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The Relationship Between Resistivity and Mineralogy at Travale, Italy

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Keywords

Larderello-Travale, geothermal field, resistivity, mineralogy, fluid inclusions

ABSTRACT

A study on cuttings and cores of geothermal wells was carried out in order to identify the types and abundance of primary and alteration minerals and to compare these data with the measured resistivity values. This study determined that lithology and heterogeneities of reservoir rocks and the alterations affecting them may only account for the small variation observed in the resistivity logs, but not for the main anomaly detected by the magnetotelluric data in the dry-steam geothermal reservoir. The occurrence of brines was suggested by the study of fluid inclusions that have shown that high-salinity fluids have circulated in the reservoir and were trapped in minerals often along healed micro-fractures. Although never highlighted by production tests, the occurrence of brine partially in a liquid phase inside the pore network or the presence of adsorbed water should be considered in further research.

Introduction

The Travale geothermal system (Tuscany, Italy) is located at the eastern margin of a wide and homogeneous geothermal area which include the Larderello field. The geological and structural setting of the Travale area involves, below a cover made of Neogenic sediments and Flysch facies formations, carbonate-anhydrite rocks of the Tuscan Nappe and the Metamorphic Basement. In the lower part of the metamorphic basement, contact metamorphic rocks (Skarn and Hornfels) are often met and represent the contact metamorphic aureole overlying granite intrusions. This aureole exhibits increased permeability due to the presence of fractures and is seismically characterised as a high amplitude seismic reflector (H Marker), that can constitute the potential target for deep wells (Bertini et al., 2006).

The main geothermal reservoir is located in metamorphic, thermo-metamorphic and magmatic rocks up to 4 km depth,

characterized by a high degree of heterogeneity and anisotropy. The exploited fluid is superheated steam with temperature above 350 °C with temperature ranging up to 350 °C and pressure values around 6-7 MPa at production depth (about 3000 m).

Aims and Analytical Techniques

A significant reduction in electrical resistivity has been observed in the dry-steam geothermal reservoir in the Travale area. This strong resistivity decrease (from 10³to 10⁰ ohm.m) has been evidenced by MT data, but not in the resistivity logs (Manzella et al., 2009). A study on cuttings on two geothermal wells for which resistivity logs are available and cores at the reservoir depths (optical petrography and EMPA) was carried out in order to identify the types and abundance of primary and alteration minerals and to compare these data with the measured resistivity values. The study of fluid inclusions has been performed to outline the type of fluid that have circulated in the field and that can be still present in the reservoir rocks.

Cutting samples were analysed on randomly oriented wholerock powder using X-ray powder diffraction (XRPD) techniques using a Philips® PW 1877 automatic diffractometer. Determination of the chlorite and illite minerals refer to the 14 Å polytype cell and 10 Å polytype cell, respectively.

Mineral microanalyses were carried out with the JEOL JXA-8600 electron microprobe. Microthermometry measurements on fluid inclusion were determined using a Linkam THMSG 600 stage on doubly polished wafer (100-200 μ m thick).

The Reservoir Rocks: Rock Types and Alterations

The main reservoir is located in the Phyllitic-Quartzitic Complex, the Micaschist Complex, thermo-metamorphic and magmatic rocks. The Phyllitic-quartzitic complex (Paleozoic) is constituted of a Phyllite Member mainly made of chloritic phyllites, graphitic phyllites and metabasites and a Carbonateanhydrite Member made of limestone with quartz, recrystallised limestones and anhydrites. The Micaschist Complex (Paleozoic) is an almandine-bearing albite micaschist with minor amphibolite. Contact-metamorphic rocks include skarn and hornfels and they represent the metamorphic aureole of underlying granitic bodies of Neogene age.

The analysed well-core samples are granite and hornfels of the deeper reservoir.

The R7BIS-3368 sample is a two-mica granite. This sample is altered with the partlial substitution of biotite in chlorite and k-feldspar in sericite. The R29-4309 sample is a granular sy-enogranite, characterised by k-feldspar, plagioclase, quartz, biotite, muscovite, cordierite, with apatite, zircon, monazite, ilmenite, tourmaline as accessories (Dini et al., 2005) of 2.25+0.04 My (Gianelli and Laurenzi, 2001). The M1-2171 sample is a hornfels crosscut by veins of quartz, adularia and chlorite. The R26B-3758 sample is a hornfels rocks made up of: quartz, plagioclase (Ab: 55-66), k-feldspar, biotite, cordierite, andalusite.

The reservoir rocks are affected by past to present-day hydrothermal alteration. Petrographic studies on well-core samples have evidenced that these alteration processes occur both as substitution of primary minerals with hydrothermal ones (e.g. chlorite instead of biotite and sericite instead of k-feldspar) and as the occurrence of hydrothermal veins filled up by quartz + chlorite \pm adularia. These alteration processes affect all the reservoir rocks as evidenced also by previous work (e.g. Pandeli et al., 1994, Carella et al., 2000 and Boyce et al., 2003).

The alteration processes of the contact-metamorphic rocks is well developed, while the alteration of studied granite is not so pervasive, producing few and scattered alteration minerals.

Resistivity-X-Ray Data

Two wells of Travale area (R7BIS and M4 wells) of which resistivity logs are present, have been selected for X-ray diffraction analyses on 103 cuttings. The samples consisted of rock cuttings belonging from the Phyllite Member, the Carbonate-anhydrite Member, the contact-metamorphic rocks, and the granitic body.

The principal mineralogical phases are quartz, alkali feldspars, carbonates, phyllosillicates and anhydrite. Carbonates consist of calcite and dolomite contents, whereas phyllosilicates include chlorite, kaolinite and a "muscovite-type" phyllosilicate characterised by an X-ray basal reflection at around 10 Å (i.e. illite and/or muscovite). The relative XRD intensity (%) of the basal reflection of chlorite and muscovite-type have been correlated with resistivity values measured by resistivity log and with the mean resistivity values extrapolated for the different drilled formation units (Figure 1).

The Phyllite Member show a relatively low-resistivity value and a relatively high-XRD intensity of the basal reflection of chlorite and in little part of muscovite, while the Carbonateanhydrite Member show higher-resistivity values and low-XRD intensity of the basal reflection of chlorite and even lower of muscovite. The Phyllite and the Carbonate-anhydrite Members samples show a mineralogical composition related to their primary metamorphic mineralogy. These Member have a variability in the mineral amounts that indicates that these lithologies are not homogeneous.

In M4 well, the contact-metamorphic rocks have low-resistiv-

R7BIS M4 (Im bgl) (m bgl) Resistivity (ohm*m) Relative XRD intensity (% Resistivity (ohm*m) Relative XRD intensity (%) Depth (DOOD Depth 0000 0000 100 1000 0 10 60 80 100 60 40 80 and could could could could could accel 0 nean resistivity of the ean intensity of the ns of resistivity log 1000 1000 mean intensity of the basal reflect of chlorite 2000 2000 mean intensity of the basa 3000 3000 esistivity of the for mean intensity of the basa reflection of "muscovite" mations drilled in the Travale 1 2 /3// 4**6**..... 5 4000 area



ity value and a high-XRD intensity of the basal reflection of chlorite and muscovite. These rocks show variable but in general abundant amount of phyllosilicates. The significant quantity of phyllosilicates of the contact-metamorphic rocks is probably related to the high degree of hydrothermal alteration that affect these rocks.

The granite rocks show a relatively high-resistivity value and a low-XRD intensity of the basal reflection of chlorite and muscovite. In these samples phyllosilicates are scarce and sparse.

Fluid Inclusions

Fluid inclusions were studied in selected quartz crystals of the M1-2171 hornfel and R29-4309 granite samples. The size of the analysed fluid inclusions are in the range 5-60 μ m. On the basis of optical observations and microthermometric data four types of fluid inclusions have been recognised (Table 1):

Type LVS: multiphase liquid-rich fluid inclusions (liquid + vapour + halite + unidentified solids in a varying number from 1 to 3). This type of inclusions was found in M1-2171 sample. They always contain a cubic transparent crystal (halite) and one or

Table 1. Summarised microthermometric data performed on the M1-2171 and R29-4309 samples. TmCO₂: melting temperature of solid CO₂. Tmlce: final ice melting temperature. TmClath: melting temperature of clathrate. ThCO₂: homogenisation temperature of CO₂. Th: total homogenisation temperature. L: liquid and V: vapour, homogenisation phase of ThCO₂ and Th. TmH: halite melting temperature. TmS: melting temperature of others solids. In brackets are reported the number of performed measurements. All values are in degree Celsius (°C). *: Some inclusions are still not homogenized at 500 °C.

Well-Depth	Туре		TmCO ₂	TmIce	TmClath	ThCO ₂		Th		TmH	TmS
			(°C)	(°C)	(°C)	(°C)		(°C)		(°C)	(°C)
R29-4309	V	range	-57.9/-57.0		10.0/11.2	15.0/25.0	V	202-246	V		
		mean	-57.5 (69)		10.8 (28)	22.5 (22)		226 (10)			
M1-2171	V	range	-57.2/-57.1	-2(1)	5.6/6.0			345/370	V		
		mean	-57.2 (2)		5.8 (2)			360 (3)			
	$L_1L_2V_2$	range	-58.5/-58.1		0.1/9.0	23.5/24.0	V	366/500*	V		
		mean	-58.2 (8)		6.0 (5)	23.8 (3)		(5)			
	LV	range		-5.7/-3.5				312/427	L		
		mean		-4.7 (10)				387 (11)			
	LVS	range								402/436	500**
		mean								414 (9)	(15)

more smaller cubic salt with rounded edges, both can be considered as daughter minerals. This fluid inclusion type does not show any change during freezing and heating between -190 °C and 248 °C. The total homogenisation occurs only in one fluid inclusion analysed by salt disappearance at 443 °C. The bubble is the first phase to disappear, halite follows, while the other solids do not melt either above 500 °C. At these temperature, these inclusion types were apparently still far from homogenisation. According to the solubility curve for NaCl in aqueous solution (Sheperd et al., 1985) and imposing the lowest homogenisation temperature of about 450 °C by halite disappearance a minimum salinity of 50 wt% can be hypothesised.

Type $L_1L_2V_2$: three-phase inclusions (aqueous liquid + carbonic liquid + carbonic vapour). This type of inclusions was found in M1-2171 sample and they are often associated with LVS fluid inclusions. These fluid inclusions generally occur along trails and can be considered secondary according to Roedder's (1984) criteria. The presence of CO₂ is testified by the appearance of a double meniscus at room temperature. The melting temperature of CO₂ well below the triple point for pure CO₂ (-56.6 °C) and the extending of the temperature interval in which the melting occurs suggest the presence of an additional gas compound, beside CO₂, in the volatile phase (Sheperd et al., 1985), probably CH₄. The CH₄ amount was roughly estimated around 10 mole % by graphical method (Sheperd et al., 1985) taking into account the final melting temperature of solid CO₂, and the temperature and mode of homogenisation of CO₂.

Type LV: bi-phase inclusions (liquid + vapour). This type of inclusions was found in M1-2171 sample and they occur along trails and can be considered secondary according to Roedder's (1984) criteria. The temperature of first ice melting between -60 and -51 °C, suggests the presence in solution of bivalent cations such as Mg^{2+} and Ca^{2+} (Crawford, 1981) in addition to Na⁺. Further temperature increase results in the melting of a salt hydrate, probably hydrohalite. Identification of hydrohalite was based on its highly birefrangent nature and higher refraction index than the solution (Roedder, 1984). Moreover, Shepherd et al. (1985) state that 'unless one has reason to believe the fluid contains more than 30 wt% CaCl₂ and has a Ca/Na weight ratio greater than 15, the hydrate formed after first melting is assumed to be hydrohalite'.

Salinity was determined using eutectic, ice and hydrate melting temperatures using the NaCl–CaCl₂–H₂O ternary plot after Oakes et al., (1990). The total salinity of the fluids is calculated by this graphic method is about 7-8 wt% NaCl eq. and in the range 6-9 wt% NaCl eq. using the equation proposed by Bodnar (1993).

Type V: mono-phase inclusions (vapour) with sometimes little amount of liquid. This type of inclusions was found in M1-2171 and R29-4309 samples. In M1-2171

sample, these inclusions are quite rare, they occur along trails and can be considered secondary according to Roedder's (1984) criteria. Some of these inclusions have an hexagonal opaque solid (probably phyrrhotite) due to accidental trapping as evidenced by the presence of this mineral both inside and outside the fluid inclusions. The presence of CO_2 is demonstrated by the appearance of a double meniscus (nucleation of liquid CO_2) during freezing runs. Because of poor optical quality of these fluid inclusions and of the small amount of liquid phase, the homogenisation temperatures of CO_2 were not observable and the temperature at which ice melts was measured only in one inclusion. The presence of an other gas compound (probably CH_4) is suggested by the low $TmCO_2$ and the extending of the temperature interval (Sheperd et al., 1985).

In R29-4309 sample, these inclusion are the only type present occurring along criss-cross cutting trails and can be considered secondary according to Roedder's (1984) criteria. The presence of CO_2 is demonstrated by the appearance of a double meniscus just below room temperature. The presence of other gas compound (probably CH_4) is suggested by the low temperature of melting of CO_2 and the extending of the temperature interval (Sheperd et al., 1985) coupled with temperature of melting of clathrate above 10 °C. The CH_4 amount was estimated by graphical method (Sheperd et al., 1985) in the 7-16 mole % range.

The fluid inclusions study have shown a multistage circulation of the fluid. The first stage is characterised by high-salinity fluids (around 50 wt. % eq. NaCl) of magmatic origin, and vapours and liquids resulting from heating of the Paleozoic rocks during contact metamorphism. The hydrothermal stage that follows is characterised by low- to high-salinity aqueous fluids with vapours produced by boiling processes. The occurrence of boiling processes is also suggested by mineralogical evidences, such as the adularia precipitation in veins. The high salinities can be explained by local boiling, or by the interaction of the reservoir fluids with evaporites and/or the remobilization of connate waters.

This multistage circulation is similar to that observed at Larderello by Valori et al. (1992) and Cathelineau et al. (1994). Previous studies on fluid inclusions of the Travale area have shown the second hydrothermal stage characterised by boiling and mixing processes (Ruggieri et al., 1999) and two phases of alteration of the granitic body, with a first phase characterised by fluids with temperatures around 340-350 °C trapped during boiling and a second phase characterised by fluids with lower temperatures (250-315 °C) showing a cooling of the system and representative of fluids circulating in the granite at present (Boyce et al., 2003).

Discussion

Comparing stratigraphy, mineral content and resistivity, the resistivity reductions observed on the resistivity logs can easily be explained as being due to the abundance of phyllosilicates (chlorite, kaolinite, muscovite and/or illite) and their distribution.

Phyllosilicate amounts are related either to primary mineralogical compositions or to secondary alteration processes. The resistivity response of the reservoir rocks is probably related also to the distribution of these minerals, where phyllosilicates are more continuous, either due to geological conditions during primary formation or to alterations, the resistivity is particularly low. Primary and secondary phyllosilicates are particularly abundant and most probably interconnected in the Phyllite Member of the Phyllitic-quartzitic Complex and in contact-metamorphic rocks of M4 well. Hydrothermal alteration played an important role in the contact-metamorphic rocks, where fracturation processes allowed the development of the intense hydrothermal flow responsible for the formation of interconnected phyllosilicates. The hydrothermal fluid did not seem to affect the granite much, suggesting that the alteration process was limited in this rock, or at least remained localized in some sparse fractures, in accordance with the resistivity log data.

Although, this study evidenced that lithology and heterogeneities of reservoir rocks and the alterations affecting them may only account for the small variation observed in the resistivity logs, but not for the main anomaly detected by the MT data. The only other possible explanation is the presence of interconnected fluid in the geothermal reservoir.

In vapor-dominated systems both interstitial and adsorbed water can be contained in geothermal reservoirs, where local conditions in microfractures and small pores might be very different from the average conditions observed on a large scale. These geothermal waters can be characterised even by high concentration of dissolved salts and ions enhancing current passage in the reservoir rocks and causing a sharp decrease in resistivity.

The occurrence of saline fluids was clearly evidenced by fluid inclusion data. The hydrothermal stage is characterised by low- to high-salinity aqueous fluids with vapours produced by local boiling processes. These fluids have circulated in the reservoir and were trapped in minerals often along healed micro-fractures. The presence of hydrothermal alteration minerals, as well as fluid inclusion study, have shown that the geothermal fluid was composed also by a liquid phase during a previous stage. Moreover, these fluids may still be present within open micro-fractures in some areas of the geothermal system.

The occurrence of brines with a salinity between 5.000 to 50.000 ppm Cl- was also suggested by Truesdell et al. (1989) who took into account the chemical characteristics and temperature of the exploited fluid. Moreover, experimental data on Monteverdi samples evidenced the presence of 2 mg/g of adsorbed liquid water inside the pore network of the rocks (Bertani et al., 1999).

Adsorption may be responsible for the existence of a liquid phase inside the pore network of the rocks and could explain the long exploitation life of the Larderello reservoirs (Bertani et al., 1996).

Conclusions

Travale field represents a particularly interesting area to assess how the electrical resistivity is affected by the circulation of geothermal fluids in a steam dominated system hosted in crystalline rocks. The results of such research may have a wide application, since crystalline rocks represent the most common scenario for EGS. Moreover, some of the results could also be extended to the exploration of sedimentary rocks.

Since the geothermal system did not show any evidence of a strong lithological change and of a pervasive alteration whose mineralogy could explain the strong resistivity decrease, the most probable explanation for the observed resistivity anomaly is the occurrence of a brine as a liquid fluid inside the pore network of the rocks or adsorbed water, even if not highlighted by production tests. Although the exploited fluid has the character of dry steam, perhaps fluid circulation might behave differently on a small and a large scale.

The knowledge of fluid circulation in the geothermal reservoir is still very limited. A multidisciplinary data integration and rock physics simulation are needed to build a complete picture of this complex geothermal fluid circulation, which in turn could provide important information regarding the origin of the field, its evolution and the duration of the geothermal resource.

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References

- Barelli A., G. Cappetti, and G. Stefani, 1995. "Results of deep drilling in the Larderello-Travale/Radicondoli geothermal area." In: Proceedings of the World Geothermal Congress, Florence, Italy, v. 3, p. 1275-1278.
- Bertani R., L. Parisi, R. Perini, and B. Tarquini, 1996. "High temperature adsorption measurements." In: Proceedings of the 21st Workshop on Geothermal Reservoir Engineering. Stanford University, Stanford, California, USA. Report number: SGP-TR-151-71.
- Bertani R., L. Parisi, R. Perini, and B. Tarquini, 1999. "High temperature measurements of water adsorption in geothermal rocks." Geothermics, v. 17, p. 166-183.
- Bertini G., M. Casini, G. Gianelli, and E. Pandeli, 2006. "Geological structure of a long living geothermal system, Larderello, Italy." Terra Nova, v. 18, p. 163-169.
- Bodnar R.J., 1993. "Revised equationand table for determining the freezing point depression of H₂O-NaCl solutions." Geochim. Cosmochim. Acta v. 57, p. 683-684.
- Boiron M.C., M. Cathelineau, G. Ruggieri, A. Jeanningros, G. Gianelli, and D.A. Banks, 2007. "Active contact metamorphism and CO₂–CH₄ fluid production in the Larderello geothermal field (Italy) at depths between 2.3 and 4 km." Chemical Geology, v. 237, p. 303–328.

- Boyce A.J., P. Fulignati, and A. Sbrana, 2003. "Deep hydrothermal circulation in a granite intrusion beneath Larderello geothermal area (Italy): constraints from mineralogy, fluid inclusions and stable isotopes." Journal of Volcanology and Geothermal Research, v. 126 (3-4), p. 243-262.
- Carella M., P. Fulignati, G. Musumeci, and A. Sbrana, 2000. "Metamorphic consequences of Neogene thermal anomaly in the northern Apennines (Radicondoli-Travale area, Larderello geothermal field – Italy)." Geodinamica Acta, v. 13, p. 345-366.
- Cathelineau M., C. Marignac, M.C. Boiron, G. Gianellli, and M. Puxeddu, 1994. "Evidence for Li-rich brines and early magmatic fluid-rock interaction in the Larderello geothermal system." Geochimica et. Cosmochimica. Acta, v. 58 (3), p. 1083-1099.
- Dini A., G. Gianelli, M. Puxeddu, and G. Ruggieri, 2005. "Origin and evolution of Pliocene–Pleistocene granites from the Larderello geothermal field (Tuscan Magmatic Province, Italy)." Lithos, v. 81, p. 1–31.
- Fiordelisi A., I. Perticone, and E. Spinelli, 2009. "Geophysical Logs and petrophysical characterization in the Travale test site (Italy)." Geothermics special issue, I-GET project, (submitted).
- Gianelli G., and G. Ruggieri, 2002. "Evidence of a contact metamorphic aureole with high-temperature metasomatism in the deepest part of the active geothermal field of Larderello, Italy." Geothermics, v. 31, p. 443-474.
- Gianelli G., and M.A. Laurenzi, 2001. Age and cooling rate of the geothermal system of Larderello. -Geothermal Resource Council *Transactions*, v. 25, p. 731–735.

- Manzella A., C. Giolito, G. Ruggieri, and C. Ungarelli, 2009. "Electrical resistivity data and their relation to geological features at the Travale geothermal field (Italy)." Geothermics special issue, I-GET project, (submitted).
- Oakes C.S., R.J. Bodnar, and J.M. Simonson, 1990. "The system NaCl–CaCl₂– H₂O: I. The ice liquidus at 1 atm. Pressure." Geochimica et Cosmochimica Acta, v. 54(3), p. 603–10.
- Pandeli E., G. Gianelli, M. Puxeddu, and F.M. Elter, 1994. "The Paleozoic Basement of the Northern Apenines: startigraphy, tectono-metamorphic evolution and alpine hydrothermal processes." Memorie Società Geologica Italiana, v. 48, p. 627-654.
- Roedder E., 1984. "Fluid inclusions." Mineralogical Society of America, Reviews in Mineralogy, v. 12, 644 pp.
- Ruggieri G., M. Cathelineau, M.C. Boiron, and C. Marignac, 1999. "Boiling and fluid mixing in the chlorite zone of the Larderello geothermal system." Chemical Geology, v. 154, p. 157-256.
- Shepherd T.J., A.H. Ranbin, and D.H.M. Alderton, 1985. "A practical guide to fluid inclusion studies." Blackic, Glasgow, 239 pp.
- Truesdell A.H., J.R. Haizlip, H. Armannsson, and F. D'Amore, 1989. "Origin and transport of chloride in superheated geothermal steam." Geothermics, v. 18, p. 295-304.
- Valori A., M. Cathelineau, and C. Marignac, 1992. "Early fluid migration in a deep part of the Larderello geothermal field: a fluid inclusion study of the granite sill from well Monteverdi." Journal of Volcanology and Geothermal Research, v. 51, p. 115–131.