

## A GEOLOGIC, HYDROLOGIC AND GEOCHEMICAL MODEL OF THE SERRAZZANO ZONE OF THE LARDERELLO GEOTHERMAL FIELD

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### INTRODUCTION

The large number of nonproductive wells lying along the northern and western margins of the Larderello field have indicated some boundaries of the productive area but have also prevented us, so far, from fully understanding the phenomena controlling the behavior of the geothermal system in these areas.

In 1980 ENEL re-opened some wells that had been shut-in immediately after drilling, thus offering us the possibility to complete the geochemical picture by means of numerous samplings of steam, gas and water in both productive and nonproductive wells. Some recent physical parameters measured in nonproductive and abandoned wells also helped in further defining the hydrogeological and thermal situation.

### GEOCHEMICAL STUDY OF THE GEOTHERMAL FLUIDS IN THE SERRAZZANO AREA

This study covered the Serrazzano area and most of the southwestern sector of the Larderello field, as shown in Figure 1. The fluids from the wells in this zone have an extremely varied geochemical composition. The study was directed at individuating the recharge mechanism prevailing in the area (local infiltration, regional water circulation, steam from high pressure zones, condensate re-evaporation, etc.) and at comparing spatial variation in composition with the results of the Raleigh condensation model.

Wherever possible we used the average values of the period 1971 through 1978 for the wells joined to the distribution network. The wells joined to the distribution network in the intensely drilled zone, all of which are pre-1950 bores, were considered to give a gas/steam ratio of the order of 20 Nl/kg. This value is the maximum for the last 15 years and also the norm in the 1950's. During the last ten years the gas/steam ratios in the zone have, in fact, been seen to decrease slightly. The gas/steam value for the Ciecciae well is that of the 1950 period (25 Nl/kg).

#### Geographic trends in steam composition

The distribution of steam composition in the Larderello field is usually clearly defined (Celati et al., 1973; Panichi et al., 1974; D'Amore et al., 1977; D'Amore and Truesdell, 1979). With the exception of the zones next to the recharge areas, the concentrations of the noncondensable gases generally increase from the center of the field outwards; the concentrations of the species more soluble in the liquid phase ( $^{180}$ ,  $H_3BO_3$ ,  $HCl$ ), on the other hand, decrease in the same direction. These distribution trends of the chemical species suggest a lateral flow of steam from zones in which steam of deep origin forms and rises, towards the margins, with a partial condensation and depletion of the species that are more soluble in the liquid phase. Figures 2, 3, 4, and 5 show the spatial distributions in the study area of  $H_3BO_3$ ,  $HCl$ ,  $^{180}$ , and the gas/steam ratio (90-98 per cent of which is  $CO_2$ ). Ammonia presented no clear geographic distribution, although the lowest recorded values (150 ppm) were found in the central zone of the study area (Val de Cornia) and around VC/10 well.

These four parameters ( $CO_2$ ,  $H_3BO_3$ ,  $Cl$ , and  $^{180}$ ) have clearly defined spatial distributions, especially in the northern part of the study area. The distributions were interpreted by means of a simple physical model based on a Raleigh's condensation process. The model was successfully applied in the "classic zone" of the Larderello field (D'Amore and Truesdell, 1979). This model traces an appropriate flow-path for the fluid coming from one or more main sources. The heat loss in the upper part of the reservoir leads to condensation of part of the steam; while the condensate is drained downwards, the residual steam continues to flow towards the margins of the reservoir. In the unexploited state the condensate flows slowly down a hydrologic gradient to the center and is revaporized.

Figure 6 is based on analysis of the trends of these four parameters along the flow line (wells VC/10, Grottitania, densely drilled area, Cioccaie, Pozzaie 2, no. 8, no. 10, no. 14) represented by the A-B line of Figures 2-5. The trends are in excellent agreement with the theoretical trends (Figure 6, D'Amore, Truesdell, 1979). They suggest that the steam coming from one major feeding source in the southeast undergoes progressive condensation, reducing the less volatile elements of the residual fluid and increasing the more volatile or lighter components. In other words, the fluid moves from a deeper, high pressure zone along the upper margin of the reservoir, dissipating heat through the cover, which gradually becomes thinner the further the steam flows on.

However, condensation does not appear to keep the temperature of the residual steam at constant values in this area, considering the temperatures calculated at well-bottom. The initial values of about 260°C become about 200°C in the densely drilled zone. Figure 7 was drawn from the distribution constants at 230°C. However, the variations in these constants, between 260° and 200°C, are of no great significance compared to the uncertainties of the data used.

The A-B flow line (from well VC/10 to no. 14) was chosen on the basis of the permeability variations, the highest permeability being in the area with the structural high of the reservoir (Celati et al., 1975). From the distribution of the low permeability wells (Figure 1) we obtain a corridor which was then chosen as the probable main flow-path of the steam.

The mathematical basis of Raleigh's condensation process is quite simple (D'Amore and Truesdell, 1979). The condensate in this process is continually removed as fast as it appears, so that the residual steam becomes richer or poorer in certain chemical and isotopic species as the initial mass of steam gradually decreases. The theoretical equation that can be used for each species is:

$$C/C_0 = (m/m_0)(1/K-1) \quad (1)$$

$m/m_0$  represents the fraction of residual steam, equal to zero for 100 per cent condensation.  $C/C_0$  is the increase or decrease in the residual steam concentration of one species with respect to the initial value  $C_0$ .  $K$  is the distribution constant between steam and liquid for each species. The following equation was used for  $\delta^{180}$ :

$$\delta - \delta_0 = 1000 (m/m_0)(\alpha-1) - 1 \quad (2)$$

where  $\alpha$  is the fractionation factor between steam and liquid.

The overall agreement between the observed and calculated trends show that Raleigh condensation along the selected steam flow path can probably explain the trend of  $\text{CO}_2$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Cl}$  and  $\delta^{180}$ . The  $\text{NH}_3$  trend is not shown in Figure 7 as it is nearly flat. However, it should be noted at this point that the  $\text{NH}_3$  content of the steam is strongly dependent on the pH value of the condensate liquid. With a pH between 5.8 and 5.2, and a temperature between 200° and 250°C about half of the ammonia is in ionic form ( $\text{NH}_4^+$ ) and remains trapped in the liquid. The pH of the liquid forming during real condensation is actually an unknown. We can only hypothesize that, in a rapid condensation simultaneous with an increase in  $\text{CO}_2$  pressure, the pH values in the condensate become so low as to camouflage any significant increase in the  $\text{NH}_3$  content of the steam in the area north of Serrazzano. This phenomenon will be studied later in greater detail.

Figure 8 shows the  $\delta^{180}$  trend versus  $\delta D$  in some wells of the study area. Analysis of Figure 8 leads us to distinguish between the various wells; Group A, including VC/10, is characterized by primary steam at 250-260°C. Groups B and C, on the other hand, probably contain D- and  $^{180}$ -depleted fluids caused by condensation (non-isothermal). The slope of the line indicates that condensation took place at temperatures of less than 220°C.

The extremely positive  $\delta^{180}$  values (+10 to +12) of the reservoir waters taken from the nonproductive wells in the northern margin of the field (wells Serra, no. 12) exclude the possibility of this fluid feeding the productive wells of Serrazzano. If these waters did contribute to the steam produced, then  $\delta^{130}$  values in the Serrazzano field would be far more positive. These waters probably consist of the residual fluid of a long boiling process within the bore, with little recharge from the reservoir water because of the very low local permeability of the formations.

The fluid from Serrazzano Sperimentale well, which lies within the densely drilled area and is much deeper than the surrounding wells, has a higher gas/steam ratio (24 Nl/kg), more than 800 ppm of  $\text{H}_3\text{BO}_3$  and about 10 ppm of  $\text{HCl}$ . This confirms that condensation takes place at the top of the reservoir where the species in question reach new equilibria.

The gas in the study area is usually far more radioactive (about 5 times as much) than in the zone of well VC/10 (D'Amore, 1975). Higher radioactivity could simply be due to stronger emanating power of the rock, together with the presence of water in the liquid phase (D'Amore et al., 1976). The latter could also have formed from the same condensation phenomenon, followed, at different times and perhaps even in different places, by re-evaporation.

#### Temperature evaluation of the area based on gas composition

A semi-empirical geothermometer was applied in the study area, based on the  $\text{H}_2$ ,  $\text{H}_2\text{S}$  and  $\text{CO}_2$  concentrations in the dry gas and on the  $\text{CO}_2/\text{H}_2\text{O}$  ratio in the fluid. A more detailed description of the theoretical and empirical basis of this geothermometer will be given in a separate report. However, the main principles are as follows:

Concentrations of  $\text{H}_2$  and  $\text{H}_2\text{S}$  have been noted to vary with respect to the gas/steam ratio as a hyperbolic function in the case of wells with similar temperature (between 240 and 260°C) and different total gas concentrations in the fluid. The geothermometer keeps the calculated temperature at a constant value when there is an increase in the gas/steam ratio and corresponding decrease in the  $(\text{H}_2+\text{H}_2\text{S})/\text{CO}_2$  ratio.

If the gas/steam ratio and the H<sub>2</sub> and H<sub>2</sub>S concentrations decrease simultaneously, the reservoir is in the cooling phase (usually because of dilution with steam from recent meteoric waters). The geothermometer used is:

$$\log(H_2/CO_2) + \log(H_2S/CO_2) + 1.25 \log(NlCO_2/kgv) = 13.87 - (6935/T) - 0.79 \log T$$

The spatial distribution of the calculated temperatures was used to construct Figure 9, which shows the calculated temperature trends. The calculated temperatures in the northern margins of the study area are about 30 degrees higher than the values calculated at well-bottom. This suggests that cooling is fast enough to prevent any rapid re-equilibration of the reactive species H<sub>2</sub> and H<sub>2</sub>S.

#### Further results of the hydrogeological and thermal surveys

The new temperature and water-level data from wells on the northern margin of Serrazzano have led to a reconstruction of the piezometric surface on this margin and of the temperature trend along a NW-SE cross-section of the field. Previous piezometric surfaces have referred only to small areas northwest of Serrazzano and Larderello (Celati et al., 1975). Using a few data on the northern part of Serrazzano, an attempt made to correlate the various zones produced the trends shown in Figures 10 and 11. Assuming the level data as reliable, we note that the piezometric surface is characterized by an isolated relative high, corresponding with the northern margin of the Serrazzano productive area. The reservoir in this zone has a very low permeability and temperatures are relatively low. There being no evidence of surface infiltration in the area of the high, we can only presume that the low permeability formations acted as cold barriers and, consequently, as condensation zones for all the nearby hot areas. These formations are, in fact, little affected by fluid circulation and have remained colder during the formation of the field.

These hot areas could be represented by the VC/10 zone, in the western part of Larderello, and the Lustignano-Canneto zone, west of Lustignano and Serrazzano. This second zone was included as past data and recent drilling results have identified it as containing a vapor-dominated system. This hypothesis is backed by the decrease in water levels across the zone.

The isotherms in the central part of the section have more or less the same trend as the top of the reservoir, but clearly decrease on the northwestern and southeastern margins. This phenomenon is much stronger in the southeastern zone, and the cooling could be attributed to the vicinity of wide absorption zones of meteoric waters. On the northwestern margin, on the other hand, where the phenomenon is less marked, the cooling could partly be ascribed to a limited infiltration through the ophiolites and underlying limestone flysch; but the main cause is the low permeability of the reservoir formations which, immediately north of the Serrazzano structure, are made up predominantly of phyllites.

#### CONCLUSIONS

The geochemical study of the northern margin of Serrazzano leads to the following conclusions,

(1) The geochemical characteristics, the temperature and present-day pressure distributions, as well as the distribution of permeability as inferred from the geographic position of the nonproductive wells (Figure 1), all suggest that the main steam source for the northern sector of Serrazzano is an area around VC/10 well in which the deep fluids are able to rise (point A in Figure 1).

(2) The condensation mechanism seems to control the distribution of the geochemical parameters.

(3) During field exploitation a part of the steam could derive from re-evaporation of condensate that accumulated in periods of higher pressure; to a lesser degree, it could even derive from a deep regional water circuit or from a steam source in layers well below those exploited at present. There appears to be no major contribution of recent meteoric waters, such as those infiltrating the ophiolitic complex.

(4) The cold area north of the productive field seems to have been caused mainly by low permeability and, consequently, by the lack of efficient fluid circulation. Slight infiltration through a cover complex that is not totally impermeable may have contributed to some extent in cooling the area. In the contact areas between these cold zones and the vapor-dominated system there once was, and in some places still is, a continuous process of steam condensation. The accumulated condensate still exists even in zones drained by the field, if permeability is very low. The piezometric gradients show where drainage is taking place. The gradient on the western margin is particularly interesting, as further evidence of the existence of an important area between Lustignano and Canneto. A careful study of the in-hole water-levels would be useful whenever the borehole encounters relatively cold marginal aquifers in poorly permeable zones.

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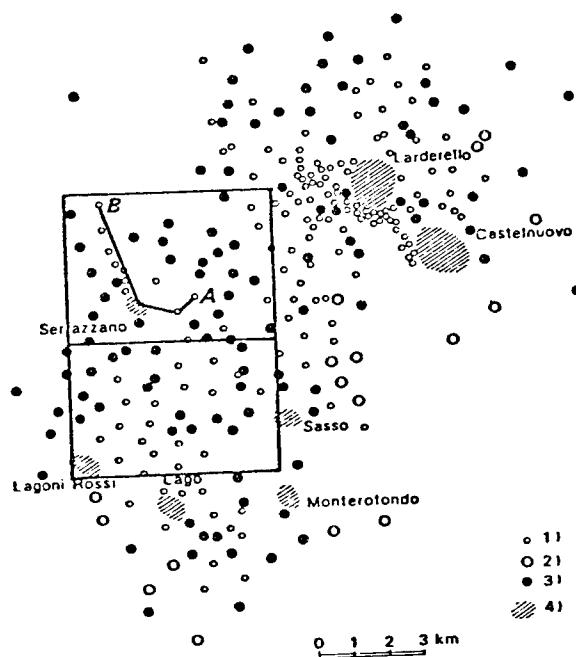


Figure 1. Geographic outline of the study area. The upper part of the rectangle represents the marginal area of Serrazzano field, which is dealt with in some detail in this report. The line from A to B is the direction taken by the fluid flow.

- (1) productive wells;
- (2) non-productive wells in areas of relatively low temperature;
- (3) non-productive wells due to low permeability;
- (4) densely drilled areas.

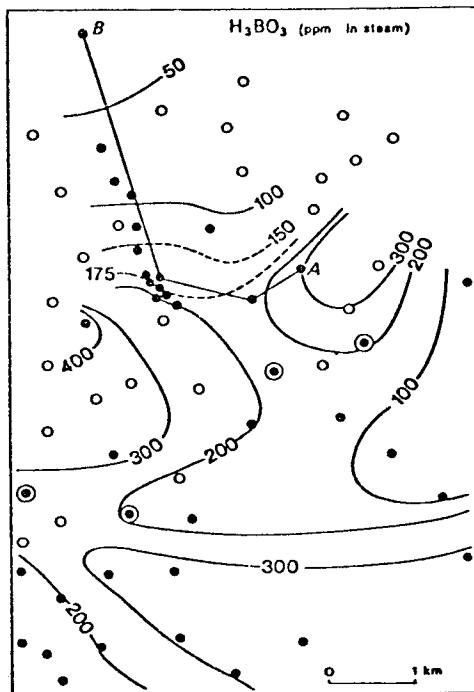


Figure 2. Spatial distribution of the  $H_3BO_3$  concentration in the steam (ppm)

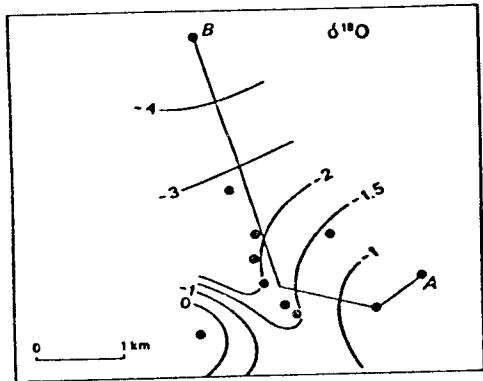


Figure 4. Spatial distribution of the  $\delta^{18}O$  content in the steam in the marginal zone of the area.

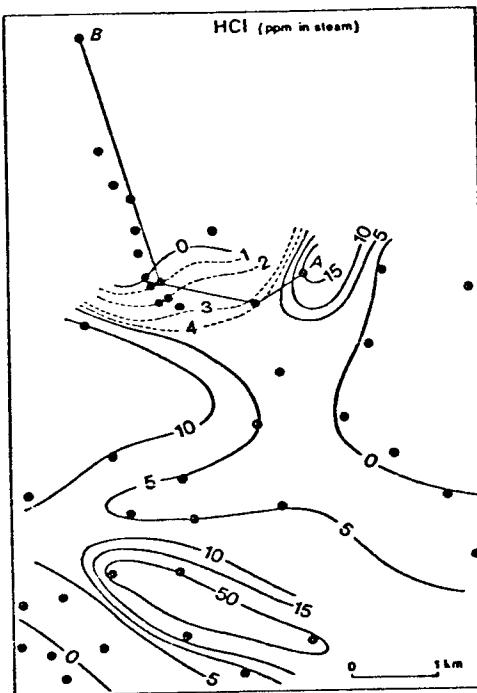


Figure 3. Spatial distribution of the HCl content in the steam (ppm)

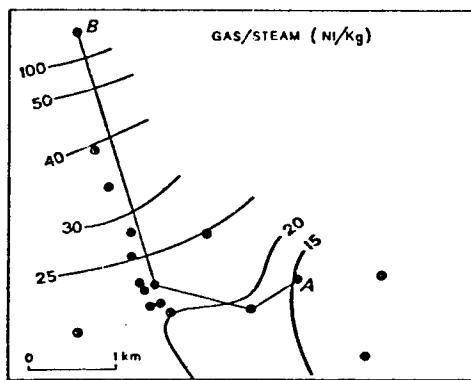


Figure 5. Spatial distribution of the gas/steam ratio expressed as liters of gas in normal conditions (STP) per kg of steam, in the marginal zone of the area.

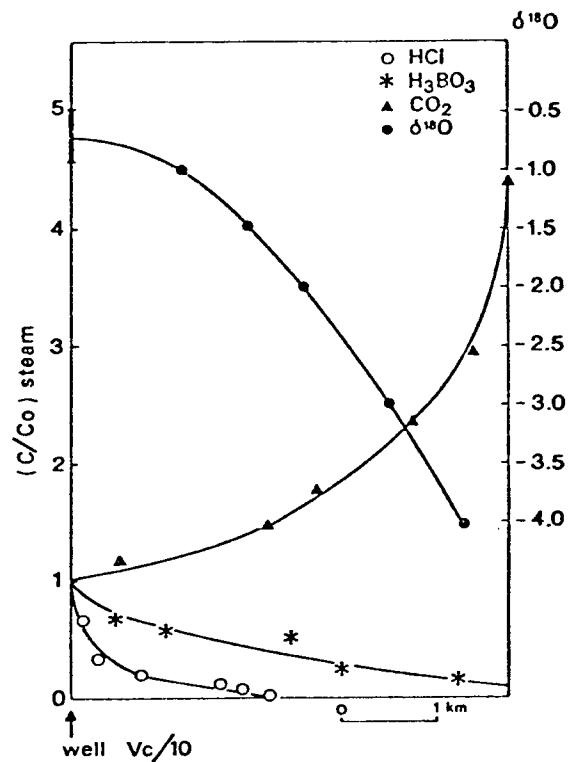


Figure 6. Trends of the gas/steam ratio of  $\text{H}_3\text{BO}_3$ ,  $\text{HCl}$  and  $\delta^{18}\text{O}$  along the profile A-B (from the spatial distributions of Figures 2, 3, 4, and 5).

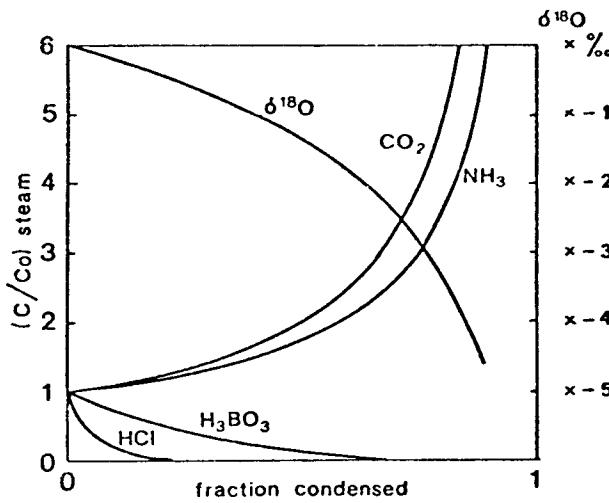


Figure 7. Solution to Raleigh condensation (1) at  $230^\circ\text{C}$  for  $\delta^{18}\text{O}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_3\text{BO}_3$ , and  $\text{HCl}$  (from D'Amore and Truesdell, 1979).

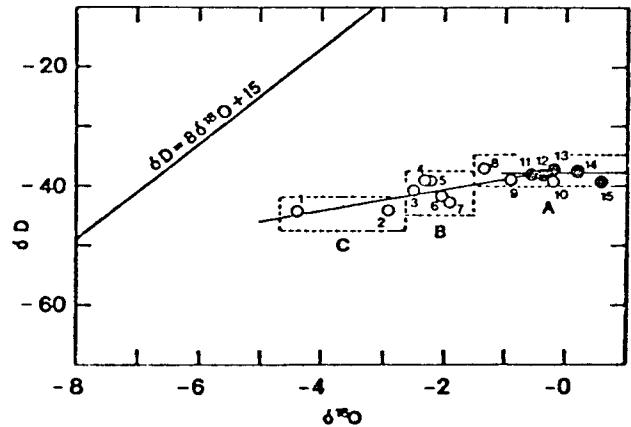


Figure 8. Trend of  $\delta^{18}\text{O}$  versus D in the steam from some wells in the study area. The black dots are well VC/10 and some others south of Serrazzano marginal zone, with temperatures of the order of  $250^\circ\text{--}260^\circ\text{C}$ .

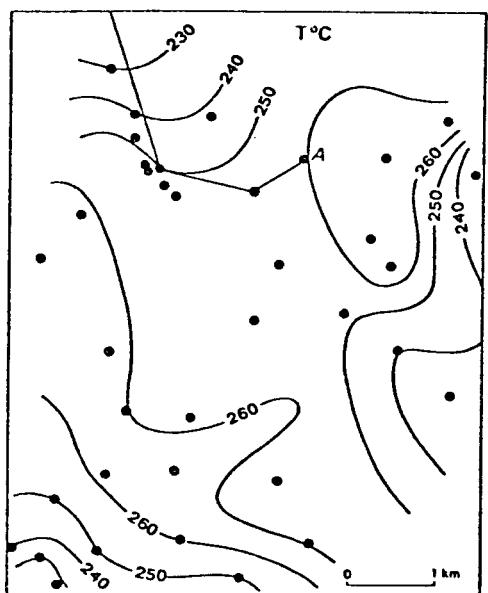


Figure 9. Spatial distribution of the reservoir temperatures, calculated by the equation described in the text, using the ratios  $H_2/CO_2$ ,  $H_2S/CO_2$  and  $CO_2/H_2O$ .

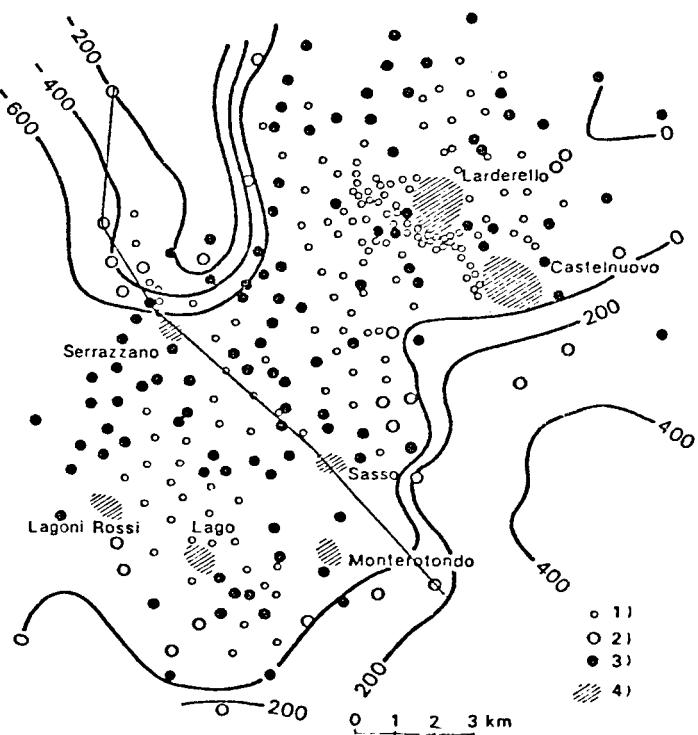


Figure 10. Piezometric surface in the boundary areas of the Larderello field. Elevation in m above sea level.

- (1) productive wells
- (2) wells where water levels have been measured
- (3) dry or low productivity wells
- (4) densely drilled areas

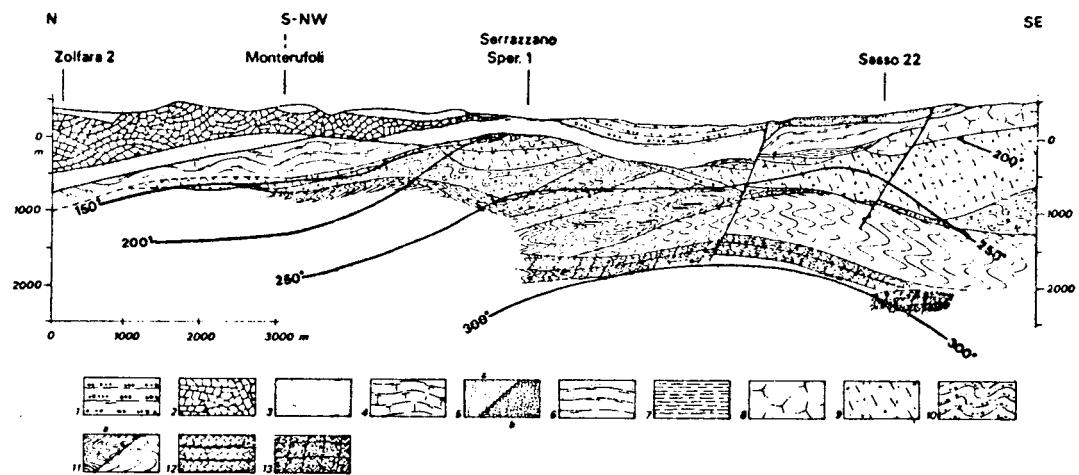


Figure 11. A geologic and thermal cross section of the Larderello geothermal field.