HYDROTHERMAL ALTERATION AND FLUID INCLUSION STUDIES IN THE VULCANO GEOTHERMAL WELLS (ITALY)

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1. INTRODUCTION

The island of Vulcano is the southernmost of the islands forming the Aeolian Archipelago in the Tyrrhenian Sea, north of Sicily (Fig. 1). "La Fossa" is the active crater on the island. Deep geothermal exploratory drilling commenced in the "La Fossa" caldera in the 1980's, after the encouraging shallow exploratory well drilled in the 50s (VU2bis, Sommaruga, 1984). Well VU2bis was a producing well, located on the northern part of the caldera. The maximum temperature encountered in this well is about 200°C at a depth of 200 m. The two deep wells were drilled on the northern (VP-I) and southern (IV-1) parts of the "La Fossa" caldera and reached maximum depths of 1000 m and 2050 m respectively. Directional drilling was also performed in both wells. The maximum temperatures encountered are about 200°C in VP-1 and 400°C in IV-1. It is interesting to note that the down-hole measured temperature in well VP-1 cannot be taken as representative of stable subsurface thermal conditions, since temperatures were recorded shortly before and after an injection test (AGIP S.p.A., 1987). No exploitable fluids were found during drilling.

Numerous studies of the compositions of gases from the fumaroles (Carapezza et al., 1981; Mazor et **al.,** 1988; Martini, 1989) and studies of stable isotopes of volcanic rocks and fumarole fluids (Cortecci et. al, 1993) in the "La Fossa" area suggest that the hydrothermal fluids result from both magmatic fluid and sea water.

The object of the present study is: (a) to unravel the water-rock interaction processes; (b) to gain information on the nature and origin of fluids that circulated through the rocks; and (c) to determine the thermal history of the system.

2. GEOLOGICAL SETTING

The geology of the island of Vulcano has been described in detail by different investigators (Keller, 1980; Frazzetta et al, 1984). **A** simplified geological map of the island of Vulcano is shown in Fig. 1. Recent studies show evidence of the tectonic control exerted by the Eolie-Tindari-Letojanni strike-slip fault in the Vulcano eruptive activity (Barberi et al., 1994). Several phases of activity can be identified in the volcanic history of this island. These phases are: (a) building of the "Vulcano Primordiale" stratocone (120-90 ka, De Astis et al., 1989) ending with the "Caldera del Piano" collapse; (b) partial upfilling of the caldera structure by mostly effusive products (90-70 ka, De Astis et al., 1989); (c) extensional tectonism leading to the collapse of the northern part of the Piano, allowing basaltic and trachybasaltic magmas to rise along fissure structures (50-25 ka, De Astis et al., 1989); (d) emplacement of the Mastro Minico-Lentia acid complex and collapse after 15 ka (De Astis et al., 1989) forming the "Caldera della Fossa" structure; (e) infilling of the caldera depression and building of the "La Fossa" volcano after the eruption of the Roia lava flow (14±6 ka, Frazzetta et al., 1984). The volcano consists mostly of pyroclastic products. The last eruption occurred during 1888-90. The eruption was fed by a magma chamber reduced in size (<< 1km^3) and located at about 2-3 km depth in the pre-volcanic basement (Clocchiatti et al., 1993).

Direct information on the subsurface formations of the "La Fossa" caldera has been obtained from the deep wells. The stratigraphic sequences are shown in Figs. 2 and 3, and can be summarized from top to bottom as follows (Faraone et al., 1986; Gioncada and Sbrana, 1991): (a) submarine hyaloclastitic and lava products filling the "La Fossa" caldera depression, that are found till depths of about 600m in VP-I and 200m in IV-1; (b) Lentia trachytic and rhyolitic lava flows (VP-1); (c) "Vulcano Primordiale" lava flows (IV-1); (d) monzodioritic intrusive rocks (IV-1).

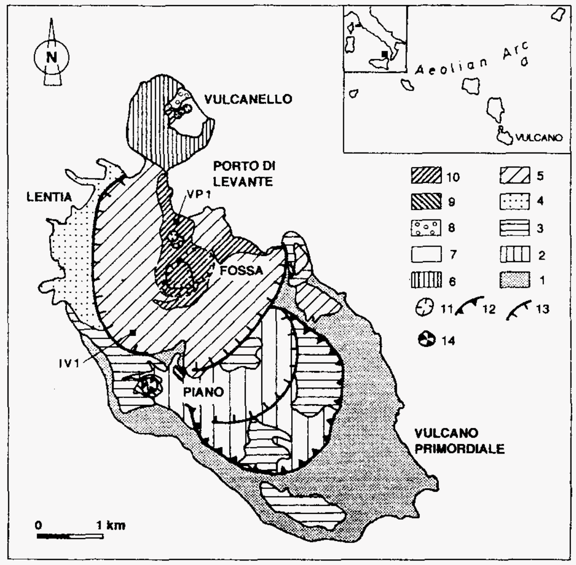

Fig. 1 - A simplified geological map of the island of Vulcano (after Keller, 1980, modified). LEGEND: 1 - Vulcano Primordiale lavas and pyroclastics (trachybasalts and trachyandesites). 2 - Piano caldera filling deposits. (tephrites and trachyandesites). 3 - Welded scoriae blankets (basalts and trachybasalts). 4 - Lavas and pyroclastics of the Lentia complex (latites to rhyolites). 5 - Pyroclastics and lavas of the Fossa cone (latites to rhyolites). 6 - Lava flows of Vulcanello platform (leucit-latites). 7 - Pyroclastics of Vulcanello cones (Lc-latites and trachytes). 8 - Roveto lava flow (trachytes). 9 - Fossil hydrothermal zones. 10 - Active hydrothermal zones. 11 - "La Fossa" and "Vulcanello" crater rims. 12 - Piano caldera rim. 13 - Extensional faults of phase (c) and "La Fossa" caldera border faults. 14 - Phreatic crater west of "Monte Saraceno".

3. SURFACE EVIDENCE OF HYDROTHERMAL ACTIVITY

The geological investigation of the island gave evidence for the existence of two phases of hydrothermal activity (fossil and active; Fig. 1). The fossil hydrothermal system is mainly located in the "Monte Saraceno" zone, where surface acid sulphate alteration is strongly developed. It affects the "Spiaggia Lunga" deposits which have yielded an age of 10 to 25 ka (Keller, 1980). A phreatic explosion crater has been found on the western flank of "Monte Saraceno' associated with phreatic breccias. The phreatic crater is related to this hydrothermal phase. The active hydrothermal system occurs within the "La Fossa" caldera and therefore developed in the last 15 ka. It is characterized by surface acid sulphate altered rocks containing natroalunite, native sulphur, kaolinite and opal. At present, intense fumarole activity affects the beach of Porto di Levante and the entire crater area.

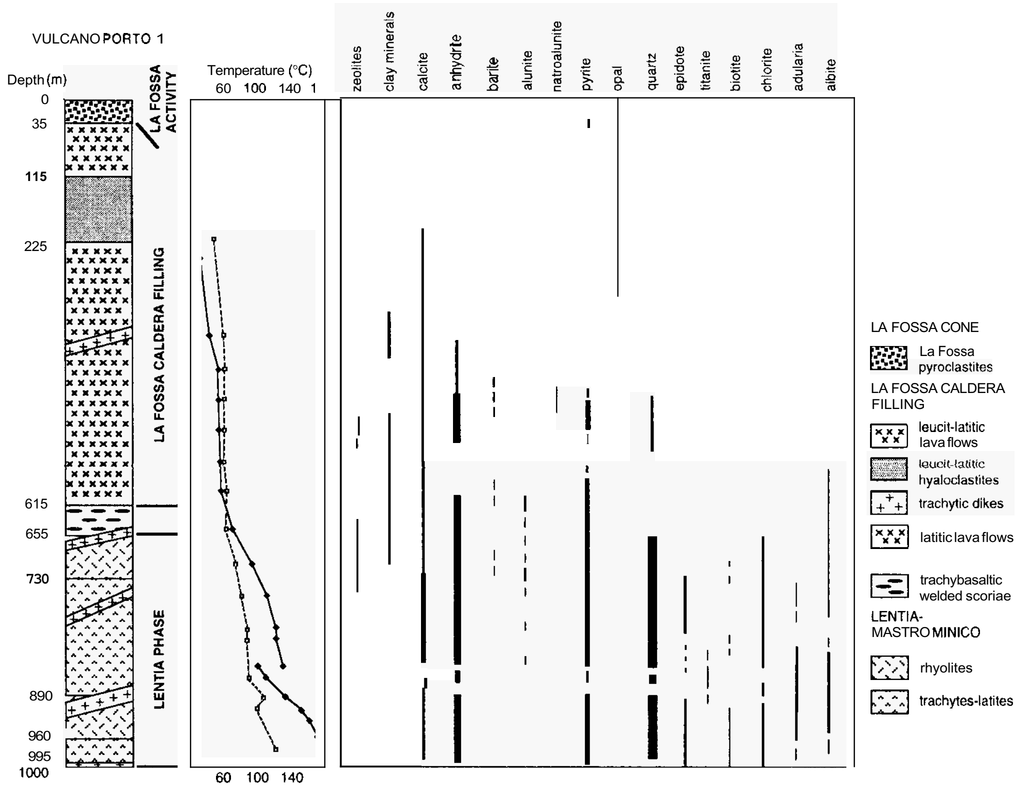

Fig. 2- Stratigraphic sequence, down-hole measured temperature (T°C) and distribution of alteration minerals in the deep exploratory well "Vulcano Porto 1" (VP-1). Open squares=temperature profile before injectivity test; dots=temperature profile after injectivity test. Dashed lines refer to rare occurrences of minerals; thin lines=abundant; thick lines=more abundant.

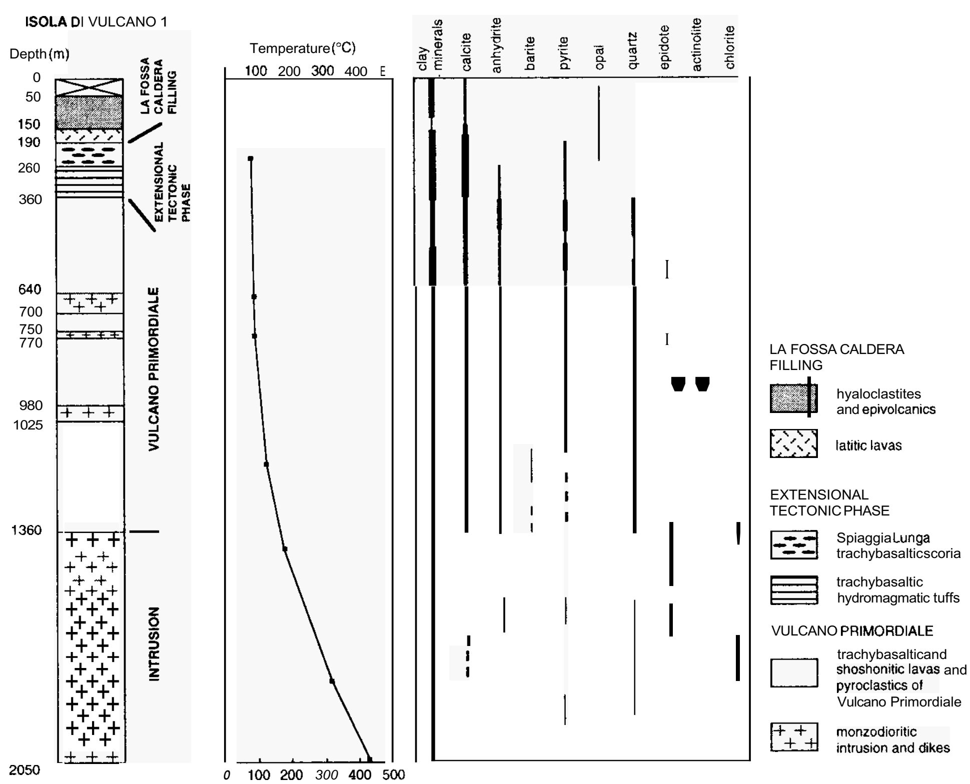

Fig. 3 - Stratigraphic sequence, in-hole measured temperature (T°C) and distribution of alteration minerals in the deep exploratory well "Isola di Vulcano 1" (IV-I). Dashed lines refer to rare occurrences; thin lines =abundant; thick lines=more abundant. (modified from Faraone et al., 1986).

4. ANALYTICAL METHODS

The study of the alteration minerals was conducted on cuttings, recovered from the wells, using petrography, X-ray diffractometry and SEM-EDS analysis. Microthermometric analyses were carried out on hand-picked unpolished anhydrite crystals from well VP-1 at depths of 615m, 800m, and 900m, using a heating/freezing CHAIXMECA stage (Poty et al., 1976) at the International Institute for Geothermal Research (IIRG). Owing to the small size of most inclusions few freezing measurements were obtained. Attempts to determine the temperature of the first melting (T_{mf}) were generally ambiguous and restricted only in a few approximate determinations.

5. ANALYTICAL RESULTS

5.1 Alteration mineralogy

Among the many factors controlling the formation of the alteration minerals, the predominant role at Vulcano is played by temperature, original rock-type and composition of the fluids. The alteration process takes place by means of replacement of the primary minerals as well as direct deposition from the fluids as vein, cavity and vesicle fillings.

The stratigraphic sequences and distribution of alteration minerals in wells VP-I and IV-1 are depicted in Figs. *2* and 3 respectively. Two types of hydrothermal regimes are observed in the Vulcano wells. These are: (i) acid-sulfate alteration characterized by natroalunite, alunite, kaolinite, opal, and pyrite, and (ii) neutral pH alteration assemblages characterized by quartz, calcite, anhydrite, barite, illite, epidote, adularia, albite, chlorite and other clay minerals.

The distribution of clay mineral assemblages and measured isotherms for wells VP-1 and IV-I are shown in Fig. 4. Clay minerals data for well IV-1 are modified from Morelli (1983) based on the petrographic observations and X-ray diffraction analysis. In these wells, the sequence of the clay mineral assemblages in order of increasing depth are characterized by: (i) smectite; (ii) mixed layer clays (illite-smectite); (iii) vermiculite-chlorite (corrensite), kaolinite and illite; and (iiii) illite-chlorite,

Although alteration in well IV-I is largely hydrothermal, a contact metamorphic aureole was also observed. This metamorphism was recognized along intrusive contacts where biotite, tremolite-actinolite and garnet were found to be common alteration minerals in association with epidote, illite and chlorite.

5.2 Fluid inclusions

Inclusion types
Both primary and secondary inclusions were recognized (Roedder, 1984). Most of the measured fluid inclusions appeared to be secondary or pseudosecondary, occurring along healed microfractures (Fig. *5)*. Both primary and secondary inclusions were generally small in size, ranging from 5 to 30 μm with rather elongated and cylindrical shape. The inclusions in all samples were predominantly two aqueous phases (L + V) with a liquid fraction of 0.8 to 0.9. However, there were also monophase inclusions (either liquid- or vapour-rich) that could be possibly due to necking down or leakage phenomena, which occur frequently in anhydrite crystals (Roedder, 1984).

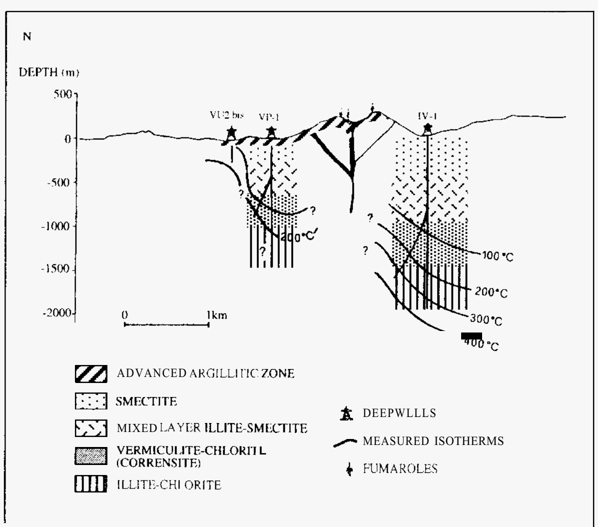

Fig. 4 - Clay mineral distribution zones and measured isotherms in wells VP-1 and IV-1.

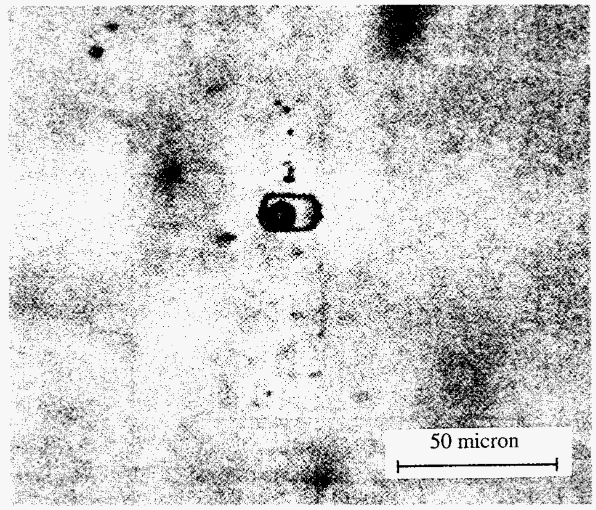

Fig. 5 - Photomicrograph of secondary inclusions along healed fracture in anhydrite crystal from 800m (VP-1) sample.

Microthermometric results
The microthermometric data from well VP-1 (summarized in Table 1) is analysed below in terms of "heating" and "freezing". The fluid inclusion data for well IV-I, which are discussed below, are taken from Cavaretta et. al. (1988).

• Heating data- The widest homogenization temperature (T_h) range and its bimodal frequency distribution (615m and 800m) reflect different generations of inclusions possibly, either the result of necking down or leaking. The frequency distributions of T_h for inclusions of well VP-1 at a depth of 615m, 800m and 900m are shown in Fig. 6a. A total of 122 homogenization temperatures were measured on liquid rich inclusions. All homogenized to the liquid phase. Assuming that pressure is hydrostatic and there has been no change of the water table since the time of trapping, the applied pressure correction is <10°C and the T_h is assumed to be the true trapping temperature.

• Freezing data- The first ice-melting temperatures (T_{mf}) range from -3.5 to -19.7°C indicating that the fluids can be modelled in the NaCl-H_2O system. Since the inclusion fluids exist in anhydrite, they must also be saturated with respect to $CaSO_4$. Therefore the fluid composition might include Ca as well as Na. The final ice-melting temperature (T_{mi}) values for inclusions fall within the range of -1.1 to -5.3, corresponding to apparent salinities of about 1.8 and *8.2* wt% NaCl eq. (Potter, 1978; Table 1). The frequency distribution of ice-melting temperatures (T_{mi}) for inclusions from well VP-I at depths of 615m, 800m and 900m are shown in Fig 7. Phenomena related to the presence of CO_2, such as clathrate formation (T melting>0°C) and CO_2 melting (-56.6°C) were not observed. During freezing runs of the anhydrite crystal, minerals were occasionaly noted inside the inclusions which might be due to retrograde dissolution of the inclusion walls and precipitation of crystals of gypsum(?).

Table 1 - A summary of the microthermometric data. D=depth; Th=homogenization temperature; Tms=down-hole measured temperature; ΔT=Tms-average Th; Tmi=ice-melting temperature; n=number of measurements; An=anhydrite; apparent salinity expressed as wt% NaCl equivalent.

			T_h (°C)			
well	D (m)	Host	range	average (n)	T_{ms} (°C)	ΔT (°C)
VP-1	615	An	121.9-304.3	241 (41)	52	-189
VP-1	800	An	176.6-304.8	234 (36)	110	-124
VP-1	900	An	199.9-308.5	226.3 (45)	140	-86.3
			T_{mi} (°C)		Apparent salinity	
well	D (m)	Host	range	average	range	aver.
VP-1	615	An	(-1.1) to (-3.6)	-2.35 (41)	1.8-6.1	3.74
VP-1	800	An	(-1.4) to (-4.3)	-2.98 (36)	2.3-6.8	4.81
VP-1	900	An	(-1.7) to (-5.3)	-3.86 (37)	2.8-8.2	6.08

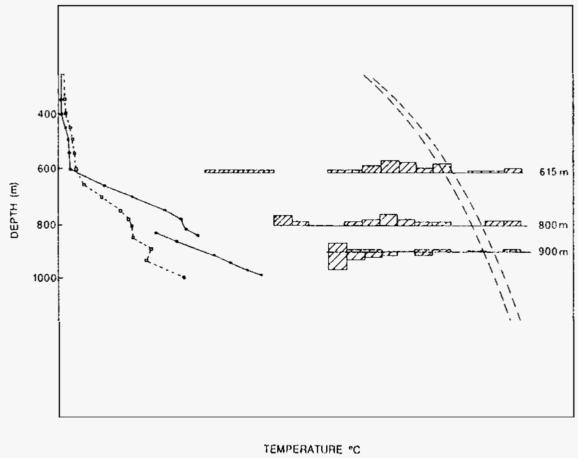

Fig. 6a - T_h, boiling point curves and thermal profile comparison for well VP-1. Open squares with dashed line=temperature profile before injectivity test; dots with heavy line=temperature profile after injectivity test. Dashed lines 1 and 2 refer to: line I, boiling point curve for pure water (B.P.C.W.), and line 2, B.P.C. for a mixture of NaCl-H_2O with a NaCl content of 5 wt% (after Haas, 1971). The NaCl content (*5* wt%) is taken as the average salinity of the fluid based on the measured T_{mi} (See Table 1).

6. DISCUSSION AND CONCLUSION

6.1 Water-rock interaction processes

Two types of hydrothermal mineral assemblages were recognized in the Vulcano wells. One group consists of alunite or natroalunite, kaolinite, opal and pyrite (acid-sulphate alteration type) whereas, the second group is represented by calcite, anhydrite, barite, illite, adularia, albite, quartz, epidote, chlorite and other clay minerals (neutral alteration type). These types of mineral assemblages are similar to those found in the Waiotapu geothermal field, New Zealand (Hedenquist and Browne, 1989) and in the Tongonan and Palinpinon geothermal fields, Philippines (Reyes, 1990) among others. Neutral pH alteration assemblages could be formed by hot, near neutral pH alkali chloride fluids while acid alteration is formed by the passage of low pH, high sulphur-bearing magmatic fluids. Such acid sulphate alteration likely result from the formation of sulfuric acid through condensation of steam and H2S in an oxidizing environment. Alteration occurs as the fluids percolate downward or laterally.

A comparison of alteration mineral geothermometry with the present-day down-hole temperatures shows evidence of the existence of higher temperature fluids in the past. In these wells, instability condition of the key hydrothermal minerals (epidote) was assumed. The assumption is based on textural evidence, such as substitution of one mineral phase by another phase or by taking into account experimental data on mineral stabilities and by making comparison with data from other geothermal fields. The replacement of high temperature mineral assemblages (e. g. epidote, adularia) by low temperature mixed layer minerals (smectite, vermiculite-chlorite) might indicate the cooling condition of the system, even though the down-hole measured temperature in well VP-1 is not representative of stable subsurface thermal conditions. The occurrence of epidote in well VP-1 and in the upper parts of IV-1 (500-1200m) at a temperature less than 200°C is not in good agreement with experimental results (Liou et. al., 1983) and other geothermal fields like Cerro Prieto (Bird et. al., 1984) and Larderello (Cavarreta et al., 1982) where the epidote first appears at a temperature >230°C. This implies significant cooling has occurred.

6.2 Nature and origin of the fluids

The microthermometric data from the Vulcano wells indicate a wide variation of temperatures and fluid salinities (Figs. 6a, 6b, 8). In well VP-1 and at the upper level of IV-I, the temperatures recorded by inclusions are found to be generally higher than the present temperatures. The fluid inclusion trapping temperatures (>225°C) are consistent with the stability condition of high temperature minerals (e.g. epidote) which are found as coexisting phases with anhydrite crystals. Besides, the same temperatures were indicated by the isotope equilibrium of anhydrite and pyrite (225°C±26°C; Cortecci, personal communication) measured on the same sample.

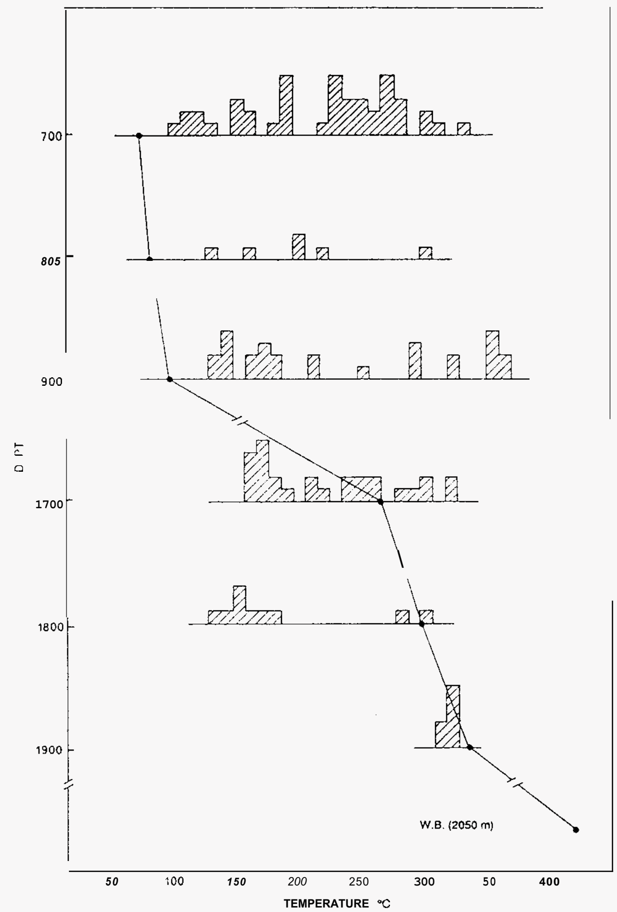

Fig. 6b - T_h and thermal profile comparison for well IV-1 (after Cavarretta et al., 1988).

Homogenization temperature vs salinity data from well VP-I is shown in Fig. 8. The T_{mi}-T_h distribution indicates a dilution between groundwaters and a saline fluid. Fluid inclusions with higher salinity (~8wt% NaCl equiv.) could be derived from magmatic fluids and/or as a result of interaction of fluid with the host rock. On the other hand inclusions with moderate salinity (almost comparable with sea water) could be originated from sea water. Inclusions with lower salinity likely result either from a dilution process where saline magmatic and/or sea water mixed with meteoric water, or as a result of steam condensates from shallower levels. This interpretation is also supported by numerous studies of stable isotopes of volcanic rocks and fumarole fluids (Cortecci et.al, 1993) and studies of compositions of gases from the fumaroles (Carapezza et al., 1981; Mazor et al, 1988; Martini, 1989). However, Bolognesi and DAmore (1993) proposed that the hydrothermal system in this area is mainly influenced by magmatic and meteoric waters, with no contribution of sea water. The presence of a low temperature aquifer shallower than 600 m can be inferred from the thermal logs of the two wells (convective region in fig. 2 and 3).

6.3 Remarks on the hydrothermal evolution of the system

Evidence of a cooling trend in the wells VP-1 and at the upper part of IV-I is furnished by comparison of the temperature-depth profile to fluid inclusion data where present temperatures are found to be at least 100-180°C lower than during fluid inclusion formation (Fig. 6a and b). Besides, evidence for cooling is also registered by the occurrence of key hydrothermal minerals such as epidote at a measured temperature lower than 200°C and replacement of propylitic paragenesis by low temperature clay minerals.

This cooling trend is postulated to be a) due to the incursion of the cooler fluids and b) self-sealing processes which led to reduction of permeability and prevent the circulation of high-temperature fluids to the system. Possible cold water inflow is also indicated by the presence of Mg-rich minerals such as vermiculite. Clear evidence of cooling has also been reported in other geothermal fields like Broadlands, New Zealand (Hedenquist, 1992); Palipinon,

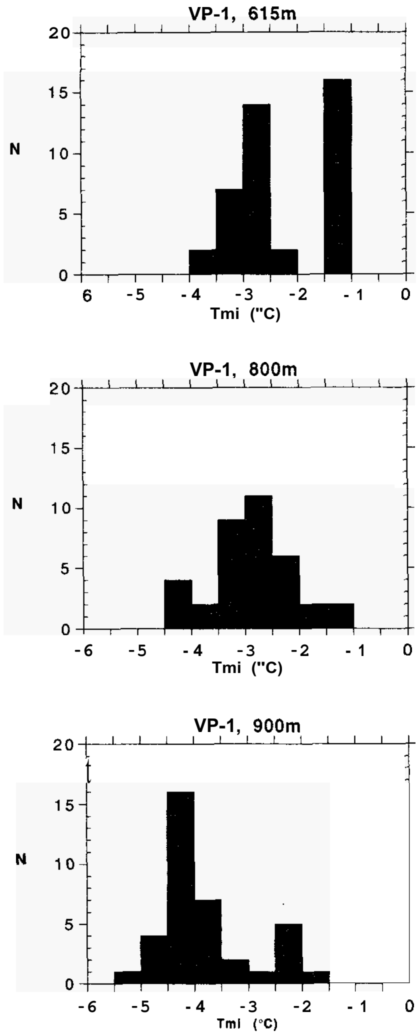

Fig. 7 - Frequency distributions of melting ice temperature (T_{mi}) of primary and secondary inclusions of well VP-1.

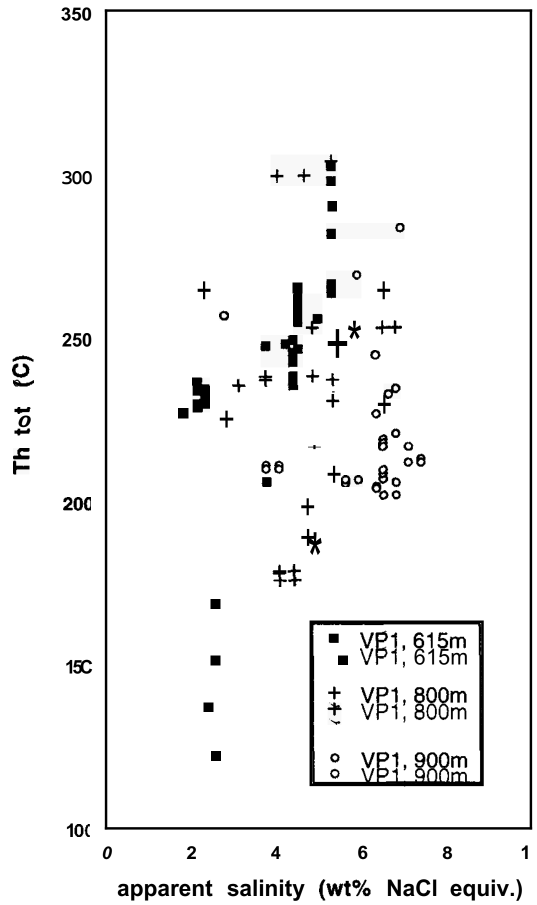

Fig. 8 - Apparent salinity and Th relations for secondary and primary fluid inclusions from well VP-1.

Phillipines (Scott, 1990), Krishmi, Japan (Taguchi and Hayashi, 1983) and the Valles Caldera, New Mexico (Hullen and Neilson, 1986).

Evidence for heating has been found at the deeper levels of IV-1 (1400-2050m) where the present day temperature is found to be higher than or equal to the trapping temperature of the inclusions (see fig. 6b). Heating has also been reported in other geothermal fields, for example at Tongonan, Philippines (Reyes, 1990) and Langano, Ethiopia (Gianelli and Teklemariam, 1993).

Based on these data together with the geological evolution of the island, an interpretation for the thermal history of the system can be proposed as follows. The fossil hydrothermal and thermometamorphic halo observed in the upper part of well IV-1, where cooling occurred, may be related to the superficial fossil hydrothermal alteration found at "Monte Saraceno" whose age is estimated at 15-25 ka, since they affect formations of this age. The hydrothermal pulse producing the observed fossil alteration may be related to the emplacement of the intrusion encountered in the lower part of well IV-1, probably occurred around 50-25 ka ago (Gioncada and Sbrana, 1991). The heating in the lower part of well IV-1 may be presently produced by the active magmatic system at "La Fossa".

The active hydrothermal system present in the Fossa area affects the volcanic units of Lentia, Fossa caldera infilling and Fossa cone, suggesting an age younger than 15 Ka. Considering the magmatic history of La Fossa (Clocchiatti et al., 1994), a release of magmatic fluids to the hydrothermal system might have occurred in relation to the volcano-tectonic activity and to the evolution of the magmatic reservoir. For example, in the 6th century a strong hydrothermal pulse has developed at La Fossa in correspondence to a shallow intrusion and differentiation of magma, leading to phreatomagmatic-hydrothermal explosive activity (Gioncada et al., 1994).

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