Journal of Volcanology and Geothermal Research 328 (2016) 222–229

Contents lists available at ScienceDirect

Journal of Volcanology and Geothermal Research

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

The chemistry and isotopic composition of waters in the low-enthalpy geothermal system of Cimino-Vico Volcanic District, Italy

Maria Battistel [a,b,*], Shaul Hurwitz [c], William C. Evans [c], Maurizio Barbieri [a]

[a] Dipartimento Scienze della Terra, Università "Sapienza" di Roma, Piazzale A. Moro 5, 00185 Roma, Italy
[b] Department of Environmental Engineering, Technical University of Denmark, Miljøvej, Building 115, 2800 Kgs. Lyngby, Denmark
[c] U.S. Geological Survey, 345 Middlefield Rd., Menlo Park, CA, USA

ARTICLE INFO

Article history:
Received 10 January 2016
Received in revised form 8 November 2016
Accepted 9 November 2016
Available online 10 November 2016

Keywords:
Low-enthalpy geothermal system
Fluid geochemistry
Boron isotopes
Strontium isotopes
Central Italy

ABSTRACT

Geothermal energy exploration is based in part on interpretation of the chemistry, temperature, and discharge rate of thermal springs. Here we present the major element chemistry and the δD, $\delta^{18}O$, $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ isotopic ratio of groundwater from the low-enthalpy geothermal system near the city of Viterbo in the Cimino-Vico volcanic district of west-Central Italy. The geothermal system hosts many thermal springs and gas vents, but the resource is still unexploited. Water chemistry is controlled by mixing between low salinity,HCO_3-rich fresh waters (<24.2 °C) flowing in shallow volcanic rocks and SO_4-rich thermal waters (25.3 °C to 62.2 °C) ascending from deep, high permeability Mesozoic limestones. The (equivalent) SO_4/Cl (0.01–0.02), Na/Cl (2.82–5.83) and B/Cl ratios (0.02–0.38) of thermal waters differs from the ratios in other geothermal systems from Central Italy, probably implying a lack of hydraulic continuity across the region. The $\delta^{18}O$ (−6.6‰ to −5.9‰) and δD (−40.60‰ to −36.30‰) isotopic composition of spring water suggest that the recharge area for the geothermal system is the summit region of Mount Cimino. The strontium isotope ratios ($^{87}Sr/^{86}Sr$) of thermal waters (0.70797–0.70805) are consistent with dissolution of the Mesozoic evaporite-carbonate units that constitute the reservoir, and the ratios of cold fresh waters mainly reflect shallow circulation through the volcanic cover and some minor admixture (<10%) of thermal water as well. The boron isotopic composition ($\delta^{11}B$) of fresh waters (−5.00 and 6.12‰) is similar to that of the volcanic cover, but the $\delta^{11}B$ of thermal waters (−8.37‰ to −4.12‰) is a mismatch for the Mesozoic reservoir rocks and instead reflects dissolution of secondary boron minerals during fluid ascent through flysch units that overlie the reservoir. A slow and tortuous ascent enhances extraction of boron but also promotes conductive cooling, partially masking the heat present in the reservoir. Overall data from this study is consistent with previous studies that concluded that the geothermal system has a large energy potential.

1. Introduction

In the past few decades the development of geothermal energy resources has expanded worldwide as a sustainable and renewable source for electricity generation and heating applications (e.g. Moore and Simmons, 2013). Geothermal systems are classified based on the reservoir temperature (Williams et al., 2011). Low-enthalpy (or low-temperature) geothermal systems have been classified by the U.S. Geological Survey (USGS) as those with reservoir temperatures of <90 °C (e.g. Reed, 1983; Williams et al., 2008) and by others at <125 °C (Hochstein, 1988), and <150 °C (e.g., Nicholson, 1993). Low-enthalpy geothermal systems are widely spread around the world and their exploitation is advantageous in terms of accessibility, distribution and costs. In many cases thermal springs can be used directly as an energy source. In many countries low-enthalpy geothermal resources are used for bathing, heating, greenhouses, and ground-source heat pumps (Lund et al., 2011; Moore and Simmons, 2013); they can also be exploited for electric power generation if sufficiently low temperatures are available for cooling the working fluid in a binary power plant (Williams et al., 2008).

To reduce the costs of exploratory drilling in the past several decades many geochemical indicators have been developed to assess the state of the geothermal reservoir (e.g. Arnórsson, 2000; Boschetti, 2013; Capaccioni et al., 2014; Fournier, 1981; Fournier and Truesdell, 1973; Fournier, 1977; Giggenbach, 1988, 1992; Spycher et al., 2011). Geochemical indicators were developed to get insights on the reservoir fluid composition, rock chemistry, reservoir permeability, and the

* Corresponding author at: Dipartimento Scienze della Terra, Università "Sapienza" di Roma, Piazzale A. Moro 5, 00185 Roma, Italy.
E-mail address: maria.battistel@gmail.com (M. Battistel).

http://dx.doi.org/10.1016/j.jvolgeores.2016.11.005
0377-0273/

rates of water recharge into the reservoir. Among exploration techniques, the stable isotope composition of water ($\delta^{18}O$ and δD) is widely used as a tracer to determine the origin of groundwater, for assessing the degree of water-rock interaction, and as an indicator for mixing of waters from different sources. Similarly the isotopic composition of strontium ($^{87}Sr/^{86}Sr$) provide**s** information on flow paths and mixing of waters because the strontium isotopes directly reflect the various source rocks (e.g. Boschetti et al., 2005; Dotsika et al., 2010; Lee et al., 2011; Negrel et al., 1999; Peiffer et al., 2011; Pennisi et al., 2006). Boron stable isotope studies are applied in geothermal exploration, because boron is highly incompatible during water-rock interaction and incorporation of boron into secondary minerals fractionates its isotopes (e.g. Ellis and Mahon, 1964, 1967; Leeman et al., 2005; Millot et al., 2012; Palmer and Sturchio, 1990).

In this study we present the major element chemistry and the isotope composition (δD, $\delta^{18}O$, $^{87}Sr/^{86}Sr$ and $\delta^{11}B$) of groundwater from a low-enthalpy geothermal system near the city of Viterbo in the Cimino-Vico volcanic district of west-Central Italy (Fig. 1a). The region hosts many thermal springs and gas vents and is a part of a larger thermal anomaly that extends from southern Tuscany in the north to the active volcanic areas of Phlegrean Fields and Vesuvius in the south (Fig. 1a). The geothermal resource in the area is unexploited despite estimates that the extractable electrical power using binary cycle power plants in the Vico area can contribute to the energetic autonomy of the region (Cinti et al., 2014; Procesi et al., 2013). The specific goals of this study are to (1) characterize the processes controlling water chemistry in the Cimino-Vico area, (2) characterize the processes controlling the isotopic systematics of boron and strontium in low enthalpy hydrothermal systems, and (3) provide new insights on groundwater circulation in the area, which in turn, give information on the potential for geothermal energy production.

2. Geological framework

Volcanic activity which gave rise to the Cimino and Vico complexes started with explosive and effusive activity at 1.35 Ma at the Cimino complex. Between 0.8 and 0.3 Ma, the Vico complex was active, producing a central caldera that now hosts Vico Lake (Fig. 1b). The Cimino volcanic products include rhyodacites, latitic ignimbrites and olivine-latitic lavas, and are mostly covered by the K-alkaline pyroclastic deposits from the Vico volcanics, consisting of undersaturated trachytes, phonolites, tephritic phonolites, tephrites, and subordinate tuffs (Arnone, 1979; Gambardella et al., 2005; Sollevanti, 1983). The pyroclastic products are intercalated with lavas belonging to potassic and highly potassic series, mostly latities and trachytes and leucitites (Peccerillo and Manetti, 1985; Beccaluva et al., 2004). Northwest and northeast striking extensional faults divide the substratum rocks and produce horst and graben structures (Baiocchi et al., 2013). Ongoing magmatic activity is manifest as several geothermal anomalies, thermal springs, CO_2-rich vents and active travertine deposition.

The hydrogeology of the Cimino-Vico geothermal area has been widely studied and the hydrostratigraphic sequence was defined by several authors (Angelone et al., 2008; Arnone, 1979; Baiocchi et al., 2013; Chiocchini et al., 2010; Piscopo et al., 2006) (Fig. 2). Two main aquifers were defined in the area: a deep geothermal reservoir, located in highly permeable Mesozoic carbonate rocks, which include limestones and anhydrites; and a fresh water volcanic aquifer that flows within the volcanic products that cover the study area. The Mesozoic unit is several thousand meters thick and is the primary regional groundwater aquifer in Central Italy It hosts numerous low-enthalpy geothermal reservoirs with temperatures ranging between 48 °C and 115 °C (Minissale, 2004), including the Cimino-Vicano one, that has an estimated temperature of ~94 °C (Battistel et al., 2014). The shallow

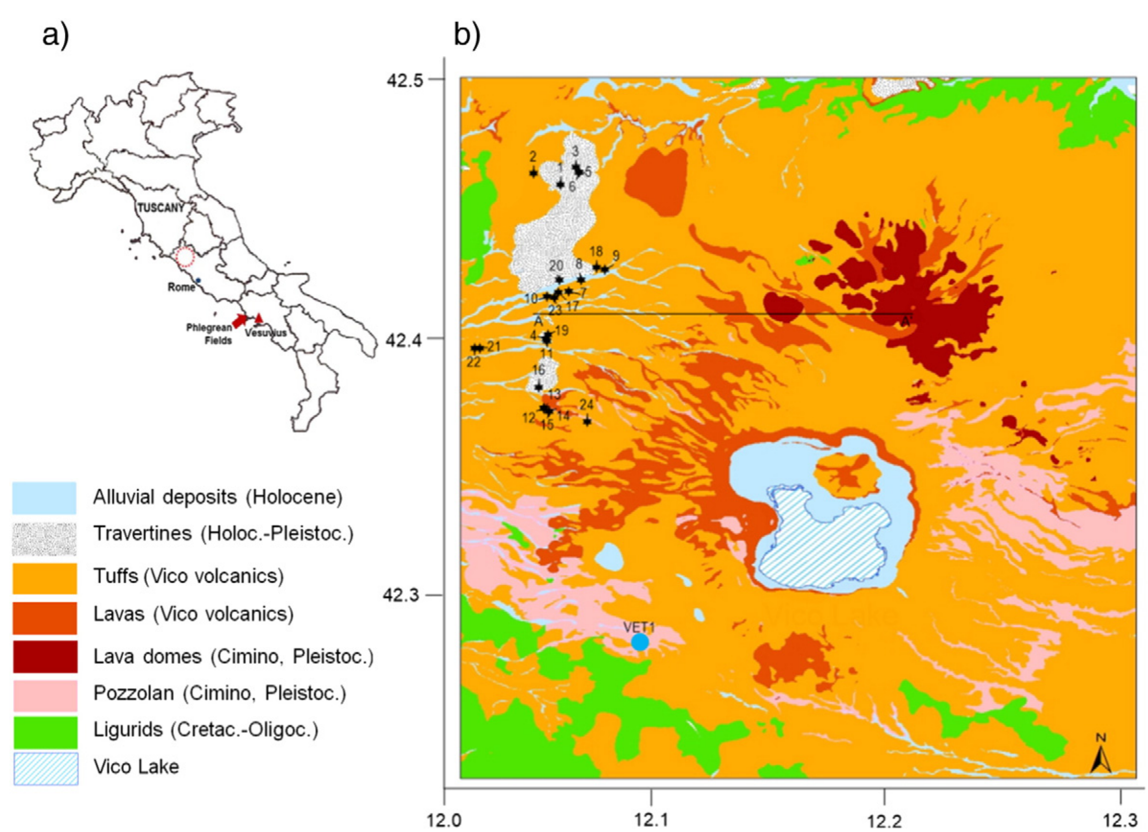

Fig. 1. Map of the study area. a) The dotted circle in the map on the top left represents the enlarged area from where samples for this study were collected. b) Geological map of the study area. The stars represent the sampling points and A-A' is the location of the hydrogeological cross-section in Fig. 2. The blue circle represents the geothermal well VET1, see text for references.