FLUID INCLUSION DATA FROM THE CARBOLI 11 WELL, LARDERELLO GEOTHERMAL FIELD, ITALY

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Abstract

In the well "Carboli 11", a temperature of 427 °C at a depth of 3328 below the ground level was measured. The well is located SW of "San Pompeo 2" well which reached a high temperature (>420 °C). high pressure (>24 MPa) in the deep part ol'the geothermal field.
Fluid inclusion and hydrothermal mineral data on a quartz-biotite-tourmaline veinlet, found at 3455 below the ground level. indicate the presence of a high salinity (– 32 wt% NaCl equiv.) Li-Na-Cl brine ot magmatic derivation, during the early stage of the geothermal field. Estimated trapping temperatures at lithostatic pressures ranges between 440 and 455 "C. These temperatures are comparable with those furnished by the biotite/tourmaline geotherniometer (~475 °C). Fluorine and chlorine contents of biotite are comparable with those found in biotites of hydrothermal ore deposits and associated acidic intrusives.
Late stage fluid inclusions are characterized by relatively low salinity (0.7-10 wt% NaCl equiv.), trapping temperature around 395-405 °C and the presence of small amounts of CO_2. These temperature values confirm the present high temperature of the deepest part of the geotherinal field which is close to 400 °C.

1. INTRODUCTION

The deepest part of the Larderello geothernial field (3-4.5 km) is characterized by the presence of a widespread thermal metamorphic aureole with an estimated thickness of some hundreds of m (Bertini *et al.*, 1985: Cavarretta and Puxeddu, 1990: Gianelli, 1994). Boron and potassium metasomatism are indicated by the widespread occurrence of small (few mm) biotite-tourmaline veins, which in some cases precede the discovery of granite. micropegmatite and aplite intrusions. The presence of acid igneous rocks has been ascertained in 5 wells so far. and is inferred on the base of a large number of geophysical data (Batini *et al.*, 1983a: Puxeddu. 1984: Gianelli *et al.*, 1994: Gianelli. 1994). Fluid inclusion studies on the hydrothermal mineral assemblages and magmatic quartz from granite samples and high temperature hydrothermal veins revealed the presence of Li-Na-Cl brines of magmatic origin, and C-O-H-N contact metamorphic fluids. These fluids are interpreted to represent the early stage of the hydrothernial circulation of the geothermal system (Valori *et al.*, 1992; Cathelineau et al., 1994). The Carboli area lies SW of the hottest part of the Larderello geothermal field (Fig. 1), where temperatures in excess of 400 °C and genpressurized fluids were found. It is worth mentioning the situation in "San Pompeo 2" well (Fig. 1), where the bottoinhole temperature was hiphcr than 420 "C. Before blow out, the well found a high pressure (>24 MPa) fluid at about 3 km depth (Batini *et al.*, 1983b). In the well "Carboli 11", at 3455 m below ground level (b.g.l.), drilled by ENEL (Italian Electricity Board), an interesting tourmaline. biotite, quartz assemblage was found. In the same well. at 3328 m, a temperature of approximately 427 °C was estimated. The stratigraphy and the temperature data of "Carboli 11" are reported in Fig. 2. "Carboli 11" well is located at a greater distance from the K horizon than "San Pompeo 2" well. The K horizon is a seismic reflector that is thought to be permeated by a saline brine (Gianelli. 1994). The aims of the present paper are: 1) to evaluate the reliability of the thermal profile of the well, on the base of fluid inclusion study; 2) to evaluate the temperature-pressure-compositions condition of formation of the tourmaline-bearing assemblages through fluid inclusion analyses and mineral chemistry studies: to compare the results with those obtained for other deep wells. and to clarify some aspects ofthe water-rock processes occurring in a near-magma environment.

1. STUDIED MATERIALS AKD METHODS

Microchemical analyses of biotite and tourmaline were performed on a Jeol 8600 electron microprobe. Fluid inclusions have been studied in hydrothermal quartz crystals from the "Carboli 11 - 3455" core sample. Microtherniornetric analyses on fluid inclusions were carried out using a Chaixmeca heating-freezing stage (Poty *et al.*, 1976); the stage was calibrated with melting-point standards and natural CO_2 pure fluid inclusions. The accwacy of the measurements was estimated at ±0.2 °C on freezing and ±2 °C on heating

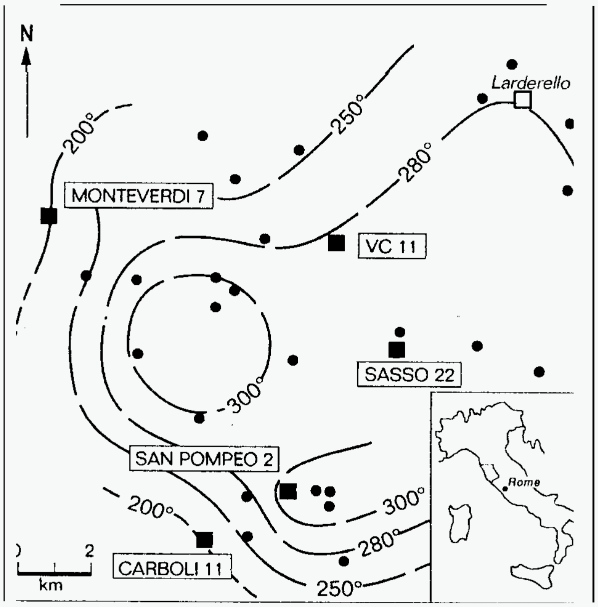

Figure 1. Location of Carboli 11 well in the Larderello field. Isotherms at 2000 m depth, from Bertini et al. (1985). Dots = Wells; Squares = Wells reaching granite and/or thennornetainorphic rocks.

3. RESULTS

3.1 Mineral chemistry and petrographic data

The "Carboli 11 - 3455" core sample is a thermometamorphic quartz phyllite. Small fractures (5-10 mm) displacing the Alpine schistosity of the rock are filled by tourmaline, biotite and quartz. Other hydrotherinal minerals. such as pyrite and plagioclase, were sporadically observed. Tourmaline and biotite replace the syn-metamorphic muscovite extending from the hydrothermal veins. Tourmaline, biotite and quartz seem to be in textural equilibrium.
The chemical composition of the biotite and tourmaline of "Carboli 11 - 3455" are reported in Tables 1A and 1B. For comparison these tables also show the compositions of micas and tourmaline of granite and thennometamorphic rocks from other deep wells. A brief description of the analyzed rocks is given below:

- The rocks of the contact metamorphic aureole are usually phyllite and micashist characterized by the late crystallization of biotite. andalusite. and, in places. corundum (Batini *et al.*, 1993b). Tounnaline with schorl-dravite to schorl-elbaite composition is reported for some hundreds of meters above the granite intrusions (Cavarretta and Puxeddu. 1990). In places few mm thick micropegmatite veins are present (e.g. sample "MV5-3045"). The biotites of the thennometamorphic rocks (Car11 of table 1a) are usually richer in mole fraction of phlogopite (Xphl)than the igneous biotites

(Sug3G, Rad26). The thermometamorphic muscovites (Sug3T, MV5, Pad2) are usually richer in Mg than those of the igneous rocks (Rad30), and still contain an interesting amount of F. Chlorite is a very common mineral in these rocks and shows a ripidolite to daphnite composition.

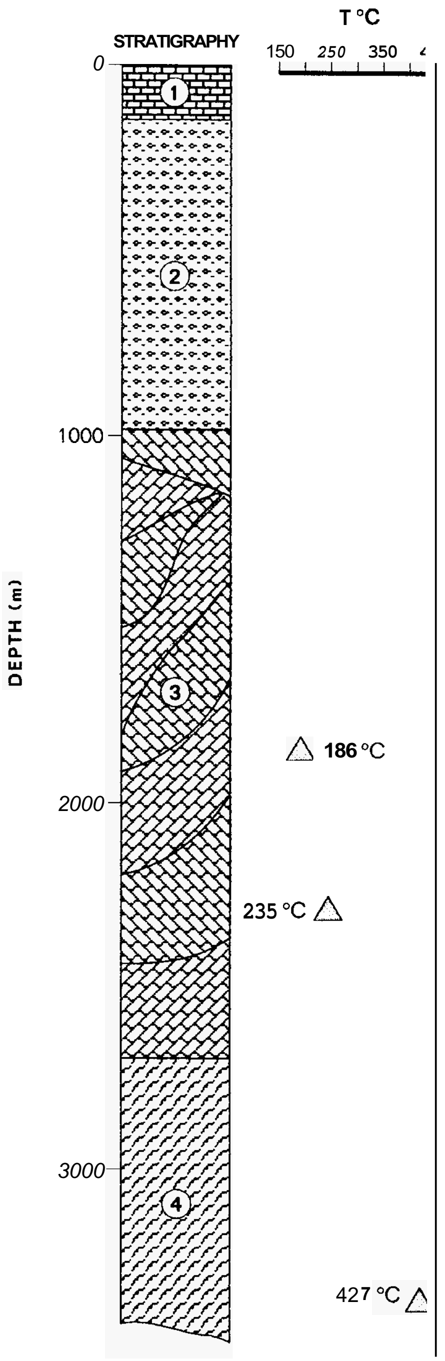

Figure 2. Simplified stratigraphy and temperature data of the well Carboli 11. Depth in m below ground level. Legend: 1) Cretaceous Flysch formations; 2) Middle-Upper Triassic formations; 3) Complex of tectonic wedges, mainly consisting of Triassic units; 4) Paleozoic metamorphic complex.

Chemically, the tourmaline of "Carboli 11" well, and that found in other thennometamorphic rocks, are close in composition to the tourmaline present in the granite dyke of well "VC 11" (Cavarretta and Puxeddu, 1990) and also to some tourmalines of "San Pompeo 2" well, drilled in a high temperature part of the field. The tourmalines consist mainly of the end members dravite, schorl and elbaite. Li content was not analysed, but its presence is suggested by an alkali deficiency and by the vacancy of the Y site (see also Cavarretta and Puxeddu, 1990)

- Granites (quartz, K-feldspar, plagioclase, biotite and ilmenite) are typically peraluminous and characterized by the occurrence of Al-rich minerals, such as primary muscovite, cordierite and andalusite as minor phases. Li (23-38 ppm), B (<20 ppm) and F (660-1100 ppm) data are available for the leucogranitic dyke found in the well "Monteverdi 7" at 3485 m b.g.l. (Cathelineau *et al.*, 1994 and unpublished data). They are comparable with the data of other granite outcrops near the geothermal area. The tourmaline leucogranite "VC 11" 2946 m b.g.l. is likely to be a differentiated product of a peraluminous granite (Cathelineau ***et** al*., 1994). The core samples of granite (Rad26, Rad30 of table 1a and Ib) show a more or less widespread alteration. Biotite is very often chloritized. A granite sample from the well "Sughere 3" (Sug3G) displays secondary chlorite, potassic white mica (sericite) and albite. Microprobe analyses of biotite and primary muscovite of granites reveal significant amounts of F and Cl (Table 1A).

Table 1A. Representative microprobe analyses of biotite and muscovite (wt%) and structural formula on the basis of 22 oxygens. Sug3T and Sug3G = Sughere 3 well (2919); Rad26 = Radicondoli 26b well (4600 m); Car11 = Carboli 11 well (3455 m); Rad30 = Radicondoli 30 well (4230 m); MV5 = Monteverdi well (3045 m); Pad2 = Padule 2 well (2782 m).

	BIOTITES			MUSCOVITES			
	Sug3G	Rad26	Car11	Rad30	Sug3T	MVS	Pad2
SiO_2	35 74	34.56	36.51	46.95	46.70	48.47	46.98
TiO_2	3 58	3 37	1.00	0.00	0 12	0.00	0.00
Al_2O_3	19.58	18.52	19.16	35.48	32.52	34.27	35.42
FeO	19.17	23.26	17.75	1.50	2.50	0.84	1.63
MnO	0.21	0.23	028	0.03	0.00	0.00	0.02
MgO	7.90	5.00	11.55	0.63	1.37	0.89	1.20
CaO	0.05	0.06	0.00	0.00	0.00	0.00	0.03
Na_2O	0.13	0.12	0 21	0.47	0.13	0.13	0.41
K_2O	9.51	8.64	9.35	9.01	10.70	9.18	9.83
F	1.60	1.18	1.56	0.50	0.33	0.08	0.10
Cl	0.13	0.26	0.30	0.00	0.00	0.00	0.03
Si	5.460	5.438	5.530	6.255	6.318	6 441	6.209
AlIV	2.545	2.562	2.471	1.745	1.682	1.559	1.790
AlVI	0.798	0.873	0.771	3.826	3.502	3.809	3.730
Ti	0.414	0.399	0.113	0.00	0.277	0.000	0.000
Fc	2.448	3.061	2.248	0.167	0.283	0.094	1.180
Mg	1.800	1.172	2608	0.126	0.277	0.176	0.237
Mn	0.027	0.030	0.049	0.004	0.000	0.000	0.002
K	1.854	1.735	1.806	1.532	2.015	1.557	1.658
Na	0.039	0.037	0.066	0.122	0.037	0.033	0.237
Ca	0.014	0.010	0.000	0.000	0.000	0.000	0.004
F	0.872	0.588	0.746	0.211	0.330	0.032	0.043

Table 1B. Representative microprobe analyses (wt%) of tourmaline and structural formula on the basis of 24.5 oxygens. Car11 =Carboli 11 well (3455 m), Pad2 = Padule 2 well (2782 m). Rad26 = Radicondoli 26b well (4600 m).

	Car11-1	Car11-2	Car11-3	Pad2	Rad26
SiO2	36.22	36.50	36.38	36.50	36.13
TiO2	0.41	0.36	0.21	0.23	0.65
A1203	32.84	31.04	32.26	34.55	30.42
FeO	6.90	7.64	6.05	7.20	10.83
MnO	0.09	0.10	0.05	0.10	0.09
MgO	6.11	6.52	6.73	4.79	4.91
CaO	0.79	0.96	0.82	0.79	0.46
Na2O	1.72	1.89	1.94	1.23	2.01
K2O	0.00	0.02	0.02	0.00	0.02
F	0.22	0.33	0.14	0.22	0.90
Cl	0.01	0.03	0.00	0.00	0.00
Total	85.31	85.52	84.64	85.19	86.52
SI	5.973	6.058	6.012	5.993	6.060
AlIV	0.027	0.000	0.000	0.007	0.000
AlVI(Z)	6.000	6.000	6.000	6.000	6.000
AlVI(Y)	0.309	0.072	0.292	0.671	0.020
Fe	0.951	1.060	0.837	0.989	1.520
Mg	1.502	1.614	1.661	1.172	1.228
Mn	0.012	0.014	0.007	0.014	0.010
Ti	0.050	0.044	0.018	0.029	0.080
Na	0.551	0.609	0.624	0 393	0.653
K	0.000	0.003	0.004	0.000	0.003
Ca	0.140	0.171	0.146	0.050	0.008
F	0.115	0.176	0.075	0 116	0.480

The fluorine content of biotite is comparable with that of the acidic rocks associated with some porphyry copper deposits (Gunow *et al*., 1980). Apatite analysis revealed a very high F content in these minerals (3.78 wt%), so that it is a fluoro-apatite. The chlorine content is roughly negatively correlated with Xphl in biotite. Chlorine content decreases and Xphl increases in the more altered samples. The fluorine content is positively correlated with Xphl. The primary muscovite composition recalls that of strongly peraluminous granites (Miller *et al*., 1981).

3.2. Fluid inclusions

The microthermometric results are suniinarized in Table 2. On the basis of the microscopic and microthermometric results, we have distinguished four fluid inclusion types, whose characteristics are quite similar to those reported for fluid inclusions observed in other deep wells of the Larderello geothermal field by Valori *et al*. (1992) and Cathelineau *et al*. (1994). Following their nomenclature we identified:

1) Three phase liquid + vapour + halite (L+V+H) inclusions (L'wh). The halite was recognized from its cubic shape and dissolution behaviour during heating (Roedder. 1984). L'wh inclusions are small (5-20 μm) and occur either isolated or in small clusters or in healed fractures, which do not completely crosscut the host crystals. On cooling, L'wh, inclusions show metastable behaviour: many of them never froze or froze partially. Only 10 inclusions freeze between -130 and -80 °C after repeated cooling-warming slow-rate runs. Failure of freezing has been noted in small inclusions containing very saline brines (Roedder. 1984). The frozen inclusions show eutectic temperatures (Te) in the -84 to -69 °C range. suggesting the presence of dissolved LiCl in the fluid. After Te. some crystals. which seems to be hydrates. melt between -62 and -57 °C. Melting temperatures of ice (Tin-ice) were observed after sequential freezing (Haynes, 1985) between -53.9 and -35.5 "C. In a few inclusions an hydrate (possibly hydrohalite) melts within a wide range of temperatures (~ -30/+13 °C). By heating. the NaCI cubes dissolve between 122 and 239 "C, and total homogenization temperatures to the liquid phase (Th_L) occur in a range of 349-393 "C. with an average of about 385 °C. Salinity estimation of L'wh inclusions based on the halite melting temperature (Tmh) in the NaCl-H2O binary system range between 28.7 and 34 wt% NaCl equiv.. with an average of 32 wt% NaCl equiv. (Sterner et al.. 1988). This estimate might not be precise because of the possible presence of LiCl in the solution.

2) L'w two phase (L+V) high salinity inclusions. These inclusions are relatively small (<15 μm) and were found only in one healed fracture. During freezing runs L'w inclusions also displayed metastable phenomena and some of them never froze; only 3 inclusions froze, showing Te between -75 and -66 "C: this indi :ates that L'w may also contain dissolved LiCl, in addition to NaCl. Because of the sinall size ofthe inclusions it was possible to clearly observe only the Tm-ice between -30.0 and -27.2 °C. whereas hydrate crystals should melt before Tm-ice. No other solids were noticed in the fluid after ice melting. From the Tn-ice we estimate an average salinity of 15.7 LiCl wt% equiv. (Linke, 1965). The Th_L of L'w are in the 390'401 °C range, with an average of 397 °C

3) Lw two phase (L+V) low to inoderate salinity inclusions. These inclusions range from 10 to 60 μm in sire and they usually occur along secondary trails. Lw inclusions exhibit Te between -44 and -29 "C indicating that other dissolved salts (such as $CaCl_2$, $MgCl_2$, KCl) may be present together with NaCI. Tn-ice varies between -0.4 and 6.6 °C, yielding a salinity of 0.7/10.0 wt% NaCl equiv. (Hall *et al*., 1988), Th_L are in the range of 358/401 °C.

4) Vc-W two phase (L+V) aqueous-carbonic inclusions. This type of fluid inclusion has variable size (5-100 μm) and occurs in secondary planes. The formation of clathrate during freezing runs indicates that the vapour phase of these inclusions contains CO_2. No liquid CO_2 was observed prior to clathration (– -25 °C), proving that the density of the CO_2 phase is very low (<0.05 g/cm3). The melting temperature of the CO_2 phase ($TmCO_2$) was clearly observed in 23 inclusions and ranges between -57.4 aiid -56.6 "C; in the other inclusions solid CO_2 shows sublimation or was not detected. Clathrate dissociation temperatures (Tdcl) are in the 6.0'10.1 °C range. Such Tdcl is too high for a fluid containing a very low density CO_2 phase (Collins, 1979); however the presence of sinall amounts of other volatile compounds (such as CH_4) may increase the Tdcl. The occurrence of other volatiles is also evidenced by the average $TmCO_2$, which is lower than the triple point of pure CO_2. In few inclusions it was also possible to detect Te (-36/-30 °C) and Tm-ice (-5.0/-2.5 °C). Salinity could not be calculated by the method of Diamond *et al*. (1992) because liquid CO_2 forms at temperature below clathrate nucleation. The estimated salinity from the Tm-ice is 4.1/7.8 wt% NaCl equiv.: because of the presence of clathrate during ice melting these are maximum values. On heating. Vc-w inclusions homogenized either to liquid (Th_L=339/363 "C) or to vapour (Th_V=345/383 °C) or show critical homogenization (Th_C= 357/362 °C). Such behaviour indicates that Vc-w inclusions have a critical density or are close to the critical density. In some cases Vc-W Inclusions belonging to the same secondary trails may display either critical and liquid and/or vapour homogenization. This suggests that the slight density differences between these inclusions may be due to post-entrapment phenomena (necking-down and/or stretching of the fluid inclusion) rather than P-T-composition changes of the hydrothermal fluid. If only H_2O and CO_2 were present in the fluid. we could estimate the molar fraction of the two components from the Th (– 360 "C) of the inclusions with critical composition. In this case the XH_2O is 0.96 and the XCO_2 is 0.04 (Takenouchi and Kennedy. 1964).

4. DISCUSSION

The occurrence of some primary isolated L'wh inclusions in the studied quartz crystals are indicative that these inclusions represent the fluid generating the quartz-tourmaline-biotite veinlet. In contrary. Lw inclusions and Vc-W inclusions are always present in clearly secondary planes and should record late hydrothemial activity. L'w inclusions are of secondary or pseudosecondary origin and do not show clear relationships with the other types of inclusions. We consider that these inclusions were trapped at an intermediate stage between L'wh inclusions and Lw. Vc-W inclusions. Some informations about the chemistry of the early hydrothermal fluid may be inferred from fluid inclusion. In particular L'wh inclusions indicate the presence of a high salinity brine during this stage. Fluid inclusions showing very low Te. such as L'wh and L'w. were found in other deep core samples by Cathelineau *et al*. (1994). In these inclusions. the same authors identified LiCl-hydrates at low temperature by Raman spectroscopy. As in their interpretation of these inclusions, we propose that the L'wh inclusions in the "Carboli 11" well represent a Li-Na-Cl rich brine exsolved from an underlying granite body during the early stage of hydrothermal activity. The Lw and Vc-W inclusions. on the other hand. trapped low density fluids that probably circulated during the late to present-day stage of the hydrothermal system. In particular, the XCO_2 (~ 0.04) of the aqueous-carbonic fluid, trapped in Vc-W inclusions. is consistent with values commonly found in the steam. of mainly meteoric origin. produced by the Larderello wells (Bertrami et. al. 1985). The interpretation of the Li-rich fluid trapped in L'w inclusions is more problematic. One possible genesis of L'w inclusions, which would explain the intermediate salinity of these inclusions. is a mixing process between the high salinity Li-Sa-CI brine and a relatively low salinity fluid. similar to those trapped in Lw inclusions. The absence of Lapour-rich inclusions clearly coeval with L'wh. L'w and Lw inclusions suggests, that boiling did not occur during their trapping. Vc-W inclusions, which are characterized by a critical density. might be trapped at or near the critical point on the solvus curve or above it.

Table 2: Summary of the microthermometric data of fluid inclusions. Abbreviations: Te=first ice melting temperature. $TmCO_2$=CO_2 melting temperature. Tm-ice=final ice melting temperature, Tdcl=clathrate dissociation temperature, Tmh=halite melting temperature. Th=total homogenization temperature, L=homogenization to liquid, V=homogenization to vapour, C=critical homogenization. Number of measurements are given in parentheses: temperatures are in "C.

	Composition		Te	$TmCO_2$	'Tm-ice	Tdcl	Tmh	Th
L'wh	H2O-NaCl-LiCl	range	-84 -69		-53.9/-35 5		122'239	349'393 L
		average			-42 (10)		199 (25)	385 *(31)*
L'w	H2O-NaCl-LiCl	range	-75 -66		-30/-27.2			390/401 L
		average			-28.5 (3)			397 *(5)*
Lw	H2O-NaCl	range	-44/-29		-6.6/-0.4			358/401 L
		average			-3.9 (28)			373 (28)
Vc-w	$H2O-CO_2-NaCl \pm CH_4$	range	-36/-30	-57.41-5h.6	-5.0/-2.5	6.0'10.1		339/383 L/V/C
		average		-57.1 (23)	-3.9 (9)	9.0 (65)		357 (66)

In order to define the temperature of the hydrothermal fluids. represented by the fluid inclusions, we must know the pressure at the time of inclusion entrapment and the isochore followed by the trapped fluid. Representative isochores for the four types of fluid inclusions are shown in Fig. **3.** The isochores for Lwh, L'w and Lw inclusions were constructed in the system NaCl-H_2O on the base of the average Th and salinity (for L'w inclusions we consider the salinity in wt% of NaCl equiv. equal to the wt % LiCl equiv. calculated from Tmi) using the Zhang and Frantz (1987) data. For Vc-W inclusions. we modelled the critical isochore in the system H_2O-CO_2 for a fluid homogenizing at 360 °C from the Bowers and Helgelson (1983) equation. **As** demonstrated by Cathelineau *et al.* (1994), the confining pressure during the early stages of the Larderello hydrothermal system was lithostatic. Thus, if L'wh were trapped under lithostatic conditions the minimum pressure (calculated from the present-day depth and an average density of2.64 g/cm^3) would be –92 Mpa. while the maximum pressure would be ~110 Mpa (assuming an average density of 2.62 g/cm^3, an average erosion rate of 0.2 mm/year and a emplacement age for the hydrothermal activity of 3.8 million years (Del Moro *et al.*, 1982)). These two pressures lead to a temperature range of 4401455 °C for the formation of the biotite-tourmaline-quartz vein (Fig. 3). These values fall between those estimated by Cathelineau *et al.* (1994) for the early fluid inclusions in "VC 11" well (425 ±15 "C) and "Monteverdi 7" well **(490** ±45 "C), but are significantly lower than the values calculated for "Sasso 22" well (630 f60 "C) and "San Pompeo 2" well (670 f25 °C). Temperature evaluation of the early stage geothernial fluid of "Carboli **11",** "Padule 2" and "Radicondoli 26b" wells can be also obtained from the coexisting tourmaline-biotite pair, using the equation of Colopietro and Frieberg (1987):

$$\ln Kd = -3150/T + 4.52$$

where T is in °K and Kd is the Mg/Fe partitioning coefficient between tourmaline and biotite. The average values calculated for "Carboli 11", "Padule 2" and "Radicondoli 26b" samples are 475 °C, 416 °C and 490 °C respectively.

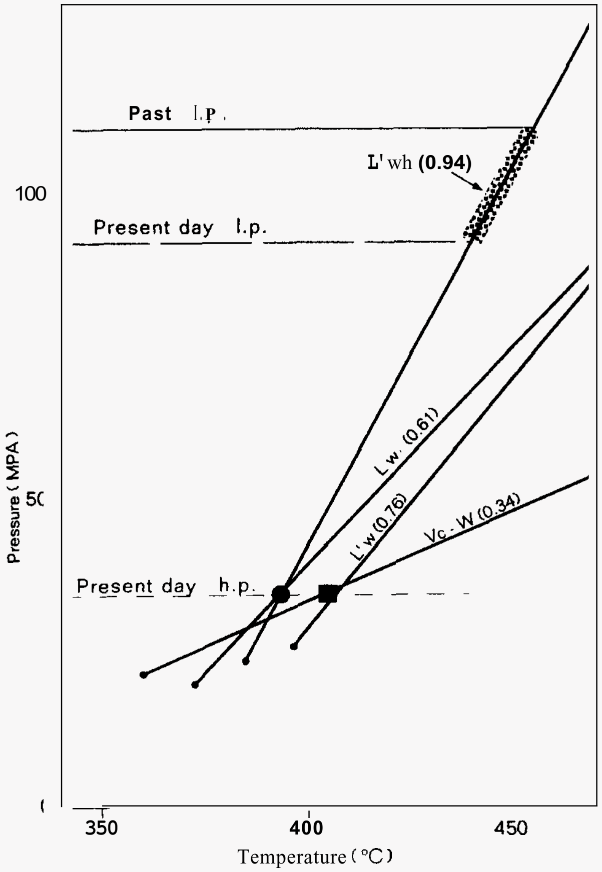

Figure 3. P-T plot showing representative isochores for the four fluid inclusion types found in the "Carboli 11 - 3455" core sample. P-T trapping conditions for L'wh inclusions (stippled area). Lw inclusions (black circle) and Vc-W inclusions (black square) are also shown. In parentheses are reported the bulk fluid densities in g/cm^3; l.p.=lithostatic pressure, h.p.=hydrostatic pressure.

The temperature obtained by means of this geothermometer for the "Carboli 11" well is in relatively good agreement with the trapping temperature (440/455 °C) of the inclusions (L'wh) related to the early hydrothermal stage.

The Larderello geothermal system evolved from lithostatic to hydrostatic and then to vapourstatic conditions with time. We therefore assume that the LA' and Vc-W inclusions were trapped under hydrostatic conditions. In this case the Lw inclusions would be trapped at about 395 "C and Vc-W inclusions at around 405 °C. L'w inclusions may be trapped at intermediate temperature and pressure between lithostatic and hydrostatic conditions.

5. CONCLUSIONS

1) The fluid inclusion thermometric data lead to some interesting considerations on the thermal state of "Carboli 11" well. Three temperature values are available along a depth interval of 1489 m (Fig. 2). Interpolating the temperature values at 1X45 and 2345 m with the trapping temperatures of the Lw (–395 °C) and Vc-W (–405 °C) inclusion, we obtain a temperature gradient ranging from 130 to 140 °C/km. In this case, the value of 427 °C measured from the melting of metallic alloy standards, could be the result of an overestimation. On the other hand, if we accept this value, then we have to admit an increase of the temperature gradient in the deepest part ofthe well, with in-hole temperatures higher than the temperatures of the late stage fluids trapped in hydrothermal quartz. Evidence of recent heating trend has not been found so far in fluid inclusion studies at Larderello. Major increase in the geothermal gradient is not uncommon.

2) Fluid inclusions and mineral chemical compositions permit us to estimate the temperature and composition of the early geothermal fluids. In particular, fluid inclusions indicate that during early hydrothermal stage. high salinity (28.7-34 wt% NaCl equiv.). high temperature (440/455 °C) fluids were circulating, in the deep part of the "Carboli 11" well. High temperature values were also obtained from the tounnaline-biotite geothennometer for the wells"Carboli 11" (475 °C), "Padule 2" (416°C) and "Radicondoli 26b" (490 °C).

Regarding the composition of the early stage geothermal fluid, we would like to focus our attention on the origin of Li, B and halogens. The occurrence of boron silicates at Larderello (tourmaline and the more rare datolite) has been explained by a thermal metamorphic-metasomatic aureole around a granite intrusion (Cavarretta and Puxeddu. 1990). The same origin is invoked by Cathelineau *et al.* (1994) for lithium and fluorine. However. the chemical data for Li and B are few and inconclusive. These authors note that an F and Li enrichment typical of leucogranite differentiates of peraluminous batholiths is not present at Larderello. They assume the presence of a late intrusion with such characteristics somewhere in the field. The best evidence for a magmatic origin for Li is its presence in primary fluid inclusions and the high trapping temperature computed for them.

The presence of fluorine and chlorine can suggest either a magmatic origin (e.g. Kovalenko **et** *al.*, 1984) or a remobilization of metamorphic fluids (Sisson, 1987). We cannot exclude a contribution of halogens from metamorphic fluids pre-existing the granite intrusion. For the micas of the granites and the rocks of the thermometamorphic aureole there is evidence of an increase of F with the phlogopite mole fraction of biotite, as already reported for a number of igneous and hydrothermal biotites (Gunow *at al.*, 1980; Brimhall and Crerar, 1987). On the contrary, the so-called Mg-Cl avoidance (i.e. a negative correlation between Cl content and the Xphl of micas, see Munoz, 1984) is not evident for the analyzed rocks. This could be due to the influence of temperature on the chlorine content of micas. or to the effect of circulation of late hydrothermal fluids. The fluorine content of the biotites of "Carboli 11" well is the highest among the analyzed samples and they plot in the field of the magmatic biotites of granitoids and porphyry copper deposits (compare with Fig. **4** of Gunow *et al.*, 1980). This further supports the hypothesis that the deep rocks of this well interacted with early fluids from an igneous source, with modifications by late fluid circulation.

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