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ORIGINAL ARTICLE

An overview of the structure, hazards, and methods of investigation of Nyos-type lakes from the geochemical perspective

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ABSTRACT

Limnic eruptions represent a natural hazard in meromictic lakes hosted in volcanoes releasing CO_2-rich magmatic gases. Biogeochemical processes also contribute to dissolved gas reservoirs since they can produce significant amounts of gases, such as CH_4 and N_2. Dissolved gases may have a strong influence of the density gradient and the total dissolved gas pressure along the vertical profile of a volcanic lake. An external triggering event, possibly related to uncommon weather conditions, volcanic-seismic activity, or landslides, or spontaneous formation of gas bubbles related to the progressive attainment of saturation conditions at depth, may cause a lake rollover and the consequent release of dissolved gases. This phenomenon may have dramatic consequences due to i) the release of a toxic CO_2-rich cloud able to flow long distances before being diluted in air, or ii) the contamination of the shallow water layer with poisonous deep waters. The experience carried out over the past twelve years at Lake Nyos, where a pumping system discharges CO_2-rich deep water to the surface, has shown that controlled degassing of deep water layers is the best solution to mitigate such a hazard. However, the application of this type of intervention in other lakes must be carefully evaluated, since it may cause severe contamination of shallow lake water or create dangerous density instabilities. Monitoring of physical and chemical parameters controlling lake stability and the evolution in time of dissolved gas reservoirs can provide essential information for evaluating the risk associated with possible rollover phenomena. Conceptual models for the description of limnological, biogeochemical and volcanic processes regulating water lake stability have been constructed by interpreting compositional data of lake water and dissolved gas compositions obtained by applying different sampling and analytical techniques. This study provides a critical overview of the existing methodological approaches and discusses how future investigations of Nyos-type lakes, aimed at mitigating the hazard for limnic eruptions, can benefit from i) the development of new technical and theoretical approaches aimed to constrain the physical-chemical mechanisms controlling this natural phenomenon, and ii) information from different scientific disciplines, such as microbiology, fluid dynamics and sedimentology.

Key words: limnic eruption, volcanic hazard, dissolved gases, Nyos-type lake, meromictic lake, lake water geochemistry.

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INTRODUCTION

Volcanic lakes, a common feature of active and quiescent volcanoes (Simkin and Sieber, 1994; Delmelle and Bernard, 2000a), have been classified based on their water physic-chemical characteristics, mainly depending on the input of heat and volcanic-hydrothermal fluids from the hosting system (Pasternack and Varekamp, 1997). *High-activity* lakes commonly consist of warm-to-hot acidic or hyperacidic brines, whose chemical composition and volume is strictly controlled by the dynamic balance between i) inputs of meteoric precipitation and magmatic fluids from a shallow source, and ii) outputs, related to evaporation, mineral precipitation and water seepage through lake bottom (Varekamp, 2003; Taran and Rouwet, 2008, Rouwet and Tassi, 2011). *Low-activity* lakes, *i.e.* those located in systems having a deep magmatic source, are defined by typically low salinity and near-neutral pH, with minor input of fluids from depth. Volcanic lakes exert a strong control on the eruptive style of active volcanoes, since lake water may interact with i) magma, producing violent phreatic or phreatomagmatic eruptions that can generate hazardous base surges and tephra emissions (from ash to ballistic); and/or ii) non-juvenile volcanic products, which may lead to major lahars and floods (Nairn *et al*., 1979; Badrudin, 1994; Christenson, 2000; Mastin and Witter, 2000; Rodolfo, 2000; Matthews *et al*., 2002; Kilgour *et al*., 2010; Morrissey *et al*., 2010). In quiescent volcanoes, the stability of the flanks may decrease after prolonged acid attack of infiltrating lake water, favouring landslide events (*e.g.*, Pasternack and Varekamp, 1994; Rowe *et al*., 1995; Sanford *et al*., 1995; Delmelle and Bernard, 2000b; Kempter and Rowe, 2000; Varekamp *et al*. 2009). A second classification system by Varekamp *et al*. (2000) reveals a contradiction as demonstrated for Lake Nyos: a *CO_2-dominated*, but *rock-dominated* lake, instead of *gas-dominated*. For these apparently low activity lakes a further

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hazard is represented by the so-called *limnic eruptions* (Sabroux *et al.,* 1987; Kusakabe, 1996; Halbwachs *et al*., 2004; Kusakabe *et al*., 2008). This feature, which was intensively studied after the two disasters at Monoun and Nyos Lakes (Cameroon, Fig. 1) in 1984 and 1986, respectively (Kerr, 1986; Kling, 1987; Kling *et al*., 1987; Sigurdsson *et al*., 1987; Le Guern, 1989; Evans *et al*., 1993), consists of a sudden outburst of massive amounts of dissolved gases, mainly CO_2, accumulated in deep layers of meromictic lakes, *i.e*. those not subject to seasonal layer turnover. Despite the fact that Lake Kivu (DRC; Fig. 1) is not really a volcanic lake, it is also considered a potential site for limnic eruptions (Haberyan and Hecky, 1987; Schmid *et al*., 2004; Tassi *et al*., 2009) since a CO_2- and CH_4-rich gas reservoir up to three orders of magnitude larger than that in Lake Nyos is stored in its bottom waters (Tietze *et al*., 1980; Schoell *et al*., 1988; Schmid *et al*., 2004, 2005). These three African *killer lakes* (Fig. 1) are characterized by significant contribution of CO_2 of magmatic origin (Kling, 1987; Schoell *et al*., 1988; Evans *et al*., 2003; Kusakabe *et al*., 2000; Nayar, 2009), and CO_2 accumulation in the hypolimnion (the deepest layer of stratified lakes; Fig. 2) is one of the main pre-requisites for the occurrence of a gas outburst in case of lake strata perturbation. In recent times, a large number of geochemical studies, aimed at evaluating the hazard related to a possible limnic eruption from other, apparently quiescent volcanic systems worldwide hosting meromictic lakes in France, Italy, Germany, Vanuatu Islands, and Chilean Andes, were carried out (Aeschbach-Herting *et al*., 1996, 1999; Aguilera *et al*., 2000; Anzidei *et al*., 2008; Caliro *et al*., 2008; Bani *et al*., 2009; Caracausi *et al*., 2009; Gunkel *et al*., 2009). These studies proposed different sampling and analytical methods to provide data for their interpretative models.

We believe that these low activity lakes could pose significant and peculiar risks to nearby human activity and therefore, if only for the sake of volcanic surveillance, deserve a dedicated review paper. Moreover, a recent data base (VHub, CVL group page) surprisingly totalled 345 volcanic lakes worldwide, most poorly studied or even unknown and that represent a potential hazard for local population. This data contrasts with the earlier much, lower number of 114 volcanic lakes suggested by Delmelle and Bernard (2000a).

The present study reports an up-to-date and comprehensive overview of sampling and analytical methods and theoretical physical-chemical models proposed and adopted by different scientific groups in the framework of geochemical surveys of Nyos-type lakes. Different scientific approaches are evaluated and criticized to provide information of the most useful tools that can be used for future investigations aimed to study and mitigate the limnic eruption hazard.

ORIGIN OF DISSOLVED GASES IN NYOS-TYPE LAKES

Dissolved gases in meromictic volcanic lakes are typically dominated by CO_2, followed by significant amounts of CH_4 and N_2, and minor concentrations of H_2 and noble gases. Sublacustrine vents discharge magmatic CO_2 into the lake bottom layer (Evans *et al*., 1993; Aeschbach-Hertig *et al*., 1996, 1999; Cioni *et al*., 2003; Caliro *et al*.,

Fig. 1. Map of Africa with the location of Nyos, Monoun (Cameroon) and Kivu (DRC) lakes (stars).

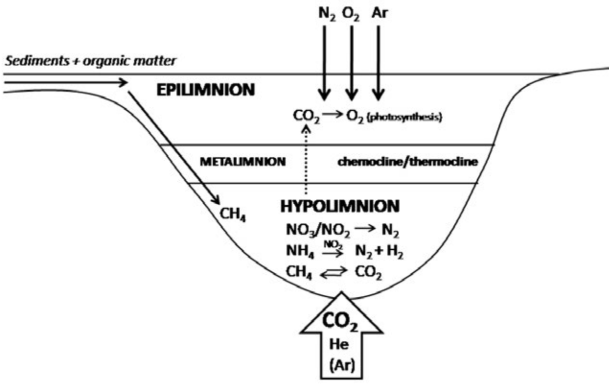

Fig. 2. Sketch of the lake stratification of a meromictic lake, and related processes to describe the origin of the dissolved gases in the various lake strata.

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2008; Caracausi *et al*., 2009; Gunkel *et al*., 2009; Tassi *et al*., 2009), although significant CO_2 contribution may also derive from biotic respiration, anaerobic decomposition of organic matter and microbial oxidation of CH_4 often entering the lake by the inflow of sediment- and organic-loaded rivers or surface run off (Rudd *et al.*, 1974; Rich, 1975, 1980) (Fig. 2). In the hypolimnion, biogenic and geogenic inputs of CO_2 are counteracted by microbial reduction processes mainly carried out by methanogens, a group of microorganisms phylogenetically affiliated to the kingdom Euarchaeota of the domain Archaea (Woese *et al*., 1990) (Fig. 2). In sulfate-free marine sediments, methanogenesis mainly proceeds using acetate from decomposing organic matter as substrate (acetate fermentation), whereas in freshwater environments this process is competitive with CO_2 reduction pathways (Deuser *et al*., 1973; Tietze *et al*., 1980; Whiticar *et al*., 1986; Schoell *et al*., 1988; Whiticar, 1999). Recent studies have shown that, in the hypolimnion of meromictic lakes, anaerobic methanotrophy, coupled to Fe or Mn reduction (Valentine, 2002) and using nitrates as substrates (Raghoebarsing *et al*., 2006), can occur. Nevertheless, CH_4 oxidation is mostly carried out in the epilimnion (the top layer of stratified lakes, subject to frequent water mixing) (Hanson and Hanson, 1996; Lopes *et al*., 2011) (Fig. 2), where CO_2 consumption also proceeds through oxygenic photosynthesis (Nelson and Ben-Shem, 2004).

Dissolved N_2 in volcanic lakes originates from air through meteoric water inflow or directly at the lake-atmosphere interface (Fig. 2). Nitrogen production by i) denitrification, *i.e.* the reduction of NO_3^- to NO_2^- and then to N_2 (Ahlgren *et al*., 1994), and ii) anammox (Anaerobic AMMonium Oxidation), *i.e.* NH_4 oxidation with NO_2^- as electron acceptor (Mulder *et al*., 1995; Jetten *et al*., 1998), commonly occur in a lake hypolimion (Fig. 2). Heterocyst-forming species such as cyanobacteria (Moeller and Roskoski, 1978), as well as by CH_4-oxidizing bacteria (Rudd and Taylor, 1980) are able to fix N_2. Microbial activity regulating biogenic N_2 has also a strong influence on H_2, since this gas can be produced by cyanobacteria through both photosynthesis and anaerobic fermentation processes (Greenbaum, 1982; Asada and Kawamura, 1986; Bergman *et al*., 1997; Asada and Miyake, 1999). Several enzymes are involved in H_2 metabolism: i) nitrogenase that catalyzes the H_2 production concomitantly with the reduction of N_2 to NH_4; ii) uptake hydrogenase that catalyzes the H_2 consumption; and iii) bidirectional hydrogenase, able to both take up and produce H_2 (Houchins, 1984; Tamagnini *et al*., 2002).

Oxygen supplied to lakes by air rapidly decrease with depth due to biological oxidation of organic matter (Fig. 2). In the epilimnion this process is frequently offset by O_2 renewal mechanisms, *i.e.* water circulation and photosynthesis, that are not active in the hypolimnion. Radiogenic Ar may be present in significant concentrations in lakes characterized by strong fluid contribution from an underlying hydrothermal system, such as Lake Kivu (Tassi *et al*., 2009), although it is generally accepted that in Nyos-type lakes this gas has a dominant atmospheric origin.

The origin of He in volcanic lakes is related to that of the primary fluid source(s), since the behavior of this chemically inert gas along the vertical water column only depends on physical processes, such as advection and diffusion. The occurrence of significant mantle He contribution, typically recognized in Nyos-type volcanic lakes (Sano *et al*., 1987; Igarashi *et al*., 1992; Kipfer *et al*., 1994; Aeschbach-Hertig *et al*., 1996; 1999; Caliro *et al*., 2008; Carapezza *et al*., 2008; Caracausi *et al*., 2009), testifies to the presence of sublacustrine springs (Fig. 2).

LAKE STRATIFICATION AND STABILITY

The distribution of dissolved gases in lake strata depends on i) the rate of gas addition, by an external source and/or biogeochemical processes within the lake and bottom sediments, and ii) vertical mixing processes, which depend on the available energy to overcome buoyancy forces favoring stratification and preventing the mixing of the lake to uniform density and temperature. As such, active magmatic-hydrothermal systems underlying crater lakes provide excess heat and fluid input leading to dynamic lake convection causing a complete water mixing (Hurst *et al*., 1991; Rowe *et al*., 1992). On the contrary, lakes in quiescent volcanic systems, typically affected by moderate inputs of salt- and CO_2-rich fluids generally from the lake bottom, tend to stratify. Water density increases with increasing salinity and dissolved CO_2 content, although an increase of water temperature with depth, often caused by the input of warmer fluids of volcanic origin, and the presence of dissolved biogenic CH_4, have an opposite effect on water stratification. In the chemocline (the horizontal layer separating two lake strata with a clear jump in chemical composition; Fig. 2) of meromictic lakes, mixing along the vertical lake profile is mostly controlled by slow diffusive mechanisms, a condition that favours gas accumulation at depth. However, certain configurations of salinity, CO_2, CH_4 and water temperature along the vertical profile may develop double-diffusive (DD) instabilities, which is known to generate local convective mixing of the water column (Stern, 1960; Veronis, 1965; Hoare, 1966; Baines and Gill, 1969; Schmid *et al*., 2010; von Rohden *et al*., 2010; Carpenter *et al*., 2011, 2013). This process may spontaneously result in a staircase-like density layering (Kelley, 1984, 1990; Kelley *et al*., 2003; Nogusho and Niino, 2010), consisting of a sequence of sharp high-gradient interfaces of temperature and salinity surrounded by nearly homogeneous mixed layers, such as those observed in the northern basin of Lake Kivu (Newman, 1976; Schmid *et al*., 2010) and

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in Lake Nyos (Schmid *et al*., 2004). Despite the fact that the presence of a staircase structure may affect the stability of the water column at a local scale, the stability of the stratification of overall chemocline is not necessarily degraded by this process (Wüest *et al*., 2012). Rice (2000) suggested that, under a DD convection regime, a rollover event may proceed by layers telescoping together from the bottom up, a process that may lead to gas over-saturation in higher layers and consequent explosive venting. Both theoretical and experimental approaches to highlight the mechanisms regulating gas bubble formation and growth, as well as the behaviour of a bubble plume in a stratified environment, have been exhaustively explained (Kieffer and Sturtevant, 1984; Wüest *et al*., 1992; Mader *et al*., 1996,1997; Zhang, 1996, 1998, 2005; Zhang and Xu, 2003; Zhang and Kling, 2006). A recent study by Mott and Woods (2010) provided quantitatively evidence that mixing of bottom lake layers at close to saturation conditions may produce a limnic eruption. Notwithstanding these studies provided important information for the knowledge of chemical-physical processes controlling the exsolution of dissolved gases from deep lake waters, there is still debate on whether the initial destabilization of an apparently stable stratified lake is related to external triggering or a lake rollover that rather occurs *spontaneously*, *i.e.* when the concentrations of geogenic and biogenic dissolved gases gradually increase until saturation.

TRIGGERING MECHANISM FOR LIMNIC ERUTPIONS

A limnic eruption may become a hazard when a meromictic lake has a great depth and a large volume to store large amounts of dissolved gases. One possible scenario is that gradual gas accumulation causes oversaturation of deep lake layers producing spontaneous nucleation and bubble growth (Zhang, 1996; Woods and Phillips, 1999). At a certain volume fraction of bubbles, depending on the density gradient, bubbly water becomes unstable and rises, causing a bubble expansion and a consequent increase of the rise rate. This process rapidly leads to an eruption of a gas-water mixture at the surface, giving rise to a so-called *ambioructic flow*, *i.e.* a flow of CO_2 and water droplets at ambient temperature formed by the collapse of a lake eruption column (Zhang, 1996). Considering that the CO_2 concentration at 58 m depth in Lake Monoun in January 2003 was very close to saturation (Kusakabe *et al*., 2008), the occurrence of a limnic eruption without the intervention of an external trigger seems a plausible mechanism, as also proposed by Tietze (1987) for the 1986 event of Lake Nyos. An external trigger related to a volcanic event from beneath the lake, initially hypothesized by a group of scientists (Tazieff, 1988; Sigvaldasson *et al.,* 1989), was considered unlikely for that limnic eruption due to i) lack of evidences for the presence of volcanic fluids in the lake after the eruption (Kling *et al*., 1989; Kusakabe *et al*., 1989), and ii) the results of the follow-up studies indicating steady supply and accumulation in the lake bottom water of magmatic CO_2. Similarly, the model of gas buildup and release proposed by Chau *et al.* (1996), which was based on a gas injection from the bottom of the lake and the degassing process through a simple diffusion-driven process, is in conflict with the observation that sediments were not disturbed at the lake bottom (Kling *et al*., 1987). Lorke *et al*. (2004) examined the possibility of a limnic eruption at Lake Kivu triggered by a lava flow into the lake. The lava flow occurred during the January 2002 eruption of Nyiragongo Volcano (just N of Lake Kivu) was not able to induce any gas release from the lake, suggesting that only strong lava outflows from sublacustrine vents could affect the lake stability.

Earthquakes may provide an energy input causing a perturbation of bottom layers theoretically able to trigger a limnic eruption (Kling, 1987, Kling *et al*., 1987), although a direct relationship between these two natural phenomena has not been demonstrated. Nevertheless, Chiodini *et al.* (2012) observed that the CO_2 concentrations measured in the hypolimion of Lake Albano (Central Italy) in the last two decades has followed a exponentially decaying pattern. The initially high CO_2 content in Lake Albano bottom waters was attributed to increased CO_2-rich fluid input from an underlying regional reservoir after a seismic swarm in 1989-1990 (Amato *et al*., 1994). In that case, neither the seismic swarms themselves nor the resulting increase of CO_2 in bottom waters were able to trigger a lake water rollover. However, similar earthquake-induced events have likely occurred in the past. This may explain the repeated overflows of this lake in the Holocene (Funiciello *et al*., 2003).

Another possible limnic eruption mechanism is the migration of undersaturated lake water upward to shallower depth where CO_2 will enter a state of oversaturation. The actual trigger to unchain this dynamics can be variable and multiple. Sigurdsson *et al.* (1987) proposed that the 1984 eruption at Lake Monoun was induced by a landslide that slumped into deep water that pushed up CO_2-rich water. A similar mechanism was suggested for the 1986 Lake Nyos event by Kling *et al.* (1987, 1989), whereas Kanari (1989) and Giggenbach (1990) hypothesized a dominantly climatic trigger, related to the descent at depth of a parcel of unusually cold (18.5°C), denser rain water. Based on results from laboratory experiments on stability in stratified water tanks (Shy and Breidenthal, 1990), Cotel (1999) calculated that a disturbances able to cause mixing of deep and shallow strata even in well stratified lakes may be generated by wind blowing in the vicinity of the lake producing internal waves (Mortimer, 1953; Carmack and Weiss, 1991; Pannard *et al*., 2011). Eventually, Evans *et al.* (1994) suggested

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that a combination of different processes, such as seasonal decline in stability, landslide and seiche, could have contributed to trigger the Lake Nyos disaster. Strikingly, both the Lake Monoun and Nyos limnic eruptions occurred in August, during the period of least thermal stability of the lakes (Kling *et al*., 1987, 1989): during the rainy season the clouds release colder rainwater to the lakes, while blocking sun radiation and thus heating of the lake surface waters.

Historical data cannot and will never resolve the precise triggering mechanism of the 1984 and 1986 Lake Monoun and Nyos disasters. However, it seems quite clear that the internal structure of meromictic volcanic lakes corresponds to conditions favorable for the occurrence of rollover that can be responsible for sudden and dangerous releases of toxic gases. This phenomenon can only be predicted by monitoring the CO_2 concentrations along the vertical lake profiles. Analytical results from studies adopting an empirical approach, *i.e.* direct measurement of water and dissolved gas chemical compositions along vertical profiles of meromictic volcanic lakes, are thus of fundamental importance for developing and refining conceptual models able to explain how and when a limnic eruption can occur. However, a protocol describing the most appropriate techniques to be adopted for geochemical investigations of volcanic lakes is still a challenge. Accordingly, a large part of the present study is devoted to a critical overview of the existing sampling and analytical methods.

INTERVENTION PLANS: EXAMPLES FROM LAKE NYOS AND LAKE KIVU

Avoiding the release of the a hazardous CO_2-CH_4 cloud out of a Nyos-type lake by artificial degassing of bottom waters is probably the only way to mitigate volcano-related hazard in its most strict sense: eliminating the cause of the limnic eruption, *i.e.* the gas dissolved in bottom waters. Within this hazard mitigation strategy, if a limnic eruption does unexpectedly take place, volcanic risk can be mitigated through an alarm system, warning the surrounding population on time of the presence of lethal CO_2 concentrations in the atmosphere. These two major set-ups ask for meticulous scientific preparations and background, and will also have strong implications for social and economic activities of areas around the lakes, or even entire countries involved.

The following holds for Nyos-type lakes: the higher the volume and deeper the lake and the longer the duration of CO_2 storage, the more CO_2 will eventually be released during lake rollover. External factors (*e.g*., climate, trigger mechanism) will decide whether the stored gas will be released or not. Under NMDP (Nyos Monoun Degassing Program), funded by the U.S. Office of Foreign Disaster Assistance (USAID), a permanent degassing apparatus was installed at Lake Nyos in 2001 and at Lake Monoun in 2003. At both lakes, the degassing system was expanded in 2006 and 2011-2012, respectively. These installations provided for the self-lifting discharge of a gas water mixture of sufficient flow to reduce the dissolved gas content in the hypolimnion. Despite the apparently effective hazard mitigation intervention, the possible destabilizing effect of controlled degassing (Freeth, 1994) was modeled and evaluated, on the grounds that, although a stable stratification has been maintained in both the lakes, a frequent monitoring of the state of gas-storage along the vertical profiles should continue during artificial degassing (Kusakabe *et al*., 2000, 2008; Schmid *et al*., 2003, 2006; Kling *et al*., 2005). Beside the hazard directly related to the extremely high recharge rate of magmatic CO_2 from the lake bottom, a second risk must be considered for Lake Nyos, where a weak dam composed of pyroclastic deposit ~100 m wide and ~40 m thick impounds the surface water (Fig. 3a). The age of these deposits has been strongly debated in literature (Lockwood and Rubin 1989; Freeth and Rex 2000; Aka and Yokoyama, 2013), in order to reveal the erosion rate of this dam, as seeping and seasonally overflowing lake water has unquestionably debilitated the natural dam (Fig. 3b). Dam breakage at Lake Nyos can cause the sudden release of $6x10^7$ m^3 of water flooding towards the Nigerian border (~50 km north of Lake Nyos), affect ~10,000 people, and definitely trigger a limnic eruption as lake level will be dropped by at least 40 m, leading to supersaturation of CO_2 contents at bottom waters (Aka and Yokoyama, 2013). Two hazard mitigation strategies can be envisioned: i) after making the lake gas free by artificial degassing, the dam can be removed, and lake water can be lowered by pumping; or ii) the weak natural dam can be reinforced by engineering works, avoiding dam breakage. Recently, the second scenario was chosen (T. Ohba, *personal communication*). In any case, the *dam problem* at Lake Nyos should be resolved, not only to save lives but also to avoid geo-political questions between Nigeria and Cameroon. To minimize the risk for limnic eruptions at Lake Nyos, Schuiling (2011) recently proposed to transform CO_2 into bicarbonate in a layer of olivine spread over the lake bottom, a project called LANCELOT (Lake Nyos carbon emission lowering by olivine treatment). Although the author did not clearly explain how carry out this intervention in the Cameroonian lakes, this idea could find some useful application in for the sequestration of CO_2 emissions from both natural and industrial sources.

At Lake Kivu, the gas reservoir represents a huge energy resource, being composed of CH_4 and CO_2 in comparable amounts (Schoell *et al*., 1988). Methane exploitation from this lake has been considered important not only as a huge economic resource but also to prevent the progressive saturation of deep water layers (Hirslund,

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2012), especially due to the increase of gas accumulation rate observed over the past decades (Pasche *et al*., 2010). However, contamination of the surface layer with toxic deep water possibly caused by artificial gas extraction may strongly affect the ecology of the lake (Pasche, 2009), with dire consequences for the ~2 million people living around the lake and dependent on lake water for personal use and a fishery. Although scientific research in this area is heavily biased by the influence of foreign energy companies and the complicated socio-political situation (Nayar, 2009), further biogeochemical, limnological and ecological studies are needed to provide an exhaustive evaluation of the possible advantages and disadvantages related to gas extraction from this lake. This considerations suggest that intervention plans to mitigate the limnic eruption hazard in other volcanic lakes should take into serious account the possible environmental impact of the artificial degassing approach.

SAMPLING AND ANALYTICAL TECHNIQUES FOR GEOCHEMICAL SURVEYS

Geochemical surveys of Nyos-type lakes basically focus on the distribution of the main parameters characterizing water and dissolved gas chemistry along vertical lake profiles. Measurements of water temperature at various depths in Lakes Nyos and Monoun were first carried out with an analog telethermometer and thermistor probe (Tuttle *et al*., 1987), whereas in the following years a four-conductor thermistor ohm-meter (Sass *et al*., 1981) was used (Evans *et al,*. 1993). In more recent times, contemporaneous measurements of different physical-chemical parameters, such as temperature, pH, electrical conductivity, and dissolved oxygen at depth intervals of a few cm, were carried out in different volcanic lakes by using multi-sensor probes (Aguilera *et al*., 2000; Cioni *et al*., 2003; Schmid *et al*., 2005; Caliro *et al*., 2008; Carapezza *et al*., 2008; Kusakabe *et al*., 2008; Sarmento *et al*., 2008; Caracausi *et al*., 2009; Pasche *et al*., 2009; Cabassi *et al*., 2013) (Fig. 4a-d). These instruments commonly have high accuracy and precision (*e.g.,* temperature: 0.01ºC accuracy and 0.001ºC precision) and they are able to store huge amounts of data, allowing the construction of almost continuous vertical profiles of the measured parameters that can be used to identify extremely thin (a few cm) water layers.

In situ analysis of lake water and dissolved gases for determining their chemical and isotopic compositions have rarely been carried out due to technical and logistic problems. Moreover, the use of different sampling and analytical techniques by the various groups of scientists provided compositional dataset that are difficult to be compared. Silicone rubber tubing was used by Evans *et*

Fig. 3. a) The north wall of the *Nyos dam*, composed of pyroclastic rocks; note the people for scale. b) M. Kusakabe inside a pothole on top of the *Nyos dam*, demonstrating the mechanical weakening of the dam structure.

al. (1993) to measure the total pressure of dissolved gases at Lake Nyos (Fig. 5). This technique, which has long been used to monitor dissolved gases (Enns *et al*., 1965), is based on the principle regulating gas diffusion through a semi-permeable membrane. More specifically, the transport of gas molecules through a homogeneous polymer matrix consists of i) condensation and solution of the penetrant at the surface of the membrane; ii) diffusion, in liquid form, through the matrix under the influence of a concentration gradient (chemical potential); and iii) evaporation at the opposite surface to the gaseous state (Klopfer and Flaconneche, 2001). The equilibrium between the partial pressure of dissolved gases and the pressure of the gas in the tubing is regulated by Henry's law, whereas the transport of gases through the semi-permeable membrane is described by Fick's law. Gas pressure build-up inside the probe due to the diffusion of gases from the surrounding fluid was measured with a pressure gauge, which was later changed to a pressure transducer able to provide a continuous monitoring of the total gas pressure of Lake Nyos at depth. Detailed vertical profiles of CH_4 at Lake Kivu were carried out with a Capsum Mets sensor, which was able to record a CH_4 concentration every 0.5 second with an estimated error of 2-5% (Schmid *et al*., 2005). Unfortunately, this type of instrument does not allow the measurement of other gas species.

A new gas sensor device based on the membrane technique (Zimmer and Erzinger, 2009) was recently used for continuous subsurface measurements of dissolved CO_2 in deep boreholes, as described in detail by Zimmer *et al.* (2011) (Fig. 6 a,b). As suggested by preliminary tests carried out in volcanic lakes in Italy (Zimmer, *personal com-*

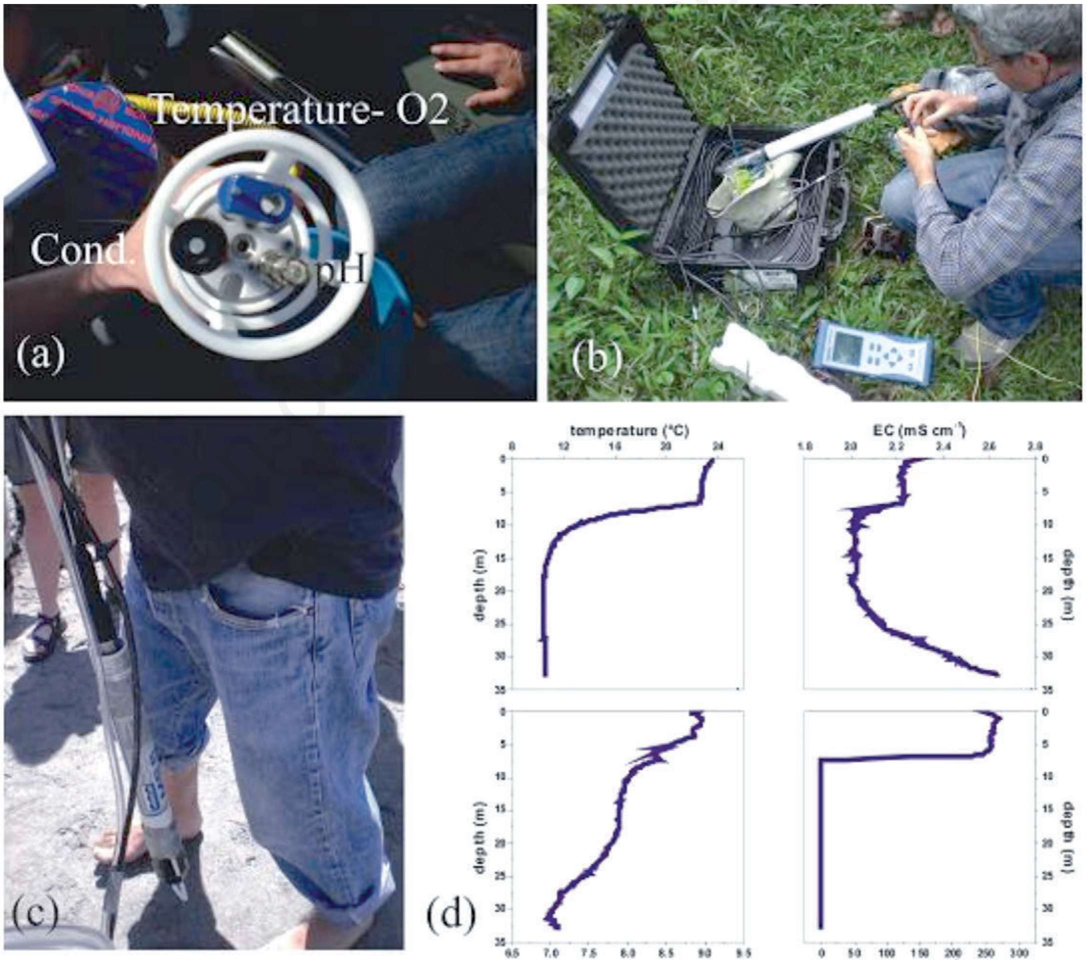

Fig. 4. The multi-sensor probe. a) View of the electrodes in the protected case on the bottom of the probe. b) Preparing the probe prior to measurement. c) Moving the probe towards the raft. d) Output data from the multi-sensor probe (example of Lake Averno, modified from Cabassi *et al.,* 2013). EC, electrical conductivity.

munication), the gas membrane sensor (GMS) method, coupled with a portable gas-chromatograph, may be successfully used to obtain measurements of partial pressures of various gas species (*e.g.*, CO_2, CH_4, N_2) at any depth required. Although to be confirmed by further investigations and tests, this approach would have the significant advantage to provide, directly in the field, a comprehensive chemical composition of dissolved gas reservoirs. The performances of the GSM method could be improved by using a portable mass spectrometer that would allow to measure the isotopic composition of the main gas species (CO_2 and CH_4), as well as the $\delta^{18}O$ and δD values of water along the whole lake vertical profile. These results encourage further development of *in situ* analytical approaches. However, past and current investigations are generally carried out on water and gas samples analyzed in laboratory. A large variety of methods has been devised and utilized to collect water and dissolved gases from below the surface. One of the most common sampling device is the Niskin bottle that consists of a glass (or plastic) cylinder equipped with stoppers at each end, connected with an elastic cord attached to a release mechanism (Fig. 7a,b). The open bottle is lowered into the lake with a cable until it reaches the sampling depth. Then, a small weight (messenger) is sent down the cable from the surface, striking the release mechanism and resulting in the two stoppers being pulled into the ends of the cylinder, thereby trapping water from that depth. Other devices, known as Van Dorn (Fig. 7c) and Ruttner water samplers (Fig. 7d), basically operate according to the same principles as the Niskin bottle, although they are characterized by a different geometry. All these instruments have a relatively low cost and are easy to use. However, they cannot be utilized when the pressure of dissolved gas largely exceeds the atmospheric pressure, such as in the hypolimnion of Nyos, Monoun and Kivu Lakes, because the closing mechanisms allow the escape of gases that exsolve at decreasing pressure during bottle retrieval. To prevent this problem different solutions have been proposed.

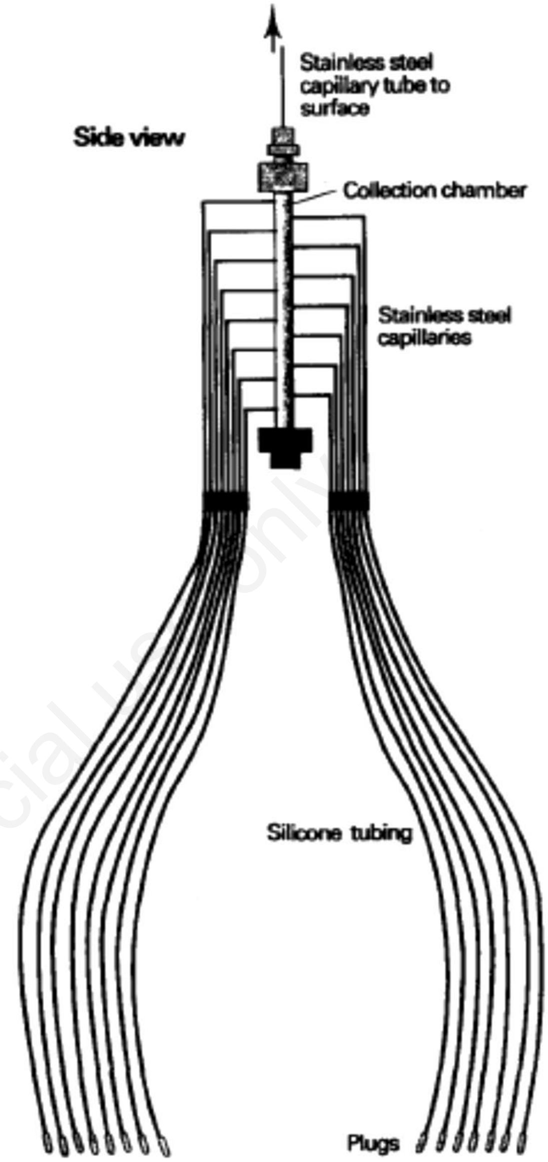

Fig. 5. Gas pressure probe (Enns *et al*., 1965, reported by Evans *et al*., 1993).

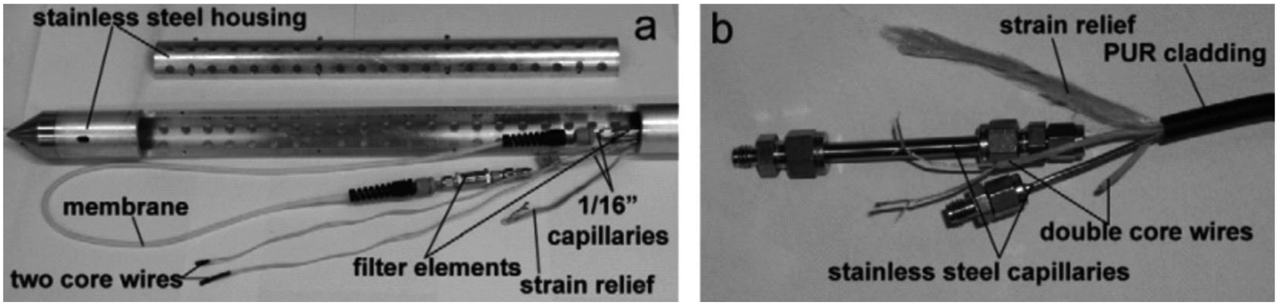

Fig. 6. a) Membrane gas collector tool. b) Cable with fittings (Zimmer *et al*., 2011).

Evans *et al*. (1993) collected samples for water analysis in a Niskin sampler equipped with a vent valve that allowed exsolving gases to be released, whereas dissolved gas analyses were carried out on samples collected in stainless steel cylinders fitted with two ball valves and one check valve and equipped with a trigger activated by a sliding messenger (Fig. 8a,b). During the bottle retrieval from the sampling depth, the check valve was closed by the increasing internal pressure excess, impeding any gas loss. In the laboratory (at 25°C), the samples were transferred to a pre-evacuated cylinder, where gases separated from the liquid phase, and then were analyzed by gas chromatography. The composition of dissolved gases was determined on the basis of headspace gas composition, cylinder inner volume, gas pressure and lab temperature. Solubility data (Weiss, 1974; Wilhelm *et al*., 1977) were used to calculate gases remaining in the liquid phase. The *stainless steel cylinder* is to be considered an effective tool for measurements of water and dissolved gas compositions along the vertical profiles of Nyos-type lakes. This method was indeed adopted, with minor modifications, by Caracausi *et al.* (2009, 2013) and Pasche *et al*. (2011), to collected water samples from Monticchio's lakes (southern Italy) and Lake Kivu, respectively.

In 1999, Nagao *et al.* (2010) collected water samples for noble gas measurements at Nyos and Monoun Lakes with a Niskin sampler connected to an evacuated 10 L laminated aluminum-plastic bag that received exsolving gases. The gases were then transferred at the surface to a 100 mL gas bottle attached with vacuum-tight stopcocks at both ends. As highlighted by the same authors, this method (called *Al-bag*) caused a strong air contamination,

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Fig. 7. a) Niskin sampler, opened before sampling. b) Niskin sampler, closed after sampling (Greg Tanyileke, Lake Miike, Kirishima Volcano, Japan). c) Van Dorn bottle. d) Ruttner bottle.

Fig. 8. a) Stainless steel gas samples picture. b) Sketch.

significantly higher than that found in samples collected using, the stainless steel cylinder (compared for the same sampling campaign). In January 2001, this Japanese scientific group repeated the sampling of dissolved gases from Lake Nyos using a series of 11 plastic hoses, each having a different intake depth. Using a two-mouth 100 mL glass syringe, water was pumped from the hoses until bubble formation, caused by decompression of the deep water, triggered spontaneous (self-lifting) outflow of a gas-water mixture. Bubbling gases spouting out of the hoses were introduced in a basin filled with surface lake water and collected in a glass bottle using a funnel. This method (known as *Flute de Pan*) was also adopted to collect a separated gas phase in December 2001, when a single plastic hose (12 mm I.D.) was utilized instead of the hose series (Nagao *et al*., 2010) (Fig. 9). The *single hose* technique was then slightly modified by connecting a plastic separator to receive the gas-water mixture spouting from the hose as the intake was lowered to each of the desired sampling depths. The new device allowed the *in situ* measurement of the gas/water ratio and the collection of both the liquid and the gas phase in the two Cameroonian killer lakes (Yoshida *et al*., 2010) and at Lake Kivu (Tassi *et al*., 2009). This method was also used in meromictic volcanic lakes characterized by a dissolved gas pressure

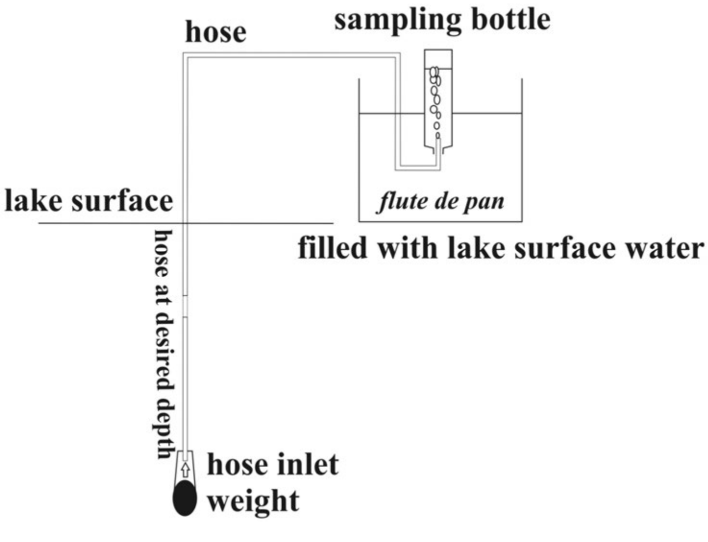

Fig. 9. Flute de pan method. The single hose is lowered to the desired depth. At the surface a reservoir is filled with surface lake water. The hose outlet is submerged in the reservoir. Due to the gas self-lift principle, dissolved gases in the lake water from depth will exsolve as bubbling gas. A previously evacuated sampling flask (*e.g*., Giggenbach bottle) is connected to the hose outlet, or a previously water filled bottle is overturned above the hose outlet (water replacement method).

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too low to trigger gas self-lifting (Aguilera *et al*., 2000; Cioni *et al*., 2003, Tassi *et al*., 2004; Caliro *et al*., 2008; Carapezza *et al*., 2008; Cabassi *et al*., 2013). To prevent the effects of the possible formation of micro-gas bubbles during sampling, the hose was connected, through a three-way valve, to an evacuated glass vial equipped with a Teflon stopcock (Fig. 10). After displacement of a water volume at least twice the pipe inner volume by means of a pump and/or a syringe, the stopcock was opened to fill the pre-evacuated vial (Giggenbach bottle without NaOH solution) with lake water up to about three fourths of the vial volume (Fig. 10). The partial pressures of each gas compound in the exsolved gas phase occupying the vial headspace were then determined by gas-chromatography. These data served to reconstruct the composition of dissolved gases according the same calculation procedure described for the stainless steel cylinder method.

Eventually, interesting results are obtained by applying the *syringe* method (Kusakabe *et al*., 2000) (Fig. 11a-c), a rapid and cost-effective approach to measure CO_2 concentrations. The total dissolved carbonate (H_2CO_3+HCO_3^-+CO_3^{2-}) is fixed in situ by collecting water with a 50 mL plastic syringe containing a 5 M KOH solution and later analyzed in laboratory by acidimetric titration or micro-diffusion techniques. The CO_2 concentrations were calculated by subtracting the HCO_3^- and the blank carbonate (in the KOH solution) concentrations from the total dissolved carbonate. Geochemical surveys of Nyos-type lakes should consider the application of relatively simple but necessary monitoring methods, as follows: i) climate monitoring by automatic meteo-stations (ambient air T, wind speed and direction, rain gauge) (Fig. 12); and ii) automatic T station for surface waters. In temperate climates, as the difference between the lake water surface temperature in winter and summer is large, a lake overturn may seasonally occur as a consequence of the cooling of epilimnetic waters. For example, when the temperature of surface water at Lake Averno (Italy) is lower than 7°C (in winter), it becomes denser than bottom water (Caliro *et al*., 2008), resulting in a complete mixing. In tropical climates, the $\Delta T_{epilimnion}$ between summer and winter is often too small to cause a seasonal lake rollover thus favoring a prolonged gas accumulation, the lake surface temperature may drop during the rainy season (summer) due to the direct input of cooler rain water, or the blocking of solar radiation by cloud cover. In conclusion,

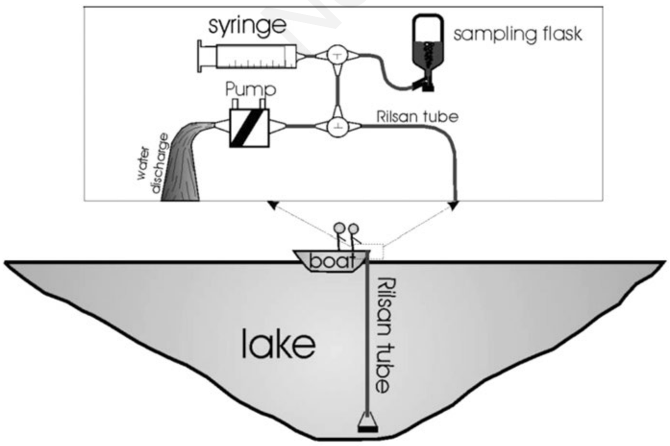

Fig. 10. Single hose method. The hose lowered to the desired depth is connected to a pump and a syringe to collect water and dissolved gas samples after displacement of a water volume at least twice the pipe inner volume.

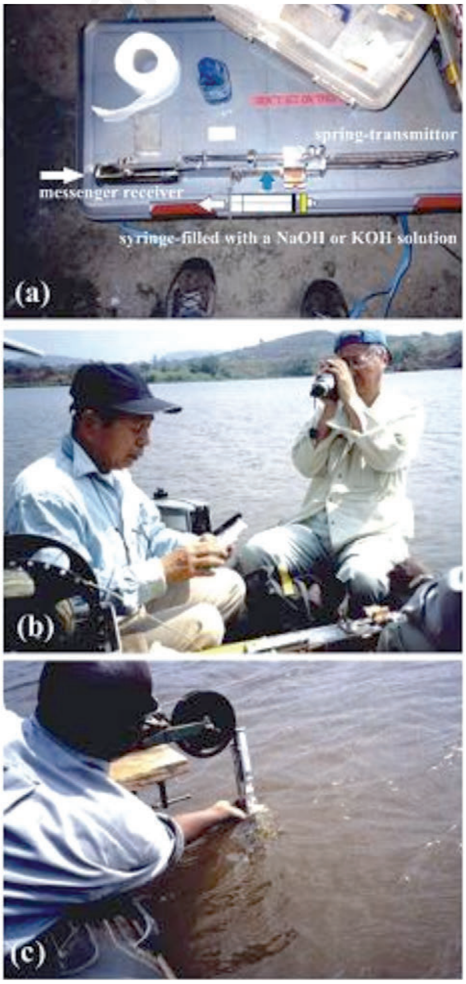

Fig. 11. The syringe method (Kusakabe *et al*., 2000). a) The syringe holder before sampling and the representation of where the syringe should be attached to the system. b) M. Kusakabe attaches the syringe to the syringe holder, before sampling lake water at depth. c) Issa lowers the syringe holder + syringe into the lake (Lake Monoun, January 2006).

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a simple monitoring of the lake surface temperature can thus be a first measure to consider to mitigate risk.

CONCLUSIONS

Limnic eruptions represent a true hazard in volcanic areas, where meromictic lakes are commonly fed by magmatic CO_2 contributing to the formation of dissolved gas reservoirs in deep water layers. The stability of the lake stratification, mainly depending on salinity and temperature vertical profiles, may be perturbed by external events, that can be difficult to predict. Magmatic gas addition, coupled with the production of gas species by biogeochemical processes (*e.g.*, CH_4 and N_2), may lead to saturation in the hypolimnion. At these conditions, a lake rollover may occur without a triggering event.

Artificial removal of dissolved gases from Nyos and Monoun Lakes, where dissolved CO_2 naturally increases at alarming rates, is the only possible intervention to mitigate the hazard for a limnic eruption. Nevertheless, this solution may pose a severe risk for the shallow aquatic environment in natural systems intensely populated by living organisms. Monitoring the vertical gradients of the water density through physical-chemical data is thus to be considered the most reliable approach for evaluating the potential hazard in volcanic meromictic lakes. As highlighted in this study, a number of different sampling methods have been developed to collect water and dissolved gas samples for chemical and isotopic analyses along lake vertical water profiles. Nevertheless, the promising results obtained by using semi-permeable membranes, commonly adopted for the measurement of geochemical parameters in deep water (marine) environments, encourage the application of this new techniques in volcanic lakes. Notwithstanding the fundamental importance of the results from these technical and theoretical approaches, an alarm system for high CO_2 contents in the atmosphere near the lake is to be considered particularly effective to mitigate the risk under the unfavorable hazardous situation of a gas release.

Fig. 12. The meteorological station raft at Lake Monoun (Cameroon, January 2006).

It is worth mentioning that preliminary microbiological investigations on samples collected from different depths in some volcanic lakes in Costa Rica (Mapelli *et al*., 2011) have shown the strong relationship between the distribution and behavior of microbial populations and the chemical and isotopic features of dissolved gas reservoirs. Stratigraphic data related to volcanic and post-volcanic activity of Colli Albani Volcano, in the area of Lake Albano (Italy), have provided evidence for the occurrence of recurrent limnic eruptions from this lake in the recent past (Funiciello *et al*., 2003). Recent studies concerning high resolution acoustic mapping (Anzidei *et al*., 2008), core radiocarbon dating (Chapron *et al*., 2010) of lake bottom sediments, and numerical modeling of landslide impact in lakes (Mazzanti and Bozzano, 2009) have provided useful results to shed light on driving processes resulting in gas bursts. These experiences strongly encourage the integration of geochemical studies on Nyos-type lakes with other scientific disciplines to improve the knowledge of those mechanisms regulating the occurrence of dangerous gas releases.

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