Chemical Geology 371 (2014) 96–114

Contents lists available at ScienceDirect

Chemical Geology

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

# Fluid geochemistry and geothermometry in the unexploited geothermal field of the Vicano–Cimino Volcanic District (Central Italy)

D. Cinti [a,*], F. Tassi [b,c], M. Procesi [a], M. Bonini [c], F. Capecchiacci [b], N. Voltattorni [a], O. Vaselli [b,c], F. Quattrocchi [a]

[a] Istituto Nazionale di Geofisica e Vulcanologia (INGV), Via di Vigna Murata 605, 00143 Roma, Italy
[b] Dipartimento di Scienze della Terra, Università di Firenze, via G. La Pira 4, 50121 Firenze, Italy
[c] CNR — Istituto di Geoscienze e Scienze della Terra, via G. La Pira 4, 50121 Firenze, Italy

ARTICLE INFO

*Article history:*
Received 17 October 2013
Received in revised form 29 January 2014
Accepted 6 February 2014
Available online 15 February 2014

Editor: David R. Hilton

*Keywords:*
Geothermal resource
Central Italy
Fluid geochemistry
Water–gas–rock interaction
Hydrothermal reservoir

ABSTRACT

The Vicano–Cimino Volcanic District (VCVD) is related to the post-orogenic magmatic activity of the peri-Tyrrhenian sector of Central Italy. The chemical and isotopic compositions of 333 water discharges and 25 gas emissions indicate the occurrence of two main sources: 1) cold Ca-$HCO_3$ to Ca(Na, K)-$HCO_3$ type waters from relatively shallow aquifers hosted in volcanic and sedimentary formations; and 2) thermal Ca-$SO_4$($HCO_3$) type waters located in a deep $CO_2$-pressurized reservoir, hosted in carbonate–evaporite rocks and separated from the shallow aquifers by thick sequences of low-permeability formations. Carbon dioxide is mainly produced by thermal metamorphic decarbonation within the deepest and hottest parts of the carbonate–evaporite reservoir ($\delta^{13}$C–$CO_2$ from −3.1 to +2.2‰ vs. VPDB), likely affected by a mantle-rooted $CO_2$. Release of $CO_2$-rich gases from the deep aquifer into the overlying shallow aquifers produces high-$CO_2$ springs and bubbling pools. The spatial distribution of thermal waters and $CO_2$-rich cold discharges is strongly controlled by fractures and faults located in correspondence with buried structural highs. Stable isotopes ($\delta$D and $\delta^{18}$O) suggest that meteoric water feeds both the shallow and deep reservoirs. The relatively low $R/R_a$ values (0.27–1.19) indicate that He is mainly deriving from a crustal source, with minor component from the mantle affected by crustal contamination related to the subduction of the Adriatic plate. Consistently, relatively high $N_2$/Ar and $N_2/^3$He ratios and positive $\delta^{15}$N–$N_2$ values (from 0.91 to 5.7‰ vs. air) characterize the VCVD gas discharges, suggesting the occurrence of a significant "excess" nitrogen. Isotopic compositions of $CH_4$ ($\delta^{13}$C–$CH_4$ and $\delta$D–$CH_4$ values from −28.9 to −22.1‰ vs. VPDB and from −176 to −138‰ vs. VSMOW, respectively), and composition of light alkanes are indicative of prevalent thermogenic $CH_4$, although the occurrence of abiogenic $CH_4$ production cannot be excluded. The $\delta^{34}$S–$H_2S$ values (from +9.3 to +11.4‰ vs. VCDT) are consistent with the hypothesis of $H_2S$ production from thermogenic reduction of Triassic anhydrites. Gas geothermometry in the $H_2O$–$H_2$–Ar–$H_2S$ system suggests that the VCVD gases equilibrated in a liquid phase at redox conditions controlled by interactions of fluids with the local mineral assemblage at temperatures lower (<200 °C) than that and measured in deep (>2000 m) geothermal wells. This confirms that secondary processes, i.e. steam condensation, gas dissolution in shallow aquifers, re-equilibration at lower temperature, and microbial activity, significantly affect the chemistry of the uprising fluids. Thermal water chemistry supports the occurrence in this area of an anomalous heat flow that, coupled with the recent demographic growth, makes this site suitable for direct and indirect exploitation of the geothermal resource, in agreement with the preliminary surveys carried out in the 1970's–1990's for geothermal exploration purposes.


## 1. Introduction

The Vicano–Cimino Volcanic District (VCVD) is part of a thermally anomalous area that extends from southern Tuscany down to the Campanian volcanic areas of the Phlegrean Fields and Vesuvius, where $CO_2$-pressurized reservoirs developed in a complex geodynamic setting (Barberi et al., 1994, and references therein). Thermal emissions and mineral springs, as well as areas characterized by an anomalously high $CO_2$ diffuse degassing from the soil, are spatially controlled by fractures and faults related to an extensional tectonic regime (Minissale, 2004, and references therein). Most VCVD thermal manifestations are located W of the town of Viterbo along a N10°E tectonic alignment (Fig. 1). Here, the thermal activity is known since Etruscan and Roman times and acknowledged by Dante in the *Divina Commedia* (Dante Alighieri, *Inferno* XIV, 76–84). Thermal discharges are currently used as spa thermal resorts for health therapies and public pools (Chiocchini et al., 2001). A thermal spa near Nepi (*Terme dei Gracchi*), constructed in Roman times (Fig. 1), exploits sulfur-rich and sparkling waters that are currently bottled for commercial use. The VCVD, as well as the whole region between southern Tuscany and northern Latium, was intensively investigated for evaluating geothermal potential (Conforto,

* Corresponding author. Tel.: +39 06 51860254; fax: +39 06 51860507.
*E-mail address:* daniele.cinti@ingv.it (D. Cinti).

http://dx.doi.org/10.1016/j.chemgeo.2014.02.005
0009-2541/

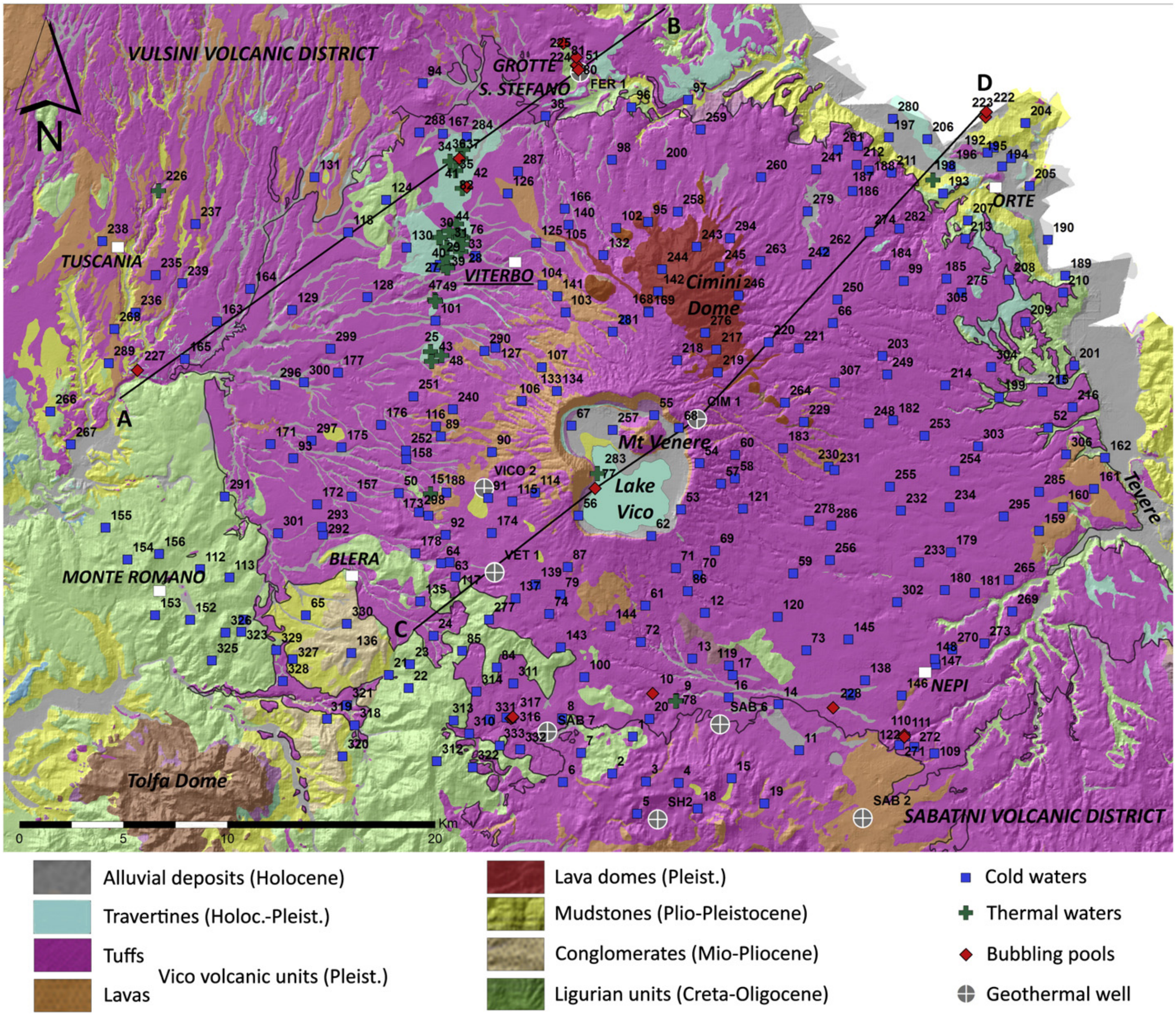


**Fig. 1.** Geological sketch map of the VCVD showing the location of the fluid sampling sites and the main towns. Interpretative sections corresponding to traces A–B and C–D are reported in Figs. 2 and 17, respectively.

1954; Cataldi and Rendina, 1973; Calamai et al., 1976; Cataldi et al., 1978; Borghetti et al., 1983; Bertrami et al., 1984; Cavarretta and Tecce, 1987; Cataldi et al., 1995; Barelli et al., 2000). Starting from the early 1950's, 9 deep wells and 76 test-holes (Fig. 1) were drilled by Terni Company (Conforto, 1954) and then, by the Italian energy provider (ENEL) and the national oil company (ENI-AGIP). A maximum temperature of 218 °C was measured in the Cimino 1 well, at the depth of 2153 m. Despite the significant potential highlighted by these preliminary explorations, the geothermal resources at VCVD have not yet been exploited.

Geochemical data of some fluid discharges from VCVD were reported in studies carried out at regional scale (Baldi et al., 1973; Arnone, 1979; Duchi et al., 1985; Chiodini et al., 1995, 1999; Minissale et al., 1997a; Minissale, 2004), whereas recent investigations have dealt with the reconstruction of a hydrogeological conceptual model of the Viterbo thermal area (Piscopo et al., 2006; Baiocchi et al., 2012) and VCVD (Baiocchi et al., 2006; Angelone et al., 2009; Chiocchini et al., 2010).

This study presents an original and detailed dataset of chemical and isotopic analyses of 333 fluid discharges (cold and thermal waters) and 25 gas emissions collected from VCVD. The main goals are to: 1) evaluate the fluid contributions from different source regions and their relationship with the tectonic assessment, 2) constrain the chemical–physical conditions controlling the chemistry of the fluid reservoirs, and 3) investigate the effects of secondary processes occurring during the uprising of deep-originated fluids toward the surface. Geochemical data were integrated with the available information concerning the stratigraphical, geophysical, hydrogeological and structural setting aimed to define a detailed conceptual model for fluid circulation and provide insights into the most promising areas for geothermal exploitation.

## 2. Geological and hydrological setting

VCVD is located along the peri-Tyrrhenian sector of Central Italy and covers a surface area of approximately 1400 $km^2$. This sector has undergone a post-collisional Plio-Quaternary extension that has led to the development of NW–SE and NE–SW-trending fault sets (Barberi et al., 1994). The former fault set is dominantly extensional, while the transverse NE–SW-trending faults are transtensive/transfer structures