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Multicomponent geothermometry applied to a medium-low enthalpy carbonate-evaporite geothermal reservoir

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Abstract

To improve knowledge of the thermal state of medium to low-enthalpy thermal systems hosted in carbonate-evaporite rocks, a mineral-solution equilibrium model was compared to other theoretical geothermometers. We use the GeoT code, which uses as input the chemical composition of water and saturation indices of minerals to calculate water-rock equilibrium over a temperature range of interest. The calculations were applied to the medium and low enthalpy geothermal systems in the Tyrrhenian-Apennine area (central Italy). The lithology consists of a Paleozoic metamorphic basement, overlain by Mesozoic carbonate–evaporite- and Oligocene–Middle Miocene flysch formations, and Quaternary volcanic complexes associated with crustal extension. A regional aquifer is hosted in the carbonate-evaporite formations, and smaller aquifers are hosted in the volcanic rocks. Reservoir temperatures were calculated based on the chemical composition of springs and wells in Central Italy (sampled previously), and in the Cimino-Vicano hydrothermal system (sampled in 2012). Chalcedony and quartz geothermometers provide realistic temperatures. The sensitivity of the model is tested for CO_2 degassing and input minerals. The results of optimized GeoT simulations show that all the samples are affected by degassing during their rise to the surface and that for computing a realistic reservoir temperature it is necessary to consider the principal minerals of the geothermal reservoir (particularly gypsum, quartz, dolomite, aragonite and calcite). The equilibrium temperatures range from 48-115°C. The statistical approach of "best clustering minerals" solves the problems related to cation or single component geothermometers. Multicomponent geothermometry coupled with optimization provides a reliable approach to reconstruct fluid composition at depth and estimate reservoir temperatures.

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1. Introduction

The major goals of geochemical studies in geothermal systems are to predict the subsurface temperatures, to understand the circulation of the thermal fluids and to have information on their origin. The basic assumption is that the concentrations of many components in the geothermal fluids reflect thermal conditions at depth [2]. The use of geochemical surveys reduces significantly the costs of geothermal exploration. Relying on the assumption that the concentration of dissolved constituents in thermal fluids are related to the reservoir's temperature, many authors have developed geothermometers to investigate geothermal fluids at different conditions, mostly cation- [3–5] and silica-based [6–8]. Whereas the main factors affecting thermal fluid chemistry are reservoir temperature and mineral assemblage, other processes such as cooling, mixing, or degassing may alter the chemical composition. For these reasons interpretation of geothermometers is a non-trivial problem. The multicomponent chemical geothermometry method developed by Spycher et al. [9] aims to improve the prediction of geothermal reservoir temperature using the full chemical analysis of waters samples, taking into account the possible surface processes that could mask the chemical signature of deep reservoir temperatures [1]. The method estimates reservoir temperature based on the computation and a statistical analysis of saturation indices of potential reservoir minerals. The aim of this study is to investigate the applicability of this approach to the medium-low enthalpy carbonate-evaporite geothermal reservoir located in Central Italy and to assess the geothermal conditions of the area. Results of the multicomponent chemical geothermometry calculations are compared to silica (quartz [7] and chalcedony [6]) and cation (Na-K [3], Na-K-Ca and K-Mg [5]) based geothermometers.

2. Geological and hydrogeological settings

The study area is located in west-central Italy, between the Tyrrhenian coast and the Apennines chain (Fig. 1). The area is characterized by a NW-SE trending structural grain resulting from the stacking of several Jurassic-Eocene flysch units above the Umbrian-Marche sequence (thick Mesozoic carbonate evaporite sequence, and Oligocene-Miocene sandstones) [10,11]. After the Miocene and the Tyrrhenian Sea opening, several extensional tectonic events affected the Tyrrhenian coast of Italy, forming marine and continental sedimentary basins. Since the Pliocene the area was intersected by intense volcanic activity [12], first in the northern Tuscany sector and northwest of Rome, then in the Roman area, and later in the currently active Neapolitan area [13]. The magmatic activity produced several geothermal anomalies, linked to active geothermal systems, thermal springs, CO_2-rich vents and active travertine deposition. The Mesozoic limestone is the major, and the lowermost, tectonic-stratigraphic unit affecting the morphology of central Italy. Due to its high permeability, the Mesozoic limestone is the primary regional groundwater aquifer, which hosts numerous geothermal reservoirs in central Italy [10]. Abundant CO_2 emissions, due to the metamorphic processes, affect this aquifer [14–16].

The volcanic activity which gave rise to the Cimino and Vicano complexes started 1.35 Ma, with the explosive and effusive activity of the Cimino complex. Between 0.8 and 0.3 Ma, the Vicano complex was active, with a central caldera that now hosts Vico lake. The Cimino volcanic products include rhyodacites, latitic ignimbrites and olivine-latitic lavas, currently mostly covered by the K-alkaline pyroclastic deposits from the Vicano volcanics, consisting of undersaturated trachytes, phonolites, tephritic phonolites, tephrites, and subordinate tuffs [17,18]. A Mesozoic evaporite-limestone unit underlies the volcanic units, separated by a Pliocene-Pleistocene sedimentary complex including conglomerates, sandstones, sands and clays and an Upper Cretaceous-Oligocene flysch.

The hydrogeology of the Cimino-Vicano geothermal area has been widely studied [17,19–22]. Two main aquifers recharged by present-day meteoric waters have been identified: a shallow fresh-water aquifer in the volcanic units and a deep geothermal reservoir in the Mesozoic carbonate units. The Pliocene-Pleistocene sedimentary complex is an aquitard or aquiclude.

Fig. 1. Study area. The red circle in the map on the right represents the enlarged area and the yellow square in the map on the left shows the Cimino-Vicano area from where samples for this study were collected.

3. Sampling and analysis

Nine water samples were collected from the Cimino-Vicano hydrothermal system between October 2011 and August 2012 (Fig. 1). Water temperature, electrical conductivity and pH were determined in the field. Bicarbonate was determined by titration with 0.1 N HCl in the field. Major ions were determined with a Dionex DX-120 ion chromatograph (precision ±2%). A Dionex CS-12 column was used for determining cations, whereas a Dionex AS9-SC column was used for anions. The analytical accuracy of these methods ranged from 2% to 5%. Data from the Tyrrhenian-Apennine area in Central Italy used for the comparison with the samples from the Cimino-Vicano volcanic district are from Chiodini et al. [23].

4. Geochemical Characterization

Chemical compositions of groundwater and thermal springs of Cimino-Vicano thermal area are reported in Table 1. Analytical error as computed from anion/cation balance [24] is within ±4%. The pH of the samples at the time of collection ranged between 5.8 and 7.9 and water temperatures ranged between 18.1°C and 62.2 °C.

Waters, with T< 25°C are classified as Ca-HCO_3 or NaK-HCO_3 type and have an EC between 303 and 753 µS/cm. Thermal waters, with T>25°C, have high EC ranging between 2460 and 3190 µS/cm and are classified as CaMg-SO_4 type, suggesting interaction with the Mesozoic evaporite unit. These waters are rich in Ca (473-681 mg/L), Mg (98.5-149 mg/L), HCO_3 (638-1,086 mg/L), and SO_4 (1,118-1,826 mg/L). The concentrations of these ions increase with increasing temperature. In contrast, Cl concentration is higher, ranging between 17.1 and 27.9 mg/L in cold waters and 7.6 and 14.4 in thermal waters). The comparable Na and K concentrations in both cold and thermal waters is attributed to the volcanic products covering the Cimino-Vicano area [17,18].

5. Water temperature at depth

We use an equilibria-based method to estimate reservoir temperatures. This method is based on the assumption that deep circulating waters are in thermal equilibrium with the host rocks and reach saturation with respect to the minerals which constitute the geothermal reservoir [25]. In systems with temperatures lower than 280°C the effects of rock type are the most significant factor controlling water chemistry. The use of silica and cation based geothermometers appears to be inappropriate, since they are calibrated for high temperature geothermal systems [2–5]. In addition, even if potentially any constituent whose concentration is controlled by a temperature-dependent

reaction could be used as a geothermometer [26], the lack of information of the geochemical conditions at reservoir depth prevents us from using an ion-based geothermometer.

We use the computer simulator GeoT [9] to calculate reservoir temperatures. This method uses the mineral assemblage of the geothermal reservoir to compute the saturation indices of the reservoir minerals over a temperature range. The clustering of the saturation indices near zero is inferred to indicate the reservoir's temperature. The code takes the smallest median absolute value of mineral saturation indices (MEDIAN) to estimate the temperature of the reservoir. The chemical composition of the waters suggests equilibrium with minerals of the carbonate-evaporate reservoir: calcite, dolomite and anhydrite, and secondary minerals typical of thermal systems.

The sensitivity of predicted temperatures to degassing was assessed using gas composition at single well. We also assessed the effect of different input minerals on saturation indices and reservoir temperature. Results from the sensitivity test applied to the data from a well in the Cimino-Vicano (M1) hydrothermal area are shown in Fig. 2. The sensitivity tests show that variations in the calculated reservoir temperature can be minimized by manual optimization that allows reconstructing the original thermal fluid mineral assemblage. Optimized results show that the sample M1 undergoes CO_2 degassing during the rise from reservoir to the surface. The sensitivity test also shows that the minerals, which affect the computation results (Fig. 2c,d) are the principal constituents (gypsum, quartz, dolomite, aragonite and calcite) of the geothermal reservoir. The aluminum silica minerals play little role in the computation of temperature thermal reservoir, and their inclusion in the model does not affect the calculated temperature or reduce the error by 1°C (Fig. 2d). The estimated temperature of Cimino-Vicano reservoir calculated from the composition of sample M1 is 96 ±6.18 °C and a temperature spread of 16°C. The main output parameters include the median (RMED), mean (MEAN), standard deviation (SDEV) and root mean-square error (RMSE), Fig. 2b-d show a tight clustering near zero. The average temperature estimate applying the optimized model to all the considered thermal samples from Cimino-Vicano hydrothermal systems is 94 ±8.32°C.

The comparison between calculated temperatures based on cation and silica geothermometers and those calculated by GeoT for water samples from Central Italy is shown in Fig. 3. Because the geothermal reservoirs in the Central Italy are located in the Mesozoic evaporite-carbonate units, results of the multicomponent geothermometers are likely the most reliable. The reservoir temperature in Central Italy ranges from 48°C (in Rapolano) to 115°C (in F. di Tiberio). Temperatures derived from silica geothermometers display less variation compared to those calculated by the GeoT code, but in most cases the quartz and chalcedony geothermometers overestimate and underestimate reservoir temperatures, respectively. Calculated temperatures based on cation geothermometers vary greatly across the region.

Table 1. Water chemistry of vicano volcanic groundwater

Id	T(°C)	pH	EC	Ca	Mg	Na	K	HCO_3	Cl	SO_4	SiO_2	Al
			mS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
M1	62.2	6.1	3,170	496	119	38.8	34.9	946	13.9	1,300	49.4	0.029
M6	62.0	6.5	3,010	533	115	38.5	44.2	915	14.4	1,345	49.7	0.030
M18	57.9	6.2	3,190	681	149	32.5	31.1	1,086	8.6	1,826	48.3	0.023
M30	31.1	5.8	2,660	524	98.5	31.1	31.5	1,040	7.6	1,118	64.8	0.042
M5	27.3	6.0	2,460	473	120	34.2	32.9	638	9.0	1,497	55.1	0.020
M19	24.2	7.0	446	67.0	13.8	24.7	17.0	186	17.1	107	78.1	0.016
M11	20.0	7.6	603	91.0	13.4	31.8	28.6	244	33.3	75.6	75.4	0.008
M21	18.7	7.9	303	17.8	6.2	18.5	21.9	122	16.7	21.4	61.2	0.008
M31	18.1	6.8	753	107	13.8	36.0	25.6	397	27.9	0.2	63.5	0.010

6. Conclusions

The reservoir temperature of several medium-low enthalpy hydrothermal systems in Central Italy was computed using the GeoT simulator, which optimizes multicomponent geothermometers. The results indicate that reservoir temperatures ranges between 48°C and 115°C comparable to previous estimates [23. The geothermal reservoir in the Cimino-Vicano volcanic district has a temperature of 94±8.32°C. The GeoT simulation results for the Cimino-Vicano system show that all water samples are affected by degassing during their ascent to the surface and that realistic reservoir temperatures are calculated when considering the principal minerals of the reservoir (particularly gypsum, quartz, dolomite, aragonite and calcite). Compared with silica and cation geothermometers, multicomponent geothermometry coupled with optimization provides a reliable approach to estimate reservoir temperatures in medium-low enthalpy carbonate-evaporite geothermal reservoir. The statistical approach of "best clustering minerals", used in this model, solves the problems related to cation or single component geothermometers.

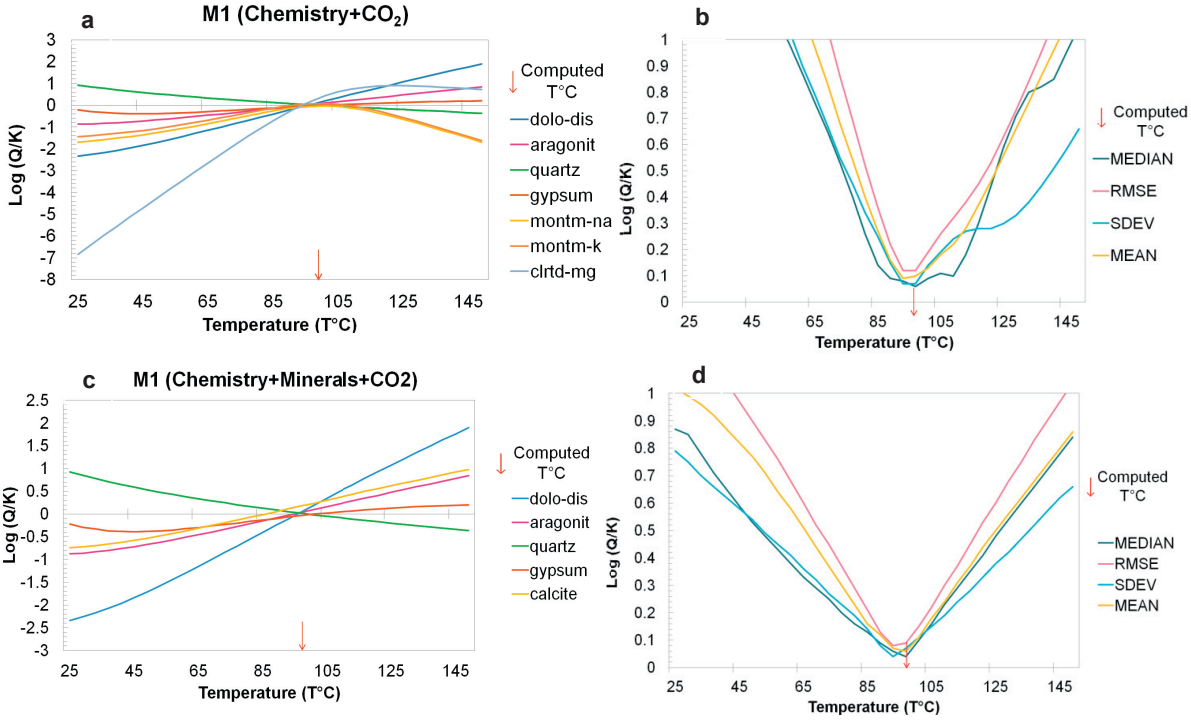

Fig. 2 (a) Computed mineral saturation indices and (b) statistical analysis for geothermal fluids from Cimino-Vicano hydrothermal system for "no minerals optimized" model. Plot (c) shows the saturation indices and (d) show the statistics for the reconstructed fluid by selecting mineral composition and CO_2 degassing.

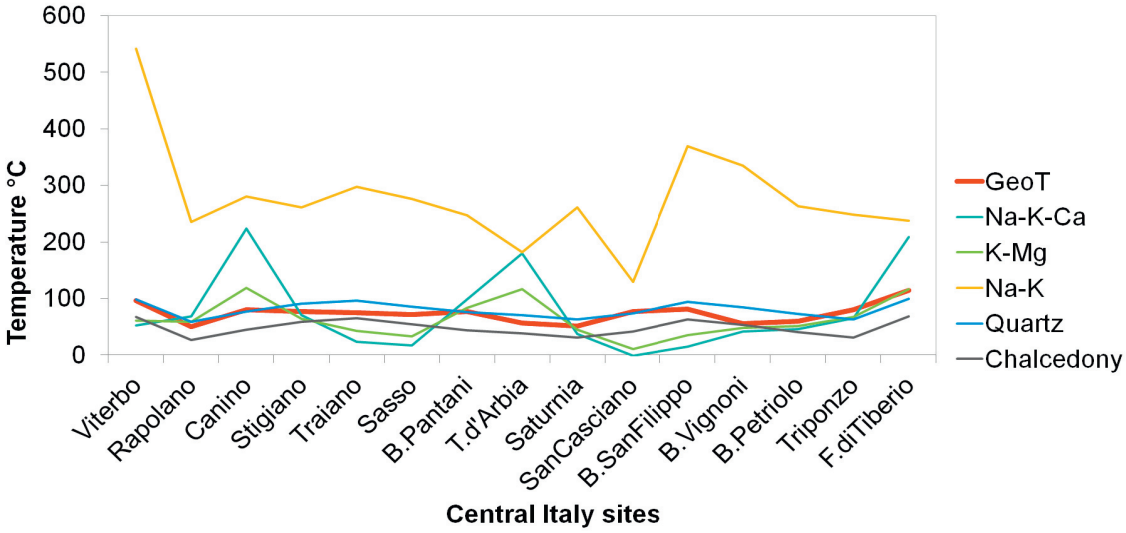

Fig. 3 Comparison between GeoT results and other ion based geothermometers in different sites in Central Italy [23].

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