Journal of Geochemical Exploration 163 (2016) 10–18

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

Depth influence on the distribution of chemical elements and saturation index of mineral phases in twins maar lakes: The case of the Monticchio lakes (southern Italy)

Michele Paternoster [a,b,*], Giovanni Mongelli [a], Antonio Caracausi [b], Rocco Favara [b]

[a] Department of Sciences, University of Basilicata, Campus di Macchia Romana, Viale dell'Ateneo Lucano 10, Potenza, Italy
[b] Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Palermo, Via Ugo La Malfa 153, Palermo, Italy

ARTICLE INFO

Article history:
Received 17 April 2015
Revised 23 December 2015
Accepted 3 January 2016
Available online 5 January 2016

Keywords:
Lake water
Meromictic lake
Chemical elements and saturation index
Depth control
Mineral phases

ABSTRACT

In this paper we provide a systematic geochemical study of the Monticchio maar lakes, on the Mt. Vulture volcano, southern Italy, to understand the processes affecting the distribution of chemical elements. A high-resolution conductivity–temperature–depth profile was obtained, and water samples were collected at various depths for analyses of major and trace elements. Although the two lakes are separated by less than 200 m, they exhibit different behaviour. The Ca–Na–HCO_3 composition of "Lago Grande" water suggests that low-temperature fluids are leached from the host volcanic rocks. Na–Ca–HCO_3 in near-surface "Lago Piccolo" water is derived from the dissolution of local volcanic rocks, while the deepest water samples are bicarbonate alkaline-earth in composition and generally show an enrichment in solutes with respect to the epilimnion layer (except for SO_4^{2-} content). The hypolimnion water is principally governed by both the input of saline groundwater from the lake bottom and authigenic processes within bottom sediments. In addition, the occurrence of anoxic conditions and microbial activity is responsible for the transformation of sulphates to hydrogen sulphide, and for the precipitation of Fe sulphide phases. Both processes cause a change in the chemical composition of saline groundwater as it moves upwards. Overall, the water chemistry of the Monticchio lakes is principally affected by: i) the input of CO_2-rich volcanic gas; ii) evaporative processes that deplete near-surface water in some elements; and iii) the occurrence of chemical, physical and biological conditions causing the transformation of molecular complexes and consequently promoting mineral precipitation.

1. Introduction

There have been increasing concerns about water quality in lakes (Kingsford, 2011), and a growing interest in understanding their physico-chemical features. The evaluation of processes governing the chemical stratification of lake water is, therefore, a powerful tool for lake management practices (Gal et al., 2009). Lakes support important freshwater ecosystems and biodiversity, regulate the water cycle, supply water resources, and maintain ecological balance (Rubec and Hanson, 2009). The Lago Piccolo (hereafter LP) and Lago Grande (hereafter LG) lakes occupy two explosive maar craters on the Mt. Vulture volcano, southern Italy. Both the LP and LG maar craters were created by intense explosive volcanic activity when a relatively small volume of erupted magma sprayed out over a large area. The Mt. Vulture hydrogeological basin is one of the most important aquifers in southern Italy (e.g., Parisi et al., 2011a, 2011b), and is also situated on a popular tourist route because of its high scenic and ecological value. Various studies have been conducted in the lakes for paleoclimate reconstruction (Brauer et al., 2000), the genesis of sediments (Schettler and Albéric, 2008) and geochemical characteristics (conductivity–temperature–depth profiles, major ions, isotopic (O and H) composition and dissolved gas content, e.g. Caracausi et al., 2009, 2013b; Chiodini et al., 1997, 2000a). Water chemistry data show that although the two lakes are separated by less than 200 m, they have different dynamics: LP is a meromictic lake, whereas LG is a warm monomictic lake, which exhibits complete water turnover in winter and a subsequent new chemical stratification during the spring (Caracausi et al., 2013b). Previous studies on the isotopic composition (δD and $\delta^{18}O$) of groundwater and rainwater in the Mt. Vulture area (Caracausi et al., 2013b; Marini, 2006; Mongelli et al., 1975) indicate that LP waters deeper than 25 m fall along the local meteoric water line (LMWL, Paternoster et al., 2008), whereas LP shallow water and all LG water exhibit a linear trend, which is typical of evaporative processes as in other volcanic lakes (e.g. Varekaamp and Kreulen, 2000).

The trophic state and pollution level in lakes can mask minute compositional changes in water geochemistry. Therefore, these changes may be more efficiently recorded by the geochemical behaviour of

* Corresponding author at: Department of Sciences, University of Basilicata, Campus di Macchia Romana, Viale dell'Ateneo Lucano 10, Potenza, Italy.
E-mail address: michele.paternoster@unibas.it (M. Paternoster).

http://dx.doi.org/10.1016/j.gexplo.2016.01.001
0375-6742/

trace elements (e.g. Sugiyama et al., 2005) than solely from the distribution of major ions and the isotopic composition. In this respect, the two Mt. Vulture lakes, which share the same origin, hydrogeological basin and climate, offer a unique opportunity to evaluate how different water dynamics affect the distribution of trace elements with depth. With this in mind, we present the first large chemical dataset from the lakes that includes Li, B, Al, V, Mn, Co, Fe, Ni, Cu, Zn, As, Rb, Se, Sr, Mo, Sb, Cd, Cs, Ba and Pb, in addition to major ions. These data are used to evaluate processes that affect the distribution of chemical elements as a function of the depth through the water column of both lakes.

2. Hydrogeology of the Mt. Vulture area

Mt. Vulture is a Quaternary stratovolcano, located along the external edge of the Apennine Chain (Fig. 1) in the northeastern sector of the Basilicata region (Italy). Volcanic activity began during the middle–upper Pleistocene (0.73 M.yr. ago) and ended 0.13 M.yr. ago (Büettner et al., 2006). Recently Caracausi et al. (2013a) show that the region around Mt. Vulture is affected by an active degassing of mantle-derived fluids through a NE–SW lithospheric discontinuity (Vulture Line). Volcanics are undersaturated silica pyroclastic deposits and subordinate lava flows composed of tephritic-phonolite, phonofoidite, foidite, melilitite and carbonatites (Beccaluva et al., 2002; Giannandrea et al., 2006). The area is characterized by NW–SE, NNW–SSE and E–W oriented normal fault systems (Beneduce and Giano, 1996; Schiattarella et al., 2005) that control the evolution of the drainage system, principally oriented along NW–SE and E–W axes (Ciccacci et al., 1999). The average rainfall is 830–900 mm/yr. and the average annual temperature is 13.7–14.1 °C (AA.VV, 2006), indicating a sub-humid (C2B′2sb′3) climate according to the classification scheme proposed by Thornthwaite and Mather (1957).

The Mt. Vulture aquifer core is mainly composed of pyroclastic and subordinate lava flow layers of different permeabilities, which give rise to distinct aquifer layers. The principal hydrogeological complexes are therefore volcanic products, with high-medium permeability values. The structural hydraulic parameters and anisotropy features of the aquifer are the major factors that control groundwater flow pathways (Parisi et al., 2011a). A recent hydraulic and hydrogeochemical study (Parisi et al., 2011a) enabled a detailed characterization of the aquifer. This study found that:

i). Groundwater geochemistry is heterogeneous between different sectors, and there are two hydrogeochemical water types, reflecting different low-temperature water–rock interactions. The first water type has bicarbonate alkaline and alkaline-earth composition with a relatively low salinity (hereafter LS), whereas the second water type has bicarbonate-sulphate alkaline composition with higher salinity (hereafter HS).

ii). Three main sectors can be distinguished within the Mt. Vulture hydrogeological system. The first W–NW sector, which constitutes the main recharge area, has an isotopic signature similar to rainwater. The second and third sectors represent the main S–SE and N–NE discharge areas.

Lake volumes are 3.98×10^6 m^3 and 3.25×10^6 m^3 for LG and LP, respectively. Surface areas are 4.3×10^5 m^2 and 1.7×10^5 m^2 for LG and LP, respectively. The two lakes are connected by a 200 m long channel, through which LP water flows toward LG (Caracausi et al., 2013b). The Monticchio lakes are situated at 660 m a.s.l. and the estimated mean recharge altitude is about 925 m a.s.l. (Caracausi et al., 2013b).

3. Sampling and methods

Water samples were collected in June 2010 in both Monticchio lakes. Water was collected vertically along a water column from the surface down to the bottom at the deepest point of each lake. A 2 L clear polycarbonate sampler was used to collect deep lake water. Physical and chemical parameters were obtained using a high-resolution probe (Ageotec IM71) equipped with a pH sensor. The temperature probe has an accuracy of 0.01 °C and resolution of 0.001 °C; the accuracy values of the electrical conductivity (EC) and pH sensors are 0.005 mS cm^{-1} and 0.01 units, respectively. The spatial acquisition step of temperature, EC and pH data was 1 m (Table 1). All water samples were filtered through a 0.45 μm MF-Millipore membrane

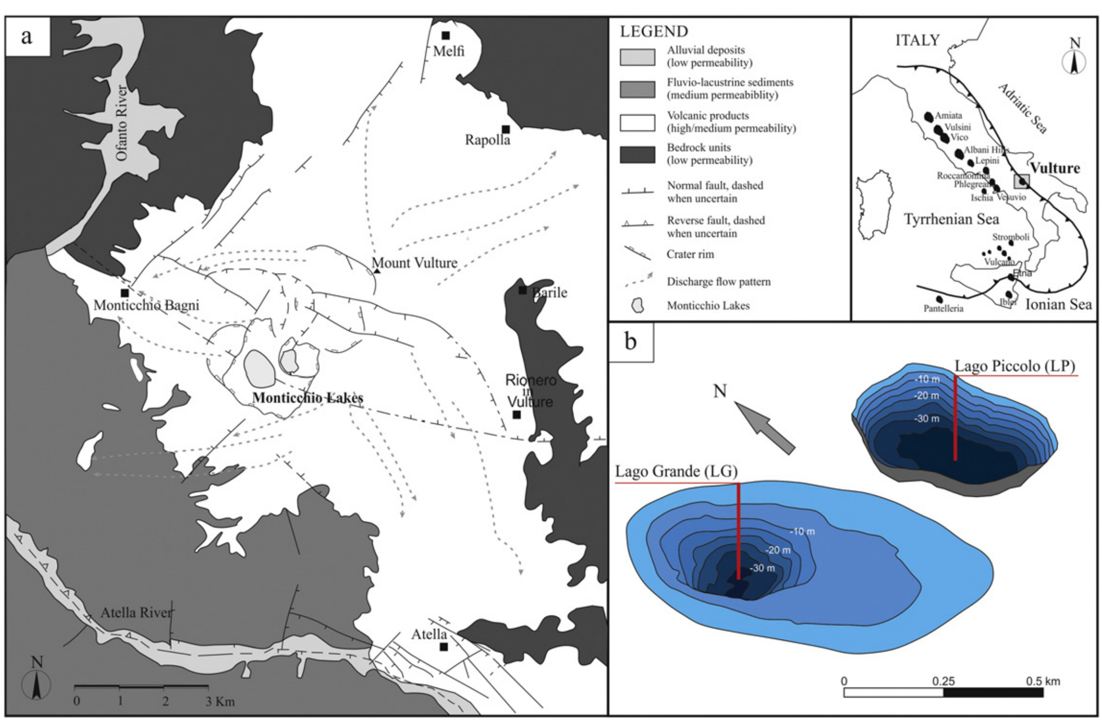

Fig. 1. (a) Simplified geological map of the Mt. Vulture volcano (modified from Giannandrea et al., 2006). (b) Bathymetric map of the Monticchio lakes showing the sampling points. The discharge flow water lines from Parisi et al. (2011a).