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Geochemical study of a crater lake: Lake Pavin, France: a view through Li-O-H isotopes

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Abstract

Here we report $\delta^{18}\text{O}$ values and for the first time δD and lithium isotopic data for the Pavin crater lake (French Massif Central). In its deeper unmixed part, this meromictic lake presents low H and O isotope compositions as a result of CO_2 intrusion and the presence of mineral water ingress. This influence of sub-lacustrine water contribution is confirmed by lithium isotopes with low $\delta^7\text{Li}$ values.

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1. Introduction

The Pavin crater lake (elevation 1197 m a.s.l.) is located in the French Massif Central at 45°55'N and 2°54'E (Fig. 1). The Lake Pavin is a near circular volcanic lake, whose diameter is around 750 m and the surface area 0.44 km². Its hydrological basin is reduced (2.07 km²). Owing to a great depth (92 m) and a high hollow coefficient (0.14), the lake water volume reaches 23x10⁶ m³. The Lake Pavin has two main singularities. First, it is located in the youngest volcanic edifice in continental France (6700 ± 200 yrs. B.P.; Boivin *et al.* [1]). Second, it is a meromictic lake: its upper layer (mixolimnion) undergoes climatically-induced mixing, while the lower part

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(monimolimnion) is anoxic and unmixed. The monimolimnion accumulates dissolved species and gases that are thought to be partly brought from sub-lacustrine springs. This additional input was first suggested by studying the water budget of the lake (Meybeck *et al.* [2]) and is still advocated in recent research (Bonhomme *et al.* [3]).

The Lake Pavin has been intensively studied to evaluate the risk of limnic eruption. Concentrations and origins of gases along the water column are reported by Camus *et al.* [4] for CO₂ and Aeschbach-Hertig *et al.* [5] for helium thus allowing to establish a conceptual model of the behavior and the evolution of species within the lake (*e.g.* Olive and Boulègue [6]). The risk of gas eruption has been quantified as low, since the hydrostatic pressure within the monimolimnion is far greater than the total pressure of dissolved gases. Stable isotope studies help to enhance the understanding of the complex behavior of the lake and to propose the location of sub-lacustrine springs with one spring in the mixolimnion and one mineral water in the monimolimnion (Assayag *et al.* [7]).

Here we present new data especially based on hydrogen and lithium isotopes that have not been reported previously. Two sampling sessions coupled with a series of physico-chemical loggings (Fig. 1B) were done, the first in September 2009 and the second in July 2012.

From one hand, the contribution of ¹⁸O/¹⁶O and ²H/¹H isotope ratios of the water to the knowledge of water mass evolution, sensitivity to fractionation processes or mixing effects is well established and can be applied to the Lake Pavin. Simultaneously, new δ¹⁸O data along the water column will be compared to the preexisting datasets.

From the other hand, assessing the behavior of Li and the distribution of Li isotopes in Earth's surface and subsoil reservoirs is crucial for constraining the global Li cycle. This highly mobile element has two isotopes with very different abundances (⁶Li ~7.5% and ⁷Li ~92.5%) and, due to the large relative mass difference between the two stable isotopes, significant mass fractionation is observed in natural materials. The resulting variations in isotope ratios observed in nature thus provide key information on the origin, fate and processes affecting Li behavior.

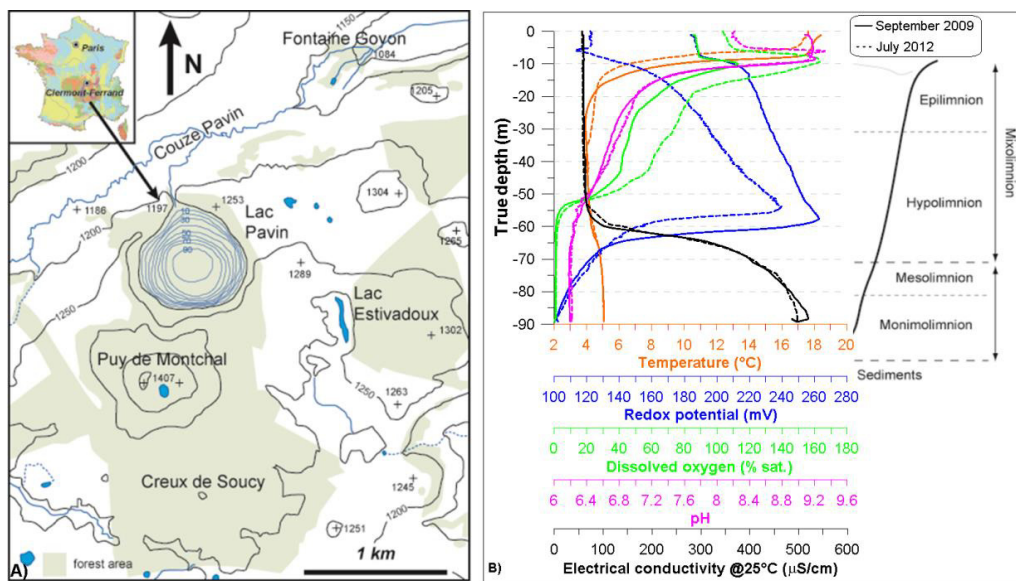


Fig. 1. A) Map of the Pavin Lake and vertical structure of the lake; modified from Assayag *et al.* [7]. B) Physico-chemical loggings performed in September 2009 (sampling for lithium analyses) and July 2012 (sampling for water isotopes analyses).

2. Samples and analytical methods

Prior to water sampling, the water column of the Lake Pavin was investigated using Idronaut 316*Plus* probes. This probe allows determining each 10 cm in depth the values of water physico-chemical parameters: temperature, pH, electrical conductivity, redox potential and dissolved oxygen concentration. Figure 1B gives the shapes of the

vertical profile of each of these parameters measured at the center of the lake in September 2009 and July 2012 respectively, but numerous other similar investigations were performed from the center to the border of the lake.

The water samples were collected using nitrogen driven deep sampler (BRGM patent FR1259214) each 10 m in depth. Unfiltered samples for $\delta^{18}\text{O}$ and δD determinations were collected in 100 ml plastic bottles and fully filled to avoid exchange with the atmosphere. Samples for lithium isotope determinations were collected in 100 ml plastic bottles, the water been filtered at 0.45 μm and then preserved by add of sub-boiled concentrated nitric acid ($\text{pH} < 2$).

Water isotope compositions were measured using gas phase mass spectrometry (Mat252 dual inlet IRMS) and gas phase equilibration method (H_2 for hydrogen, CO_2 for oxygen) at BRGM's Isotopic Geochemistry Laboratory. $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ ratios were normalized to VSMOW international standard.

Lithium isotopic compositions were measured using a Neptune Multi-Collector ICP-MS at BRGM's Isotopic Geochemistry Laboratory. $^7\text{Li}/^6\text{Li}$ ratios were normalized to the L-SVEC standard solution (NIST SRM 8545) following the standard-sample bracketing method (see the method reported by Millot *et al.* [8]).

3. Results and discussion

The physico-chemical structure of the lake described in Figure 1B is in line with that of previous studies with a perennial transition between the mixolimnion and the monimolimnion highlighted by a disappearance of oxygen, a decrease of redox, a reach of a constant pH value and a strong increase of the concentrations in dissolved elements.

Oxygen isotope ratios (Fig. 2A) have a similar shape compared to previous acquisitions. The waters remaining in the unmixed layer have lower ratios whereas the upper part of the lake (from the thermocline at *c.a.* 8 m depth in July 2012 down to 50 m depth) has a nearly constant ratio. This suggests that the mixolimnion is in steady state as a consequence of a good mixing between surface water runoff and spring discharges. The upper part of the water column is sensitive to fractionation processes linked to evaporation at lake's surface (sampling in July) especially considering that this surface represents 1/5th of the whole hydrologic basin. Once the chemocline (*c.a.* 60 m depth) is reached, the waters become depleted in ^{18}O as a result of the impact of CO_2 intrusion from deeper horizon – CO_2 of magmatic/mantle origin – and the ingress of a mineral water having chemical composition similar to that of the neighboring Fontaine Goyon spring, also depleted in ^{18}O (e.g. Assayag *et al.* [7]).

Very similar conclusions can be made considering hydrogen isotope ratios (Fig. 2B). Near the surface, the ratio is heavier than deeper in the mixolimnion. Under 60 m in depth, the depletion in D isotope ratio becomes more prominent. This suggests that the imprint of mineral waters (Fontaine Goyon) having lower δD values is very sensitive in the monimolimnion.

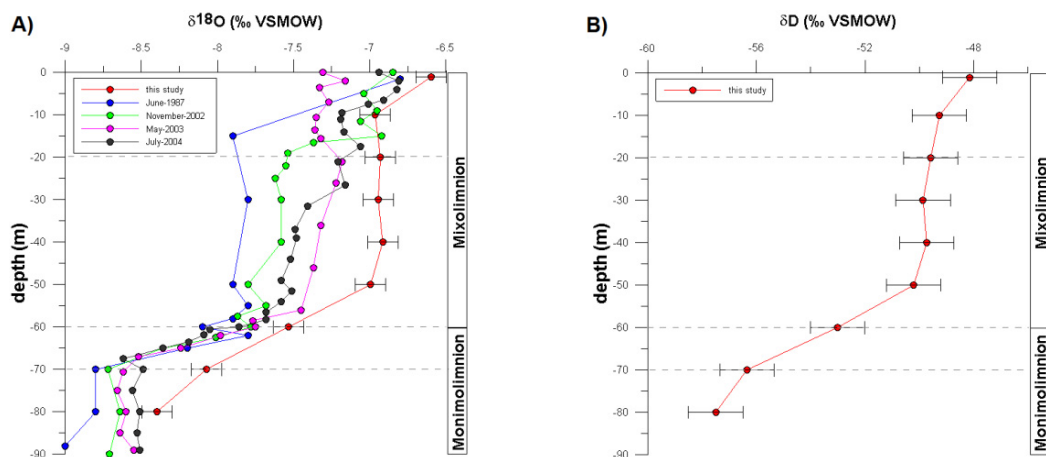


Fig. 2. A) Vertical evolution of the oxygen isotope ratio with comparison to previous studies. B) Associated evolution of hydrogen isotope ratio. Samples from July 2012.

As a consequence of this similar behavior of oxygen and hydrogen isotopes with increasing depth, the plot of δD vs. $\delta^{18}O$ gives a regression line with a very good correlation coefficient ($R^2 = 0.99$; Fig. 3). The slope of this correlation line is close to 5.46 with an intercept of -11.9. Such a slope is often related to evaporation processes (*e.g.* Fontes [9]). This can be postulated for the waters in the shallower part of the mixolimnion. The isotope ratios for the samples between 10 m and 50 m depth are similar when taking into account error bars on the ratios. This may reflect the effect of lake mixing together with the presence of depleted waters linked to recharge during winter times. This may also be the consequence of mixing between superficial end member enriched in D and ^{18}O and a deep one depleted in those isotopes and approaching the Fontaine Goyon composition (Fig. 3). Indeed, the deep spring that necessarily feeds the lake is thought to have similar isotope ratios as a consequence of interaction at low temperature with CO_2 like other springs in the French Massif Central (Fouillac *et al.* [10]). Nevertheless, a simple mixing line between two end members and the absence of detectable discontinuity at the mixolimnion – monimolimnion interface is somewhat surprising and needs further investigations to be fully understood.

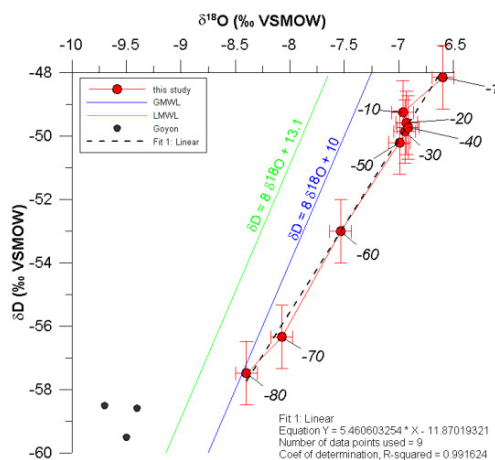


Fig. 3. δD vs. $\delta^{18}O$ relationship for Lake Pavin waters with comparison with local mineral water (Fontaine Goyon) and Local and Global Meteoric Water Lines (resp. Fouillac *et al.* [10] and Craig [11]). The labels represent the depth of sampling.

The marked lithium enrichment in the monimolimnion reported by Michard *et al.* [12] and Viollier *et al.* [13] is confirmed in the samples collected in September 2009 (Fig. 4A). Nonetheless the enrichment seems to be smaller with only a 3 fold rise in concentration (4 to 5 fold in the literature). Similar to the statement made for oxygen and hydrogen isotopes, this enrichment is likely to be linked to lithium brought by the presence of a mineral spring in the monimolimnion (the Li content of Fontaine Goyon reaches 0.2 mg/L). When considering lithium isotopes (Fig. 4B), additional conclusions can be made. The isotopic homogeneity of the mixolimnion is less clear than for O and D isotopes. As some sub-lacustrine springs can also be located in this compartment, especially around 40 to 50 m depth, the changes in lithium isotopes may be associated with the imprint of such a sub-lacustrine spring of freshwater composition (ratio close to that of the upper part of the lake). Further in depth in the monimolimnion, as the lithium concentration increases and the isotope ratio decreases, the influence of mineral water can be invoked.

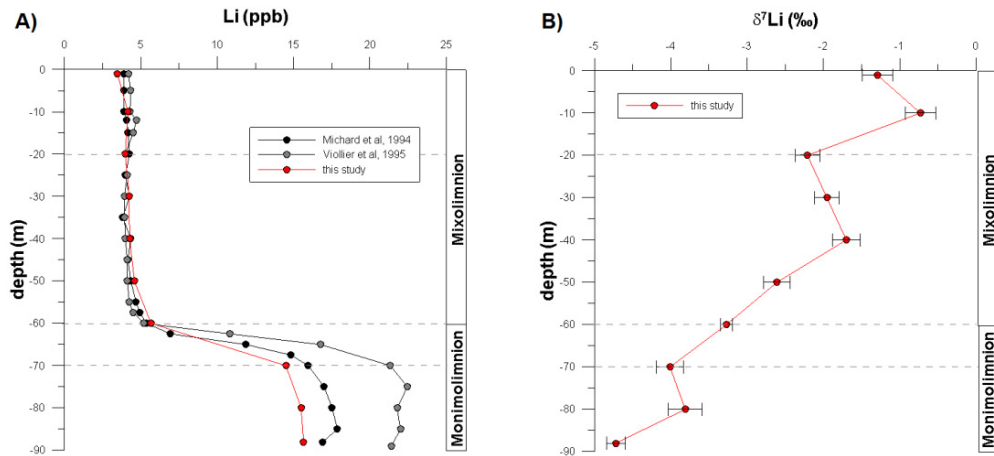


Fig. 4. A) Vertical evolution of the lithium concentration with comparison with previous studies. B) Associated evolution of lithium isotope ratio. Samples from September 2009.

Acknowledgments

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