Accumulation of mantle gases in a permanently stratified volcanic lake
(Lac Pavin, France)

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Abstract—Lac Pavin is a volcanic crater lake in the Massif Central (France), characterized by a permanent vertical density stratification resulting from a strong and persistent chemocline between about 60 and 70 m depth. The deep water below the chemocline forms the monimolimnion, in which most dissolved ions as well as helium, carbon dioxide, and methane are strongly enriched. The 3He/4He ratio of the excess helium is (9.09 ± 0.01) × 10^{-6}, or (6.57 ± 0.01) × 10^{-6}, or (6.57 ± 0.01) × 10^{-6}. These findings clearly indicate a flux of mantle-derived magmatic gases into the monimolimnion.

In order to derive the fluxes of magmatic volatiles into Lac Pavin, it is essential to understand the hydrologic characteristics of the lake. Previously published two-box models have assumed groundwater input at the lake bottom, a short residence time in the monimolimnion, and biogenic origin of the CO2. We propose an alternative model with a flux of magmatic gases, but not of water, into the monimolimnion, and a weak diffusive coupling between the monimolimnion and the overlying mixolimnion which leads to a long deep-water residence time (~70 yr). We reassess the carbon budget of the lake and conclude that the major part of the accumulated CO2 in the monimolimnion is of magmatic origin. From the model-derived water exchange rates, we calculated a mantle 4He flux of (6 ± 2) × 10^{11} atoms m^{-2} s^{-1}. This value lies near the lower end of the range found in comparable volcanic lakes. The flux of magmatic CO2 is estimated as (1.2 ± 0.4) × 10^{-3} mol m^{-2} s^{-1}, which is also comparatively low. The monimolimnion appears to be in steady state with respect to these fluxes, therefore no further, potentially hazardous, accumulation of CO2 takes place. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

Several studies have used the ratio of He isotopes to investigate the origin of gases in the deep water of lakes in volcanic areas (Lake Nyos, Sano et al., 1990; Crater Lake, Collier et al., 1991; Lake Mashu, Igarashi et al., 1992; Lakes Van and Nemrut, Kipfer et al., 1994; Laacher See, Aeschbach-Hertig et al., 1996b). In spite of its presence as a trace element in magmatic gases, He is a rather uniform and close to 2 \times 10^{-9} (Marty and Jambon, 1987; Giggenbach et al., 1991; Martin et al., 1993). The ability of volcanic lakes to store magmatic gases can be used to quantify mantle degassing. However, a thorough understanding is required of the physical characteristics of the investigated lake, particularly deep-water residence time, in order to be able to convert measured He concentrations into He fluxes (Kipfer et al., 1994; Aeschbach-Hertig et al., 1996b). The fluxes of mantle-derived 3He vary significantly among lakes studied until now (between 5 × 10^{10} atoms m^{-2} s^{-1} in Crater Lake and 2 × 10^{9} atoms m^{-2} s^{-1} in Lake Nyos). These fluxes and observed C/3He ratios can be used to estimate the flux of magmatic CO2.

Lac Pavin is a small (0.44 km^2), but deep (92 m), nearly circular lake located at an altitude of 1197 m in the French Massif Central (Fig. 1). It occupies a maar crater which was formed about 6000 years ago (Camus et al., 1993; older sources cited even younger ages: 4–5 kyr, Meybeck et al., 1975; 3.5 kyr, Camus et al., 1973). It represents the most recent period of volcanic activity in the Massif Central. Its geological setting is similar to that of other maar lakes such as Lake Nyos (Cameroon) or Laacher See (Germany). The catastrophe at Lake Nyos in 1986, when 1700 people were killed by a cloud of CO2 gas released from the lake (Kling et al., 1987) sparked an investigation of the risk of similar catastrophic CO2 degassing at Lac Pavin (Camus et al., 1993). This study concluded that the CO2 concentration in the deep water is far from saturation and

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that most of the carbon is of biogenic origin. In this current study, we use He isotope data to reassess the origin and flux of He and CO₂ in Lac Pavin.

A peculiar property of Lac Pavin is the presence of a stagnant deep-water layer, called monimolimnion. This was first described in detail by Pelletier (1968), although some indications had been observed earlier (Olivier, 1952). The monimolimnion is not affected by seasonal mixing; it is permanently anoxic and has an elevated temperature. It is separated from the overlying mixolimnion, the seasonally mixed layer, by a chemocline between about 60 and 70 m depth. The sharp increase in concentrations of dissolved ions in the chemocline assures the stability of the stratification despite the concurrent increase of temperature. The key quantity needed to calculate fluxes of dissolved species in Lac Pavin is the water residence time in the monimolimnion.

Several studies have tried to answer questions about the origin and evolution of the monimolimnion of Lac Pavin. Because the surficial water input to the lake appears to be smaller than the output, the existence of sublacustrine springs has been suggested (Glangeaud, 1916). Tritium data have repeatedly been used to assess the water balance. Alvinerie et al. (1966) found no evidence for a spring in the first tritium profiles from the lake. Meybeck et al. (1975) postulated a spring of mineralized water discharging into the monimolimnion. Martin (1985) quantified this hypothesis with a box-model based on tritium data. Camus et al. (1993) updated this model using new tritium results, confirmed the presence of a spring in the monimolimnion, but suggested based on K/Li ratios that its water was not of thermomineral origin. This model was used in subsequent geochemical studies to calculate element fluxes through the chemocline (Michard et al., 1994; Viollier et al., 1995). The model implies a short residence time of about 3 yr in the monimolimnion, and consequently large fluxes of dissolved and particulate matter across the oxic-anoxic interface at the chemocline.

In recent years, however, two independent approaches have raised doubts about the validity of this model. New tritium modeling in our group showed that our tritium data from 1993 are inconsistent with the assumption of a large input of tritium-free water into the monimolimnion (Waldner, 1995). Moreover, all tritium data from Lac Pavin, including our results from 1993 and 1996, can be explained by a model with very slow diffusive exchange across the chemocline and a residence time of about 70 yr in the monimolimnion (Schmid, 1997). In a parallel study, Viollier et al. (1997) dismissed the model with a spring in the monimolimnion because settling particle fluxes observed by using sediment traps were much smaller than predicted by the model; they estimated a residence time of about 300 yr in the monimolimnion.

In this study, we use He not only as a geochemical tracer to investigate the origin of the gases in the monimolimnion, but also as a conservative physical tracer to constrain the deep-water residence time. Because He is a chemically inert noble gas, it is a useful tool for the study of transport processes in lakes. A new box model is used to estimate the fluxes of He and
CO₂ into Lac Pavin. Our complete data set, including an extensive temperature and conductivity survey and transient tracer data (tritium, CFCs) will be discussed in a complementary article (Aeschbach-Hertig et al., submitted).

2. EXPERIMENTAL METHODS

Three water samples for He isotope analysis were taken with the most elementary methods during a reconnaissance at Lac Pavin in August 1993. A Niskin bottle on a rope was lowered by hand from a small row boat. Temperature was measured with a thermometer after recovery of the bottle. Given these conditions, we estimate the accuracy of the sampling depth as ± 5 m and that of the temperature as ± 0.5°C. During two expeditions in September 1994 and 1996, water samples were taken in 5–15 m intervals in vertical profiles, using Niskin bottles and a hand-driven winch with a counter to determine depth with an accuracy better than ±2%. Water samples were analyzed for He and Ne isotoxps, tritium, CFCs, CH₄, N₂, Ar, O₂, and alkalinity. Furthermore, high resolution CTD (conductivity, temperature and depth) profiles were recorded with a Seacat SBE-19 probe, which was also equipped with sensors for O₂, pH, and light transmissivity. The CTD-probe recorded data twice per second, and it was lowered slowly enough to obtain results every 10–20 cm. Temperature was measured with an accuracy of 0.01°C and a resolution of 0.001°C. The pH electrode was calibrated with standard buffer solutions. All samples and CTD-profiles discussed here were taken at positions near the center of the lake, where it is deepest.

For the He analysis, the water was transferred into copper tubes immediately after recovery from the lake and tightly sealed by stainless steel clamps on both ends. This standard procedure was problematic for samples taken deeper than 70 m depth, where bubbles were observed in the transparent tubing used for the transfer of the water to the copper tubes. Such degassing indicates the presence of high concentrations of dissolved gases in the deep water, most likely CO₂ or CH₄, which exsolve with pressure reduction as the water is brought to the surface. No special measures were taken to avoid degassing or to collect the exsolving gas, but corrections can be made for the effect of degassing.

In the laboratory, the dissolved gases were extracted from the water under vacuum. By several cold traps and getter pumps, the He and Ne fractions were separated and then simultaneously analyzed for concentration and isotopic composition in separate, non-commercial mass spectrometers. These were both statically operated 90° sector mass spectrometers equipped with the highly linear Baur-Signier ion source (Baur, 1980). They were calibrated with an air standard. Experimental uncertainties mainly result from fluctuations of instrument sensitivity and are estimated from the standard deviation of the calibrations within a measurement run. Average 1σ-errors on water samples from Lac Pavin are 0.4% for 3He/4He-ratios, 0.6% for 4He concentrations, and 1.0% for Ne concentrations (Table 1). These values are close to the long-term mean reproducibility of the system. More detailed discussions of the analytical procedures for He and Ne can be found in Kipfer et al. (1994), Aeschbach-Hertig et al. (1996b), and Beyerle et al. (submitted).

Samples for the analysis of CFCs, CH₄, N₂, and Ar were also taken in copper tubes. The gases were analyzed on a gas chromatograph equipped with an electron capture detector (ECD) for the sensitive measurement of trace amounts of CFCs. CH₄, N₂, and Ar were measured with a thermal conductivity detector (TCD). Calibration was performed with an air standard. Accuracy is on the order of a few percent. The experimental procedures for these gases are in detail described by Hofer and Imboden (1998). Samples for titration of dissolved oxygen and alkalinity were taken in glass tight glass bottles. Alkalinity was determined in the laboratory a few days after sampling by titration with HCl solution and the Gran function. Precision is estimated to ±2%.

Cross-sectional areas of the lake at intervals of 10 m depth were produced by digitizing the bathymetric map of Delebecque (1898). For box model calculations, volume weighted concentrations were estimated using interpolations from both cross-section and concentration profiles.

3. RESULTS

3.1. Conductivity, Temperature and Depth Data

The main large scale features of the vertical profiles of temperature and electrical conductivity taken near the center of the lake in September 1994 and 1996 can be seen in Fig. 2. Three relatively uniform layers of water and two interfaces can be clearly distinguished: (1) The epilimnion, or surface mixed layer, with a seasonally varying temperature and depth. In September 1994 and 1996, the epilimnion was about 10 m deep and had a temperature of 12.6 and 14.5°C, respectively; (2) The thermocline (10–20 m), characterized by a steep temperature gradient between the seasonally varying value above and the practically constant value below; (3) The layer between about 20 and 60 m depth, which we will refer to as the hypolimnion. It is a seasonally mixed layer whose temperature is very close to the temperature of maximum density of water (about 4°C). Layers 1–3 form a layer called the mixolimnion, because in spring and late fall, when the temperature of the epilimnion reaches 4°C, the thermocline vanishes and the waters of these layers are mixed (Restitiuti, 1987); (4) The chemocline (60–70 m), characterized by a strong increase of electrical conductivity. In the chemocline, the temperature increases from about 4–5°C (see inset of Fig. 2a); and (5) The monimolimnion below about 70 m depth, which never takes part in the seasonal circulation of the mixolimnion. The monimolimnion is moderately mineralized with conductivity around 400 µS/cm and permanently anoxic.

The water density, ρ, is determined mainly from temperature, T, and salinity, S, which can be derived from conductivity. Schmid (1997) applied the general method given by Wüst et al. (1996) to derive the relationship between conductivity, salinity, and density for the specific composition of the dissolved ions in Lac Pavin (taken from Michard et al., 1994). For the analysis of the vertical density stratification, it is convenient to examine the local stability or Brunt-Vaisälä frequency, which is given (e.g., Imboden and Wüst, 1995) by:

\[ N^2 = \frac{g}{\rho} \frac{\partial \rho}{\partial z} = g \left( \frac{\partial T}{\partial z} \alpha - \beta \frac{\partial S}{\partial z} \right), \]

where \( \alpha \) represents the coefficient of thermal expansion, \( \beta \), the coefficient of haline contraction, and the \( z \) coordinate is positive upwards. Evaluation of Eqn. 1 shows that stability is very low both in the epilimnion and hypolimnion, and highest in the thermocline, where it is dominated by the temperature gradient. In the chemocline, temperature increase with depth has a destabilizing effect, which must be compensated by the concurrent increase of dissolved solids. Indeed, the increase of density as a result of dissolved ions overcompenses the density decrease due to temperature by a factor of more than 50, as calculated from the respective terms in Eqn. 1. As a result, the chemocline is a very stable feature. Stability of the monimolimnion lies between that of the mixolimnion and the chemocline. A detailed discussion of density stratification for Lac Pavin will be given in Aeschbach-Hertig et al. (submitted).

The details of the thermal structure below the thermocline are shown in the inset of Fig. 2a. Below the chemocline, temperature remains practically unchanged over a period of two years, and below 75 m depth the two profiles were identical.
of gases in water is described by Henry's law:  

\[ C_i = K_i \cdot p_i \]  

where \( C_i \) represents the molar concentration of gas \( i \) in the water; \( K_i \) is the Henry coefficient of the gas and \( p_i \) is the partial pressure of \( i \) in the gas phase. In lakes, if no sources or sinks are present, gas concentrations are expected to be in equilibrium with their partial pressure in the atmosphere. Atmospheric equilibrium concentrations for Lac Pavin were calculated using the methods described by Aeschbach-Hertig et al. (in press), based on the following solubility data: Weiss (1971) for He and Ne, Weiss (1970) for Ar and N\(_2\), Weiss (1974) for CO\(_2\), and Wilhelm et al. (1976) for CH\(_4\). Solubilities were evaluated at the measured temperature for samples from the mixolimnion and at a temperature of 4°C for samples from the monimolimnion. That is, it is assumed that the deep water formed at the temperature of maximum density and has since been heated to its measured temperature in isolation from gas exchange. Furthermore, a salinity of 0.04%, as calculated from electrical conductivity, and an atmospheric pressure of 0.87 atm (corresponding to the altitude of 1197 m) were used.

Because the hydrostatic pressure rises rapidly with depth (\( \sim 0.1 \text{ atm m}^{-1} \)), deep waters of lakes can hold much higher

- **3.2. Gas solubilities and degassing**

The observation of degassing of the deepest samples from Lac Pavin requires a discussion of gas solubilities, from which a correction model for degassing can be derived. The solubility of gases in water is described by Henry’s law:

\[ C_i = K_i \cdot p_i \]  

Errors are absolute 1σ-errors determined from the reproducibility of calibrations.

- **Table 1. He and Ne data (analyzed by mass spectrometry).**

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<th>Depth [m]</th>
<th>( ^{4}\text{He} \cdot 10^{8} ) [cm(^3) STP/g]</th>
<th>( \Delta^{4}\text{He}^{a} ) [%]</th>
<th>( ^{3}\text{He}^{i}^{i}\text{He} ) ( \times 10^{-4} )</th>
<th>( R/R_{a}^{b} ) [-]</th>
<th>( \text{Ne} \cdot 10^{7} ) [cm(^3) STP/g]</th>
<th>( \Delta\text{Ne}^{c}^{e} ) [%]</th>
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<td>4.63</td>
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Errors are absolute 1σ-errors determined from the reproducibility of calibrations.

- **a** Percent deviation of measured \( ^{4}\text{He} \) (Ne) concentration from atmospheric solubility equilibrium according to Weiss (1991), calculated for 4°C, except for the warmer surface samples.
- **b** Ratio of measured \( ^{3}\text{He}^{i}^{i}\text{He} \) to the atmospheric value \( R_{a} = 1.384 \cdot 10^{-4} \) (Clarke et al., 1976).
- **c** Relative error of the Ne concentration and absolute error of \( \Delta\text{Ne} \) is about ± 1% for all samples.
- **d** Sample lost during analysis.
- **e** He and Ne concentration corrected for degassing, based on the assumption of \( \Delta\text{Ne} = 0 \).
concentrations of gases in solution. Saturation concentrations are reached when the sum of the partial pressures corresponding to the concentrations according to Eqn. 2 equals the total in situ (atmospheric + hydrostatic) pressure. Degassing during sampling occurs when the sum of the partial pressures exceeds the atmospheric pressure at the lake surface. It has been observed in other volcanic lakes (Sano et al., 1990) and in groundwaters. Stute (1989) has developed a model to correct noble gas concentrations in groundwaters for the effect of degassing. It is assumed that gases partition between the water and gas bubbles according to their solubility. Thus, the initial amount of gas dissolved in the water volume, \( V_w \), is distributed between \( V_w \) and a finite gas volume (bubble), \( V_g \), such that the concentrations in the two phases obey Henry’s law. Using the condition of mass conservation, one obtains an equation for the ratio between the initial gas concentration, \( C_i^0 \), and the remaining gas concentration, \( C_i \) (compare Stute, 1989):

\[
\frac{C_i^0}{C_i} = 1 + \frac{V_g}{V_w} \frac{1}{K_i R T}.
\]  

An equivalent model of equilibrium partitioning between a gas and a water phase has also been used to interpret noble gas abundances measured in gases and waters from mineral springs of the Massif Central (Matthews et al., 1987). For the correction of degassing during sampling, the model may appear too simple, because the available time may not be sufficient to attain solubility equilibrium. Stute (1989) also proposed a model that takes kinetic effects resulting from the different diffusivities of the gases into account. However, for the weak degassing observed in Lac Pavin (see below), the difference between the models is negligible.

3.3. Helium and neon data

In lakes, He is the only noble gas for which significant non-atmospheric sources may be expected. Although mantle He has been found in some volcanic lakes, crustal (radiogenic) He and \(^3\)He from the decay of tritium are ubiquitous, though often as small components (e.g., Aeschbach-Hertig et al., 1996a; Kipfer et al., 1996). Except for He, noble gas concentrations in lakes are usually close to equilibrium with the atmosphere (Aeschbach-Hertig et al., in press), although only Ne has been regularly measured (e.g., Torgersen et al., 1977; Aeschbach-Hertig et al., 1996a, 1996b; Hohmann et al., 1998).

In Lac Pavin, Ne is indeed generally close to atmospheric equilibrium (Table 1), except for the 1994 samples from the deep monimolimnion, which are up to 8% undersaturated. The \(^4\)He concentrations, however, are near atmospheric equilibrium only in the epilimnion. In the hypolimnion, they are higher by up to a factor of 3, in the monimolimnion by up to a factor of 70 (Fig. 3a, Table 1). The profiles from 1994 and 1996 are very similar, suggesting that the deviation of the 70 m sample from 1993 results from an overestimation of depth, because depth control was insufficient in that sampling campaign. In 1994, the highest \(^4\)He concentration was observed at 80 m depth, with a slight decrease at greater depth. The deepest samples taken in 1996 were unfortunately lost in the usually rare event of breaking of the copper tube upon opening. The Ne deficit and the He decrease below 80 m in 1994 most probably result from the observed degassing during sampling.

Assuming that Ne had been in atmospheric equilibrium in the deepest samples from 1994 before degassing occurred, we can calculate the gas/water volume ratio from Eqn. 3. With this result, we can then correct the effect of degassing for all other gases. The ratio of the assumed initial Ne concentration to the
measured Ne concentration is 1.05 for the 85 m sample and 1.09 for the two 90-m samples from 1994 (compare Table 1). The Henry coefficients \( K_i \) in Eqn. 3 were calculated for the actual water temperature of 5°C (5.2 \( \times \) \( 10^{-2} \) mol l\(^{-1}\) atm\(^{-1}\) for Ne, 4.05 \( \times \) \( 10^{-4} \) mol l\(^{-1}\) atm\(^{-1}\) for He). The calculated gas/water volume ratio is 0.0005 (85 m) and 0.001 (90 m). Thus, the loss of 1 cm\(^3\) of gas per liter of sampled water is sufficient to explain the observed Ne depletion. From Eqn. 3 we find that the measured He concentrations have to be multiplied by a factor of 1.06 (85 m) and 1.11 (90 m) to correct for degassing. This correction yields smooth He profiles (Table 1, Fig. 3a), which lends additional confidence to it. Note that degassing affects the He/Ne elemental ratio minimally, and has a negligible effect on the \(^3\)He/\(^4\)He isotope ratio.

The large He excesses in the monimolimnion clearly indicate an input of He from the underground. The origin of this He can be interpreted from the \(^3\)He/\(^4\)He-ratio (Fig. 3b). This ratio continuously increases from values close to the atmospheric ratio \( R_a \) in the epilimnion to more than six times larger values at the chemocline. In the monimolimnion, the \(^3\)He/\(^4\)He-ratio remains almost constant at values close to 6.5 \( R_a \). Although the \(^3\)He concentration profile has exactly the same shape as the \(^4\)He profile shown in Fig. 3a, the profile of the \(^3\)He/\(^4\)He-ratio is very different. The shape of the \(^3\)He/\(^4\)He profile reflects the depth dependent variation of the mixing ratio of two He components with distinct \(^3\)He/\(^4\)He-ratios. The atmospheric component is dominant near the surface and the excess component dominates in the monimolimnion. The exact isotope ratio of the excess He component, \( R_{ex} = \frac{\text{\(^3\)He}}{\text{\(^4\)He}} \), can conveniently be determined from graphical representations of the data.

In a plot of \(^3\)He versus \(^4\)He concentrations (Fig. 4), all data from Lac Pavin fall perfectly on a line \( (R = 0.99998) \) starting at the point representing air-saturated water (ASW). The slope of the regression line, corresponding to the isotopic ratio of the excess component, is very well defined and yields \( R_{ex} = (9.09 \pm 0.01) \times 10^{-6} \), or \( (6.57 \pm 0.01) R_a \). Another useful graphical representation of the data shows the relationship between the He isotope ratio and the Ne/He element ratio (Fig. 5). In this plot, the ASW end-member is slightly temperature dependent, because the solubilities of He and Ne are different functions of temperature (Weiss, 1971). The two samples from near the surface fall close to the ASW point for 14°C, which was approximately the temperature of the surface water during sampling. These points were excluded from the linear regression. The remaining data lie on a mixing line \( (R = 0.9996) \) between ASW at 4°C, the temperature at which deep convection takes place, and an excess He endmember, the \(^3\)He/\(^4\)He ratio of which is defined by the intercept of the line with the y-axis. The value derived from this plot is in perfect agreement with the result interpreted from Fig. 4.

The high \(^3\)He/\(^4\)He-ratio of the excess He in Lac Pavin clearly indicates its origin from a mantle source. The isotopic ratio of this source is lower than typical values for the MORB mantle \( (\approx 8–9 R_a) \), Lupton, 1983), and higher than He isotope ratios measured by Matthews et al. (1987) from mineral springs of the Massif Central (up to 5.5 \( R_a \)), which were interpreted as mixtures between a mantle-derived and a crustal He component. However, the \(^3\)He/\(^4\)He-ratio in Lac Pavin is identical to ratios measured in fluid inclusions in xenoliths from the Massif Central \( (6.53 \pm 0.25) R_a \) (Dunai and Baur, 1995). Thus, we interpret that He in Lac Pavin is derived from the regional sub-continental mantle reservoir, without significant further addition of crustal He.

The good correlations in Figs. 4 and 5 rule out a significant...
contribution from tritium decay to the observed $^3$He excess. Indeed, even total decay of the highest ever observed tritium concentration in the monimolimnion of about 20 TU (Meybeck et al., 1975) would cause a $^3$He excess of only $5 \cdot 10^{-14}$ cm$^3$STP g$^{-1}$, less than 2‰ of the observed maximum excess. Thus, tritiogenic $^3$He plays a negligible role in Lac Pavin and cannot be used to determine $^3$H-$^3$He water ages (Torgersen et al., 1977). This deprives us of a powerful tool to quantify the water residence time in the monimolimnion, which would allow determination of the flux of He to the lake.

3.4. The Carbonate System

Given the observation of degassing, the methods to determine the dissolved CO$_2$ concentration should be carefully chosen. The carbonate system in water consists of six solute components, namely CO$_2$, H$_2$CO$_3$, HCO$_3^-$, CO$_3^{2-}$, H$^+$, and OH$^-$. These six components are interrelated by four equations, which define the equilibrium of the reactions between the components (e.g., Stumm and Morgan, 1981). Because the respective equilibrium constants are known functions of temperature, measurement of any two of the six components as well as temperature allows calculation of the other four. In practice, it is often convenient to measure linear combinations of the individual components, such as alkalinity or total CO$_2$ ($\Sigma$CO$_2$). As pointed out by Stumm and Morgan (1981), it is more expedient to measure pH in the field than alkalinity, because degassing of CO$_2$ affects pH but not alkalinity. In fact, in the case of Lac Pavin it is probably necessary to measure pH in situ, as we have done by using a sensor on our CTD-probe. Samples for alkalinity can be brought to the laboratory for later titration. Problems occur if CaCO$_3$ precipitates, but this was not observed in the samples from Lac Pavin.

Our alkalinity and pH data from September 1996 (Table 2) are generally in close agreement with published results from 1992 (Michard et al., 1994) and 1987 (Camus et al., 1993). Some deviations of pH observed in the zone of a decreasing gradient between thermo- and chemocline probably result from the slow response of the pH-sensor on our CTD-probe. The temperatures listed by Michard et al. (1994) deviate slightly from ours (higher in the mixolimnion, lower in the monimolimnion), but they do not have an accuracy comparable to our CTD data. In principle, the measured total alkalinity should be corrected for the effects of non-carbonate bases to obtain the carbonate alkalinity. Such corrections were made by Michard et al. (1994), and proved to be small (<2% of total alkalinity). Because we do not have complete chemical analyses of the sampled water, and because the correction is within analytical error, we neglect it. The concentrations of the various carbon species determined from pH and alkalinity are listed in Table 2.

The pH can be regarded as the master variable which defines the speciation of the carbonate system (e.g., Stumm and Morgan, 1981). In Lac Pavin, it changes from relatively alkaline conditions in the epilimnion (pH $\approx$ 8) to rather acidic conditions in the monimolimnion (pH $\approx$ 6). This change occurs gradually within the mixolimnion and is obviously related to increasing concentrations of dissolved CO$_2$. In this whole range of pH values, the concentration of CO$_3^{2-}$ is negligibly small, and alkalinity is practically identical to the concentration of HCO$_3^-$, which is the dominant anion in Lac Pavin. In the epilimnion, the concentration of dissolved CO$_2$ (given as

![Figure 4. Correlation of the He isotope concentrations in Lac Pavin. Surface samples plot near the point for air-saturated water (ASW), deep-water samples are enriched by He from a source with a $^3$He/$^4$He ratio of $(9.09 \pm 0.01) \cdot 10^{-6}$, as indicated by the slope of the regression line.](image-url)
\( \text{H}_2\text{CO}_3 = \text{CO}_2 \text{ (aq.)} + \text{H}_2\text{CO}_3 \) is low, in fact below the atmospheric equilibrium concentration of 0.015 mmol l\(^{-1}\). The concentration of \( \text{H}_2\text{CO}_3 \) rises rapidly in the mixolimnion and dominates the carbonate system in the monimolimnion, where the corresponding equilibrium partial pressure, \( p\text{CO}_2 \), reaches a value of about 0.25 atm. This high value explains the tendency for degassing of the deep water, although \( \text{CO}_2 \) on its own could not form bubbles under atmospheric pressure. Under the total pressure of about 10 atm at the lake bottom, the concentration of dissolved \( \text{CO}_2 \) is far from saturation. Note that complete degassing of the \( \sim 16 \) mmol of \( \text{CO}_2 \) dissolved per liter of water would form a gas volume of more than 400 cm\(^3\) at the surface of Lac Pavin. Thus, the loss of 1 cm\(^3\) l\(^{-1}\) estimated above from the Ne deficit suggests that actual degassing was minimal. Equation 3 yields a correction factor of only 1.0007 for \( \text{CO}_2 \) in the deepest samples. However, the \( \text{CO}_2 \) concentrations calcu-

Fig. 5. Correlation of \(^3\text{He}/^4\text{He}\) with Ne\(^4\text{He}\) in Lac Pavin. Surface samples plot near the point for air-saturated water (ASW) at the September surface temperature of 14°C. Because of the temperature dependence of the Ne/He ratio, the surface samples were excluded from the linear regression through all other data. The deep-water samples define a mixing line between ASW at the turnover temperature of 4°C and a He source with a \(^3\text{He}/^4\text{He}\) ratio of \((9.09 \pm 0.01) \times 10^{-6}\), as indicated by the intercept of the regression line.

Table 2. The carbonate system.

<table>
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<tr>
<th>Depth</th>
<th>Temp</th>
<th>pH</th>
<th>Alkalinity</th>
<th>H₂CO₃</th>
<th>pCO₂</th>
<th>ΣCO₂</th>
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<td>[°C]</td>
<td>[−]</td>
<td>[mM]</td>
<td>[mM]</td>
<td>[atm]</td>
<td>[mM]</td>
</tr>
<tr>
<td>12 September 1996</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
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<td>0.454</td>
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<td>4.35</td>
<td>16.5</td>
<td>0.259</td>
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Error* ±0.01 ±0.1 ±2% ±20% ±20% ±20%

* Errors for T, pH, and alkalinity are estimated measurement uncertainties. The 20% error of the calculated quantities \( \text{H}_2\text{CO}_3 \) and \( p\text{CO}_2 \) follows from the error of pH, and the error of \( \Sigma\text{CO}_2 \) can be calculated by error propagation for the sum of alkalinity and \( \text{H}_2\text{CO}_3 \).
Table 3. Ar, N₂, and CH₄ data (analyzed by GC).

<table>
<thead>
<tr>
<th>Depth [m]</th>
<th>Ar [mM]</th>
<th>ΔAr [%]</th>
<th>N₂ [mM]</th>
<th>ΔN₂ [%]</th>
<th>CH₄ [mM]</th>
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12 September 1996

<table>
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<tr>
<th>Depth [m]</th>
<th>Ar [mM]</th>
<th>ΔAr [%]</th>
<th>N₂ [mM]</th>
<th>ΔN₂ [%]</th>
<th>CH₄ [mM]</th>
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<td>0.523</td>
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<td>0.668</td>
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</table>

Relative errors of the concentrations and absolute errors of the Δ-values are about ±5% for all samples.

a Percent deviation of measured Ar (N₂) concentration from atmospheric equilibrium according to Weiss (1970), calculated for 4°C, except for the warmer surface samples.

b All concentrations from these samples have been corrected for degassing according to equation (3) in the text.

For N₂, and 2.21 · 10⁻³ mol l⁻¹ atm⁻¹ for CH₄. The corresponding correction factors from Eqn. 3 for the 90 m samples are 1.02 for Ar and CH₄ and 1.05 for N₂. The concentrations of Ar were up to 9% higher than atmospheric equilibrium in 1994, but generally below atmospheric equilibrium in 1996. We think these deviations result from a combination of statistical (±5%) and systematic measurement errors. In contrast, concentrations of N₂ in the monimolimnion were systematically higher than atmospheric equilibrium in both years, by up to 19%. These excesses might result from denitrification in the anoxic environment.

The atmospheric equilibrium concentration of CH₄ is only about 3 · 10⁻⁶ mmol l⁻¹; hence it is not surprising that CH₄ could not be detected in the mixolimnion. In the monimolimnion, however, CH₄ reached concentrations of almost 4 mmol l⁻¹. The corresponding equilibrium partial pressure is 1.7 atm, thus CH₄ is strongly supersaturated at atmospheric pressure and in fact the major driving force of degassing. High concentrations of biogenic CH₄ and associated degassing are not uncommon in highly productive (eutrophic) lakes. Note, however, that Lac Pavin has been classified as low-productive (oligotrophic) by Restituito (1987). Nevertheless, the CH₄ may be of biogenic origin, if the deep-water residence time is sufficiently large to allow its accumulation.

All these gas data are in strong contrast to data from 1987 given by Camus et al. (1993). These authors obtained up to 7 times higher Ar concentrations than we have measured, and their Ar concentrations scatter within a factor of 3, whereas our data are almost constant and near atmospheric equilibrium. Their N₂ concentrations are relatively constant but about 6 times higher than ours. Note that their reported N₂ concentration of 4.6 mmol l⁻¹ at 40 m depth is just at saturation at the in situ pressure of 4.9 atm. We see no plausible explanation for such high excesses of Ar and N₂ above atmospheric equilibrium. The CH₄ concentration at 80 m depth reported by Camus et al. (1993) is 18 mmol l⁻¹, again 6 times higher than our result, and again near saturation at the in situ pressure of 8.9 atm. In fact, adding the 4 atm partial pressure corresponding to the reported N₂ concentration implies supersaturation and in situ formation of bubbles, which has not been observed. At 90 m depth, the reported N₂ and CH₄ concentrations are somewhat lower, but still supersaturated. As noted before, the CO₂ results reported by Camus et al. (1993) are far lower than ours. We have no explanation for these discrepancies, but in the light of their internal inconsistencies (supersaturations, irregular depth profiles) we reject the 1987 gas data.

4. DISCUSSION

4.1. Fluxes Through the Chemoèline

The primary goal of this study was to determine the flux of He and other magmatic gases into Lac Pavin. To this end, we make the basic assumption of steady state conditions in the monimolimnion. Temperatures and He concentrations in the monimolimnion did not change measurably between 1994 and 1996. There is also a close agreement between the two profiles in the mixolimnion, probably because both sampling events occurred in September, minimising the effects of seasonal variation. Additional evidence that conditions in the monimolimnion are close to steady state comes from comparison...
with earlier studies. Even the oldest temperature data from the
monimolimnion (Olivier, 1952; Pelletier, 1968) agree with our
CTD-data within the limits of their accuracy, irrespective of
the season. Michard et al. (1994) and Viollier et al. (1995, 1997)
used the steady state assumption to calculate element fluxes in
the monimolimnion, and justified it by the agreement of their
results for several geochemical parameters with previous data.
If the assumption of steady state in the monimolimnion holds,
all input fluxes of conservative species must be balanced by
vertical transport across the chemocline. All we need to know
to calculate the fluxes is the water exchange across the chemo-
cline, or the water residence time in the monimolimnion.

The two-box models of Martin (1985) and Camus et al.
(1993) postulate a spring in the monimolimnion. Camus et al.
(1993) calculated a spring water input \( Q_{sp} \) of 35 l s\(^{-1}\) and
an exchange flux \( Q_{ex} \) of 11 l s\(^{-1}\) between mixo- and monimolim-
nion, resulting in a total upward flow, \( Q \), across the chemocline
of 46 l s\(^{-1}\). The water residence time in the monimolimnion
with a volume, \( V \), of 4.4 \( \times 10^6 \) m\(^3\) is given by \( V/Q = 3 \) yr in
this model. With respect to the cross-sectional area, \( A \), of 2 \( \times 10^5 \) m\(^2\)
at 60 m depth, the upward advective flow, \( Q \), gives rise to an
upwelling velocity, \( v_{adv} = Q/A \) of 7 m yr\(^{-1}\). This strong
upward advection implies that the interface between mon-
imolimnion and mixolimnion, which is marked by large gradi-
ents of temperature, salinity, and dissolved gases, should rise
rather quickly. To keep the upper boundary of the chemocline
at a constant depth of 60 m and the concentration, \( C_{mixo} \), in
the mixolimnion at steady state, regular and vigorous mixing down
to 60 m is necessary to remove the constantly advected excess
of heat and dissolved substances. The excess flux that has to be
removed is given by \( F_{exc} = v_{adv} \cdot (C_{moni} - C_{mixo}) \). Using
volume weighted average He concentrations of 2.20 \( \times 10^2 \) cm\(^3\) STP g\(^{-1}\) for the monimolimnion and 0.07 \( \times 10^2 \) cm\(^3\) STP g\(^{-1}\) for the mixolimnion, one obtains an excess He flux of
5 \( \times 10^{-5} \) cm\(^3\) STP m\(^{-2}\) s\(^{-1}\). Similarly, from the mean temper-
ature excess of about 0.7°C in the monimolimnion, a heat flow
of 0.7 W m\(^{-2}\) is calculated.

In contrast, four out of five direct measurements of the heat
flow from the sediment of Lac Pavin gave results between
0.021 and 0.028 W m\(^{-2}\) (Camus et al., 1993). Thus, the
assumed spring in the monimolimnion must be responsible for
most of the excess heat flow in this model. Such a spring would
constitute a point source of heat, which might easily have been
missed by the heat flow measurements. Interestingly, one heat
flow station yielded an enhanced flux of 0.15 W m\(^{-2}\). Yet, this
station was located above the chemocline at a depth of 50 m.
This result may be an indication of a sublacustrine spring in the
monimolimnion, consistent with the small temperature signal vis-
able in Fig. 2a. Such a spring must have a dissolved ion content
typical for surface water, because no anomaly in the electrical
conductivity was observed. Note that only slightly elevated
spring temperatures are necessary to explain the observed tem-
perture anomalies, both in the mixo- and the monimolimnion.
In particular, the temperature of the hypothetical spring in
the monimolimnion can easily be calculated from the postulated
water fluxes and the steady state assumption. The steady state
temperature of the monimolimnion, \( T_{moni} \), is the weighted
average of the temperature of the mixolimnion, \( T_{mixo} \), and the
spring, \( T_{sp} \), with the respective fluxes into the monimolimnion,
\( Q_{ex} \) and \( Q_{sp} \), as weights. Using \( T_{moni} = 5°C \), \( T_{mixo} = 4°C \),
\( Q_{ex} = 11 l s^{-1} \), and \( Q_{sp} = 35 l s^{-1} \), one obtains a temperature
of only 5.3°C for the spring. Analogous balance calculations
show that the concentrations of all conservative species in the
deep spring must be similar to those measured in the monim-
olimnion.

The observation of an elevated temperature in the mon-
imolimnion does not necessarily imply that a high heat flow or
a spring must be present. The temperature anomaly may be the
result of the mean measured heat flow (0.025 W m\(^{-2}\), exclud-
ing the high result from the mixolimnion), if only the heat
exchange across the chemocline is low enough. Thus, we
consider an alternative model of Lac Pavin with a uniform heat
flow to the monimolimnion of 0.025 W m\(^{-2}\), and with a purely
diffusive exchange through the chemocline. Assuming that the
temperature profiles in the monimolimnion are at steady state,
we can calculate the vertical turbulent diffusivity \( K_z \) from the
temperature gradient. The vertical heat flux, \( F_h \), from diffusion
is given by:

\[
F_h = -K_z \rho \frac{dT}{dz},
\]

where \( c \) represents the heat capacity of water, and \( \rho \) denotes
water density. Using the steady state condition that this diffu-
sive heat flow must equal the geothermal heat flow of 0.025 W
m\(^{-2}\), we can estimate \( K_z \) from Eqn. 4.

The strongest temperature gradient and hence the minimum
\( K_z \) value occurs in the chemocline between 60 and 70 m depth.
Equation 4 yields average \( K_z \)-values in this layer of 0.8 \( \times 10^{-7} \)
m\(^2\) s\(^{-1}\) in 1994 and 1.1 \( \times 10^{-7} \) m\(^2\) s\(^{-1}\) in 1996. Note that these
values are somewhat lower than the molecular heat diffusion in
water (\( D_T = 1.35 \times 10^{-5} \) m\(^2\) s\(^{-1}\) at 4°C), which is the lowest
possible value. This indicates that the assumptions made for the
calculation are not completely valid. Certainly the assumption
of stationarity is only an approximation in the upper part of the
chemocline, where some warming occurred between 1994 and
1996 (Fig. 2a). More importantly, the result indicates that the
true heat flow is likely somewhat larger than 25 mW m\(^{-2}\), a
value which is rather low even for non-volcanic lakes. How-
ever, a heat flow within a factor of two of the measured value
and very low turbulence in the chemocline would be consistent
with the observed temperature profiles. If the heat flow through
the chemocline is dominated by molecular rather than turbulent
diffusion, the above derived diffusivities cannot be applied to
calculate diffusive mass fluxes. The molecular diffusivities of
dissolved substances are about two orders of magnitude lower
than that of heat. However, we know of no example from open
lake water where diffusion of dissolved substances is at the
molecular level.

Thus, we take \( K_z = 10^{-7} \) m\(^2\) s\(^{-1}\) as an upper boundary of
the turbulent diffusivity in the chemocline, and calculate the
maximum He flux from the equivalent to Eqn. 4, assuming that
the He profile is at steady state:

\[
F_{He} = -K_z \frac{dHe}{dz}.
\]

Note that here, as well as in the following, we use the total He
concentration, which for all practical purposes is identical with
the 4He concentration. Total He fluxes can be converted to 4He
fluxes using the constant isotope ratio of the inflowing He
component of $9.09 \times 10^{-6}$ (Fig. 4). The He gradients in the chemocline between 60 and 70 m were very similar in both years and Eqn. 5 yields a maximum He flux of about $2 \times 10^{-8}$ cm$^3$STP m$^{-2}$ s$^{-1}$ or $5 \times 10^{14}$ atoms m$^{-2}$ s$^{-1}$.

For comparison with box models, any diffusive flux through the chemocline defined by $K_z$, and a concentration gradient, $dC/dz$, may be expressed by an advective exchange flux, $Q_{ch}$, and the concentration difference $\Delta C$ across the chemocline by setting

$$Q_{ch} = K_z \frac{A_{ch}}{d_{ch}},$$

where $A_{ch}$ and $d_{ch}$ represent the cross-sectional area and the thickness of the chemocline, respectively. With $K_z = 10^{-7}$ m$^2$ s$^{-1}$, $A_{ch} = 2 \times 10^5$ m$^2$, and $d_{ch} = 10$ m, Eqn. 6 yields $Q_{ch} = 21$ s$^{-1}$. This weak exchange flux corresponds to a water residence time $V/Q_{ch}$ of 70 yr in the monimolimnion.

### 4.2. Box Models

Thus, we have two completely different models of the water exchange in the monimolimnion of Lac Pavin: the “advective” model with a spring in the monimolimnion and hence an upward advection through the chemocline, and the “diffusive” model with only a weak diffusive link between mixo- and monimolimnion. To assess which model is more realistic, we examine the total He balance in the lake, based on the assumption that the concentration in the monimolimnion remains constant. For this discussion we use box models, although the previous two-box models are too simplified to correctly describe the He balance. The output of He from the lake occurs primarily by gas exchange at the surface. This process depends critically on the He concentration at the surface, which is not equal to the mean concentration of the entire mixolimnion during most of the year. Therefore, the epilimnion was introduced as a third layer, existing during the summer and winter thermal density stratification.

The division between the epilimnion and the hypolimnion is taken at a depth of 10 m based on the temperature profiles. As in previous studies, the division between mixo- and monimolimnion is set at a depth of 60 m. Volumes, surface areas, and mean He concentrations for the three boxes are given in Fig. 6. The epilimnion is mixed with the hypolimnion to form the mixolimnion during fall and spring overturn. According to Restituito (1987) as well as to regularly taken temperature profiles in the upper 40 m of the lake (Amblard, pers. comm.), the fall overturn in December is clearly weaker than the spring overturn in April. Although the data show that homothermal conditions endure for about a month in spring, the period of full mixing should be shorter in the model, because actual mixing occurs intermittently depending on wind energy input. Because the effective duration of the mixing periods in spring, $\tau_{mix,s}$, and fall, $\tau_{mix,f}$, are difficult to estimate, we used different scenarios for these parameters. From May through November the lake is thermally stratified and in winter an inverse stratification and usually an ice-cover develop, also limiting gas exchange. According to Alvinerie et al. (1966) and Meybeck et al. (1975) the ice cover can extend from late December until April in cold winters, whereas in mild winters no permanent ice cover forms. Thus, the model parameter for the duration of the ice cover was set as average, at 2 months.

On this model structure we impose the water and He fluxes corresponding to the advective model of Camus et al. (1993) and our diffusive model (Fig. 6. Table 4). In the advective model, a water input, $Q_2$, of $35 \text{ l s}^{-1}$ occurs into the monimolimnion. To conserve the water balance, in the diffusive model a sublacustrine freshwater spring $Q_1$ of the same size is assumed, however discharging above rather than below the chemocline. Surface water input, $Q_0 = 23 \text{ l s}^{-1}$, and output, $Q_{out} = \sum Q_i = 58 \text{ l s}^{-1}$, are the same in both models. In the advective model, the He input occurs through the spring in the monimolimnion as a point source. In the diffusive model, the input of He is assumed to be unrelated to sublacustrine springs and uniformly distributed over the entire sediment area, thus flowing both into the mixo- and the monimolimnion. Both scenarios are certainly simplified pictures of the geological reality, because Lac Pavin is situated in a complex environment of volcanic deposits (Camus et al., 1973; 1993). In particular, the crater of Lac Pavin cuts through the basaltic lava flow of the neighboring Puy de Montchal, which erupted just shortly before the formation of Lac Pavin. The activity of sublacustrine springs as well as the transport of He and other gases might be related to a higher permeability or fracturing of this zone. However, in the framework of the box models used here, only the distribution of the inputs between the boxes and not their precise location is relevant.

The assumption of a uniform flux of He from the sediments has also been used in other volcanic lakes to quantify the He flux (Lake Nyos, Sano et al., 1990; Lake Van, Kipfer et al., 1994). In Crater Lake, (Collier et al., 1991) the input of He has been associated with hydrothermal activity, whereas this attribution is unclear in the case of Lake Mashu, (Igarashi et al., 1992). In Laacher See (Aeschbach-Hertig et al., 1996b) a superposition of a uniform sediment flux and a point source in the form of a gas vent could be identified. The exact nature of the transport mechanisms for heat, He, and other magmatic gases into volcanic lakes may be variable. Giggenbach et al. (1991) have proposed a model of such lakes as high-CO$_2$, low-temperature systems in which transport both by a water or a gas phase is possible.

The gas exchange velocity, $v_{gas}$, can be estimated from wind speed. Wanninkhof et al. (1990) and Upstill-Goddard et al. (1990) derived empirical relationships from experiments in lakes, which were confirmed by the results of Clark et al. (1995). The average wind speed on Lac Pavin is expected to be rather low, because the lake is protected against high winds by the crater walls. A typical value for much larger Swiss lakes is $2 \text{ m s}^{-1}$ (Livingstone and Imboden, 1993), which may be taken as an upper limit for Lac Pavin. With a wind speed of $2 \text{ m s}^{-1}$, the empirical relationships yield gas exchange velocities of 0.3 and 0.6 m d$^{-1}$ for a Schmidt number of 600, which translates to 0.5 and 1 m d$^{-1}$ for He at 10°C (Wanninkhof, 1992). For a wind speed of 1 m s$^{-1}$, the empirical relationships yield gas exchange velocities of less than 0.2 m d$^{-1}$ for He. We adopt a value of 0.5 m d$^{-1}$ as a realistic estimate for the following calculations.

### 4.3. Analytical Considerations

Some general properties of the He balance equations of the box models can be derived from analytical considerations. For
instance, it is easy to see that the He output is dominated by gas exchange, because $v_g$ is much larger than $Q_{out}/A_0 (0.01 \text{ m d}^{-1})$.

It is interesting to compare the He loss from gas exchange to the He input supposed by the models. The He flux, $F_g$, from gas exchange is given by:

$$F_g = v_g(C_s - C_{eq}),$$

where $C_s$ represents the He concentration at the surface and $C_{eq}$, the atmospheric equilibrium concentration which varies slightly with temperature. For September surface temperatures

![Diagram of three-box model](image)

**Table 4. Parameter values for the advective and diffusive model.**

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>$Q_2$ [l/s]</th>
<th>$Q_1$ [l/s]</th>
<th>$Q_0$ [l/s]</th>
<th>$Q_{12}$ [l/s]</th>
<th>$Q_{01}$ [l/s]</th>
<th>$C_{in,2}$ [cm$^3$STP/g]</th>
<th>$F_{He}$ [atoms m$^{-2}$ s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advective</td>
<td></td>
<td>35</td>
<td>0</td>
<td>23</td>
<td>11</td>
<td>?</td>
<td>?</td>
<td>0</td>
</tr>
<tr>
<td>Diffusive</td>
<td></td>
<td>0</td>
<td>35</td>
<td>23</td>
<td>?</td>
<td>?</td>
<td>0</td>
<td>?</td>
</tr>
</tbody>
</table>

Q-values for the advective model are taken from Camus et al. (1993). Water output $Q_{out} = Q_0 + Q_1 + Q_2$ is the same in both models (58 l s$^{-1}$). $C_{in,0}$ and $C_{in,1}$ are set to $C_{eq}$ in both models. Question marks denote the fit parameters.
of about 14°C, $C_{eq}$ is $3.95 \cdot 10^{-8}$ cm³STP g⁻¹. The surface concentration $C_s$ is either the concentration $C_0$ of the epilimnion in the stratified situation, or the weighted average concentration of the entire mixolimnion, which we denote as $C^*_s$.

The average $C_0$ observed in September was $4.09 \cdot 10^{-8}$ cm³STP g⁻¹ (Fig. 6). Thus, Eqn. 7 yields a flux of $0.8 \cdot 10^{-8}$ cm³STP m⁻² s⁻¹ for $v_g = 0.5$ m d⁻¹. In contrast, the mean value of $C^*_s$ for September would be $6.66 \cdot 10^{-8}$ cm³STP g⁻¹, yielding a theoretical flux of $16 \cdot 10^{-8}$ cm³STP m⁻² s⁻¹. In other words, in September, He loss by gas exchange is reduced by a factor of 20 because of thermal stratification. In the stratified situation, the total output of He through the lake surface by gas exchange ($A_0 \cdot F_g = 4 \cdot 10^{-3}$ cm³STP s⁻¹) is much smaller than the total input through the chemocline in the advective model ($Q_{2.12} \cdot (C_2 - C_1) = 100 \cdot 10^{-3}$ cm³STP s⁻¹), but comparable to input from the maximum He flux as estimated from Eqn. 5 through the entire sediment area in the diffusive model ($A_0 \cdot F_{He} = 9 \cdot 10^{-3}$ cm³STP s⁻¹). Thus, the He flux of the advective model leads to a strong accumulation of He in the hypolimnion during the period of summer stratification. With a net accumulation of $96 \cdot 10^{-3}$ cm³STP s⁻¹, the complete He excess contained in the hypolimnion in September ($5.2 \cdot 10^3$ cm³STP) could be accumulated in two months. However, we must assume that the accumulation lasted at least since early May, i.e., for four months prior to our sampling date in September.

Yet, in the presence of the strong He flux of the advective model, the steady state concentration in the mixolimnion even for permanent full mixing must be larger than the atmospheric equilibrium concentration. This steady state concentration can be estimated from the balance equation for He, simplified by neglecting surface in- and outflow (compare Fig. 6):

$$0 = V^*_s \frac{dC^*_s}{dt} = (Q_2 + Q_{1.2}) \cdot (C_2 - C^*_s) - A_0 v_g \cdot (C^*_s - C_{eq}) \quad (8)$$

where $V^*_s$ represent the volume of the entire mixolimnion. With $v_g = 0.5$ m d⁻¹, Eqn. 8 yields a steady state value for $C^*_s$ of $7.7 \cdot 10^{-8}$ cm³STP g⁻¹, similar to the average $C_1$ observed in September ($7.4 \cdot 10^{-8}$ cm³STP g⁻¹). In other words, a gas exchange velocity of at least 0.5 m d⁻¹ and permanent overturn of the upper 60 m of Lac Pavin and are required to remove the high He flux imposed by the advective model and create the sharp He decrease at the chemocline observed in September. Yet, the He profiles were obviously taken within a period of stratification, when mixing reached no deeper then 10 m.

Since reasonable assumptions about removal of He from the mixolimnion by gas exchange and seasonal mixing cannot balance the advection of He from a significant spring in the monolimnion, the advective model has to be rejected. This conclusion was not reached from the profiles of many dissolved reactive substances, although they generally look very similar to the He profile (Michard et al., 1994; Viollier et al., 1995), because it was assumed that these substances would be removed from the mixolimnion by sedimentation. Only the direct observation of settling fluxes in sediment traps revealed the inconsistency of the advective model (Viollier et al., 1997). Because He is not affected by any chemical processes, it can be used to constrain the physical processes in Lac Pavin better than any reactive species.

### 4.4. Numerical Solutions

The diffusive box model was solved numerically, using AQUASIM, a flexible simulation tool for aquatic systems (Reichert, 1994). The seasonal variation of the water temperature in the epilimnion was implemented using historical data sets (Pelletier, 1968; Amblard, pers. comm.) because the temperature affects both the equilibrium concentration and the gas exchange velocity of He. Fit parameters were the exchange fluxes $Q_{1.2}$ and $Q_{0.1}$ during stratification (Table 4). To simulate overturn in December and April, $Q_{0.1}$ was raised by a factor of 10000. A uniform He flux $F_{He}$ from the sediment was assumed. It was coupled to $Q_{1.2}$ in such a way as to maintain steady concentrations in the monolimnion. Since parameters governing the He input ($F_{He}$, $Q_{1.2}$) and output ($\tau_{max}$, $Q_{0.1}$, $v_g$) are unknown, the He profiles on their own cannot yield a unique solution. However, the range of $\tau_{max}$ and $v_g$ can be reasonably constrained, as discussed above. Three scenarios were calculated, with low, mean, and high He output from mixing and gas exchange (Table 5). Optimum values of $Q_{0.1}$ and $Q_{1.2}$ were calculated for each scenario by least squares adjustment of the model output to the measured concentrations.

All three scenarios yield satisfactory fits (Table 5, Fig. 7). Since the model is strictly periodic over one year, it is not possible to reproduce the interannual variability which is present in the data. The optimum values for $Q_{1.2}$ range from 1.5 s⁻¹ in the low mixing scenario to 3.71 s⁻¹ in the high mixing scenario. As expected, the information from two He profiles taken at the same time of the year is not sufficient to precisely constrain the water exchange across the chemocline. A simple way to obtain a better constraint on the He flux would be the method applied in Laacher See (Aeschbach-Hertig et al., 1996b), i.e., to take He profiles in spring and fall and directly observe the increase during the period of summer stratification.
The available data do, however, provide clear evidence against the model of the lake with a significant spring in the monimolimnion. For comparison, the advective model was also implemented, with $Q_{01}$ as the only free parameter. As expected, only very high values of $Q_{01}$ can yield the low He concentrations observed in the hypolimnion. Even in the high output scenario, a $Q_{01}$ of 30,000 l s$^{-1}$ is needed, practically equivalent to permanent mixing of the entire mixolimnion. Therefore, modeled concentrations in the epilimnion and hypolimnion are almost identical, and the fit to the observed data is poor. This again shows that the advective model is not appropriate. If a deep spring is present at all, it cannot deliver more water than a few l s$^{-1}$; otherwise too much He would be advected upwards through the chemocline.

From the temperature profiles and Eqn. 4 we estimated $10^{-7}$ m$^2$ s$^{-1}$ as an upper limit of $K_z$ in the chemocline, equivalent to a $Q_{12}$ of 2 l s$^{-1}$. This first “maximum” estimate lies between the results of the low and mean mixing scenarios in the diffusive model. The concentrations of the transient tracers tritium and CFCs have been used in a more detailed model of Lac Pavin, in order to constrain mixing in the lake (Schmid, 1997; Aeschbach-Hertig et al., submitted). There are many unknown factors related to the in- and output of the transient tracers, which do not allow much more precise conclusions than provided here. However, the results of the tracer modeling argue for low values of $Q_{12}$. Violette et al. (1997) obtained $K_z$ values in the chemocline on the order of $10^{-8}$ m$^2$ s$^{-1}$ from models of the concentration profiles of several trace elements. All these results provide arguments for a low water exchange between monimolimnion and mixolimnion. Hence, it seems fair to dismiss the high mixing scenario and to adopt the average of the other two scenarios as best estimate, with uncertainties which include the two scenarios.

To summarize, our best box model of Lac Pavin comprises no (or a very small) spring in the monimolimnion and a small water exchange of $(2.1 \pm 0.6)$ l s$^{-1}$ across the chemocline. This exchange in the box model corresponds to an eddy diffusivity of $1 \cdot 10^{-7}$ m$^2$ s$^{-1}$ in the chemocline and a water residence time of 66 yr in the monimolimnion. Our best estimate for the $^4$He flux into Lac Pavin is $2.2 \cdot 10^{-8}$ cm$^3$ STP m$^{-2}$ s$^{-1}$ or $6 \cdot 10^{11}$ atoms m$^{-2}$ s$^{-1}$. The corresponding $^3$He flux is $2.0 \cdot 10^{-13}$ cm$^3$ STP m$^{-2}$ s$^{-1}$ or $5.4 \cdot 10^6$ atoms m$^{-2}$ s$^{-1}$. The heat flow is estimated to be 30 mW m$^{-2}$. All these estimates have an uncertainty of $\pm 30\%$.

4.5. Flux of Mantle CO$_2$

Experience from other volcanic lakes suggests that the elevated CO$_2$ concentrations in the monimolimnion of Lac Pavin are of magmatic origin and related to the observed mantle He. However, Camus et al. (1993) concluded from high observed CH$_4$/CO$_2$ ratios that the CO$_2$ is mainly of biogenic origin. Yet, as discussed above, we obtain lower CH$_4$ and higher CO$_2$ concentrations, thus substantially lower CH$_4$/CO$_2$ ratios. Whereas Camus et al. (1993) mentioned fluctuating ratios between 1.66 and 22, we obtain quite stable values between 0.12 and 0.16, with an average of 0.15 in the deep monimolimnion. Thus, a new assessment of the CO$_2$ budget is necessary.

From the data of Table 2 we calculate an average CO$_2$ concentration in the monimolimnion of 15 mmol l$^{-1}$, corre-
responding to a total CO$_2$ of 64 $\times$ 10$^6$ mol, with an estimated uncertainty of 20% because of high sensitivity to pH. Camus et al. (1993) suggested that methanogenesis is the dominant process of biogenic CO$_2$ production. With the new low CH$_4$/CO$_2$ ratio, this reaction can account for only 15% of the total CO$_2$. Oxidation of organic matter can at most account for 1 mmol l$^{-1}$ of CO$_2$ (% of the total), according to a balance of possible oxidants presented by Camus et al. (1993). According to the solubility of CO$_2$, only a negligible contribution (0.02 mmol l$^{-1}$) can be of atmospheric origin. Thus, we conclude that at least 78% of the CO$_2$ in the monimolimnion (11.5 mmol l$^{-1}$, or 50 $\times$ 10$^6$ mol in total) is of magmatic origin. This conclusion is not in conflict with the $\delta^{34}$C balance of the dissolved carbon in Lac Pavin presented by Camus et al. (1993), because the $\delta^{34}$C value of magmatic CO$_2$ is similar to that of average crustal CO$_2$, as pointed out by Matthews et al. (1987).

By dividing the calculated magmatic CO$_2$ excess in the monimolimnion with the $^3$He excess, which is almost purely of mantle origin, we obtain the atomic C/$^3$He ratio of the magmatic source. The resulting ratio of 13 $\times$ 10$^9$ falls near the lower end of the range observed in mineral springs of the Massif Central (Matthews et al., 1987). These authors interpreted their $^3$He/$^4$He and C/$^3$He data as the result of a mixing between a mantle endmember with a C/$^3$He ratio of 10$^9$ and a crustal endmember with a C/$^3$He in the range of 10$^{12}$ to 10$^{14}$. The C/$^3$He ratio from Lac Pavin would thus indicate only minimal addition of crustal carbon. This is consistent with the fact that the $^3$He/$^4$He in Lac Pavin is somewhat higher than the highest values observed in the springs by Matthews et al. (1987). It is also in agreement with our interpretation of the He in Lac Pavin as derived from the regional sub-continental mantle reservoir, with little further addition of crustal $^3$He. Combining the C/$^3$He ratio with the $^3$He flux, we obtain a CO$_2$ flux of 1.2 $\times$ 10$^{-7}$ mol m$^{-2}$ s$^{-1}$. The total amount of magmatic CO$_2$ released from the lake in one year is 1.7 $\times$ 10$^8$ mol or about 70 tons. These flux estimates are accurate to ±40%.

The yearly turnover of magmatic CO$_2$ at Lac Pavin is 70 times less than at Laacher See (Aeschbach-Hertig et al., 1996b), and several orders of magnitude less than the amount of CO$_2$ that was instantaneously released during the catastrophe at Lake Nyos in 1986. The estimates for the latter range between 2.4 $\times$ 10$^5$ tons (Giggenbach, 1990) and 2.4 $\times$ 10$^6$ tons (Kling et al., 1987). Since the monimolimnion of Lac Pavin appears to be in steady state, CO$_2$ is not accumulated any more but continuously released to the atmosphere. Therefore, no danger of catastrophic degassing exists.

The above estimated heat flow of 30 mW m$^{-2}$ yields a heat/$^3$He-ratio of 6 $\times$ 10$^{-9}$ J/atom. This is much less than values measured in hydrothermal springs in the ocean (e.g., Baker and Lupton, 1990; Jenkins et al., 1978), but comparable to values derived from other maar lakes (Lake Nyos, Sano et al., 1990; Laacher See, Aeschbach-Hertig et al., 1996b). However, the result from Lac Pavin does not fit in the tentative relationship between formation age of the maar and the heat/$^3$He flux ratio proposed by Aeschbach-Hertig et al. (1996b) based on the data from Lake Nyos and Laacher See. Still, it may be interesting that the C/$^3$He ratio appears to vary systematically with age. With a C/$^3$He-ratio of 13 $\times$ 10$^9$ and an age of 6000 yr, Lac Pavin lies in between the younger Lake Nyos (30 $\times$ 10$^9$, 400 yr), and the older Laacher See (9 $\times$ 10$^9$, 11,000 yr).

5. CONCLUSIONS

This study confirms the potential of lakes for the detection and quantification of mantle volatile fluxes in volcanically active areas. However, it highlights the need for a thorough understanding of the physical processes in the investigated lakes in order to obtain reliable quantitative results. The dynamics of Lac Pavin are particularly complicated, and the hitherto published studies differ greatly in their assessment of the water balance and the water residence time of the monimolimnion. In this study, He proved to be useful not only as a geochemical tracer to reveal the magmatic origin of some gases in Lac Pavin, but also as a non-reactive tracer used to constrain the physical parameters of the lake. Because He in the water column is only affected by the physical processes of advection, diffusion, and gas exchange, the shape of the He profile allows assessment of the relationship between these processes. The change of He concentration by a factor of about 30 across the chemocline proves that water exchange across this boundary must be low, and therefore contradicts previous models with a large spring in the monimolimnion.

The constraints provided by the He balance on the exchange of water and dissolved substances across the chemocline allows quantification of the flux of magmatic CO$_2$ with an accuracy of about ±40%. Further sampling over various seasons and possibly the evaluation of transient tracer data could considerably reduce uncertainty in the future. Moreover, the observed mantle He isotope signature in Lac Pavin leads to the conclusion that the major part of the CO$_3$ in Lac Pavin is of magmatic rather than biogenic origin. Nevertheless, a danger of an outburst of CO$_2$ from the lake does not appear to exist, at least as long as the input to the lake does not tremendously increase. At the present level, the concentrations in the deep water seem to be approximately in steady state.

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