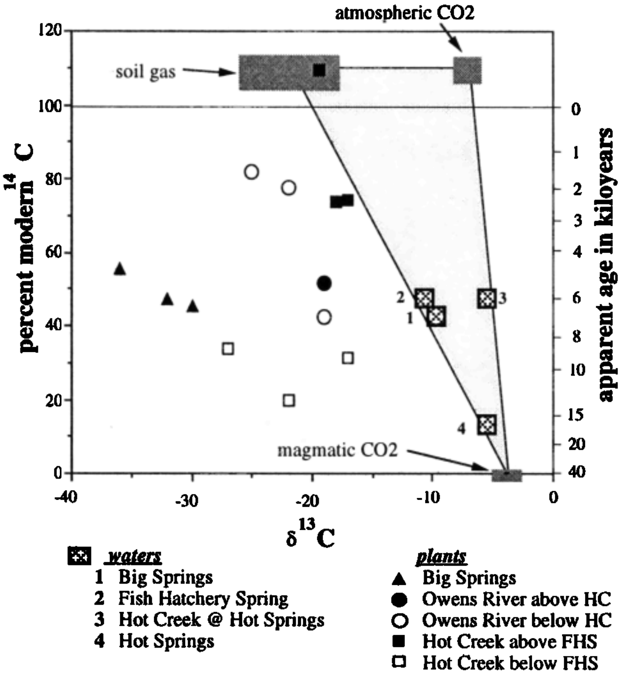

Figure 3. ^{14}C and ^{13}C variations in waters and plants of Long Valley caldera. Wide variation in ^{14}C is due to mixing of CO_2 from three reservoirs (shaded triangle), while $\delta^{13}C$ varies mainly due to fractionation during one or more stages of photosynthesis (see text).

Preserved plants below Big Spring as possible records of past CO_2 release

Dead DIC from the springs of Long Valley causes dramatic depletions in ^{14}C of live stream plants in the caldera and for many kilometers downstream. If the dead DIC is magmatic in origin, preserved stream plants could serve as records of past magmatic activity.

Magmatic CO_2 is the likely source of dead DIC in the modern Long Valley hydrothermal system. As thermal waters saturated with $CaCO_3$ rise, calcite precipitates and CO_2 evolves (White and Peterson, 1991). Hilton (1996) determined that this CO_2 is primarily magmatic in origin. Big Spring is a cold spring with a high dead DIC concentration but probably does not receive chemical inputs from the hydrothermal system (M. L. Sorey, pers. comm., 1996). The possible sources of its dead carbon are interactions with carbonates in marine metasediments, magmatic emissions of CO_2 to its recharge area on the north side of Mammoth Mountain (Heim, 1992), and decomposition of ancient organic matter buried by the moat rhyolites (M. L. Sorey, pers. comm., 1996). Since the molar Ca concentration at Big Spring is about an order of magnitude lower than that of dead DIC, only a small portion of the C is from calcium carbonates. If Mg is included, at most 40% of C is from carbonate minerals. Thus, there may be a large input of magmatic CO_2 into the recharge waters of Big Spring. Forthcoming helium isotope data from the U.S. Geological Survey should clarify this issue (M. L. Sorey, pers. comm., 1996). Heim (1992) estimated that Big Spring water averages ~12 years old based on tritium levels. Therefore, the ^{14}C contents of plants downstream of Big Spring may be sensitive indicators of magmatic CO_2 emissions.

We have discovered preserved aquatic plant material that may have recorded the isotopic character of DIC in the upper Owens River at an important juncture in its recent past. We have found a pumice-filled abandoned channel of the Owens River ~3 km. upstream of the Hot Creek confluence apparently filled in a single event at the time of the Inyo Craters eruptions, 600 years ago. AMS ^{14}C dates on 11 conifer charcoals in the pumice cluster between 600 and 700 ybp (Fig. 4). Beneath the pumice, we found the remains of aquatic plants with roots still attached to small river cobbles in anoxic groundwater in the thalweg stream gravel. AMS dates of these plant remains range from 1100 to 2040 ybp. Thus, when they were buried by pumice, they contained ~10% dead DIC, compared with ~50% in the plants of this section of the Owens River today. The only major inputs upstream of this site today are Big Spring and the Mono Craters Tunnel. Based on calcium concentrations, the total upstream contribution from dissolved $CaCO_3$ is no more than one-third of the dead DIC.

These results imply that (1) magmatic CO_2 was entering the upper Owens River at the time of the 600 ybp Inyo Craters eruptions, and (2) that modern levels there (1994-1996) are

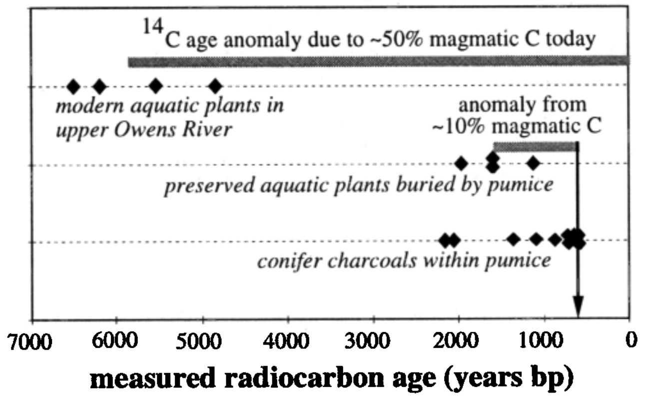

Figure 4. Apparent ages of modern and preserved stream bed plants in the upper Owens River along with true ages for conifer charcoals collected in a pumice-filled abandoned channel of the river. Charcoals cluster about 600 years in age, suggesting the pumice is Inyo Craters ejecta. Modern plants contain about 50% magmatic C, five times higher than the magmatic C content of plants growing in the river at the time of the 1400 AD eruptions.

five times higher than those recorded by the plant remains at the time of the last caldera-related eruptions.

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References

Bailey, R. A., Geologic map of Long Valley caldera, Mono-Inyo Craters volcanic chain, and vicinity, Eastern California, U.S. Geologic Survey Map I-1933, 1989.

Castle, R. O., J. E. Estrem, and J. C. Savage, Uplift across Long Valley caldera, California, *Journal of Geophysical Research*, 89, 11507-11516, 1984.

Deines, P., The isotopic composition of reduced organic carbon, in *Handbook of Environmental Isotope Geochemistry, Vol. 1, The Terrestrial Environment, A*, P. Fritz and J. Ch. Fontes (Eds.), pp. 329-390, Elsevier: Amsterdam, 1980.

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

Fritz, P., J-Ch. Fontes, S.K. Frape, D. Louvat, J-L. Michelot, and W. Balderer, The isotope geochemsitry of carbon in groundwater at Stripa, *Geochimica et Cosmochimica Acta*, 53, 1765-1775, 1989.

Giggenbach, W. F., Variations in the chemical and isotopic composition of fluids discharged from the Taupo Volcanic Zone, New Zealand, *Journal of Volcanology and Geothermal Research*, 68, 89-116, 1995.

Hainsworth, L. J., C. D. Farrar, J. R. Southron, Magmatic CO_2 record in pine needs and growth rings at Mammoth Mountain, California, *Eos*, 76, 688, 1995.

Heim, K., Hydrologic study of the Big Springs, Mono County, California, unpublished bachelor's thesis, California State University, Fullerton, 1992.

Hill, D. P., W. L. Ellsworth, M. J. S. Johnston, J. O. Langbein, D. H. Oppenheimer, A. M. Pitt, P. A. Reasenberg, M. L. Sorey, and S. R. McNutt, The 1989 earthquake swarm beneath Mammoth Mountain, California: an initial look at the 4 May through 30 September activity, *Bulletin - Seismological Society of America*, 80, 325-339, 1990.

Hilton, D. R., The helium and carbon isotope systematics of a continental geothermal system: results from monitoring studies at Long Valley Caldera, *Chemical Geology*, 127, 269-295, 1996.

Hoefs, J. Stable Isotope Geochemistry , Springer, Berlin, 1997.

Reid, J. B. Jr., The Owens River as a Tiltmeter for Long Valley Caldera, California, *The Journal of Geology*, 100, p. 353-363, 1992.

Rose, T. P. and M. L. Davisson, Radiocarbon in hydrologic systems containing dissolved magmatic carbon dioxide, *Science*, 273, 1367-1370, 1996.

Shevenell, L. and F. Goff, Addition of magmatic volatiles into the hot spring waters of Loowit Canyon, Mount St. Helens, Washington, USA, *Bulletin of Volcanology*, 55, 489-503, 1993.

Sorey, M. L., B. M. Kennedy, W. C. Evans, C. D. Farrar, and G. A. Suemnicht, Helium isotope and gas discharge variations associated with crustal unrest in Long Valley caldera, California, 1989-1992, *Journal of Geophysical Research*, 98, 15871-15889, 1993.

Sorey, M. L., B. M. Kennedy, and L. J. Hainsworth, Carbon dioxide and helium emissions from a reservoir of magmatic gas beneath Mammoth Mountain, California (abstract), *Eos Trans. AGU*, 77, F830, 1996.

Sorey, M. L., G. A. Suemnicht, N. C. Sturchio, and G. A. Nordquist, New evidence on the hydrothermal system in Long Valley caldera, California, from wells, fluid sampling, electrical geophysics, and age determinations of hot-spring deposits, *Journal of Volcanology and Geothermal Research*, 48, 229-264, 1991.

Srdoc, D., I. Krajcar-Bronic, N. Horvatincic, and B. Obelic, Increase of ^{14}C activity of dissolved inorganic carbon along a river course, *Radiocarbon*, 28, 515-521, 1986.

Sveinbjörnsdóttir, A. E.;. E., J. Heinemeier, N. Rud, and S. J. Johnsen, Radiocarbon anomalies observed for plants growing in Icelandic geothermal waters, *Radiocarbon*, 34, 696-703, 1992.

Taylor, B. E., and T. M. Gerlach, Mantle CO_2 degassing at Long Valley, Steamboat Springs at the Coso Range (abstract), *EOS Trans AGU* , 65, 1153, 1984.

White, A. F, M. L. Peterson, H. A. Wollenberg, and S. Flexser, Sources and fractionation processes influencing the isotopic distribution of H, O, and C in the Long Valley hydrothermal system, California, U.S.A., *Applied Geochemistry*, 5, 571-585, 1990.

White, A. F, M. L. Peterson, H. A. Wollenberg, and S. Flexser, Sources and fractionation processes influencing the isotopic distribution of H, O, and C in the Long Valley hydrothermal system, California, U.S.A., *Applied Geochemistry*, 5, 571-585, 1990.

J.B. Reid Jr.[1], J.L. Reynolds[2], N.T. Connolly, S.L. Getz, P.J. Polissar[3], and L.J. Winship, School of Natural Science, Hampshire College. Amherst, MA, 01002.

L.J. Hainsworth[4], Lawrence Livermore National Laboratories, Livermore, CA 94551. email: jreid@hampshire.edu

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