VARIATION OF GEOCHEMICAL PARAMETERS INDUCED BY REINJECTION IN THE LARDERELLO AREA

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ABSTRACT

Isotopic and chemical analyses of steam and gas from the producing wells, from their initial production to 1992, have been used to describe the effects of exploitation and of waste fluid reinjection. Maps of the steam isotopic distribution and of the gas content distribution respectively have been derived for the whole Larderello geothermal field. Observation of pre-reinjection and later data, reveals a good distinction between natural /meteoric inflow, induced by exploitation. and artificial waste fluid recharge. In the wells affected by reinjection, gases, apart from N_2, are substantially diluted, since condensates are attained through an evaporation process. Isotopic variations of H_2, CH_4 and CO_2 have been used to describe the disequilibrium conditions among gas components. This disequilibrium is induced by the settling of a liquid plume at the producing level in the reservoir.

1. INTRODUCTION

The Larderello geothermal field. located in southern Tuscany, produces superheated steam from a vapor-dominated reservoir. To obtain valuable information from a reinjection study in vapor-dominated systems. the most suitable methodology for the type of produced fluid. i.e. gas and steam, is to be used. Tracers are very helpful, in this respect. as they can provide informations on the processes occurring in the reservoir and on their evolution with time. The isotopic composition of the condensate sampled at the power plants cooling towers was successfully used as a "natural" tracer in the monitoring of reinjection tests at Larderello. Nuti *et al.* (1981), Bertrami *et al.* (1985) and D'Amore *et al.* (1987).

The close correlation found between stable isotopes of the steam and gas/steam ratio points to a mixing occurring at depth between reinjected condensate and a deep steam component. This process is accompanied by the formation of a liquid plume undergoing different degrees of evaporation, D'Amore *et al.* (1987).
Variations of isotopic temperatures, derived from H and C isotopic exchanges between gas molecules such **as** CO_2, CH_4, H_2 and H_2O, before and after reinjection at Larderello, were attributed by Bolognesi *et al.* (1990). to the development of a liquid phase in the producing reservoir.

The aim of this paper is to present the results obtained by considering the bulk gas composition of the fluids from Larderello in the interpretation of the reinjection process. In addition, an accurate reconstruction of the chemical features of the whole field before the reinjection. Scandiffio *et al.*, this volume, enables **us** to distinguish between the fluid variations due to the injection of waste water and those due to natural meteoric inflow or to changes in the system's physical conditions.

2. CHEMICAL AND ISOTOPIC EFFECTS OF THE REINJECTION ON THE DISCHARGED FLUID

D'Amore *at al.* (1987) showed the effects on stable isotopes and gas contents of the steam produced by wells close to the reinjection sites at Larderello. Data referring to productive wells of the inner part of the field, where additional processes such as infiltration of local cold water or steam lateral condensation are little felt or not at all. are reported by Bolognesi *et al.* (1990).
In general, δD, $\delta^{18}O$, gas/steam ratio and CO_2 contents may be successfully used in order to evaluate the amount of the reinjected water recovered by each productive well.
The correlation between gas and stable isotopes content seems to hold at any proportion of deep and reinjected components.
The isotopic composition of the steam is clearly affected by mixing with reinjected waters only close to reinjection sites, while the isotopic composition of gas appears to be modified over much wider zones, Bolognesi *et al.* (1990).

2.1 CHEMICAL AND ISOTOPIC VARIATIONS OF THE GAS AND CONDENSATE.

Figure 1 shows some XH_2O-XCO_2-Xi diagrams. where $i = H_2$, CH_4 and N_2 in the fluids discharged from the wells N.82, N.101 and N. 137.

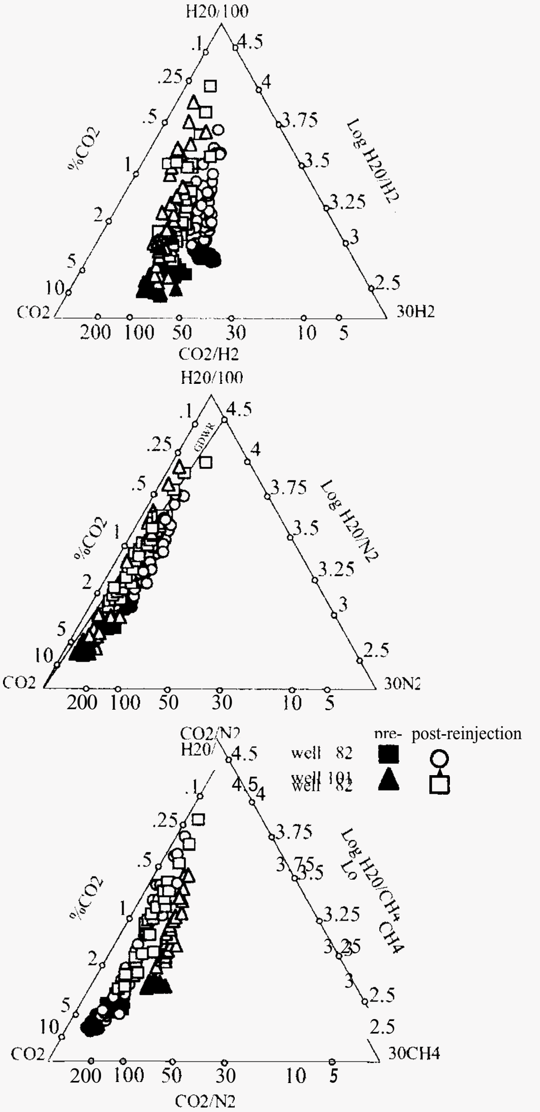

Figure 1 - Triangular diagrams for theree selected wells considering pre-reinjection period (full symbols) and post-reinjection period (empty symbols).

Of these wells, differently spaced from the reinjection sites and frequently monitored, the first two are located a little inside the northwest area of Larderello (high gas), while the third is located within the reference core (low gas): see Scandiffio *et al.*. this volume. Comparison among samples collected before and after-reinjection (full and empty symbols) proves that all the wells are strongly affected by the reinjection. The more the vapor from the reinjected water increases in the produced fluid, the more the representative points move towards the top of the diagrams. Since the waste condensate is gas-depleted. except for a small amount of N_2, the overall effect, in first approximation, can be explained as a dilution process of the original deep steam: as it is clearly seen in the upper diagrams of Figure 1

Unlike for the other gases, the distribution of N_2 suggests that reinjected water contributes largely to the content of nitrogen in the monitored wells. This is actually shown by the bottom left diagram of Figure 1, where the N_2/H_2O ratio. for a zero contribution of deep steam. corresponds to that ofthe air saturated groundwater at 20°C.

This meteoric contribution to the fluids discharged after reinjection is well documented by Figure 2. where the relative content of N_2. He and Ar is shown for samples collected before and after-reinjection.

Injected and/or infiltrated waters previously equilibrated with the atmosphere should introduce in the deep reservoir 2.4×10^{-4} mmol/mol of Ar. This amount is very similar to the average content of this component in the fluid produced during the period 1930-1965 (1.6×10^{-4}). However the two endmeinbers differ in the N_2 contents; in the former the theoretical N_2/Ar ratios are between 38 and 84 (values for the air and for the saturated underground-water respectively), while in the original fluid this ratio is about 800.

The radiogenic He is present in the deep fluid with a concentration of about 4×10^{-4} mmol/mol, but is completely absent in the secondary steam produced by reinjected waters.

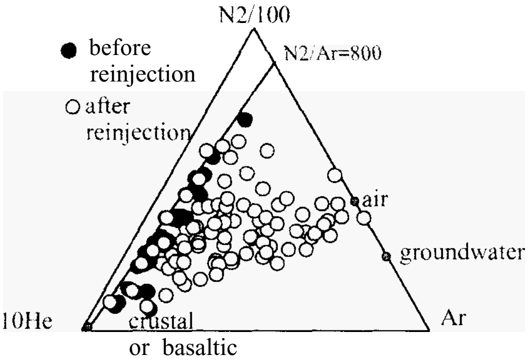

Figure 2 -Relative concentrations (mmol/mol on water free basis) of N_2, Ar and tie components. Composition of crustal and magmatic fluids. together with N_2/Ar ratio.; for the atmosphere and air-saturated groundwater are reported for comparison.

The observed trend of Figure 2 seems to be the result of a simple mixing between deep components and the meteoric ones. introduced by waste fluids. Full circle:: refer to gas emerging anywhere in the Larderello geothermal system before reinjection (1979). according to Scandiffio *et al.*, this volume. while the empty ones represent the situation recorded afterwards. In general, we can see that pre-reinjection data. and post-reinjection data reveal Ar as a very sensitive gas component with respect to the wells affected by reinjection. The Ar/He ratio in many fluids increased inore than a hundredfold with respect to prereinjection period. The usefulness of this tracer should be at least of the same order of the isotopic composition ofthe steam and the gas/steam ratio.

While the behaviour of major gas constituents. apart from N_2, is conditioned by a simple dilution of a deep steam with a depleted vapour, the resulting Ar content seems strongly depending. inore than on the initial concentration in the reinjected water, on the separated steam fraction and related partitioning phenomena.

For condensates such as H_3BO_3 and NH_3, the reinjected concentrations of which range respectively between 0.1÷ 0.25 mmol/mol and 0.2÷0.4 mmol/mol, the liquid/vapour distribution coefficient play a fundamental role.

In fact, due to the different calues of these coefficients, during boiling NH_3 is concentrated with respect to H_3BO_3; see Figure 3. Considering the steam delivered from a single well N. 137. a good consistency exists between the reinjected water composition and steam produced at the same period: here is a mixing process between the deep steam and a new vapour H_3BO_3 depleted. but NH_3 strongly enriched. Such variations of this vapour are relative to reinjection water as solubilities of these constituents are quite different: the first partitioning in the residual liquid, the second into the vapour phase. In terms of evaluation of Recovery Coefficients (i.e. of the amount of the reinjected water which is recovered from the productive wells near the reinjection sites), probably the relative concentrations of Ar, He and N_2 (or CO_2) may represent a tool which reflect "immediately" the variations occurring in the reinjection sites. On the other hand. the use of stable isotopes composition of the steam delivered at the surface (Figure 4) may give "smoothed results because the secondary (from reinjected waters) vapour consists of mixed steam.; from new evaporation fronts and from residual liquid plumes.

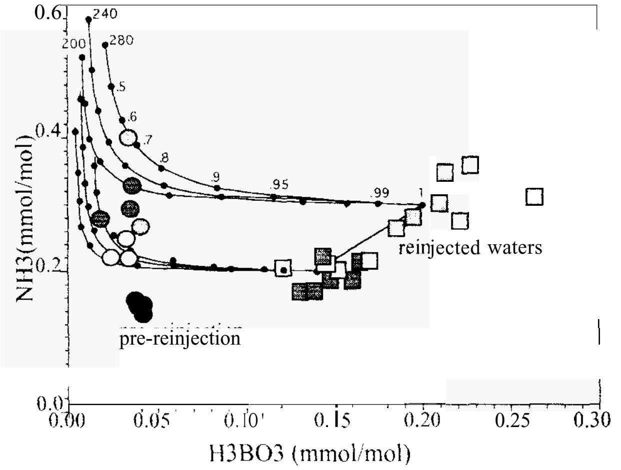

Figure 3 - Ammonia and boric acid concentrations of the fluids delivered at the same well (circles) in different time. between August 1983 and April 1985. The composition of the reinjected waters and the (squares) steam produced before reinjection are reported together with the variations expected by a s.s. steam separation.

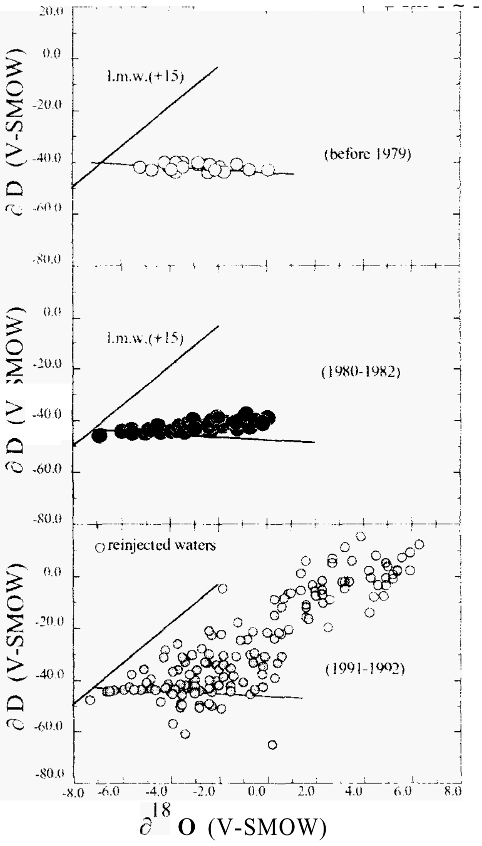

Figure 4 - Progressive changes in the $\delta^{18}O$ and δD content of the fluids produced at Larderello as a consequence of the increase in the reinjecion amount. The second diagram refers to the steam produced in the whole field after the first reinjection tests in the Valle Sccolo area.

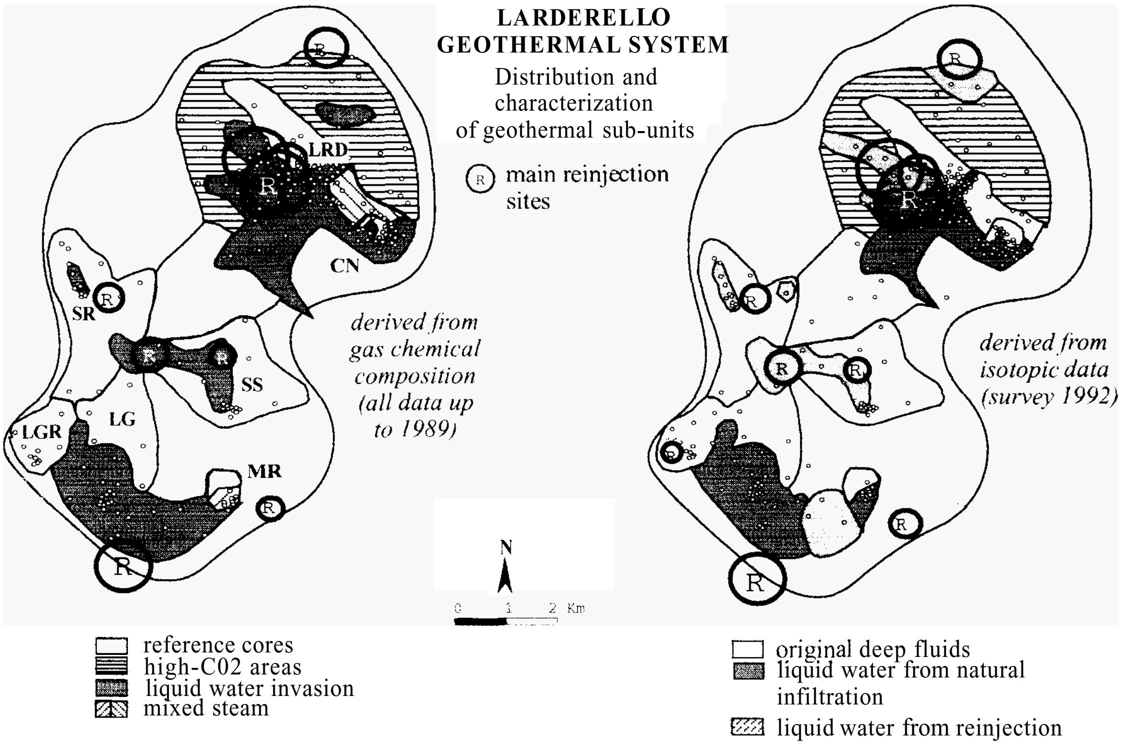

Figure 5. Zonation of the geothernial field derived from gas and isotopic analyses of steam produced during reinjection.

A picture ofthe state ofthe whole field to 1988, based on the major gas costituents, was obtained by considering all the systematic analyses performed after the start of reinjection. The reference cores. and the zones of the field in which produced fluids have an appreciable vapor content originated by natural inflow or artificial reinjection of water are shown in the left map of Figure 5.
These two different sources are recognizable on the whole. but cannot be discriminated on a gas chemistry basis: for both of them the variation introduced in the resulting fluids consists in a substantial dilution of the original gaseous mixtures.

In August 1992, an isotopic survey was carried out on the field to single out the two different contributions on the basis of the distinct features of the natural inflow with respect to the reinjected ones. Indeed, considering the range of isotopic variations **in** the vapor produced before reinjection (δD =-40±2 ‰ and $\delta^{18}O$ ranging between -6 ‰ and 0 ‰), the natural recharge (δD - -40 ‰; $\delta^{18}O$ - -7 ‰) tends to modify only the $\delta^{18}O$ content of the steam. while the share of reinjected water (δD and $\delta^{18}O$ - +5 ‰) determine variations in both the isotopes (see Figure **4).**
Here the second diagram refers to the steam produced in the whole field 1/2 years after the first reinjection test in the Larderello field..
Joint examination of the distribution of the values of $\delta^{18}O$ and δD enabled to sketch the right map of Figure 5. The agreement with the left map based on the chemical data is very good. The slight differences are justified by the changes of reinjection sites and by the different velocity of response of the two methodologies on which these maps are hased. Besides. artificial and natural recharges arc well distinguished.

3. INJECTATE RECOVERY IN VALLE SECOLO AREA

In the Valle Secolo area the productive wells network is developed enough to compute a mass-balance.
Up to now it is impossible to use any other geochemical tracers than the stable isotopes and the gas content of the steam for a quantitative evaluation of the recovery coefficients.
Assuming a complete evaporation of the reinjected water, the recovered discharge from each productive well is given by (1):

$$Q_I = Q_{WH}*(X_{WH}-X_R)/(X_I-X_R) \tag{1}$$

where I = reinjected contribution. R = deep steam contribution. M'H = (wellhead)total amount. and X= G/S or $\delta^{18}O$ **or** δD, according to the used tracer.
Bertrami et al. (1985)for the 1979 ÷ 82 period calculated a recovery, of about 100% as regards to G/S, while using the isotopic composition the value was of 85%. In 1992 similar results were obtained.
In particular, between October 1991 and March 1992. the computed recovery was 100% according to the G/S and 85 ÷ 90% using the stable isotopes.
In the following period, April-September 1992, these values were lower. about 90 ÷ 100% with G/S and 50 ÷ 70% with the isotopes.

Theoretical recoveries obtained using the gas content always exceed the ones based on the isotopes, hut they are less reliable because the reference values for the deep steam gas content (X_R) refer to pre-1979.
However, the isotopic values are also affected by the following uncertainties:
- the remjected water isotopic composition (X_I) is variable, with averaged $\delta^{18}O$ = 5 ± 2 and δD = 0 ± 10, moreover; some fractionation occurs as a consequence ofthe existing residual plumes;
- before 1979 the average deep steam composition (X_R) was estimated as $\delta^{18}O$ = -2.5 and δD = -40. hut nothing can be said on occurred variations.

The decreased recovery at the end of 1992 is due to the change in the reinjection sites: indeed, in this period the reinjection wells were deeper and farther located form the monitored ones.

4. DISEQUILIBRIUM CONDITIONS IN THE RESERVOIR FROM ISOTOPIC DATA

Preliminary evaluations of the isotopic disequilibrium induced by reinjection among gaseous components of the geothermal fluid was described by Bolognesi *et al.* (1990). Starting from 1992. further analyses, of O. H and C isotopes of the fluid discharged by 20 wells of a S-N oriented transept crossing the whole field, confirm that after-reinjection samples show isotopic temperature always different than those obtained during precious period.

The reinjection effects on productive wells are a function of both the distance from the reinjection sites and the reservoir permeability. Both steam stable isotopes and major gas constituents clearly point to the different degree of interaction between deep and waste fluids. This is shown. for example. by the representative points of wells N. 137 (circles)and LePr.2 (stars) in the (a) and (b) diagrams of Figure *6.* The first one is strongly affected by reinjection, but it is not so for the second. Such disagreements disappear looking at the gas isotopic

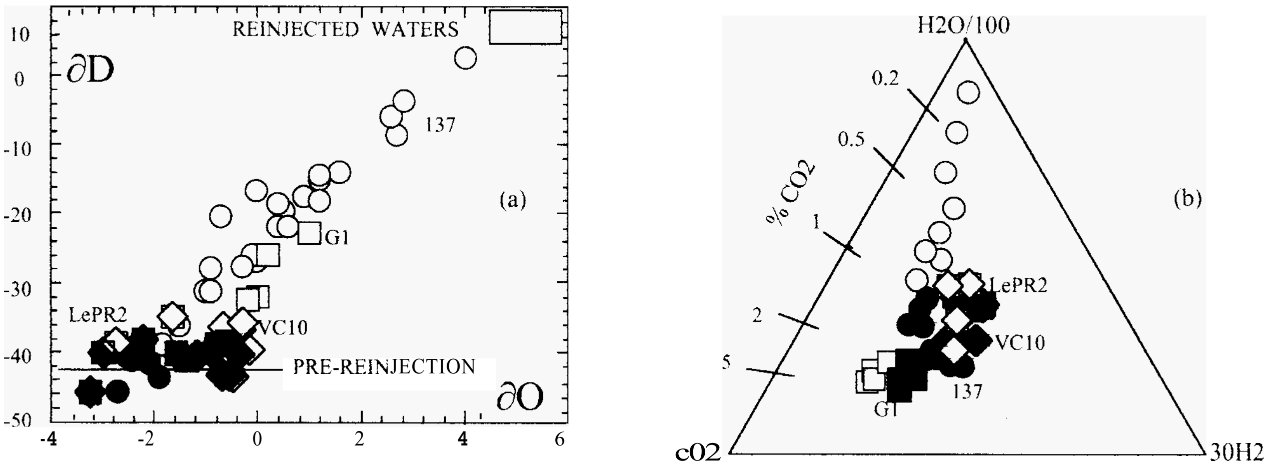

Figure 6 . Comparison between isotopic and chemical compositions of steam from some wells of Larderello collected before (full symbols) and after (empty symbols) reinjection. Among the different wells. N. 137 is located nearest to the reinjection site.

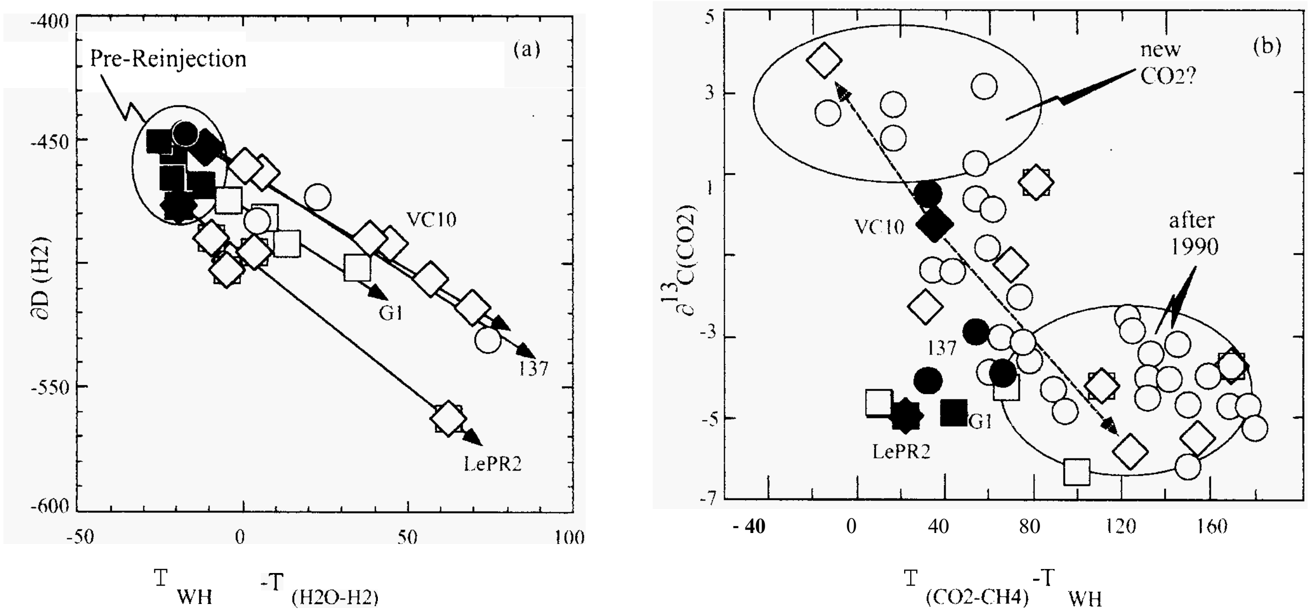

Figure 7. Observed variations of the isotopic tempertures before and after reinjection in the selected wells of Fig.6. Diagram (c) shows these variations computed with the pair (H2O-H2) in relation to the well-head temperatures. Diagram (d) shows these variations computed with the pair (CO2-CH4) in relation to the well-head temperatures.

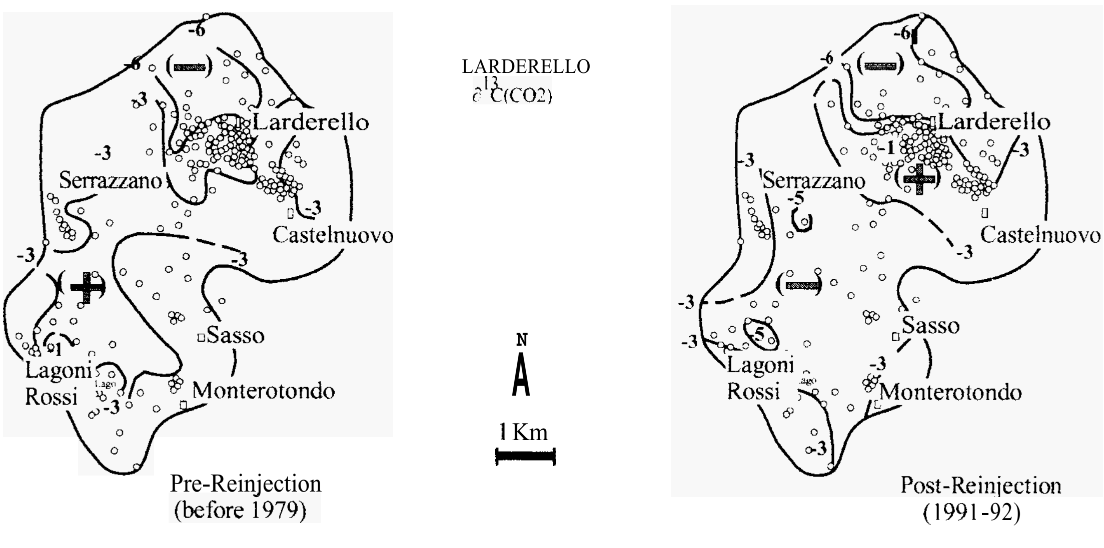

Figure 8. Carbon isotopic composition of carbon dioxide produced by the wells before and after reinjection.

composition. The $\delta D(H_2)$ vs T_{WH}-$T_{(H2O-H2)}$ diagram. (a) of the Figure 7, illustrates the difference between the temperature actually measured at the wellhead and the isotopically computed one. Before1979 (full symbols), the ΔT for all the wells was = 0°C or just -30°C; afterwards (empty symbols). the ΔT values increased to fifty degrees. showing that a similar isotopic disequilibrium was established.

Different is the behaviour ofthe $\delta^{13}C$ (CO_2) vs $T_{(CO2-CH4)}$ -T_{WH} in diagram (b) of Fig.7; the ΔT values. ≈ 40°C before 1979. during the first stages of reinjection underwent a considerable decrease. while after 1990 these rose up to 160°C. In this case the isotopic disequilibrium affects all the wells. These occurrences could be explained by the production of new H_2 and CO_2 in the presence of a boiling liquid plume in the producing reservoir.

A supporting argument is given by Figure 8, where the geographical distributions **of** ^{13}C contents of CO_2 in the field before and after reinjection are represented. Here important variations presumably induced by the injection of liquid in the steam reservoir are shown.

Just below the Larderello reference core, in fact. an enrichment of at least 2 ‰ can be observed, the more positive values being probably due to newly formed CO_2, by reaction of liquid water with limestones occurring in that area. In the area of Serrazzano and Lagoni Rossi. on the contrary. a very light carbon dioxide of unknown origin lowered the local $\delta^{13}C$ tag from - 3 to - 5. **As** regard the peripheral areas sensible variations of $\delta^{13}C$ have not been found until now

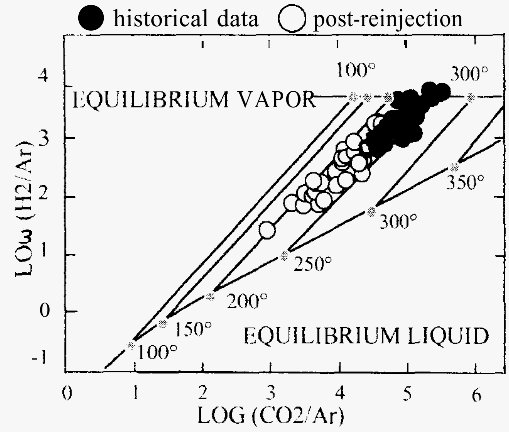

Figure 9. Evaluation of H2-Ar and CO2-AR equilibrium conditions. The concentrations are expressed in mmol/mol on water free basis.

Disequilibrium conditions at depth. besides isotopes. could be also supported by the relationship among H_2, CO_2, and Ar shown in Figure 9, after Giggenbach (1989). Here the representative points of the wells selected for the already mentioned transept are compared with some "historical' data from Sborgi (**1934)** and other unpublished data from 1932 to 1950. From an original composition representing a near-vapor equilibrium condition at about 250°C, a progressive influence of the injected water on the deep component implies an alignment along the 200°C isotherm.This occurrence requires further studies. because these values may not be the result of the attainment of full equilibrium, but rather the result of a meteoric Ar addition to the geothermal system.

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