GEOCHEMICAL EVOLUTION OF FLUIDS IN THE LARDERELLO GEOTHERMAL FIELD

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ABSTRACT

The sixty years production history of the Larderello geothermal field is represented by over 14000 items of chemical data. Some anlyses of fluid at the start of exploitation are included providing suitable data also on Ar and He content.
Correlation diagrams based on XH_2O-XCO_2-Xi ratios (where i = H_2 H_2S. CH_2 and N_2), taking into account all production areas, show temporal or geographical variations. The Larderello. Castelnuovo. Lago, Lagoni Rossi, Monterotondo. Serrazzano and Sasso sub-areas are characterized by "reference cores" which maintained almost costant ratios among gas components. These "cores" are generally located in the central part of each subarea. Mixing and boiling processes are invoked to explain the occurred compositional variations.

1. INTRODUCTION

Initially (1980s) reinjection in the Larderello field was succesfully traced with variations in the stable isotopes content and the G/S ratio of the produced fluids. Subsequent studies, based on chemical analyses performed at the same time as the isotopic ones, achieved such useful results that for any further evaluation a better knowledge of the prereinjection conditions in the tested areas was required. A first examination. notwithstanding the available chemical data before 1970 were very few. showed that, already before reinjection. significant temporal variations in fluid composition had occurred and in certain zones substantial differences existed among wells a few hundred meters apart. To understand these changes all existing data were recovered to carry out a synthesis of the entire exploitation history of the Larderello field during the prereinjection period (1926-1978).

2. HYSTORY OF THE INDUSTRIAL DEVELOPMENT

Between 1926 and 1940, 136 wells (82% productive) were drilled reaching the top of carbonate reservoir in an area less than 4 km^2. Steam output gradually increased up to 1500ton/h.

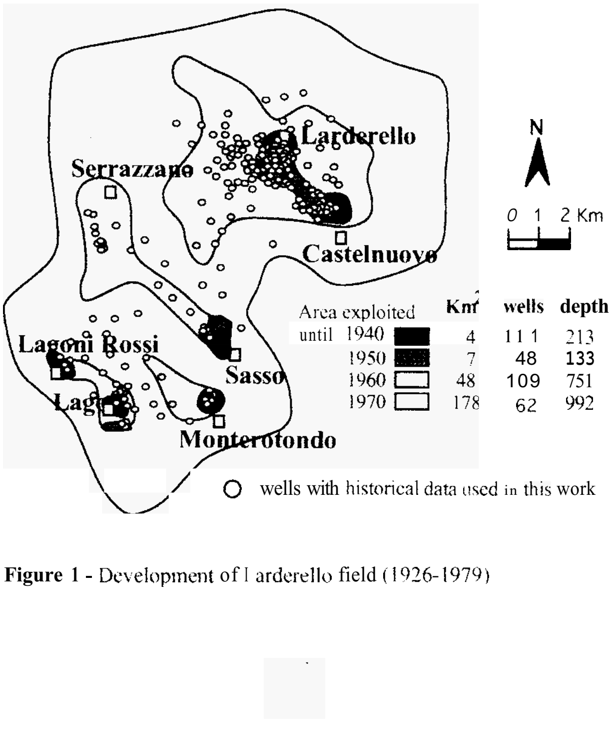

Figure 1 - Development of Larderello field (1926-1979)

Between 1940 and 1950 the exploited area almost doubled *to* 7 km^2 and the total production arose to 2200 ton'h in spite of the decrease occurred in the older production zones.
During the next thirty years the exploited area was extended up to 180 km^2 drilling outside of the high structures of carbonates. The new deeper and wider spaced (1 well/km^2) wells. notwithstanding the less favourable permeability conditions. enabled to reach a steam output of 3000 ton/h in the early 60s.
A sketch map is given in Figure 1.

3. CHEMICAL COMPOSITION OF MAIN GASES

The chemical analyses of all the fluids sampled in the whole field. expressed in terms of mmol/mol. were used to draw triangular diagrams such as XH_2O-XCO_2-Xi where i = H_2, CH_4, H_2S, N_2, NH_3 and H_3BO_3. Only some of them will be discussed in this paper,
Figure 2 shows XH_2O-XCO_2-XH_2 and XH_2O-XCO_2-XCH_4 diagrams for all fluids sampled before 1979 (over 6000 records). Points spread over 60% of both the plots with a common distribution between two straight lines. These represent the boundaries of a smaller triangle containing the H_2O and CO_2 corners and having respectively $\log XH_2O/XH_2 = \log XH_2/XCH_4 = 3.2$ and $XCO_2/XH_2 = XCO_2/XCH_4 = 18$ as limiting values.
Considering the time trend of each well in greater detail, for some of them variations in the percentage of CO_2 of over 25 times and in both the CO_2/H_2 and CO_2/CH_4 ratios of over 10 times have been observed: whereas for others a very little scattering around an average value was found.
For example. see Figure 3 (left). data of all the wells located in the centre of the Larderello sub-unit shift lower than 50% around the average values of the two parameters, namely 2.0±1.0 and 60±30 for the CO_2 and the CO_2/H_2 ratios respectively.
Because the same pattern is shown considering respecticely H_2S. CH_4, N_2. NH_3 and H_3BO_3 by those same wells. they can he singled out as a set apart from the rest of sub-unit. As in the others sub-units of the field the same behaviour can be observed, the wells which kept almost unchanged their chemical composition during the whole production history were then separated. Such small areas where these selected wells. generally drilled between 1930 and 1940, are located, will be indicated as "reference cores". There, in the past. have been existing large thermal manifestations which have now disappeared.
The average chemical composition of fluids in some of the "reference cores" are shown in Table 1; these same data were plotted as open symbols in the triangular diagrams of Figure 3 (right). These appear quite distinct in the plots. confirming that the fluids produced in the various areas of the Larderello field differ in the main gas components. The fluids sampled from drillings, made in the early 1930s and shallow

Table 1 - Fluid composition *of* some Larderello sub-units

Molar	Larderello	Castelnuovo	Monterot.	Lago
H_2O	979.948	974.690	990.253	982.948
CO_2	18.992	23.817	8.519	15.282
H_2	.412	.288	.329	.584
H_2S	.428	.430	.234	.463
CH_4	.312	.260	.371	.370
N_2	.181	.161	.095	.110
NH_3	.212	.227	.107	.107
H_3BO_3	.115	.127	.092	.136

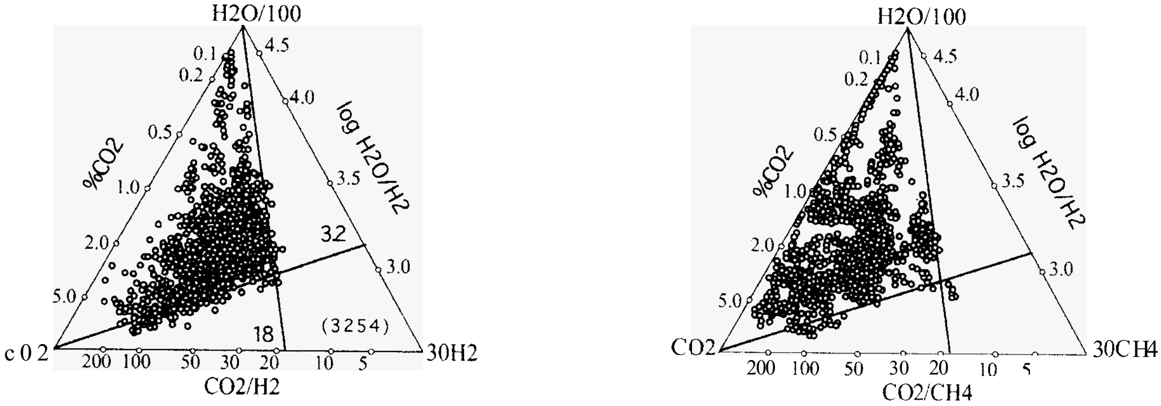

Figure 2 - XH_2O-XCO_2-XH_2 and XH_2O-XCO_2-XCH_4 diagrams for all produced fluids up 1979

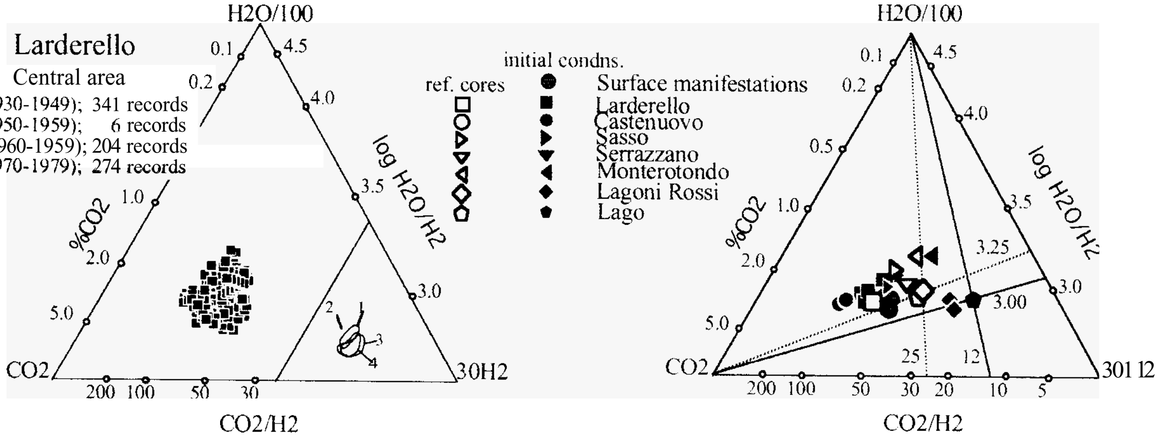

Figure 3 - Relative stability of H_2 concentration ofthe Larderello reference core (left), and coinparison (right) between averaged values of all the reference cores with the early produced fluids in the field (initial conditions)

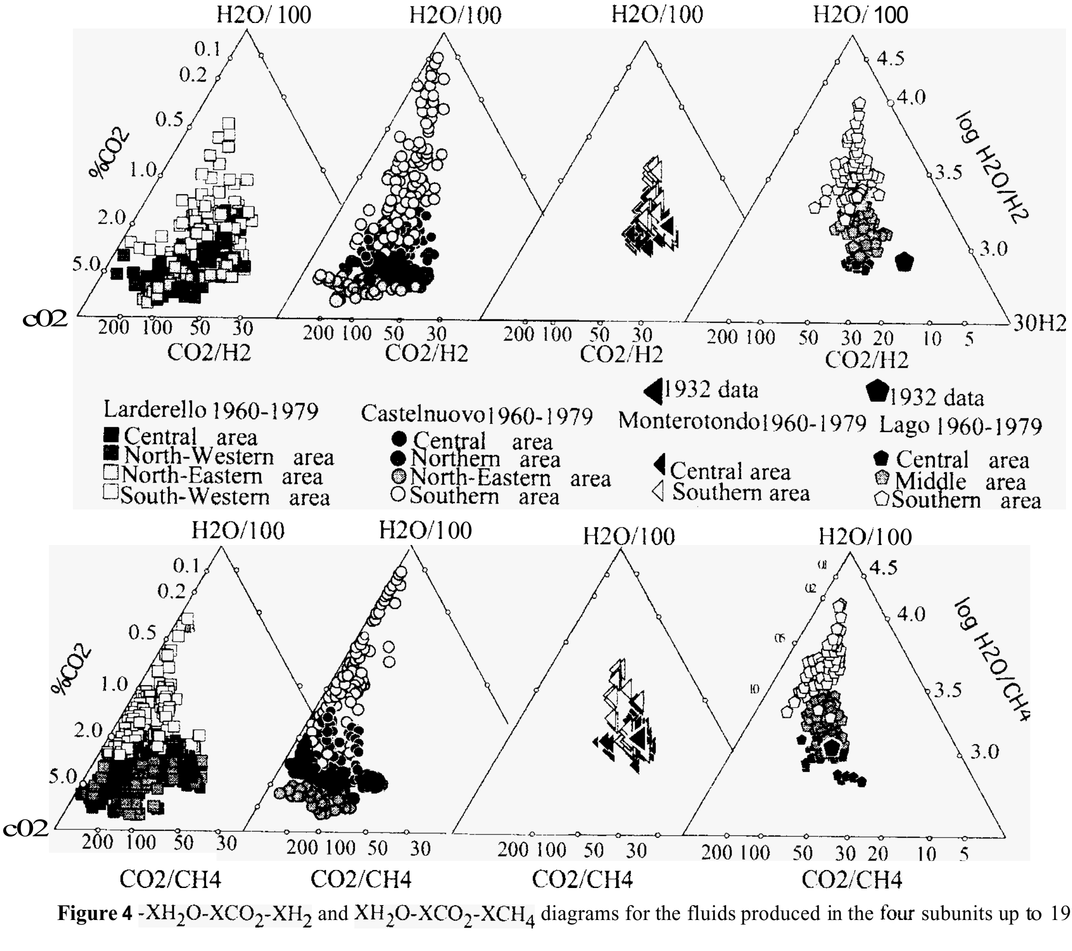

Figure 4 -XH_2O-XCO_2-XH_2 and XH_2O-XCO_2-XCH_4 diagrams for the fluids produced in the four subunits up to 1979

wells dating back to the beginning of industrial period, as from Sborgi (1934). are plotted as black symbols. while the rapresentative points of some steam jets analyzed between 1895 and 1911 as from Nasini (1930) are shown as shaded rings. All these fluids show an excellent overlapping with the average values of central areas ("reference cores"). These data should be considered as valuable initial references, the more so since. in addition to the main constituents of gases. even at that early date their He and Ar content were determined.

The same behaviour is observed in the similar XH_2O-XCO_2-Xi diagrams, where Xi refers to CH_4, H_2S and N_2 not represented in this paper.

From the foregoing. it is evident that. though based on a limited set. these data rapresent the initial conditions of the field.

One important consequence of the nearly perfect overlap between the "initial conditions" and the "reference cores" is that the fluid produced by the wells located near the old manifestations stayed practically stable in the course of the whole industrial history of the field. Starting from the these values, the next step is to analyze any change in the gas composition through the end of prereinjection period (1979). The aim is to evidence temporal variation due to the depressurization of the field and/or to the progressive expansion of production areas.

Figure 4 shows the XH_2O-XCO_2-XH_2 and XH_2O-XCO_2-XCH_4 diagrams for wells drilled in the outlying zones of Larderello. Castelnuovo. Lago and the Monterotondo sub-units. The first three of them show sets of points assuming quite different positions from those belonging to the "reference cores", while Monterotondo displays only a slight shift.

Larderello sub-unit

The further northeast and northwest the wells are located in comparison with the reference core the more the CO_2 content increases. The representative points shift towards the left corner of the diagrams and the CO_2/H_2 and CO_2/CH_4 ratios from a typical value of about 40 and 80 reach respectively a maximum of 200 and 800. On the contrary the log H_2O/H_2 and log H_2O/CH_4 ratios retain the original values ranging between 3.5 and 3.25.

Southwestern wells up to 1970s behave as reference core ones. then show a progressive strong depletion of CO2 % keeping the original CO_2/H_2 ratio. while in the case of the CH_4 diagram. the CO_2 decrease is often coupled with an outstanding drop of methane, reaching the highest values of CO_2/CH_4 ratio in the area (R=900).

Hence. the Larderello sub-unit can be represented as a complex of four areas. the northernmost ones of which display an unchanged H_2 and CH_4 content. but more CO_2 {up to 5 times) than in the central. reference core. The last area, including the wells drilled to the southwest. is basically characterized by a progressive decreasing of the G/S ratio.

Castelnuow sub-unit

Here has been a more complex history than in Larderello. Until the mid-1960s. almost all the old wells, drilled in a limited area close to the natural manifestations, kept a costant composition nearly similar to the one observed in the Larderello central area . After this date. substantial modifications were observed in the southernmost wells. At the same time. new wells, located in the northern and north-eastern areas produced fluids differentiated from the previous ones by much higher CO_2 content.

To sum up, four areas are recognizable also in the Castelnuovo sub-unit. The first, which can considered as the reference core is the most central one. It was once larger, including before 1960 also wells further south. These from that time differentiated as separated units showing a progressive depletion in CO_2 and a considerable increase of logs H_2O/H_2 and H_2O/CH_2. In this case too, the CO_2 decrease is coupled with an outstanding drop of the methane content. The third area is made up by the wells to the northeast, and the fourth by those located to the north. The fluids produced here can be considered a mix between those present in the central core and those of the north-eastern area.

Lago sub-unit

Three main areas have been here identified. The first corresponds to the more internal. definable as the reference core, the other two outlying areas located increasingly further south. The Lago XH_2O-XCO_2-XH_2 diagram show the greatest separation. observed in the whole field. between the position of the wells belonging to the reference core and the historical data of 1932, the latter being characterized by an higher H_2 content. The most likely hypotheses for explain this differece are the following:

- the historical data for Lago refer to a well with a limited flowrate and located in the southern area which in 1963 had already undergone a considerable evolution. The period in which the changes began cannot be documented due to lack of previous data.
- the wells which, owing to their unchanged composition from 1963 to the present (reference core) are located further north and were drilled at least 25 years after the ones the historical data refer to.

Despite these limitations, the Lago sub-unit is characterized by the presence of a reference core and two peripheral areas. The latter show, to a different degree. a progressive decrease of the CO_2 content. Moreover. while the CO_2/H_2 ratio keep nearly constant (R = 25). the CO_2/CH_4 ratio increases from 30 to 500.

Monterotondo sub-unit

This one presents the lowest changes in the examined sub-units. Only a light variation of the logs H_2O/H_2 and H_2O/CH_4 can be observed. A similar behaviour is followed in the rest of the sub-units (Lagoni Rossi, Sasso and Serrazzano) not described here.

Based on the chemical composition of the produced fluids before reinjection, the summarizing map of Figure 5 has been drawn.

4. TRACE CONSTITUENTS: He AND Ar

In the N_2-He-Ar triangular diagrain of Figure 6 are shown the representative points of the fluids produced up to the start of reinjection. Starting from 1932 (left triangle), and then examining 1940-50 (central triangle). these are quite steady and well defined by the ratios $N_2/He = 300 \div 500$, $N_2/Ar \approx 800$ and $Ar/He \approx 0.5$, being the Ar and He averaged concentrations respectively $1.6x10^{-4}$ and $4.2x10^{-4}$ mmol/mol. The points are clustered on the ideal line which defines a mixing process between a pure crustal component with a magmatic one.

In 1963 (right triangle) the N_2/He ratio had increased ($700 \div 2000$) although the nitrogen content had been unchanged and the variation were more significant for wells that had produced for a longer time and/or undergone a greater pressure fall-off. It appears that the magmatic component increased, but it is not so.

A possible explaination is that the He content in the reservoir. being the result of an accumulation process occurring over very long times. is not renewable in the course of exploitation and gradually falls as the wells produce. This decrease causes the shift of the points towards the top of the diagram. Moreover the radiogenic origin of He in Larderello field. proved by a set of He_3/He_4 ratios measurements made in 1983, confirms this hypothesis with an average mantle component of less than 5 %, Hooker *et al.* (1985).

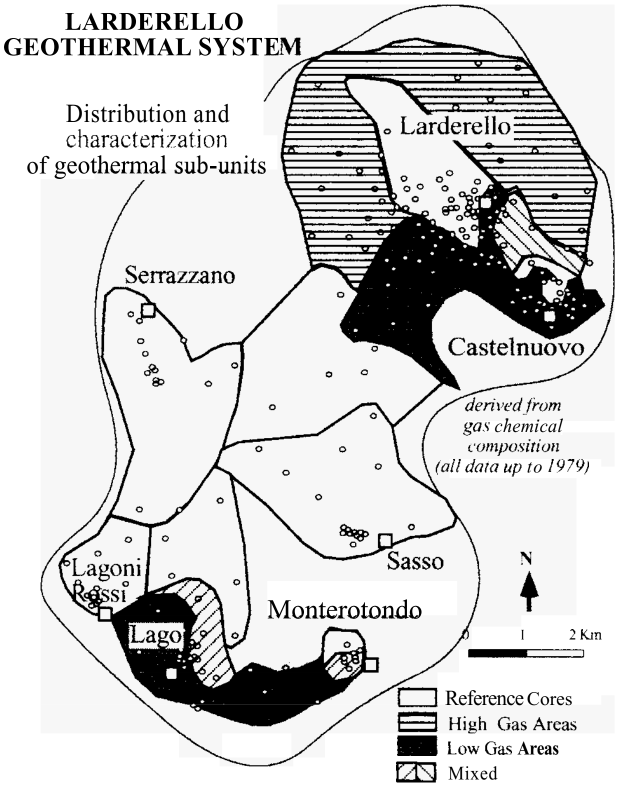

Figure 5 - Characterization of Larderello geothermal field based on gas chemical composition.

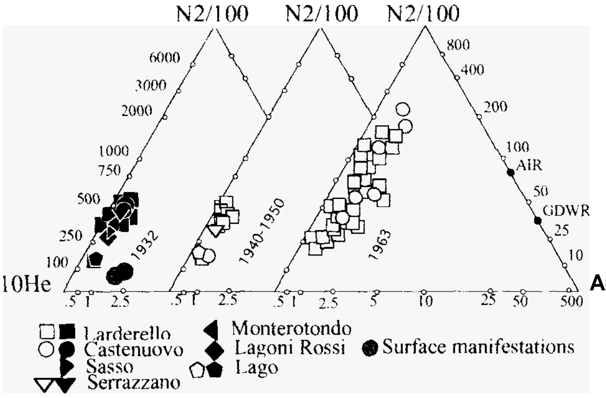

Figure 6 - Relative N_2, He and Ar contents in Larderello geothermal field up to 1963

5. A POSSIBLE TENTATIVE MODEL

The fluids evolution and geographical differences shown in the previous sections can be briefly summanzed as follows:

- each sub-unit is characterized by a "reference core" where wells have been always producing fluids with steady composition.
- in the southernmost areas of the Larderello. Castelnuovo, Lago and Monterotondo sub-units low gas content fluids have been pointed out. Their G/S ratios, initially quite similar to their own "reference core" value, decreased, at a different degree. with time keeping the initial CO_2/H_2 ratio, while this does not always hold true for the CO_2/CH_4 ratio.
- higher CO_2 content Ibr the northernmost and easternmost wells ofthe field.
- Ar content very close to that of the air saturated groundwater.

Further observations to be taken into account are the following:

Gas production. mainly CO_2, has always been high at Larderello; average G/S values from productive wells at steady conditions give a reservoir gas content highly exceeding the theoretical ones for a water-rock equilibrium under hydrostatic pressure. Such G/S valuer have been kept for a long time and only in the last few years the overall gas content has been decreasing with respect to the vapour production.

Any interpretation of the above statements can be done only after a brief introduction about the gas origin in the Larderello geothermal field. The produced CO_2 could not have been stored in the original reservoir fluid, O'Sullivan. *et ai.* (1983) and Prueas (1983). For wells located in the "reference cores" the CO_2 concentration changes only slightly in comparison with their observed strong decrease in Ilow-rate. excluding any possible external source of this component. Thus the only possible CO_2 origin is internal to the system, due to inetasoinatic interactions between water and rocks. Such a hypothesis can be applied to liquid-dominated fields without any theoretical difficulty while for vapour-dominated fields any solution is more problematic.

According to Giggenbach (1984) and Giggenbach *et al.* (1989), for a liquid equilibrated between 200°÷ 300°C with an average silicatic crust the main reaction controlling C02 partial pressure is (1):

$$\text{Ca-Al}_2\text{-silicate} + \text{K-feldspar} + CO_2 = \text{k-mica} + \text{calcite} + \text{Qz} \qquad (1)$$

the temperature dependence of this reaction is given by (2):

$$\log PCO_2 = 0.0168t - 3.78 \qquad (2)$$

where PCO2 is expressed in bar.

Again according to Giggenbach (1989) the H_2 fugacity, buffered by the $(FeO)/(FeO_{1.5})$ system, in a lot of geological environments is practically costant over a temperature range between 20" and 1200°C and is given by (3):

$$\log (fH_2/fH_2O) = -2.8 \qquad (3)$$

'Many occurrences prove the existence of hydrothennal alteration processes. like described by the equation (1). even recently active in the Larderello field, Cavarretta *et al.* (1982).

Measured CO_2/Ar and H_2/Ar values of Larderello wells are consistent with the theoretical ones for a steam produced by a liquid totally boiling between 200°÷ 300°C, and PCO_2 and fH_2O of this liquid can be derived by (2) and (3) respectively.

This holds true ifthe water-rock equilibrium is kept all over the process and the boiling is carried out without any phase segregation. **As** the liquid evaporatea, releasing C02 and H_2 in the vapour phase. new amounts of theae gases are formed in the residual liquid by feldspar alteration in the inetainorphic basement. The Ar. initially dissolved in the liquid, goes completely in the vapour phase during the early stages of the boiling. **As** this .latter proceedes. while CO_2 and H_2 are continually produced and transferred to the vapour phase. Ar content in the same vapour is diluted until reaching. at the end of the process. its original concentration in the initial liquid.

The Ar source. on the hase of Ar^{40}/Ar^{36} ratios determined before 1979 as from Mazor (1978/79), is indeed totally atmospheric, considering that its average concentration in the fluids between 1930 **and** 1963 is 1.6×10^{-4} mmol/mol, very close to that of water equilibrated with air (2.4×10^{-4} mmol/mol); more than 70 % of the produced steam should be of meteoric origin.

Maximum C02 concentration, in case of a complete evaporation under ideal equilibrium condition. will be close to 70 mmol/mol of total fluid. CO_2 content is smaller than this calue in all the Larderello productive wells.

This hypothesis is still under study, but similar conclusions have been already proposed by Calore *et al.* (1990).

By such a mechanism it is possible, introducing simple inixing processes between two end-members. to explain both the already described occurrences and the isotopic composition of the steain produced in the whole field.

The two end-members are:

- a primary deep steam **(A)** produced inside the so-called reference cores slightly differing froin one sub-unit to another by the chemical composition. Typical isotopic values are $\delta D = -40$ and $\delta^{18}O = -2$; owing to an extensive water-rock interaction undergone by the liquid phase, indeed, the original meteoric δ18O content is shifted. towards higher values. Its gas content, with particular respect to CO_2, H_2, and **Ar** is supported by the production mechanism above discussed. The compositional differences among the reference cores could occur as a function of the degree of partial equilibrium among the liquid phase and the mineral assemblages in the reservoir. This study is still in progress;
- a secondary steam (B) derived by freshwaters boiling. Because of their short residence time at depth, the water-rock interaction is slight, and so the steam contains few gas and its isotopic tag keeps typically meteoric: $\delta D = -40$, $\delta^{18}O = -7$. This occurrence can be traced back to early sixties and provides a natural recharge ofthe field.

In the diagrams of Figure 4. the deep steam is described as "central areas". Wells in the southern zones of Larderello. Castelnuovo, Lago and Monterotondo produce a different degree of mixing between the two end-members. This process results as a shift of the representative points from the reference cores towards the upper comer of the diagrams. The wells located in the north-eastern and north-western areas of Larderello and in the north-eastem area of Castelnuovo. characterized by the highest CO_2 content in the field, are found in the lower left comers of the diagrams This, can be explained as the result of a water-rock interaction and evaporation locally close to the ideal equilibrium conditions.This model is supported by the isotopic distribution of steam in the whole field, Panichi *et al.* (1978). Moreover trends similar to those of Figure4 have been observed in the wells more sensitive to reinjection. as shown in Panichi et al.. this volume.

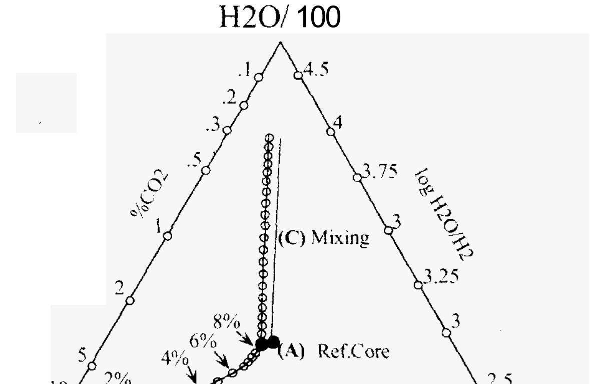

Figure 7 - Computed trend of steam produced according to a boiling process.

As an alternative to explain the compositional differences among the several zones of the Larderello field it can be invoked a boiling process. The only way to fit the representative points distribution in Figure 4 is to simulate a complex evaporation, as a linear combination of an equilibrium boiling ("single-step" type) at 10% and a Rayleigh-distillation ("continuous-steam" type) at 90%. This isothermal process. at T = *250°C.* is represented in Figure 7.

Here is shown the theorethical path of a steam produced during such a boiling. starting from a liquid system which had the average composition of the Larderello reference core (A). Each dot corresponds to an evaporation step of 0.5% by weight. It can be observed that within 6% of evaporation (early stages) a strong enrichment of CO_2 in the vapour phase occurs Since for an 8% of evaporation the gas composition of the resulting vapour phase is the same initially assumed for the dissolved gases in the original liquid as the evaporated fraction grows higher (late stages). being the residual liquid by now almost devoid of gases, the representative points of the produced steam will move straight towards the top of the diagram according line (B). In the same figure is shown. as comparison. the linear path of a fluid obtained by simple mixing between primary and secondary steam (C); the two lines. beginning from (A) are coinciding. According to the boiling process the reference core composition (A) could represent either an early stage of the boiling. or. more probably, the result of a complete evaporation of the original liquid under local conditions of full liquid-vapour equilibrium. The composition of the fluid from low G/S wells should be given by a late stage of the process, while the high G/S wells should outcome from the early stages. Such kind of a process is theoretically consistent both with the lowest gas content areas in the south of Larderello. Castelnuovo. and Lago and with the higher gas content in the northernmost and easternmost ones of the field. However limits are given by:

- the inconsistency between the computable quantities of different G/S fluids and the respectively produced flow-rates:
- the assumption of an original liquid system bearing already in solution the total amount of gases that will be produced at the end of the process.
- the fact that a liquid phase has never been encountered by drilling even deeper than 3000 m in any part of the field.

Anyway the possibility of adapting the gas production mechanism, described at the beginning of this section, to the boiling process is not yet to be ruled out. It has not been excluded that while in a part of the field the first explanation prevails. in another part the second holds true.

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