Hydrothermal alteration in the Berlin geothermal field (El Salvador): new data and discussion on the natural state of the system

Giovanni Ruggieri[1*], Chiara M. Petrone[1], Giovanni Gianelli[2],
Alessia Arias[3], Elizabeth Torio Henriquez[4]

[1] CNR - Istituto di Geoscienze e Georisorse, Via La Pira 4, 50121 Firenze, Italy
[2] CNR - Istituto di Geoscienze e Georisorse, Via Moruzzi 1, 56124 Pisa, Italy
[3] ENEL GEM, Produzione Geotermica, Via A. Pisano, 120, 56122 Pisa, Italy
[4] LaGeo S.A. de C.V., 15 Av. Sur, Col. Utila, Santa Tecla, El Salvador

Abstract. — The Berlin geothermal field (Republic of El Salvador), located about 110 km ESE of the city of San Salvador, is a water-dominated system with temperature close to 300°C in the production zone. The geothermal wells at Berlin intercepted calc-alkaline more or less hydrothermally altered lava flows and pyroclastic rocks. This study presents data on hydrothermal alterations, together with their distribution with depth, microprobe analyses of hydrothermal minerals and geochemistry of altered rocks. The stability of some minerals under natural state (i.e. before exploitation and reinjection) and present state reservoir conditions have been evaluated both using mineral saturation indices and activity vs. temperature diagrams. This information contributes to the reconstruction of the thermal and chemical characteristics of the field and their temporal evolution and they, therefore, play an important role for the correct evaluation of the geothermal resource and for the future exploration strategies. Four mineral alteration zones, occurring at increasing depths, have been distinguished on the basis of the abundance and appearance of characteristic hydrothermal minerals. The hydrothermal phases may either replace the igneous minerals, or fill cavities or fractures crosscutting the rock. The shallowest alteration zone is characterized by the presence of relatively low-temperature minerals, such as saponite, montmorillonite, heulandite etc. At greater depth, hydrothermal phases, such as epidote, wairakite, prehnite, hydro-garnets typical of higher temperature conditions, occur. Quartz, calcite and chlorite are widespread in most of these zones. Geochemical analyses show that fluid-rock interaction caused an increase of Ca and LOI, no variation of Mg and Fe and a decrease of Na and Si in an altered core sample with respect to unaltered rock. Whereas, K was totally leached out from the altered rock. The shape of the deepest alteration zones gives a record of a past natural state condition (not the most recent) and contrast with present-day thermal feature, suggesting that significant thermal variations occurred from the time of alteration formation to present-day. Recent natural state and present state conditions of the reservoir fluid were computed by using geochemical data of the present-day discharged fluids. Temperature and the CO_2 content decreased, in most of the wells, evolving from the natural state of the system to the present state conditions. These variations can be explained with variable degrees of degassing due to isoenthalpic or sub-isoenthalpic boiling. Mineral saturation indices indicate that wairakite is unstable under both present and natural state conditions. $Log[Ca^{2+}]/[H^+]^2$ vs. temperature diagram indicates that epidote is generally not stable under both present and natural state conditions, its stability depends mostly on the CO_2 partial pressure. This explains why epidote

* Corresponding author, E-mail: ruggieri@igg.cnr.it

compositions are not correlated to the temperature. Chlorite appears to be stable under both present and natural state conditions and its composition varies with temperature. The Al^{IV} content in this mineral from different wells shows, in fact, a fairly good correlation with temperature following the equation: $T(°C) = 47.238 \times Al^{IV} + 175.77$. This equation, therefore may be used for temperature estimates for the Berlin geothermal field.

Riassunto. — Il campo geotermico di Berlin (Repubblica di El Salvador), posto a circa 110 km ESE dalla capitale San Salvador, è un campo ad acqua dominante e temperature vicino a 300°C nella zona di produzione. I pozzi geotermici di Berlin hanno incontrato nel sottosuolo lave e piroclastiti calcalcaline più o meno intensamente alterate. In questo studio vengono presentati dati sulle alterazioni idrotermali, sulla loro distribuzione rispetto alla profondità, insieme ad analisi alla microsonda elettronica di minerali idrotermali e dati geochimici sulle rocce. Inoltre, viene discussa la stabilità di alcuni minerali, sia nello stato naturale del serbatoio (cioè precedente allo sfruttamento e alla re-iniezione) sia in quello attuale, utilizzando gli indici di saturazione dei minerali e diagrammi di attività vs. temperatura. Queste informazioni contribuiscono alla ricostruzione delle caratteristiche termiche e chimiche del campo e della loro evoluzione temporale, giocando, pertanto, un ruolo importante per una corretta valutazione della risorsa geotermica e per una futura strategia di esplorazione. Quattro zone di alterazione, presenti a profondità crescenti, sono state riconosciute sulla base dell'abbondanza e della presenza di minerali idrotermali caratteristici. Le fasi idrotermali possono sia sostituire i minerali magmatici, sia riempire cavità o fratture che interessano la rocce. La zona più superficiale di alterazione è caratterizzata dalla presenza di minerali di temperatura relativamente bassa, quali saponite, montmorillonite, heulandite ecc.. A profondità crescenti si trovano minerali idrotermali tipici di temperature più elevate, quali epidoto, wairakite, prehnite, idro-granato. Il quarzo, la calcite e la clorite sono diffusi in gran parte delle zone di alterazione. I dati geochimici hanno messo in evidenza che l'interazione fluido-roccia ha provocato in una roccia alterata rispetto ad una non alterata, un aumento del Ca e della LOI, nessuna variazione di rilievo di Mg e Fe, un impoverimento di Na e Si e la totale rimozione del K. Le forme delle zone di alterazione più profonde rispecchiano una condizione naturale antica (non quella più recente) e contrastano con la struttura termica attuale, ciò indica che importanti variazioni termiche sono avvenute dal tempo della formazione delle alterazioni ad oggi. Lo stato naturale più recente e quello odierno dei fluidi di serbatoio sono stati ricostruiti utilizzando dati geochimici dei fluidi attuali. Nella maggior parte dei pozzi, la temperatura e il contenuto di CO_2 sono diminuiti dallo stato naturale alle condizioni odierne del campo. Queste variazioni possono essere legate al degassamento del fluido in seguito a processi di ebollizione isoentalpico o sub-isoentalpico. L'indice di saturazione della wairakite indica che questo minerale non è stabile sia in condizioni naturali che in quelle odierne. Il diagramma $\log[Ca^{2+}]/[H^+]^2$ vs. temperatura, ha messo in evidenza che l'epidoto non è in generale stabile né in condizioni naturali né in quelle attuali. La stabilità dell'epidoto, nel campo geotermico di Berlin, dipende perlopiù dalla pressione parziale della CO_2. Ciò può spiegare l'assenza di una correlazione tra la composizione di questo minerale e la temperatura. La clorite appare stabile sia in condizioni naturali che in quelle odierne e la sua composizione varia con la temperatura. Il contenuto di Al^{IV} della clorite di vari pozzi, infatti, è ben correlato con la temperatura secondo la seguente relazione: $T(°C) = 47,238 \times Al^{IV} + 175,77$. Questa equazione, quindi, può essere utilizzata per stime della temperatura nel campo geotermico di Berlin.

Introduction

The Republic of El Salvador is the smallest Central American country, but is one of the largest producers of geothermal power. The Berlin geothermal field (in the order of 10 km^2 at a mean elevation of 800 m above the sea level (a.s.l.)) is one of the main geothermal fields of El Salvador and it is located in the central-eastern part of the country (fig. 1). The first exploratory well (TR-1) was drilled in 1968, the exploitation of the system started in 1992 with a 2.5 MW back-pressure unit. In 1999, two 27.5 MW condensing units went on-line (Arias *et al.*, 2003 and reference therein). Two wells (TR-17 and TR-18 in fig. 1) have been recently drilled by the Share Holder Agreement Enel – GESAL (now LaGeo) in the frame of a new exploration project, which has the aim to investigate the field boundaries.
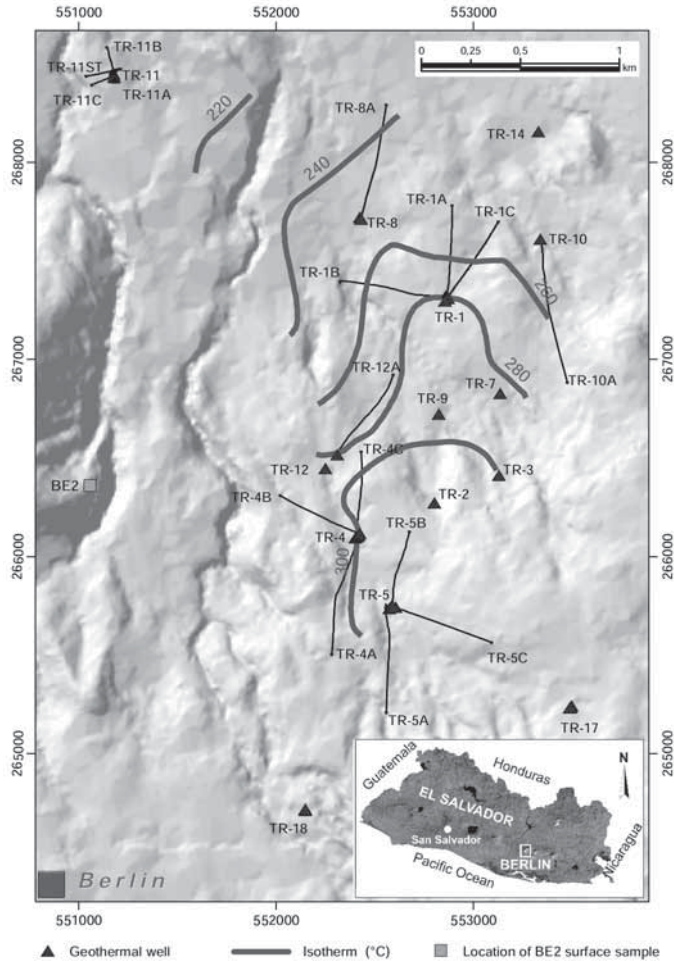
Fig. 1 – Location of the geothermal wells and temperature distribution at 1100 m below sea level of the Berlin geothermal field. Isotherm contour lines from Arias *et al.* (2003).

A recently revised model of the geothermal system has been proposed by Arias *et al.* (2003). The components of the system are: a) an impervious cover made up of altered volcanics, with clay minerals replacing most of the igneous assemblage through a thickness of approximately 1500 m; b) a reservoir consisting of altered lava flows and pyroclastics, with epidote, albite and chlorite as typical hydrothermal minerals. Calcite is common in both caprock and reservoir. The known thickness of the reservoir is at least 1000 m.

The Berlin geothermal field is a liquid dominated system showing an average temperature close to 300°C in the southern production zone, and lower temperature in the northern domain (fig. 1).

The definition of the "natural state" of the geothermal systems is a fundamental input data for any type of reservoir modelling (hydrological, geochemical, reactive transport, etc). In this paper the natural state of the system means the thermal and chemical characteristics before the exploitation and the re-injection operation, which influence

the conditions of the reservoir and produce the "present state" of the system. Mineral alteration studies integrated with geochemical data are of peculiar interest in geothermal systems as they can provide information on the water-rock interaction processes and on the related physical-chemical changes. These studies, therefore, can be used in defining the natural state of the system and in evaluating its temporal evolution.

In this paper, we present data on hydrothermal alteration of Berlin geothermal field by integrating the published and unpublished information from some existing wells and the new drilled ones.

The distribution of the hydrothermal minerals with depth and the relationships between the different hydrothermal mineral assemblages have been studied through optical microscope observations of thin sections of both core samples and cuttings. The mineral chemistry of several hydrothermal phases have been determined by microprobe analyses. In addition, whole rock analyses have also been performed and mineral stability/instability with respect to the reservoir fluid composition have been reviewed using temperature vs. log activity diagrams.

The new data will be discussed in order to: (i) reconstruct the natural state and the eventual physical-chemical evolution of the geothermal fluids; (ii) find a correlation between mineral distribution and/or the mineral compositions with temperature; (iii) characterize the mass transfer between fluid and rock by means of the analyses of the hydrothermal alteration and the chemical changes in bulk rock composition. All this information are of great importance as they can contribute to the development of the conceptual model of the system, which in turn can help the future exploration and exploitation strategies.

Geological framework

The Berlin area is located south of the so-called *Central American graben*, which was a result of the Cocos plate subduction under the Caribbean one. The subduction causes the volcanism, the geothermal anomalies and the main structural features affecting this area. A recent regional study (Corti *et al.*, 2005) points out that the tectonic setting in the Berlin area is interested by one of the

two main active fault segments recognized in the eastern part of El Salvador. This strike-slip system consists of main E-W faults, synthetic (WNW-ESE) and antithetic (NNW-SSE) Riedel shears, and NW-SE tensional structures. This last fault system, running NW-SE, is the most representative at the local scale of Berlin geothermal field.

The field is placed on the northern flank of a Quaternary volcanic complex where the maximum elevation of the peaks is around 1500 m a.s.l., then sloping down northwards to about 300 m a.s.l..

This calcalkaline volcanic complex alternates basaltic to andesitic lava flows and scoria, and andesitic to dacitic ignimbrites, which were produced during major eruptions (Raymond *et al.*, 2005). The presence of a minor amount of relict volcanic porphyritic quartz, in some core-samples and cuttings from deep drilling, suggests the occurrence at depth of more acid compositions (dacite to rhyolite?). The basaltic rocks date 1.4 Ma, whereas the andesitic-dacitic ignimbrites date from 0.1 to 0.075 Ma (Raymond *et al.*, 2005).

The hydrothermal circulation of the geothermal system is responsible of a band zonation shown by the altered volcanic rocks.

Methods

Samples have been studied by microscopic observations of thin sections. X-ray diffraction (XRD) analysis was carried out on selected samples in order to identify the types of clay minerals present (on a < 2µm fraction treated with Mg and K, glycolated and heated according to standard procedures). XRD analysis was also useful to identify microcrystalline minerals, in particular zeolites.

Microprobe analyses were performed with an automated wave-dispersive (WDS) electron microprobe (JEOL-JXA-8600) under the following operating conditions: acceleration voltage 15 kV, counting time 15 s, beam current 10 nÅ. The Bence and Albee (1968) matrix correction routine was applied. Accuracy and precision estimates are given in Vaggelli *et al.* (1999). Representative microprobe analyses of the hydrothermal minerals are reported in Table 1.

Rock chemical analysis was performed by X-ray fluorescence. Loss on ignition (LOI) was

measured by sample weight difference before and after heating at approximately 900°C.

The composition of the reservoir fluid has been reconstructed based on the water and gas compositions, sampling temperature and pressure, steam/gas ratio at the well-head sampling as reported in D'Amore and Mejia (1999) by using an updated version of the WATCH software (Arnorsson *et al.*, 1982; Stefansson, 2001).

The saturation indices of the hydrothermal minerals were then computed both with the WATCH code and the REACT code of Bethke (1996) containing a more complete mineral and chemical thermodynamic data bank as compared to the WATCH code. The calculations have been performed using quartz geothermometer (Fournier and Potter, 1982) for the well TR-1 and the Na-K geothermometer (Fournier and Truesdell, 1973) for the other wells. This method is more accurate than those of D'Amore and Mejia (1999), who used the approach of mineral saturation indices (Michard and Roekens, 1987). This approach, in fact, requires precise Al and Fe water concentrations when calculating the saturation indices, but in the case of the Berlin geothermal fluid these concentrations are largely uncertain.

Hydrothermal alteration

The rocks intersected by geothermal wells in the Berlin geothermal field mainly consist of volcanic rocks and volcanic breccias. In the breccias the clast size varies from few cm to sub-millimetric dimensions, and almost all the clasts derive from effusive rocks with minor amounts of sub-volcanic rocks; some breccias are also characterized by the occurrence of vesicles. More rarely the clasts show a granoblastic texture, consisting of hydrothermal minerals, indicating that brecciation processes involved early hydrothermal phases.

The volcanic products are affected by variable degrees of hydrothermal alteration, from slightly altered volcanic matrix and fresh phenocrysts, to totally replaced volcanic rocks. Hydrothermal minerals not only replace the original igneous minerals, the volcanic groundmass and the breccia matrix, but also fill small voids and microfractures crosscutting the volcanic rocks (fig. 2).

The volcanic rocks usually have intergranular porphyritic to trachytic or seriate textures. Phenocrysts are usually composed of plagioclase and more rarely by pyroxenes. Relict of volcanic porphyritic quartz was also sporadically observed, pointing to an intermediate to acid composition of some volcanic rocks.

Unaltered phenocrysts of plagioclase have labradorite to bytownite composition (An_{43-93}) (Table 1A), while primary plagioclases are often altered and replaced by epidote and albite (Ab_{90-98}) (Table 1A) and minor adularia, or by calcite and albite or by clay minerals (fig. 2C, 2D, 2F). The latter minerals are abundant at relatively shallow depths (<700 m b.g.l.) where nontronite, montmorillonite, saponite and corrensite have been identified by X-ray analyses. With increasing depth illite-montmorillonite mixed layers, illite and chlorite are the main phyllosilicates.

Epidote replaces both the breccia matrix and the volcanic groundmass of the clasts and, in this case, is usually associated with albite ± quartz ± chlorite ± calcite and, more rarely, adularia, pyrite and titanite. Epidote is also found in veins and filling vugs and vesicles (fig. 2A, 2B). In such occurrences epidote is usually accompanied by quartz ± calcite ± titanite ± pyrite ± anhydrite ± prehnite. Prehnite (Table 1B) is also observed as monomineralic fillings in veins (fig. 2E). In some samples, the veins consist of early euhedral epidote and of later anhydrite, filling spaces between the epidote crystals. Epidote is characterized by high variability in Fe^{3+} content (Table 1A), from relatively iron-poor (X_{Fe3+} down to 0.13) to iron-rich (X_{Fe3+} up to 0.34). Adularia shows a BaO content up to 8 wt% in the TR-2 well at about 1500 m depth (Table 1A), and relatively high F concentrations characterize apatite (up to 2.95 wt%, TR-8 at about 1800 m depth) and titanite (up to 1.3 wt%).

In addition to epidote and albite, calcite, quartz and chlorite are the most abundant hydrothermal phases. Calcite replaces plagioclase (fig. 2F), and forms veins or fills cavities. It occurs as individual crystals or associated with quartz, epidote, chlorite, anhydrite, wairakite (X_{Na} of 0.02-0.06, Table 1B). Mn-rich carbonate (possibly rodocrosite) is present, in addition to calcite. Textural relationships suggest that calcite can be either in equilibrium with epidote and quartz, but it can also

Table 1A – *Selected microprobe analysis and structural formulae of epidote and feldspar from well core samples of the Berlin geothermal field.*

		epidote					hydrothermal feldspar			magmatic feldspar		
							Ad	K-felds	Plag	Plag	Plag	Plag
Well	TR-2	TR-5B	TR-8A	TR 17A	TR-18	Well	TR-2	TR-2	TR-5c	TR-2	TR-18	TR-18
Depth m.	1650	1765	1779	2628	2600	Depth m.	1502	1502	1628	1502	1553	1553
SiO_2	38.52	38.57	38.04	38.67	37.89	SiO_2	50.1	63.9	64.8	52.5	44.58	47.8
TiO_2	0.14	0.1	0.02	0.14	0.16	TiO_2	nd	nd	bdl	0.09	0.03	0.04
Al_2O_3	28.4	26.1	22.0	26.58	22.5	Al_2O_3	30.8	19.1	21.6	29.1	35.57	33.1
FeO	6.73	9.68	15.03	10.48	16.19	Fe_2O_3	0.60	0.31	1.39	1.26	0.57	0.70
MnO	0.13	0.32	0.17	0.41	0.40	MgO	0.17	0.00	0.25	0.12	0.05	0.04
MgO	0.07	0.08	0.07	0.16	0.10	CaO	0.40	0.00	1.28	12.52	18.58	16.37
CaO	23.96	23.66	23.38	23.40	22.61	Na_2O	0.30	0.31	10.23	3.94	0.80	1.99
Na_2O	0.04	bdl	0.02	0.08	bdl	K_2O	9.55	15.94	0.03	0.36	0.05	0.10
K_2O	bdl	bdl	bdl	bdl	bdl	SrO	0.00	0.00	nd	nd	0.06	0.03
Cr_2O_3	bdl	0.03	bdl	0.09	bdl	BaO	7.93	1.35	nd	nd	0.00	0.04
Sum	98.02	98.48	98.69	99.92	99.87	Sum	99.81	100.97	99.60	99.90	100.29	100.24

Structural formulae based on 12.5 oxygens   *Structural formulae based on 8 oxygens*

Si	2.97	2.99	2.99	2.95	2.94	Si	2.42	2.96	2.86	2.39	2.05	2.19
						Al	1.75	1.04	1.13	1.56	1.93	1.79
Ti	0.01	0.01	0.00	0.01	0.01	Ti	0.00	0.00	0.00	0.00	0.00	0.00
Al	2.59	2.38	2.03	2.40	2.06	Fe^{3+}	0.02	0.01	0.05	0.04	0.02	0.02
Fe^{3+}	0.44	0.63	0.99	0.67	1.05	Sum Z site	4.20	4.01	4.04	4.00	4.01	4.00
Sum M site	3.03	3.02	3.02	3.08	3.13							
						Mg	0.01	0.00	0.02	0.01	0.00	0.00
Mn	0.01	0.02	0.01	0.03	0.03	Ca	0.02	0.00	0.06	0.61	0.92	0.80
Mg	0.01	0.01	0.01	0.02	0.01	Na	0.03	0.03	0.88	0.35	0.07	0.18
Ca	1.98	1.96	1.97	1.91	1.88	K	0.59	0.94	0.00	0.02	0.00	0.01
Na	0.01	0.00	0.00	0.01	0.00	Sr	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	Ba	0.15	0.02	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.01	0.00	Sum X site	0.80	0.99	0.96	0.99	1.00	0.99
Sum A site	2.00	2.00	1.99	1.98	1.92							
						Ab	3.6	2.8	93.4	35.5	7.2	17.9
X_{Fe3+}	0.14	0.21	0.33	0.22	0.34	An	2.6	0.0	6.5	62.4	92.5	81.4
						Or	74.7	94.7	0.2	2.1	0.3	0.6
						Cn	19.1	2.5	0.0	0.0	0.0	0.1

Abbreviations: bdl=below detection limit, nd=not detected, Ad=adularia, K-felds=K-feldspar, Plag=plagioclase, Ab=albite, An=anorthite, Or=ortoclase, Cn=celsian. X_{Fe3+} = $Fe^{3+}/(Fe^{3+} + Al^{3+})$. Complete set of analysis available on request.

TABLE 1B – *Selected microprobe analysis and structural formulae of prehnite, cholorite and wairakite from well core samples of the Berlin geothermal field.*

	prehnite			chlorite							wairakite	
Well	TR-17	TR-17	Well	TR-2	TR-2	TR-5B	TR-17	TR-17	TR-18	Well	TR-5C	TR-5B
Depth m.	1500	1500	Depth m.	1502	1650	1765	2417	2417	1553	Depth m.	1628	1765
SiO_2	43.6	38.8	SiO_2	27.9	28.5	26.2	29.4	28.4	32.3	SiO_2	52.69	54.42
TiO_2	bdl	0.10	TiO_2	bdl	bdl	0.03	0.04	0.02	0.04	TiO_2	bdl	bdl
Al_2O_3	20.9	25.4	Al_2O_3	19.4	20.8	19.9	17.8	18.5	15.3	Al_2O_3	22.18	23.70
FeO	3.84	9.21	FeO	26.49	20.24	28.35	21.74	20.33	22.43	FeO	0.11	0.36
MnO	0.19	0.23	MnO	0.52	0.66	0.59	0.64	0.70	0.66	MnO	bdl	bdl
MgO	0.90	bdl	MgO	14.07	18.21	13.26	18.82	19.48	17.61	MgO	bdl	0.07
CaO	26.07	23.04	CaO	0.17	0.16	0.22	0.07	0.08	0.57	CaO	11.43	11.60
Na_2O	0.03	bdl	Na_2O	0.03	0.11	0.07	0.02	0.10	0.13	Na_2O	0.11	0.44
K_2O	bdl	0.02	K_2O	bdl	bdl	bdl	bdl	0.02	0.06	K_2O	0.02	0.33
Sum	95.69	96.75	Cr_2O_3	0.04	bdl	0.06	0.04	0.05	0.02	Cr_2O_3	0.06	bdl
			Sum	88.55	88.74	88.53	88.57	87.67	89.06	Sum	86.54	90.92

Structural formulae based on 22 oxygens | *Structural formulae based on 28 oxygens* | *Structural formulae based on 12 oxygens*

	prehnite			chlorite							wairakite	
Si	6.12	5.50	Si	5.83	5.75	5.56	5.99	5.83	6.55	Si	3.96	3.92
Al^{IV}	1.88	2.50	Al^{IV}	2.17	2.25	2.44	2.01	2.17	1.45	Ti	0.00	0.00
Sum IV site	8.00	8.00	Sum IV site	8.00	8.00	8.00	8.00	8.00	8.00	Al	1.97	2.01
										Fe^{2+}	0.01	0.02
Al^{VI}	1.57	1.74	Al^{VI}	2.61	2.71	2.53	2.28	2.31	2.20	Mn	0.00	0.00
Fe^{3+}	0.43	0.26	Ti	0.00	0.00	0.00	0.01	0.00	0.01	Mg	0.00	0.01
Sum VI site	2.00	2.00	Mg	4.39	5.48	4.20	5.73	5.97	5.33	Ca	0.92	0.89
			Fe^{2+}	4.64	3.42	5.04	3.71	3.49	3.81	Na	0.02	0.06
Ti	0.00	0.01	Mn	0.09	0.11	0.11	0.11	0.12	0.11	K	0.00	0.03
Fe^{2+}	0.07	0.86	Ca	0.04	0.03	0.05	0.02	0.02	0.12	Cr	0.00	0.00
Mg	0.19	0.00	Na	0.01	0.04	0.03	0.01	0.04	0.05	Sum	6.88	6.95
Mn	0.02	0.03	K	0.00	0.00	0.00	0.00	0.01	0.02			
Ca	3.92	3.50	Sum VI site	11.79	11.79	11.97	11.86	11.95	11.65	X_{Na}	0.02	0.06
Na	0.01	0.00										
K	0.00	0.00	$Fe^{2+}/$	0.51	0.38	0.55	0.39	0.37	0.42			
Sum Y site	4.20	4.40	$(Fe^{2+}+Mg)$									

Abbreviations: bdl= below detection limit. X_{Na} = Na/(Na+Ca+K). Complete set of analysis available on request.

be replaced or it can be a late phase with respect to quartz and wairakite. Quartz is also found in veins, but in several cases it forms the cement of volcanic breccias with jigsaw-puzzle textures.

In some weakly altered rocks small amounts of augite and diopside phenocrysts occur as relic, but in many cases pyroxenes are replaced by chlorite and opaque minerals. Chlorite often shows ripidolite composition (i.e. a solid solution between daphnite and clinochlore with 0.37 to 0.55 $Fe^{2+}/(Fe^{2+} + Mg^{2+})$ values) (Table 1B). Chlorite can also be found in veins associated with variable amounts of calcite, epidote, quartz, pyrite. The latter mineral, even if it is usually observed in small amounts, it
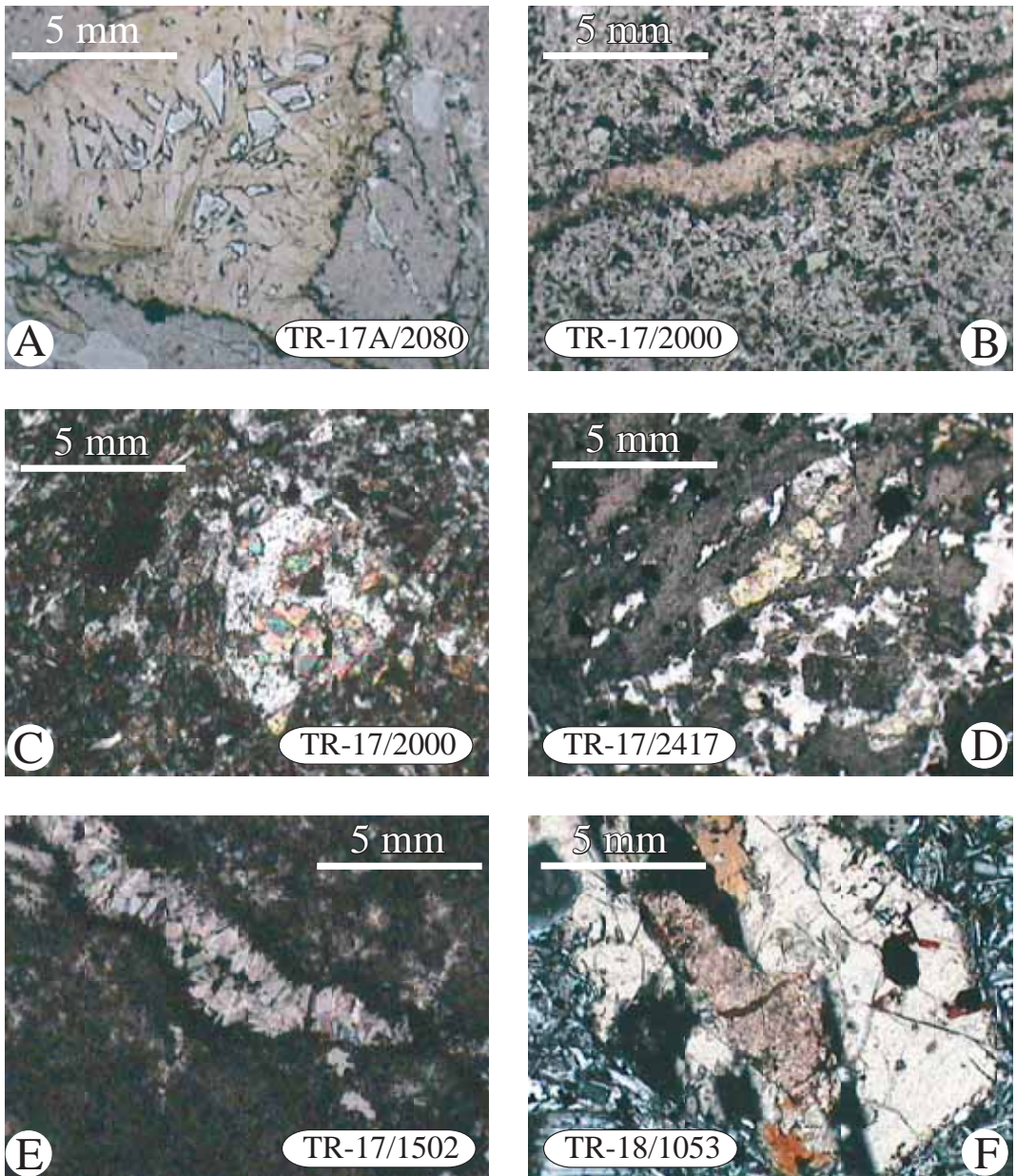
Fig. 2 – Microphotograph of alteration minerals. A) Epidote in vein and vug, with empty spaces between idiomorphic crystals; B) epidote vein; C) epidote and albite replacing igneous plagioclase; D) quartz and epidote filling microfractures and replacing plagioclase; E) prehnite vein; F) calcite replacing plagioclase. A and B: parallel nicols, C, D, E and F: crossed nicols.

is widespread in most of the studied samples as euhedral crystals sometimes with a chlorite rim. In addition to the above hydrothermal minerals, actinolite, hydro-garnet and laumontite have also been observed in the examined wells.

The abundance of the hydrothermal minerals and the alteration style in the Berlin geothermal field is partially controlled by the bulk chemistry of the rock. In fact, basaltic to andesitic rocks alter to calcite, chlorite (or clay minerals), epidote, titanite, pyrite, quartz, albite and rare adularia. Calcite and phyllosilicate are widespread in the matrix, whereas vein minerals are epidote, calcite, wairakite, quartz, chlorite in different proportions. The more silicic rocks of likely rhyolitic or dacitic composition alter to the same secondary mineral assemblages, but calcite is more rare whereas hydrothermal quartz can be abundant. In addition, hydrothermal alteration seems to be more pervasive than in the rocks of basic to intermediate compositions. The matrix, in particular, appears as a microcrystalline aggregate of quartz and feldspar, derived from re-crystallization of a felsitic matrix.

Optical observations and X-ray revealed a zoned distribution of the hydrothermal assemblages with depth. The different zones have been distinguished on the basis of: 1) the most abundant hydrothermal phases, and 2) the appearance or disappearance of some characteristic minerals (Table 2). A low-temperature assemblage consisting principally of clay minerals, heulandite, quartz and calcite occur at shallow depth between 0 and 670-800 m b.g.l.. The clay minerals occurring in this zone are mostly nontronite, montmorillonite, saponite and corrensite. Below this zone, from about 670-800 to 1100-1630 m b.g.l. (the depth limits vary depending on the different wells), the main hydrothermal phases are calcite, chlorite, quartz and lesser amount of wairakite, laumontite, anhydrite, illite and illite-montmorillonite mixed-layers. At greater depth, from 1100-1630 to 1460-1840 m b.g.l. the hydrothermal assemblage is characterized by the appearance of epidote and albite, which coexist with quartz, illite, chlorite, calcite, wairakite, adularia and prehnite. In the deepest zone (below about 1460-1840 m b.g.l.) calcite is absent or very scarce, while epidote, albite and quartz are common; adularia, prehnite, anhydrite and chlorite, actinolite, wairakite and hydro-garnet also occur in variable amounts. In several samples, minor amounts of titanite and pyrite are also observed without clear depth distribution.

RESERVOIR FLUID CHARACTERISTICS AND MINERAL SATURATION INDICES

Temperature and chemical data of the reservoir fluids discharged by the geothermal wells are

TABLE 2 – *Hydrothermal minerals and depths range of the four alteration zones recognized in the Berlin geothermal field.*

Depth b.g.l. (m)		Hydrothermal minerals	
min	max	Abundant	Moderately abundant to trace
0	670-800	nontronite, montmorillonite, corrensite, quartz, calcite, heulandite	saponite
670-800	1100-1630	calcite, chlorite, quartz	wairakite, laumontite, anhydrite, illite, illite-montmorillonite, corrensite
1100-1630	1460-1840	albite, quartz, chlorite, calcite	illite, wairakite, adularia, prehnite, epidote
1460-1840	?	epidote, albite, quartz	adularia, prehnite, anhydrite, chlorite, actinolite, wairakite, hydro-garnet, calcite
Widespread titanite and pyrite without depth distribution			

reported by D'Amore and Mejia (1999), and Montalvo and Axelsson (2000). The reservoir fluids are NaCl waters with about 5000-11000 mg/kg of total dissolved solids (TDS), 3000 to 6000 mg/kg of chloride, and 600 to 900 mg/kg of silica. The concentration of non-condensable gases in the steam are in the 0.25-0.50% range by weight, with CO_2 constituting 80 to 90% of the total gas content. CO_2 concentration in the reservoir fluids are usually between about 200 and 1900 mg/kg with partial pressures (P_{CO_2}) of 0.49-4.60 bar (D'Amore and Mejia; 1999). Fluid enthalpy varies between 1200 and 1400 kJ/kg, measured temperatures in the production zones are in the 280-300°C range (see wells TR-2, TR-3, TR-4, TR-5, TR-9 in fig. 1), while lower values, around 245-250°C, were measured at the northern part of the field where the wells are utilized for reinjection purposes (D'Amore and Mejia, 1999).

The salinity and enthalpy differences of the reservoir fluids from distinct wells have been explained in terms of fluid mixing, boiling and conductive cooling (D'Amore and Mejia, 1999).

The thermal and chemical characteristics of the reservoir in its natural state conditions were estimated on the basis of gas samples from the first production period, and considering thermodynamic equilibrium between the fluid components (D'Amore and Truesdell, 1985; Saracco and D'Amore, 1984).

Here, we re-process the existing chemical data, and compute new saturation indices (S.I.) for the mineral assemblage under present state conditions. The S.I. together with the temperature, the CO_2 fugacity or partial pressure, the pH, the $\log[Ca^{2+}]/[H^+]^2$ under present and natural state conditions are compared in Table 3. This table shows significant differences in the S.I. values obtained with the different codes, S.I., in fact, depends on the different activities of the Al and Fe species, and, consequently, on the distinct computed activity products. It is useless to perform a sensibility analysis on the Fe and Al variations because, as was said before, the concentrations of these elements are largely uncertain. It is more significant to plot the well fluid data in $\log[Ca^{2+}]/[H^+]^2$ vs. temperature and $\log[Mg^{2+}]/[H^+]^2$ vs. temperature diagrams and discuss the evolution of the fluids from their natural state to the present state conditions (see below). The advantage of the phase diagrams is that the

stability fields of the minerals are independent on the Al and Fe contents.

Rock geochemistry

The chemical analyses of 10 core-samples drilled in the geothermal wells are reported in Table 4. The LOI (2.81-6.54 wt%) indicates that all these samples were more or less affected by hydrothermal alteration.

A useful graphic method to evaluate the main changes in chemistry in rock, which underwent a chemical exchange with a permeating fluid, is the isocon or Grant's diagram (Grant, 1986). In this diagram the major elements and LOI of the altered are compared with those of the original rock. The only unaltered surface volcanic rocks comparable for their stratigraphic position to the analyzed altered rocks are represented by some basaltic lavas emplaced during the oldest volcanic activity in Berlin area. The chemical analysis of one of this lava (BE2 sample, its location in fig. 1) is shown in Table 4. Since Ti is usually an immobile element, we compare the composition of BE2 sample with that of the altered sample (TR-17/2417) showing the most similar TiO_2 content (fig. 3).

Basically, there are two ways to construct the isocon diagrams; 1) assuming that no volume changes occurred during the alteration process; and 2) assuming a nearly constant value for one or more elements which are considered immobile during the same process. The first hypothesis leads to the equation: $C^A = (\rho^O/\rho^A) C^O$, where C is the concentration of one element and ρ is the rock specific gravity, and the superscripts A and O refer to the altered and original rock respectively. In the case of the second assumption the equation is: $C^A = (M^O/M^A) C^O$, where M is the mass of the rock sample. ρ^O/ρ^A and M^O/M^A are the slopes of the straight lines defined by the two different hypotheses. If we assume constant mass, then $C^A = C^O$. The dot-dashed line of fig. 3 has been constructed assuming constant Al.

Discussion

The isocon diagram in fig. 3 shows that the most significant chemical changes in the

TABLE 3 – *Mineral saturation indices, gas partial pressures and fugacities, and chemical parameters of interest of selected geothermal fluids at Berlin under natural state and present state conditions. Present state conditions were computed using WATCH program (Arnorsson* et al.*, 1982; Stefansson, 2001) and REACT code of Bethke (1996), natural state conditions are from D'Amore and Mejia (1999).*

	Present-day reservoir condition													Natural reservoir condition						
	Computation using REACT code						Computation using WATCH code							Computation of D'Amore and Mejia (1999)						
Well	TR-1	TR-2	TR-3	TR-5	TR-9	TR-10	Well	TR-1	TR-2	TR-3	TR-5	TR-9	TR-10	Well	TR-1	TR-2	TR-3	TR-5	TR-9	TR-10
Mineral	S.I.	S.I.	S.I.	S.I.	S.I.	S.I.	Mineral	S.I.	S.I.	S.I.	S.I.	S.I.	S.I.	Mineral	S.I.	S.I.	S.I.	S.I.	S.I.	S.I.
Quartz	0.1	0.1	0.1	-0.7	0.0	-0.1	Quartz	0.0	0.1	0.0	-0.2	-0.1	-0.2	Quartz	-0.1	0.1	0.0	-0.8	-0.7	-0.1
Calcite	0.1	-1.8	0.1	0.5	0.3	0.3	Calcite	0.6	-1.0	0.8	0.8	0.2	0.8	Calcite	1.4	-2.4	-0.9	0.9	-0.7	-0.2
Anhydrite	-0.6	-1.5	-0.6	0.7	-1.3	0.7	Anhydrite	0.2	-0.4	-0.4	0.6	-1.9	0.6	Anhydrite	0.2	-1.7	-0.8	0.7	-1.3	0.6
Epidote	3.2	< -3	-0.5	< -3	-0.4	1.2	Epidote	0.6	-0.5	1.1	-0.1	0.6	0.1	Epidote	2.2	< -3	-0.7	< -3	-0.4	1.2
Prehnite	0.8	< -3	-1.3	< -3	-2.0	-0.4	Prehnite	1.0	0.1	2.1	1.3	0.4	1.3	Prehnite	-0.4	< -3	-1.4	< -3	-2.0	-0.5
Daph 14A	3.0	< -3	< -3	< -3	-1.9	-1.0	Mg-Chl	-4.1	< -3	< -3	< -3	1.1	-2.9	Daph 14A	2.5	< -3	< -3	< -3	-1.9	-0.5
Rip 14A	2.7	< -3	< -3	< -3	-0.7	-0.4	Ca-Mont	< -3	0.5	< -3	< -3	< -3	< -3	Rip 14A	1.9	< -3	< -3	< -3	-0.7	-0.3
Clin 14A	0.5	< -3	< -3	< -3	-0.3	-0.4	Mg-Mont	< -3	0.0	< -3	< -3	< -3	< -3	Clin 14A	1.1	< -3	< -3	< -3	-0.4	-0.5
Ca-Sap	3.2	-2.4	0.9	-2.8	3.2	2.3	Na-Mont	< -3	-1.4	< -3	< -3	< -3	< -3	Ca-Sap	3.9	-2.6	0.6	< -3	3.2	2.2
Mg-Sap	2.9	-2.5	0.7	< -3	3.0	2.1	K-Mont	< -3	-2.5	< -3	< -3	< -3	< -3	Mg-Sap	3.7	-2.7	0.3	< -3	3.0	1.9
Na-Sap	3.1	-2.8	0.4	< -3	2.8	1.8	Albite	-0.6	0.1	0.1	-0.8	-0.2	-0.8	Na-Sap	2.5	-3.0	0.1	< -3	2.7	1.7
K-Sap	2.4	< -3.	0.2	< -3	2.5	1.5	Wairakite	-1.5	0.2	0.3	-1.0	-1.0	-1.0	K-Sap	3.0	< -3.	-0.2	< -3	2.5	1.4
Ca-Nontr	4.0	-2.8	-0.5	< -3	0.5	0.9								Ca-Nontr	2.7	< -3.	-1.3	< -3	0.5	1.1
Mg-Nontr	3.8	-2.9	-0.8	< -3	0.4	0.7								Mg-Nontr	2.5	< -3.	-1.5	< -3	0.4	0.9
Na-Nontr	3.9	< -3	-1.0	< -3	0.1	0.4								Na-Nontr	2.5	< -3	-1.5	< -3	0.1	0.6
K-Nontr	3.4	< -3	-0.9	< -3	0.2	0.4								K-Nontr	2.1	< -3	-1.7	< -3	0.2	0.6
Albite	0.9	-0.9	-0.8	< -3	-1.3	-1.1								Albite	-0.6	-0.9	-1.0	< -3	-1.3	-0.9
Wairakite	-1.1	< -3	-2.0	< -3	-3.0	-1.9								Wairakite	-2.7	< -3	-2.1	< -3	-3.0	-1.8
pH	6.8	5.3	6.0	6.2	6.4	6.2	pH	6.7	5.3	6.0	6.2	6.4	6.2	pH	6.7	5.3	6.0	6.2	6.4	6.2
$\log[Ca^{2+}]/[H^+]^2$	10.1	6.2	8.3	9.4	8.2	9.2	$\log[Ca^{2+}]/[H^+]^2$	10.4	6.58	8.61	9.3	7.87	9.3	$\log[Ca^{2+}]/[H^+]^2$	9.8	6.0	8.0	9.0	8.2	9.2
fCO_2(bar)	0.05	3.18	2.09	0.54	2.70	0.59	PCO_2(bar)	0.04	1.70	1.21	0.39	1.34	0.39	fCO_2(bar)	0.14	0.90	0.35	2.00	0.32	0.19
(fugacity coefficients in the range 0.9 to 1.15)														(fugacity coefficients in the range 0.9 to 1.15)						
T°C*	205	289	276	250	299	250	T°C*	205	289	276	250	299	250	T°C^	260	300	300	300	300	240

Abbreviations: S.I. = saturation indices, Chl = chlorite, Mont = montmorillonite, Daph = daphnite, Sap = saponite, Nontr = nontronite, Clin = clinochlore, Rip = ripidolite, T°C* = present state temperature computed using chemical geothermometers (T_{qz} for the well TR-1 and at T_{NaK} for the other wells), T°C^ = natural state temperature computed by D'Amore and Mejia (1999) using gas data.

altered rock are an increase in Ca, and LOI and a decrease in K, Na and Si. This result reflects the type of alteration of the TR-17/2417 sample, where epidote (fig. 2D) and chlorite replace plagioclase and femics. Mg and Fe remain in the secondary chlorite, epidote and sulphide, part of the silica remains in quartz (fig. 2D) and in the other hydrothermal silicates, as also some Na in newly formed albite. However, part of Si, Na and all K were leached out of the rock and went into the fluid phase. The high LOI value is due to the presence of OH-bearing phases (chlorite, epidote) and pyrite in the altered rock.

The contrasting alteration style shown by the femic-intermediate and silicic rocks of the Berlin geothermal field has also been reported from the New Zealand geothermal fields (Browne, 1989) and explained with the different fluid pathways through the andesite (joint channels) and rhyolite (interconnected pores). Tuffs and volcanic breccias generally behave like the silicic lava. Alteration of rhyolite is largely characterized by quartz and adularia, when rocks react with upflowing chloride waters of at least 170-190°C (Hennenberger and Browne, 1988). Diffractometric analyses carried by LaGeo on Berlin samples reveal a K-feldspar with X-ray pattern comparable with the hydrothermal adularia of Wairakei (Steiner, 1970). It is, therefore, possible that the primary sanidine re-crystallized in a new feldspar under the reservoir conditions.

Table 4 – *Chemical analyses of selected rock samples.*

Label	Sample type	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$	L.O.I.	Total
BE 2	lava flow	50.68	1.22	17.92	12.10	0.20	4.27	9.51	2.73	1.39	0.32	0.21	100.55
TR-2/1250	core sample	51.20	0.97	19.55	9.29	0.14	3.23	9.65	2.30	0.96	0.23	2.81	100.33
TR-2/1350	core sample	51.16	0.93	18.35	8.08	0.18	3.10	8.43	2.21	1.33	0.38	5.70	99.85
TR-2/1600	core sample	52.86	0.88	19.93	8.60	0.15	3.89	4.82	3.85	1.70	0.17	2.98	99.83
TR-2/1650	core sample	57.38	0.56	19.37	5.98	0.15	2.37	6.71	4.42	0.89	0.13	2.04	100.00
TR-5B	core sample	45.66	0.98	16.26	11.53	0.21	3.33	11.27	2.35	0.80	0.20	6.54	99.13
TR-17	core sample	58.88	0.86	15.01	8.53	0.19	2.88	6.34	3.75	0.23	0.30	2.58	99.55
TR-17/2417	core sample	41.59	1.12	19.77	13.81	0.27	4.65	13.97	1.94	0.03	0.28	3.93	101.36
TR-18/1053	core sample	53.78	0.74	18.15	7.96	0.17	2.85	7.46	4.36	1.88	0.23	2.14	99.72
TR-2/1450	core sample	52.40	0.77	16.71	9.65	0.18	2.75	7.78	2.73	0.77	0.23	5.30	99.27
TR-2/1502	core sample	55.54	0.70	16.82	8.41	0.18	3.11	6.55	2.84	1.04	0.20	3.54	98.93

TR samples are hydrothermally altered volcanics cored in different wells, BE 2 is a lava flows outcropping in the Berlin area; first number after TR refers to well number, second number is the depth of sampling when is known.
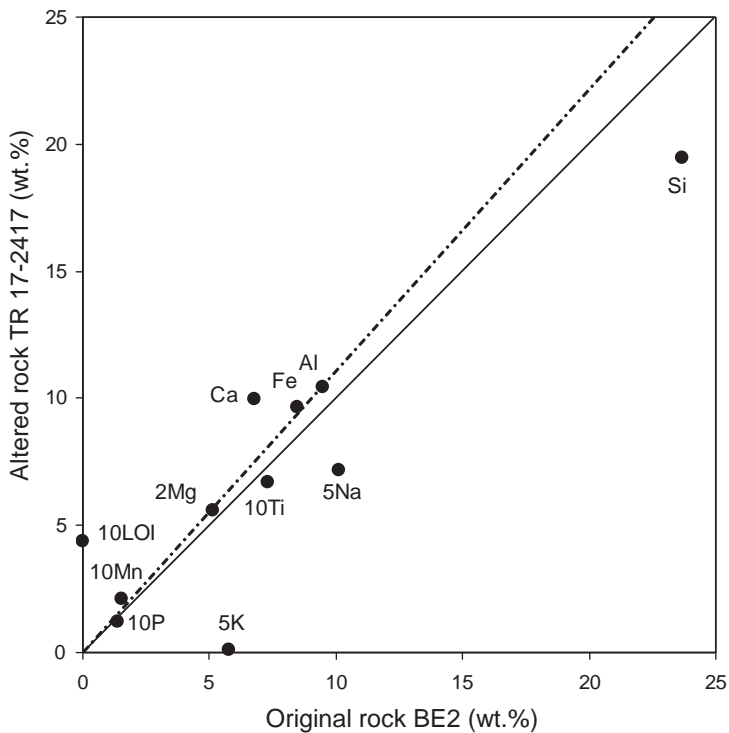
Fig. 3 – Isocon diagram, altered core sample TR-17/2417 m depth vs. original unaltered rock (BE2 surface sample). Some chemical components are increased by a multiplying factor (e.g. 5Na = 5 x Na wt.% of the rock). Full line = constant mass; dashed-dotted line = constant Al. BE2 is a basalt lava flow of the old Berlin volcano, its location is: 13°31'00" N, 88°31'42" W, elevation: 716 m.

Since the formation of specific hydrothermal minerals is correlated with the temperature and/or chemistry of the fluids, the distribution of the alteration assemblages with depth in theory can provide useful information on the natural state of the system. For example, epidote distribution and/or abundance in some geothermal fields is correlated with isotherms, although the stability of this mineral may be also influenced by other parameters such as CO_2 and O_2 fugacities, and pH (Bird and Spieler, 2004).

The distribution of the different hydrothermal assemblages, the limit of epidote appearance and the present-day isotherms along a SW-NE section in the recently explored area are shown in fig. 4A. Fig. 4B shows the same features along an area, which comprises the hottest zone of the production area (south) and the zone of fluid outflow (north). Fig. 4B is based on a model proposed by Montalvo

and Axelsson (2000), according to this model the upflow of the geothermal fluid is thought to be underneath the Tecapa volcano to the south of the field.

The transition from shallow clay-minerals alteration to the deeper epidote, albite, wairakite etc. assemblage (Table 2, fig. 4) is a clear evidence of increasing temperature with depth. Despite local irregularities the different zones are roughly sub-horizontal or moderately dipping (fig. 4), and probably reflect more or less the distribution of the isotherms during the developing of the alteration minerals. The transition from the zone dominated by calcite + chlorite + quartz to the zone beneath is marked by epidote crystallization ("epidote in" of fig. 4). On the basis of the disappearance of laumontite, a phase present in the calcite + chlorite + quartz but not below, and the appearance of epidote, it is possible to
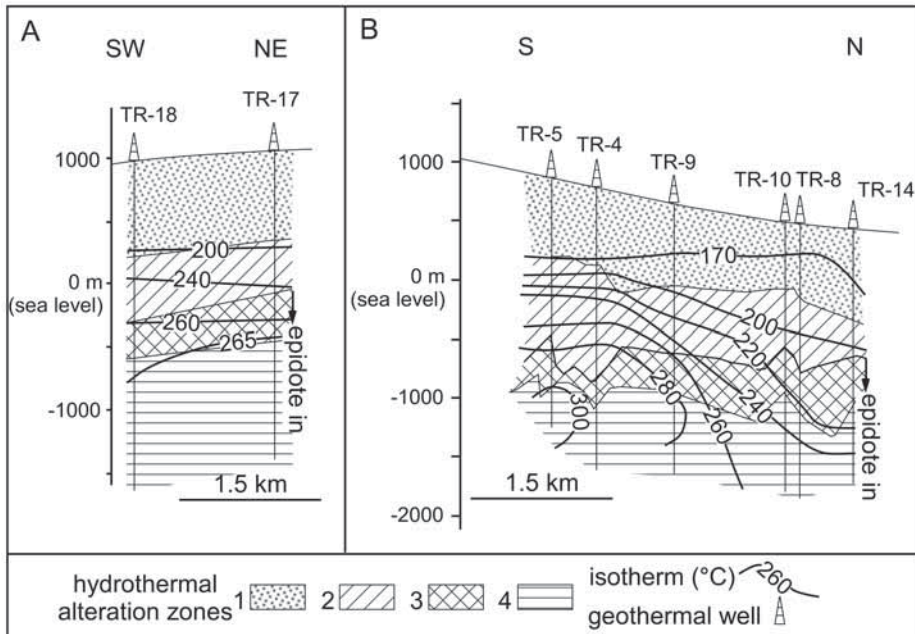
Fig. 4 – Distribution of the hydrothermal alteration zones with depths, isotherms and epidote appearance in: A) the recently explored area along a section comprising the wells TR-17 and TR-18, B) along a zone comprising the production area (south) and the zone of fluid outflow (north) (modified after Montalvo and Axelsson (2000)). The four alteration zones (1, 2, 3, and 4) are those reported in Table 2, in particular the characteristic minerals of each zone are: 1) calcite + clay minerals, 2) chlorite + calcite + quartz, 3) chlorite + calcite + quartz + albite ± epidote ± prehnite, 4) epidote + quartz + albite ± prehnite.

set this transition at a temperature between about 220 and 260°C. The upper stability limit of laumontite, in fact, was found at about 220-230°C by Liou (1970), and epidote is a common and abundant phase above 230-260°C in volcanic rocks (Bird and Spieler, 2004). The occurrence of garnet in the deeper zone (Table 2) is indicative of relatively higher temperatures (i.e. >300°C in active geothermal systems, Bird *et al.*, 1984 and reference therein).

In the production area, present-day isotherms distribution do not follow the alteration zones except for the shallow part of the field. Here, the limit between the calcite + clay minerals and the zone dominated by calcite + chlorite + quartz is, in fact, mostly comprised within 170° and 200°C. This range is in agreement with the transformation of saponite to chlorite, which is completed at temperatures higher than 200-240°C (Patrier *et al.*, 1996 and reference therein). However, the occurrence of montmorillonite and illite-montmorillonite mixed layers in the clay-mineral + calcite zone and in the calcite + chlorite + quartz zone respectively is not coherent with the relatively high present-day temperature in the two zones (up to 200°C and >200°C, respectively). As suggested by Patrier *et al.* (1996), the occurrence of such smectites and mixed-layers at temperature above their stable temperature may be considered as present or very recent metastable phases whose transformation toward illite is kinetically controlled (temperature and time dependent).

In the deeper parts of the field, the isotherms crosscut the limits between the hydrothermal assemblages, and in particular the isograd of epidote appearance ("epidote in"). A similar situation, characterizes the recently explored area, where the limit between the calcite + clay minerals and calcite + chlorite + quartz zones is sub-parallel to the 200°C isotherm. At greater depths the isotherms are not parallel to the alteration zones (fig. 4), suggesting that in the deep part of the geothermal field significant thermal changes have occurred from the time of alteration mineral deposition. The deep alteration zones, therefore, do not reflect the present-day thermal structure of the geothermal field, but testify a past natural state of the system that is different from the most recent natural state (i.e. just before exploitation).

The distribution of the hydrothermal minerals with depths is also indicative of a past variation of the fluid chemistry. The studied wells are characterized by a shallow depth calcite + clay-mineral zone, whereas at greater depth a decrease in calcite is observed and prehnite may occur. This transition suggests a CO_2 variations with depth. Prehnite is, in fact, a mineral stable in fluids having low CO_2 concentrations, whereas calcite crystallization in place of prehnite can be related to a CO_2 increase. Therefore, during the formation of the hydrothermal assemblage, a relatively shallow fluid circulation, characterized by Na-HCO_3-NaCl water, was probably responsible for calcite (and clay minerals) depositions, whereas the deeper aquifer, dominated by CO_2-poor NaCl fluid, produced prehnite and epidote formation.

The question arises whether a given hydrothermal mineral is actually in equilibrium with the reservoir fluid, and consequently may or may not give information on the natural and present state of the reservoir. Hydrothermal minerals not in equilibrium with the reservoir fluid were noted, for example, in the Tendaho geothermal field by Gianelli *et al.* (1998) where the widespread wairakite found in the altered reservoir rocks shows negative saturation indices. Another example of metastability, is the occurrence of clay minerals under the present-day reservoir conditions reported at Chipilapa by Patrier *et al.* (1996).

The occurrence of several Ca-Al silicates (epidote, prehnite, wairakite, garnet, laumontite) and calcite, and the coexistence of some of these phases in a number of samples in the Berlin geothermal field suggests different stages of mineral deposition and/or kinetic control on metastable phases. The deposition of distinct Ca-Al-silicates is indicative of some spatial or temporal changes in the physical-chemical parameters of the reservoir fluid. In particular, Ca-Al-silicate stability depends on temperature and pH (linked to the CO_2 partial pressure). For example, prehnite and andradite-grossular garnets need CO_2-poor fluids, such as degassed geothermal waters. Epidote equilibrium also depends on P_{CO_2} (Bird and Helgeson, 1980; Bird and Spieler; 2004), and this mineral is replaced by calcite and clay minerals in the gas-rich geothermal reservoirs.

As shown above, the computation of the S.I. with the WATCH and REACT codes give different

results (Table 3). A partial exception is represented by the results of the S.I. of wairakite, which can be always considered a relict mineral. Its instability under present-day conditions can probably be related to an incompatibility with present-day pH values and possibly P_{CO_2}.

Epidote and clay minerals stability can be evaluated by computing the mineral equilibria as a function of temperature and $\log[Ca^{2+}]/[H^+]^2$ (fig. 5) and $\log[Mg^{2+}]/[H^+]^2$ (fig. 6), respectively. These figures show the evolution of the fluids from their natural state to the present state conditions (arrows). Fig. 5 also reports the saturation curves of calcite for two different P_{CO_2} (0.05 and 3 bar).

Epidote can be considered stable under both natural and present state conditions in the wells TR-1 and TR-10, only if prehnite or garnet are not present, and if the partial pressure of CO_2 is less than 0.05 bar approximately (Fig. 5). However, in well TR-10 the P_{CO_2} is higher than 0.05 bar under both natural and present state conditions, and in TR-1 under natural state condition (Table 2). Similarly, in well TR-5, the high P_{CO_2} does not also allow epidote stability under both present and natural state condition. In the wells TR-2 and TR-3, epidote stability is close to natural state conditions, but in the present state conditions the high P_{CO_2} likely destabilizes this mineral in TR-3. Well TR-9 represents a particular case, as it is close to the natural state temperature, but with a high P_{CO_2}, which likely destabilizes epidote. Therefore, the stability of epidote is largely controlled by the carbon concentration rather than by fluid temperature at Berlin. Changes in the CO_2 content can be interpreted in terms of phase separation (boiling) processes. D'Amore and Mejia (1999)
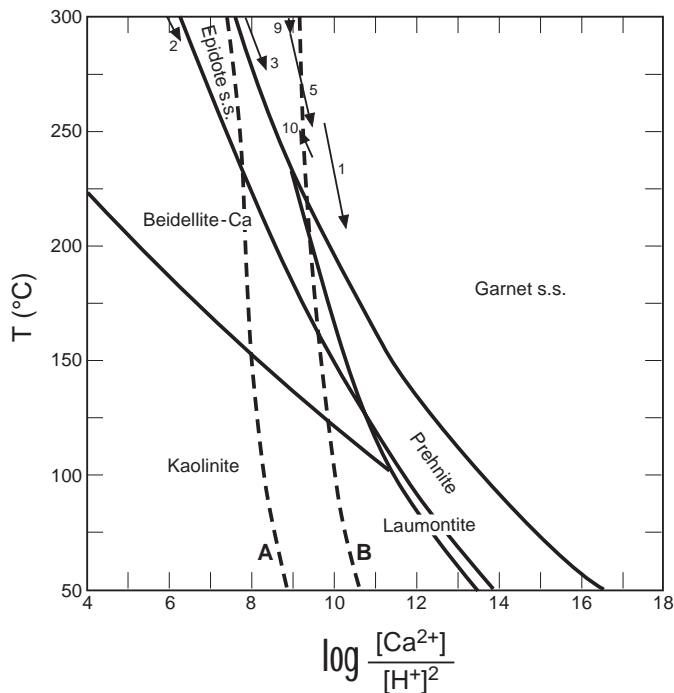

Fig. 5 – Activity-temperature (T) diagram showing the stability of epidote and other hydrothermal minerals as a function of Ca^{2+} and H^+ activities. The dashed lines indicate the saturation of calcite for a P_{CO_2} of 3 bar (A) and of 0.05 bar (B). The numbers refer to the wells whose chemical parameters and temperatures are shown in Table 3. The arrows indicate the composition of the reconstructed reservoir fluid in its natural (arrow's tail) and present state (arrow's head) (see text and Table 3).

suggested that the fluid discharged by well TR-5 is the parental water of the Berlin reservoir coming from the southern upflow zone of the field. The wells TR-3, TR-2 and TR-9 are considered waters evolved from well TR-5 by boiling, while TR-1 and TR-4 fluids evolved by conductive cooling. The estimated P_{CO_2} of the natural state (D'Amore and Mejia, 1999) in the parental reservoir water is four times higher than that measured at present. However, the reconstruction of the present state condition of the reservoir fluids of wells TR-5, TR-1 and TR-10 have a relatively low-P_{CO_2}, whereas other wells are characterized by higher P_{CO_2} (Table 3). We suggest that all the fluids have been evolved from a single parental high enthalpy fluid, which experienced variable degrees of degassing and cooling, depending on the amount and type of boiling. A completely isoenthalpic boiling fosters degassing and pH increase, whereas a "sub-isoenthalpic" boiling (i.e. when fluids lose heat to the rock, due to self-sealing and local pressure increase) keeps the fluid more acidic and gassy (Reed and Spycher, 1985).

Considering now the stability of clay minerals, we can observe that: 1) most of the fluids plot in the chlorite stability field, under both natural and present state conditions, and 2) beidellites, and montmorillonites (considered here also as proxies of mixed-layers and corrensite) are stable at temperatures not greater than 175-200°C at the $\log[Mg^{2+}]/[H^+]^2$ characterizing the Berlin geothermal fluids (fig. 6). This temperature range is in good agreement with the present-day transition temperature (around 170-200°C) from the shallow depth clay-mineral zone to the deeper zone, characterized by the presence of chlorite and the disappearance of most clay-minerals (fig. 6). This confirms that the shallow alteration zone,
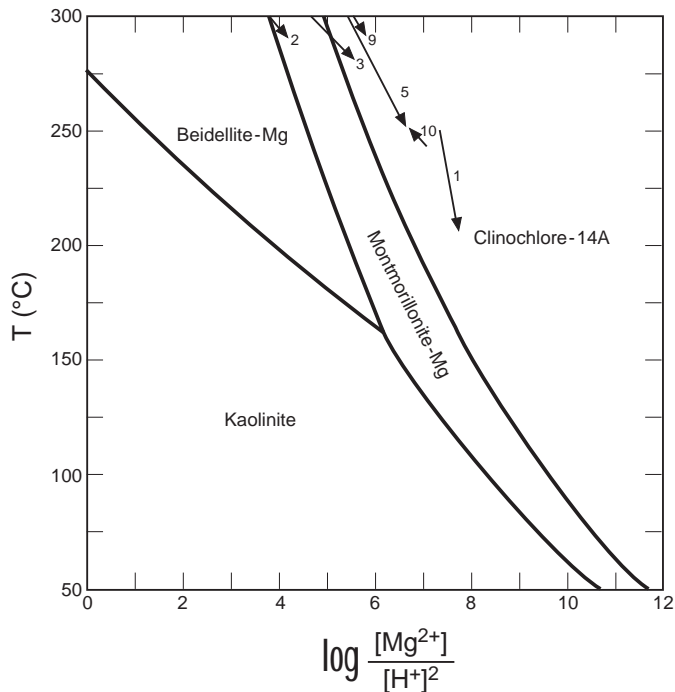

Fig. 6 – Activity-temperature (T) diagram showing the stability of chlorite and other hydrothermal minerals as a function of Mg^{2+} and H^+ activities. The numbers refer to the wells whose chemical parameters and temperatures are shown in Table 3. The arrows indicate the composition of the reconstructed reservoir fluid in its natural (arrow's tail) and present state (arrow's head).

dominated by the presence of clay-minerals, may reflect the present thermal conditions and that no important thermal changes occurred from the natural state.

The composition of some hydrothermal minerals can also be used for geothermometric estimate. Epidote compositions, specifically the mole fractions of pistacite (Xps) in epidote, are sometimes correlated with temperature (Bird and Spieler, 2004). The comparison between present-day temperature with the computed Xps from several wells, did not indicate any clear correlation. This corroborates the above hypothesis that temperature and/or chemical parameters may have varied from the crystallization of epidote in the deepest alteration zones to present-day.

The composition of chlorite in many geothermal fields, has been often correlated with temperature. Specifically the amount of Al^{IV} is positively correlated with temperature (McDowell and Elders, 1980; Cathelineau and Nieva, 1985; Cathelineau, 1988, Jowet, 1991), although, the validity of the chlorite geothermometer has been disputed (see for example De Caritat *et al.*, 1993). Here, we have compared the crystallization temperature of chlorite, using the empirical geothermometer proposed by different authors, with present-day temperature. The best results were given by the relation between temperature and Al^{IV} proposed by Cathelineau (1988). Particularly, in well TR-17 the temperature ranges and averages of chlorite temperatures correlate with the present-day thermal profile (fig. 7A). A fairly good positive correlation between present-day temperature and the Al^{IV} contents of chlorite coming from different wells and depths, except for the TR-2/1650 sample is shown in fig. 7B. This correlation suggests, as also previously evidenced in fig. 6, that the chlorites in the Berlin geothermal field are usually in equilibrium with the present-day thermal state. The following linear relation correlates the average Al^{IV} concentrations with the present-day temperatures: $T(°C) = 47.238 \times Al^{IV} + 175.77$. This equation may be used for geothermometric estimates for the Berlin geothermal field, since the difference between the computed temperature values and present-day temperatures is usually modest (within ±13°C).

Conclusions

Four alteration zones of the Berlin geothermal field formed at increasing temperature and different depths. The distribution of the hydrothermal phases at depth suggests that at the time of hydrothermal alteration development, the isotherms were in
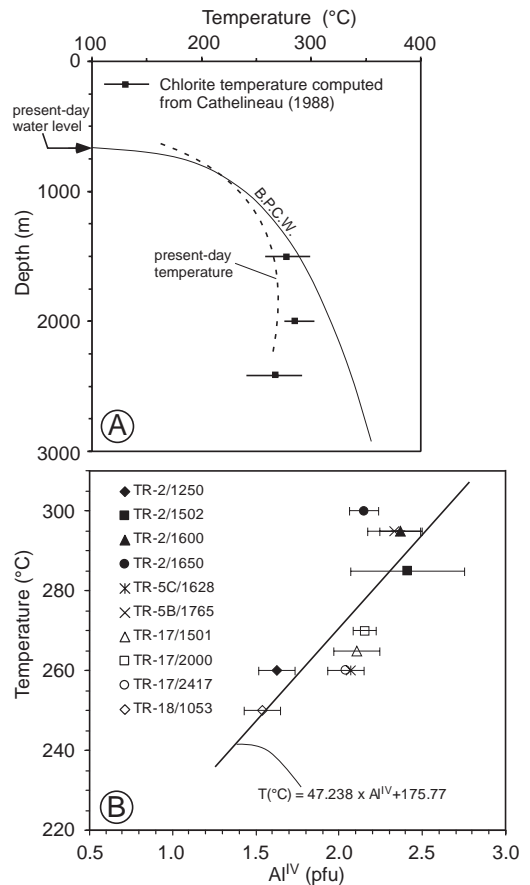

Fig. 7 – A) comparison between chlorite temperatures calculated using the equation of Cathelineau (1988) of core samples drilled at three different depths in well TR-17 and present-day thermal profile; B.P.C.W. = boiling point curve for pure water, data points are arithmetic means, bars indicate ± one standard deviation; B) diagram of Al^{IV} (atoms per formula unit = pfu) of chlorite from different core samples vs. present-day temperature, regression line for this parameters showing its equation, the data points are arithmetic means, the bars indicate ± one standard deviation.

first approximation sub-horizontal or moderately dipping and that the CO_2 content in the geothermal fluid decreased with depth. The shape of the deep alteration zones record the past thermal distribution (i.e. the past natural state) and not the most recent natural state. They also diverge from the distribution of the present-day isotherms indicating that important thermal changes may have occurred. On the other hand, the boundary between the shallow depth alteration zones is more coherent with present-day temperature data suggesting that in this part of field alteration minerals record the natural state of the system and that no large variation occurred from the start of the exploitation. Fluid-rock interaction promoted an increase in Ca, and LOI related to epidote, calcite and chlorite replacement on plagioclase and femics, a substantial constancy of Mg and Fe, which remain in hydrothermal phases (chlorite, epidote etc.), whereas part of Na, Si and most of the K are leached out.

Thermodynamic computations indicate that wairakite is always instable under present conditions and that epidote is not stable under present and natural state conditions of the reservoir fluids of most wells. Epidote stability is largely controlled by the carbon content rather than by temperature. This can explain why epidote composition at Berlin is not related to temperature. Temperature and CO_2 decreased, in most of the cases, passing from the natural state of the system to present state conditions. These variations can be explained with variable degree of degassing and cooling, during boiling processes with variable amount of boiling fraction. On the other hand, chlorite is a stable phase either in the natural state and at present state conditions. The equilibrium of this mineral to present conditions is also indicated by fairly good correlation between present-day temperature and Al^{IV} content in chlorite from different wells.

From the above results, we suggest that the distribution of the deep high-temperature hydrothermal mineral should not be used for reconstructing the present-day thermal structure of the field. In particular, the "epidote in" isograd is probably meaningless for temperature evaluation since this mineral is often in disequilibrium with respect to the fluid phase under both natural and present state condition. Present-day temperature can be evaluated using the proposed equation that relates Al^{IV} of chlorite with the temperature.

REFERENCES

Arias A., Bertani R., Ceccarelli A., Dini I., Fiordelisi A., Marocco B.M., Scandiffio G., Volpi G., Barrios L., Handal S., Monterrosa M., Quezada A. and Santos P. (2003) – *Conceptual model review of the Berlín geothermal system (El Salvador)*. In *"Geothermal Resources Council Transaction"*, October 12-15, 2003. Morelia, Michoacan, Mexico, **27**, 755-759.

Arnorsson S., Sigurdsson S. and Svavarsson H. (1982) – *The chemistry of geothermal waters in Iceland. I. Calculation of aqueous speciation from 0° to 370°C*. Geochim. Cosmochim. Acta, **46**, 1513-1532.

Bence A.E. and Albee A.L. (1968) – *Empirical correction factors for the electron microanalysis of silicate and oxides*. J. Geol., **76**, 382-403.

Bethke G.M. (1996) – *Geochemical reaction modeling*. Oxford University Press, New York, 397 p.

Bird D.K. and Helgeson H.C. (1980) – *Chemical interaction of aqueous solutions with epidote-feldspar mineral assemblages in geologic systems. 1- Thermodynamic analysis of phase relations in the system $CaO-FeO-Fe_2O_3-Al_2O_3-SiO_2-H_2O-CO_2$*. Am. J. Sci., **280**, 907-941.

Bird D.K., Schiffman P., Elders W.A., Williams A.E. and McDowell S.D. (1984) – *Calc-silicate mineralization in active geothermal systems*. Econ. Geol., **79**, 671-695.

Bird D.K. and Spieler A.R. (2004) – *Epidote in geothermal systems*. In *"Epidotes"*, A. Liebscher and G. Frantz, eds. Reviews in Mineralogy and Geochemistry, Mineral. Soc. America, Geochemical Soc., **56**, 235-300.

Browne P.R.L. (1989) – *Contrasting alteration styles of andesitic and rhyolitic rocks in geothermal fields of the Taupo volcanic zone, New Zealand.*

In: *"Proceeding of 11th New Zealand Geothermal Workshop 1989"*, 111-116.

CATHELINEAU M. (1988) – *Cation site occupancy in chlorite and illites as a function of temperature.* Clay Miner., **23**, 471-485.

CATHELINEAU M. and NIEVA O. (1985) – *A chlorite solid solution geothermometer. The Los Azufres (Mexico) geothermal system.* Contrib. Mineral. Petrol., **91**, 235-244.

CORTI G., CARMINATI E., MAZZARINI F. and GARCIA M.O. (2005) – *Active strike-slip faulting in El Salvador, Central America.* Geology, **33**, 989-992.

D'AMORE F. and MEJIA J.T. (1999) – *Chemical and physical reservoir parameters at initial conditions in Berlin geothermal field, El Salvador. A first assessment.* Geothermics, **28**, 45-74.

D'AMORE F. and TRUESDELL A.H. (1985) – *Calculation of geothermal temperatures and steam fraction from gas composition.* Trans. Geotherm. Res. Counc., **9**, 305-310.

DE CARITAT P., HUTCHEON I. and WALSHE J.L. (1993) – *Chlorite geothermometry: a review.* Clays Clay Miner., **41**, 219-239.

FOURNIER R.O. and POTTER R.W. (1982) – *A revised and expanded silica (quartz) geothermometer.* Geotherm. Res. Counc. Bull., **11**, 3-9.

FOURNIER R.O. and TRUESDELL A.H. (1973) – *An empirical Na-K-Ca geothermometer for natural waters.* Geochim. Cosmochim. Acta, **37**, 1255-1275.

GRANT J.A. (1986) – *The isocon diagram - A simple solution to the Gresens' equation for metasomatic alteration.* Econ. Geol., **81**, 1976-1982.

GIANELLI G., MEKURIA N., BATTAGLIA S., CHERSICLA A., GAROFALO P., RUGGIERI G., MANGANELLI M. and GEBREGZIABHER Z. (1998) – *Water-rock interaction and hydrothermal mineral equilibria in the Tendaho geothermal system.* J. Volcanol. Geotherm. Res., **86**, 253-276.

HENNENBERGER R.C. and BROWNE P.R.L. (1988) – *Hydrothermal alteration and evolution of the Ohakuri hydrothermal systems, Taupo zone, New Zealand.* J. Volcanol. Geotherm. Res., **34**, 211-231.

JOWET E.C. (1991) – *Fitting iron and magnesium into the hydrothermal chlorite geothermometer.* In: *"GAC/MAC/SEG Joint Annual Meeting, Program with Abstract"*, Toronto, 27-29 May, A62, p. 16.

LIOU J.G. (1970) – *P–T stabilities of laumontite, wairakite, lawsonite, and related minerals in the system $CaAl_2Si_2O_8$–SiO_2–H_2O.* Contrib. Mineral. Petrol., **27**, 259-282.

MCDOWELL S.D. and ELDERS W.A. (1980) – *Authigenic layer silicate minerals in borehole Elmore 1, Salton Sea geothermal field, California, USA.* Contrib. Mineral. Petrol., **74**, 293-310.

MICHARD G. and ROEKENS E. (1987) – *Modelling of the chemical composition of alkaline hot waters.* Geothermics, **12**, 161-169.

MONTALVO F. and AXELSSON G. (2000) – *Assesment of chemical and physical reservoir parameters during six years of production-reinjection at Berlin geothermal field (El Salvador).* In: *"Proceedings of World Geothermal Congress 2000"*, Kyushu - Tohoku, Japan, May 28 - June 10, 2153-2158

PATRIER P., PAPAPANAGIOTOU P., BEAUFORT D., TRAINEAU H., BRIL H. and ROJAS J. (1996) – *Role of permeability versus temperature distribution of the fine (<0.2 μm) clay fraction in the Chipilapa geothermal system (El Salvador, Central America).* J. Volcanol. Geotherm. Res., **72**, 101-120.

RAYMOND J., WILLIAMS-JONES A.E. and CLARK J.R. (2005) – *Mineralization associated with scale and altered rock and pipe fragments from the Berlín geothermal field, El Salvador; implications for metal transport in natural systems.* J. Volcanol. Geotherm. Res., **145**, 81-96.

REED M.H. and SPYCER N.F. (1985) – *Boiling, cooling, and oxidation in epithermal systems: a numerical modeling approach.* In: *"Geology and Geochemistry of Epithermal Systems"*, Berger B.R. and Bethke P.M. eds., Reviews in Economic Geology, **2**, 249-272.

SARACCO L. and D'AMORE F. (1989) – *CO2B: a computer program for applying a gas geothermometer to geothermal systems.* Comput. Geosci., **15**, 1053-1065.

STEFANSSON A. (2001) – *Dissolution of primary minerals of basalt in natural waters. I. Calculation of mineral solubilities from 0° to 350°C.* Chem. Geol., **172**, 225-250.

STEINER A. (1970) – *Genesis of hydrothermal feldspar (adularia) in an active geothermal environment at Wairakei, New Zealand.* Mineral. Mag., **37**, 916-922.

VAGGELLI G., OLMI F. and CONTICELLI S. (1999) – *Quantitative electron microprobe analyses of reference silicate mineral and glass samples.* Acta Vulcanol., **11**, 297-303.