MODELS FOR STEAM CHEMISTRY AT LARDERELLO AND THE GEYSERS

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ABSTRACT

Evolution with time of the chemistry of steam from three typical Larderello wells is interpreted to indicate that three sources contribute progressively to steam production. Initially and during the first ten to fifteen years of production (about 1940-1955 for two wells; 1962-1970 for the third), most steam came from vaporization of condensate just above the vapor-dominated reservoir. Initially this steam had a high flow because it originated close to the well bottoms and was low in temperature and gas and high in boron and ammonia. During this period, ammonia and boron content and flow rate decreased, and temperature and gas content increased as the condensate near the well was exhausted and the source of steam shifted to the vapor-dominated reservoir. Ten to twenty years later (after 1963) chloride appeared in the steam, and gas content decreased as vaporization of deep brine became a major steam source.

Chemical and isotopic compositional variations with geographic location are interpreted as resulting from pre-exploitation lateral steam flow from central boiling (or inflow) zones toward the edges of the system. During this lateral flow, conductive heat loss to the surface results in partial condensation; gases are concentrated in the residual steam and slightly volatile salts are removed into the condensate. This process is modeled as a Raleigh condensation obeying the equation:

$$C/C_o = (m/m_o)^{(1/K-1)}$$

where at any point C/C_o is the ratio of the concentration of a steam component to its original concentration; m/m_o is the fraction of steam condensed; and K is the distribution coefficient of the component between steam and water (C_s/C_w). The magnitudes of the variations at Larderello ($-3‰$ in $\delta^{18}O$, $+5x$ in CO_2 and $+3x$ in NH_3) suggest that the productive field is limited by excessive liquid water and non-condensable gas when 80 percent of the original steam flow has condensed. At The Geysers, a 17x increase in CO_2 and a $7‰$ decrease in $\delta^{18}O$ suggest that the limit is at 95 percent condensation. Lateral steam movement and condensation may have created the large lateral extent and cavernous porosity of these systems by leaching the reservoir rock. This model may be used with steam analyses from existing wells to guide field development.

INTRODUCTION

The compositions of steam from the vapor-dominated geothermal systems of Larderello, Italy and The Geysers, California have been shown by previous investigators to vary with position in the field (Celati et al., 1973; Panichi et al., 1974; D'Amore et al., 1977; Truesdell et al., 1977; Truesdell and Nehring, 1978; Mazor, 1978) and with time since drilling of individual wells (Sestini, 1970). In each of these studies, the compositional variations have been interpreted to be due to reservoir processes, including lateral cold-water recharge, condensation of steam, and vaporization of liquid water, but no quantitative models were proposed. In this paper, we examine variations of steam compositions with time and location and propose quantitative models for chemical and physical processes in the reservoir that could produce the variations.

These variations are complex because the composition of steam from each well changes with time as well as with its position in the field. Because exploitation has proceeded from zones in which the reservoir is close to the surface toward zones in which it is more deeply buried, some zones are very heavily exploited with many old, closely spaced wells and other recently developed zones have few, widely spaced wells. In the long-exploited zones the reservoir is at shallow depths and may have contained steam that differed in original composition from steam in the deeper, newly developed zones. Thus it may not always be possible to distinguish original differences from those induced by exploitation.

Detailed examination of the evolution with time of steam compositions from three typical wells indicates that steam from the main reservoir dominates the middle period of production. Certain constituents (H_3BO_3 and NH_3) show large decreases during early exploitation, and others (Cl) increase greatly late in the exploitation. Thus the middle period of a well's production appears to be the most reliable for modeling reservoir chemical patterns. A model for the evolution of steam compositions with time based on these data is presented in the next section.

CHANGES IN STEAM COMPOSITION WITH TIME

The changes with time since drilling of flow, temperature, gas/steam ratio, and ammonia, boric acid, and chloride concentrations of steam from three Larderello wells are shown in figure 1. In general each well showed similar evolution:

(1) The flow decreased rapidly in the first 15 years to about 10 percent of its initial value and then remained nearly constant.

(2) The flowing wellhead temperature of the steam was at first constant. After 5-10 years it increased rapidly to a broad maximum and then declined. Calculated well bottom temperatures were about 15 to 20°C higher but showed similar changes. The initial well bottom temperature was 215 to 235°C for the wells considered, but all maximum well bottom temperatures were just above 250°C.

(3) The gas/steam ratio increased more or less rapidly to a maximum 10 to 15 years after drilling and then declined.

(4) The NH_3 content of the steam rose to a maximum 5 to 12 years after drilling and then declined rapidly to generally constant values. The peak in NH_3 was independent of the peak in gas/steam ratio.

(5) The H_3BO_3 content of the steam reached a maximum shortly after drilling and declined rapidly to a nearly constant value in about 20 years.

(6) Chloride appeared in concentrations greater than 1 ppm after 1960 and increased rapidly to over 20 ppm by 1978.

(7) In the dry gas, concentrations of H_2S and H_2 decreased and those of other gases remained constant (N_2) or increased slightly (CH_4). These changes are not shown in the figure.

These observations can be explained only by an evolution of the source of the steam. We propose a model for the evolution of steam source that is based on the White et al. (1971) model of vapor-dominated systems. Our model in its simplest form explains the major features of the evolution of steam compositions and can be elaborated to explain individual differences. Only the behavior of NH_3 is not adequately explained by the model.

A THREE-SOURCE MODEL OF STEAM ORIGIN

In the geologic model of White et al. (1971), a vapor-dominated reservoir containing both ascending steam and downward-draining condensate is bounded above by rock saturated with hot condensate and below by rock saturated with hot brine. When a well is opened into such a reservoir, the resulting decrease in pressure causes existing steam to flow to the well and liquid water to vaporize in place to produce additional steam utilizing heat transfer from the rocks. The vaporization of liquid water to steam can occur in the saturated condensate and brine layers as well as in the two phase vapor-dominated reservoir so long as the liquid water is relatively immobile and does not flow to the well. Our model suggests that each of these zones contributes steam to the flow of the well; the main contributions occur in order of increasing distance from the well bottom.

The upper condensate zone and the lower brine zone both have a higher ratio of liquid water to rock than exists in the two-fluid-phase liquid-vapor reservoir where much of the void space contains steam. Steam produced from vaporization of liquid can be expected to be cooler and to contain higher concentrations of water-soluble components and lower concentrations of vapor-soluble components compared to steam from original vapor. The upper condensate and the

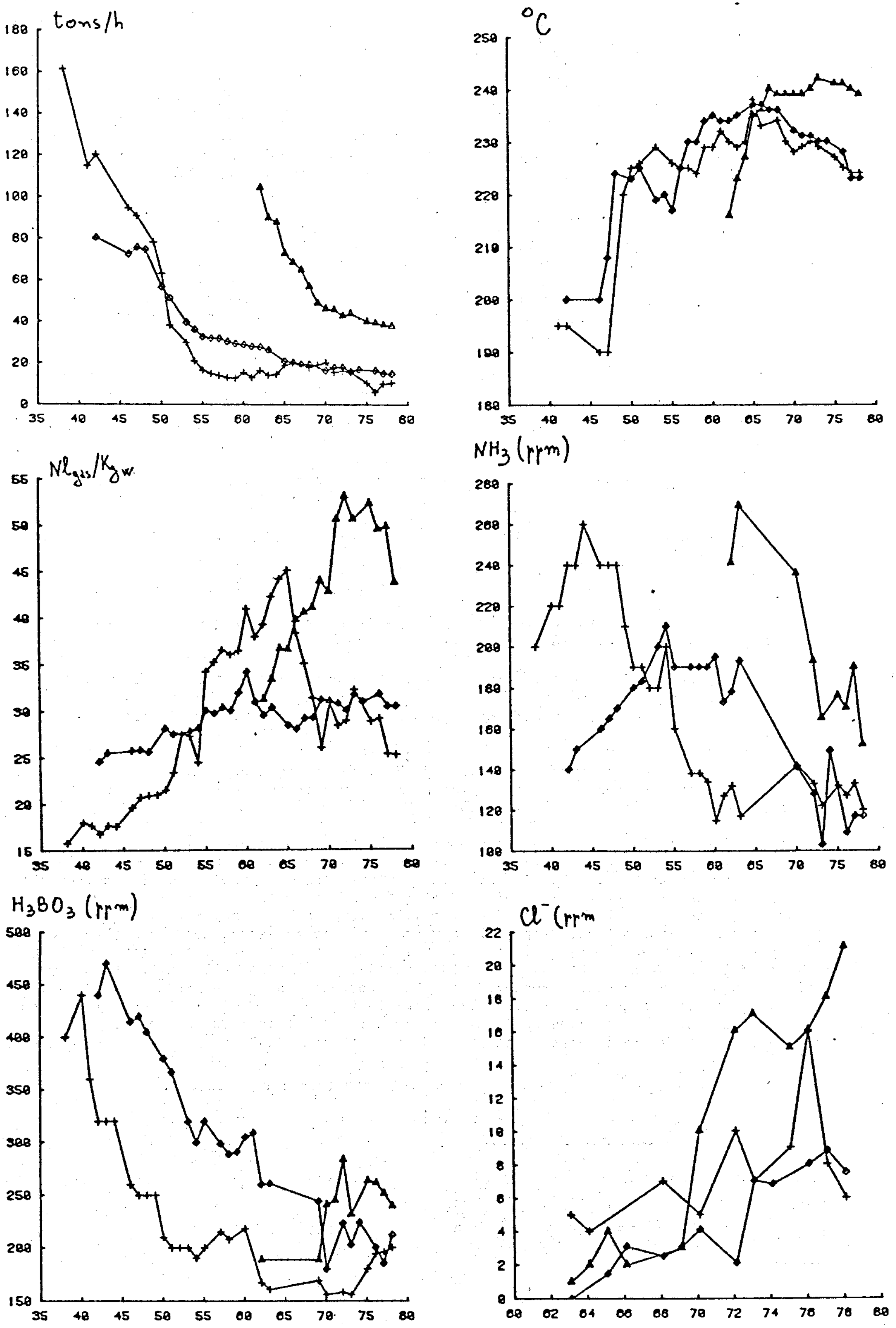


Figure 1. Yearly measurements of flow, well-head temperature and composition of steam from three Larderello wells (+ ALR, ◇ FBN, △ GR1).

brine differ in composition because certain volatile substances (NH_3, H_3BO_3) have been transferred from the hotter brine to the cooler condensate via the steam; they differ in temperature because the condensate is losing heat conducted upward to the ground surface and the brine is being heated from below; and they differ in distance from the well bottoms, which are usually near the top of the two-phase vapor-dominated reservoir, especially in older wells.

For these reasons, steam that originates from vaporization of liquid in the upper condensate zone would be expected to have the following properties relative to steam from the two-phase reservoir which consists largely of original vapor:

(1) a lower temperature because pre-exploitation temperatures were somewhat lower and because the liquid water/rock ratio is higher and more heat is required to vaporize the water;

(2) a very low gas/steam ratio because gas was selectively enriched in original vapor and is therefore deficient in steam newly vaporized from liquid;

(3) a much higher content of boron which is concentrated in liquid during condensation; and

(4) a higher flow rate because more of the water mass is close to the well and the average flow path is therefore shorter.

Steam originating from vaporization of the underlying brine would be similar to vaporized condensate except that:

(1) the flow rate would be much lower because the steam originates far from the well;

(2) the temperature lowering effect of vaporization would be masked by travel through the reservoir and heat exchange with rock;

(3) some components of the brine that are virtually insoluble in steam (e.g. chloride) and not normally present in steam or condensate may appear in the steam when the brine becomes sufficiently concentrated owing to production-induced boiling; and

(4) after sufficient time, boiling of brine may extend into deeper parts of the brine body where higher temperatures occur and the steam temperatures may then increase. This increase in steam temperature was not observed in the wells considered but has been reported in other wells (Sestini, 1970).

Our model of the evolution of steam properties suggests that progressively deeper sources of steam are tapped during the history of a well. The dominant steam source initially is vaporized liquid from the condensate layer, then original vapor and vaporized liquid from the two-fluid-phase, vapor-dominated reservoir and finally vaporized liquid from the deep brine body. This sequence may be telescoped if deep drilling bypasses the upper part of the vapor-dominated reservoir. Thus, deep wells may not show the full sequence although a recent (1962) deep well at Larderello did (figure 1). This model has been applied to the evolution of steam compositions from the ALR well from 1938 to 1978. For this well, the contribution from each source and the resulting evolution in steam composition and temperature along with the observed compositions and temperatures are shown in figure 2. The calculated compositions of steam from each of these sources are shown in table 1. The temperatures used are bottom-hole temperatures calculated by the methods of Nathenson (1975).

Table 1.--Model properties of steam reaching well ALR from three sources.

Source	Upper Condensate	Vapor-dominated reservoir	Deep brine
Temp., $^{\circ}C$	215	254	232
Gas, Nl/kg	0	44	0
NH_3, ppm	355	120	153
H_3BO_3, ppm	405	160	255
Cl, ppm	0	0	33

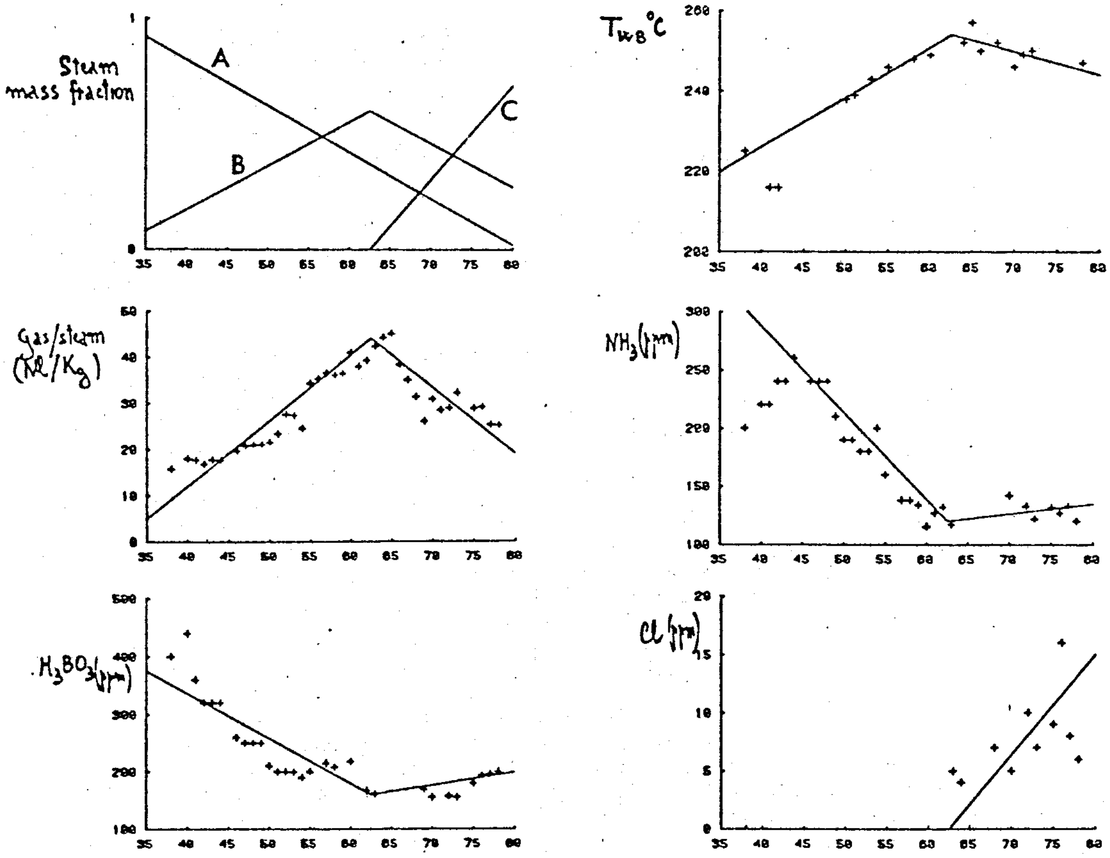


Figure 2. A simple three source model of steam from the ALR well. Source A is the condensate layer, B is the vapor-dominated reservoir, and C is the deep brine.

In our simple model of the ALR well, steam from vaporization of condensate just above the vapor-dominated reservoir predominates for the first 17 years. This steam has a low temperature (215°C, about 40°C below the original reservoir temperature) resulting from the vaporization of about 6.5 percent liquid in the rock. It is high in ammonia (355 ppm) and boric acid (405 ppm), substances carried in steam but also relatively soluble in water, and contains little gas and no detectable chloride.

Steam from the main vapor-dominated reservoir dominates the next 17 years. This steam is higher in temperature (254°C, almost the same as the reservoir temperature) because little liquid water vaporized during production and higher in gas because original vapor is produced along with vaporized condensate. The NH_3 and H_3BO_3 concentrations (160 and 120 ppm) are about one-third that of the condensate steam. Essentially all of the gas (CO_2, H_2S, etc.) produced from the well was contained in this part of the system. The flow rate of steam from the well is much lower than during the initial, condensate-dominated phase because the source of steam is dominantly vapor and thus originates at greater distances from the well. If the condensate in the two-phase reservoir is assumed to have the same composition as condensate in the overlying layer, then it constitutes only one-third of the total mass of fluid and, in a rock of 10 percent porosity, would occupy only 0.6 percent of the total volume.

Steam from the deep brine that dominates the last five years production is similar to condensate-produced steam in containing essentially no gas but differs in containing chloride and in having lower concentrations of ammonia and boron. The chloride is probably transported as ammonium chloride formed because production-induced boiling concentrated chloride in the residual brine. The absence of chloride in steam from the condensate or two-phase layers suggests that chloride is not transported upward in the natural system and that transport occurs as a result of exploitation.

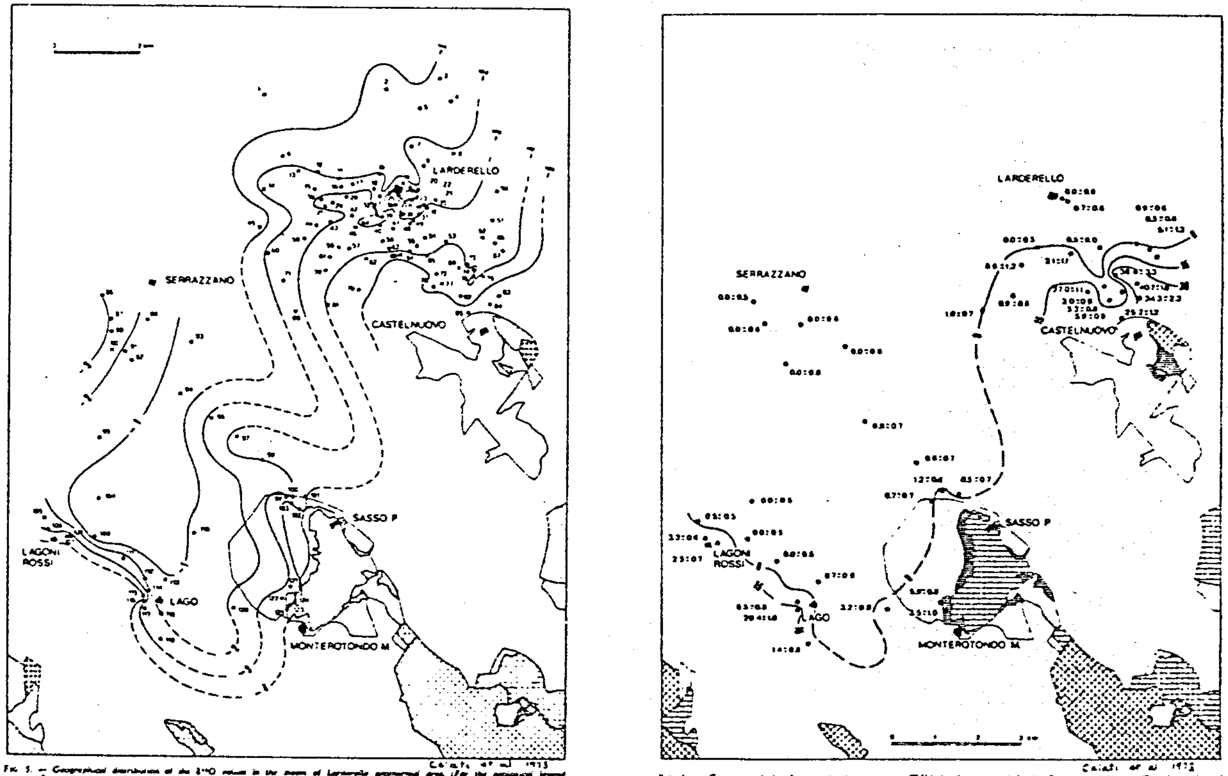
The stability of the steam flow rate during boiling from the brine indicates a near constant distance of travel. The temperature is not a reliable indicator of the fraction of liquid in this zone because the steam temperature is influenced by rock temperatures in the two-phase zone, but the observed temperature decline does suggest higher liquid water contents compared to the vapor-dominated reservoir, possibly near 2-3 percent of the total volume. The deep brine layer can be expected to be stratified, and the chemical and thermal properties of steam evaporated from this layer may change with time.

This model is semi-quantitative; the calculations of steam compositions from each layer do not have unique solutions. However, the evolution of steam compositions clearly supports the model of an upper condensate layer, a two-fluid-phase, vapor-dominated reservoir, and a deep brine layer.

This model does not satisfactorily explain the relatively high concentrations of ammonia in steam from the condensate and brine. Ammonia is a gas, and unless it is ionized, it should partition into steam rather than condensate. However, the condensate ammonia may have an independent origin and may not be in equilibrium with ammonia in the steam. Ammonia could have been formed within sedimentary layers in the shallower part of the reservoir by thermal degradation of organic material in a strongly reducing environment and held as NH_4^+ adsorbed on clay minerals (D'Amore and Nuti, 1977). The distribution of ammonia in these layers may not be uniform, and the part closest to the vapor-dominated reservoir may contain less ammonia than the upper parts. This uneven distribution may explain the initial rise in ammonia observed in each of the three wells considered and may explain why changes in ammonia are independent of changes in gas/steam ratio.

GEOGRAPHICAL PATTERNS OF STEAM COMPOSITION

The most conspicuous chemical patterns observed in the Larderello vapor-dominated geothermal field are the strong increases or decreases from the center to the edges of constituents carried in the steam (Celati et al., 1973; Panichi et al., 1974; and D'Amore et al., 1977) that are shown in figure 3. Similar patterns have been observed at The Geysers (Truesdell et al., 1977 and M. Gulati, oral communication, 1979).



Celati et al 1973

FIG. 5. — Geographical distribution of the δ18O values in the steam of Larderello geothermal area. (For the geological legend see Figure 1).

Celati et al 1973

FIG. 6 — Geographical distribution of tritium content (T.U.) in the steam of Larderello geothermal area. (For the geological legend see Figure 1).

Figure 3a. Geographical distribution of ^{18}O and tritium in Larderello steam, from Celati et al. (1973) and Panichi et al. (1974).

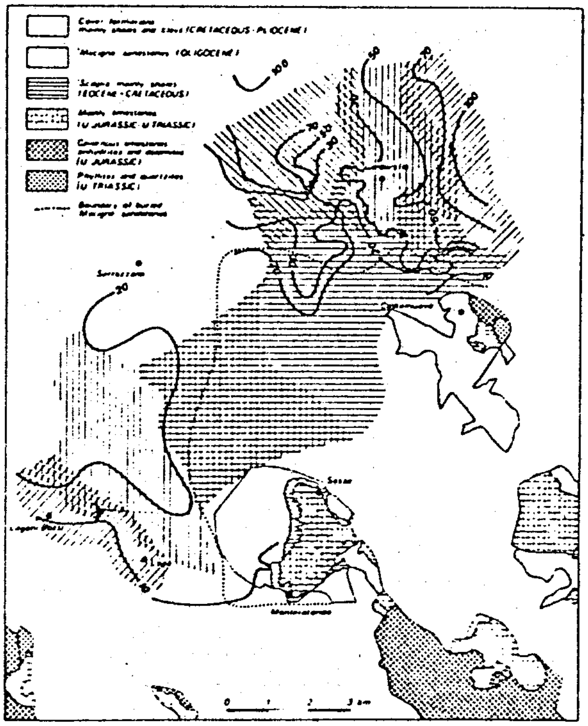


Fig. 5 Geographical distribution of the gas steam ratio in Larderello geothermal field

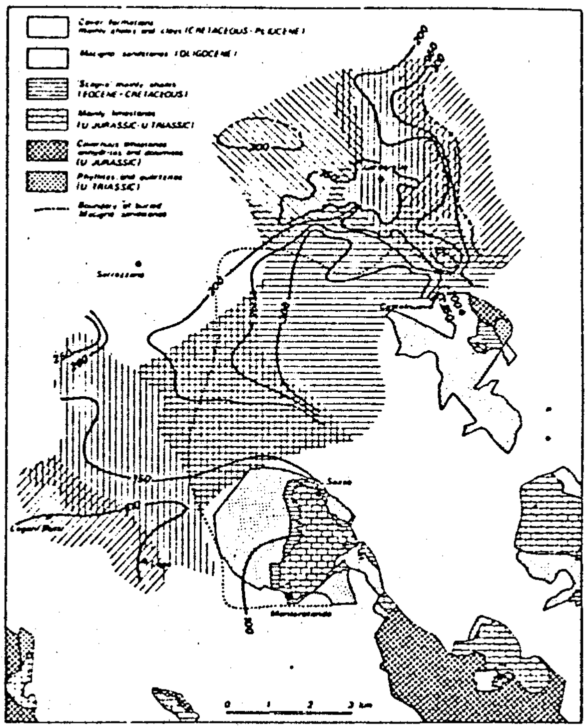


Fig. 3 Geographical distribution of NH_4^+ content (ppm) in the steam of Larderello geothermal field

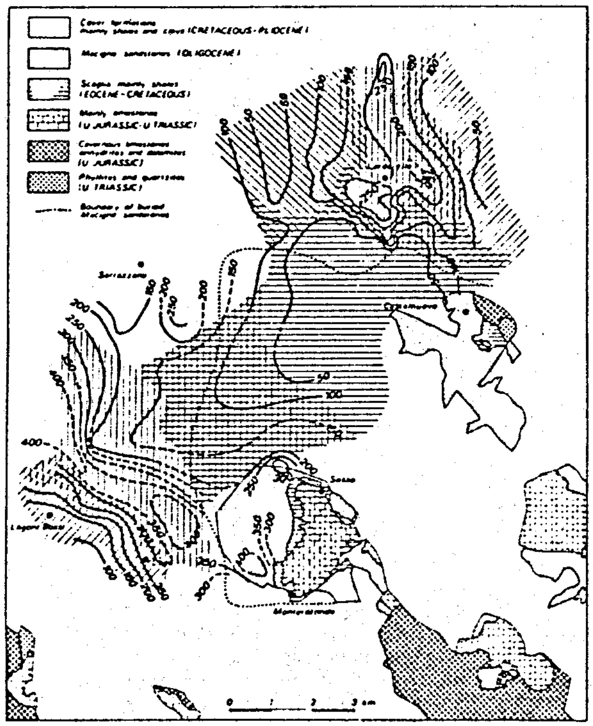


Fig. 4 Geographical distribution of H_3BO_3 content (ppm) in the steam of Larderello geothermal field

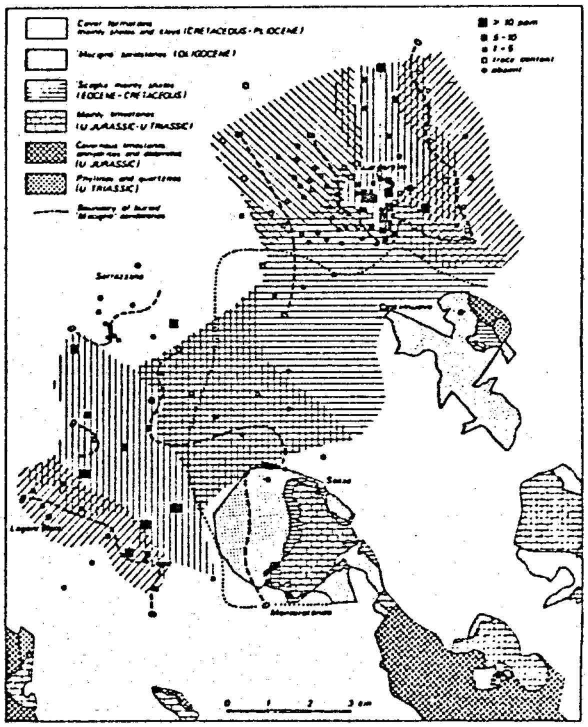


Fig. 2 Geographical distribution of Cl^- content (ppm) in the steam of Larderello geothermal field. The subdivision into zones of Fig. 6 is also shown

Figure 3b. Geographical distribution of gas/steam, NH_4, H_3BO_3 and Cl in Larderello steam, from D'Amore et al. (1977).

In general, gas concentrations (gas/steam, NH_3) increase from the center to the edge whereas concentrations of substances more soluble in liquid (^{18}O, H_3BO_3, Cl) decrease in this direction. These distribution patterns suggest lateral steam movement from the center toward the edges and partial condensation and removal of liquid-soluble constituents and residual concentration of gases. This process of lateral steam movement and condensation was suggested by D'Amore et al. (1977) to explain the gas/steam patterns at Larderello and by Truesdell et al. (1977) to explain ^{18}O distribution at The Geysers. We propose here a quantitative model of this process.

A RALEIGH CONDENSATION MODEL

In the proposed condensation model (shown schematically in figure 4) steam entering the two-fluid-phase (liquid-vapor) reservoir from a central boiling or upflow zone flows laterally and loses heat to the surface. The heat loss causes part of the steam to condense and drain downward to a liquid-saturated zone at the bottom of the reservoir while residual steam continues lateral movement toward the edges of the reservoir. The condensate may flow back to the central zone and be re-vaporized. This model differs from that of White et al. (1971) which suggested that boiling took place under the entire area of the reservoir. We propose that boiling (and steam upflow) takes place in several zones of limited area that are probably equivalent to the upflow zones of water dominated systems. The lateral flow of steam and solution of rock minerals by newly formed condensate produce the much greater areal extent of vapor-dominated systems compared with hot water systems.

The suggested lateral vapor movement with liquid condensation and phase segregation is analogous to atmospheric processes in which water vapor moves inland from warm oceanic sources and becomes depleted in ^{18}O and D as condensed phases (rain and snow) precipitate. The resulting changes in oxygen and hydrogen isotopes have been successfully modeled as a Raleigh process (Dansgaard, 1964). In a Raleigh process the products of a reaction are continuously removed as they are formed so the remaining material becomes more and more chemically or isotopically fractionated as it diminishes in mass. Because of the analogy with atmospheric condensation, we decided to model the changes in steam composition as a Raleigh process.

The mathematical basis of a Raleigh process is quite simple. It can easily be modeled numerically, but it is more compactly expressed by an analytical formulation (Manuel Nathenson, written communication, 1979). The distribution constant is defined as $K = Cs/Cw$ where Cs and Cw are the molar concentrations of a substance in steam and in water. The mass of this substance in steam of mass m is, after a small amount of condensation Δm, equal to the sum of the mass in the remaining steam $m-\Delta m$ and in the newly formed condensate Δm. The derivation follows directly:

$$mCs_m = (m-\Delta m)Cs_{m-\Delta m} + \Delta mCw_{m-\Delta m},$$

$$(mCs_m - mCs_{m-\Delta m})/\Delta m = Cw_{m-\Delta m} - Cs_{m-\Delta m},$$

$$mdCs/dm = Cw - Cs.$$

Introducing the distribution constant:

$$mdCs/dm = (1/K-1)Cs,$$

$$dCs/Cs = (1/K-1)(dm/m).$$

Intregrating from the initial conditions (C_o, m_o):

$$C/C_o = (m/m_o)^{(1/K-1)}.$$

Figure 5 shows results obtained from this equation for C/C_o versus $1 - m/m_o$ for several values of the distribution constant, K. With progressive condensation, all gas ($K > 1$) concentrations in the steam increase rapidly (are concave upward) and go to infinity as the value of $1 - m/m_o$ approaches one. The concentration in the steam of substances more soluble in water than in steam ($K < 1$) go to zero as m/m_o approaches zero. C/C_o decreases slowly (concave downward) for $1 > K > 0.5$ and rapidly (concave upwards) for $K < 0.5$.

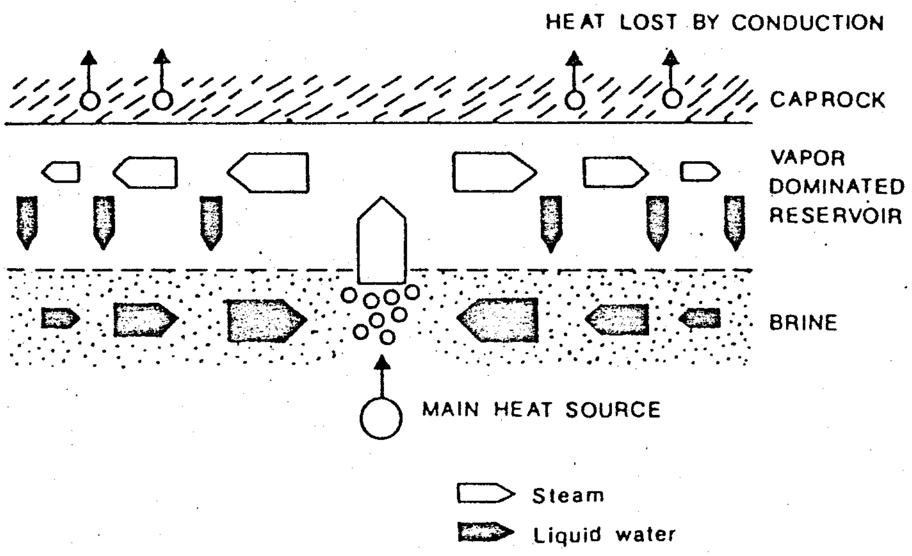


Figure 4. Lateral steam movement and condensation in vapor-dominated geothermal systems.

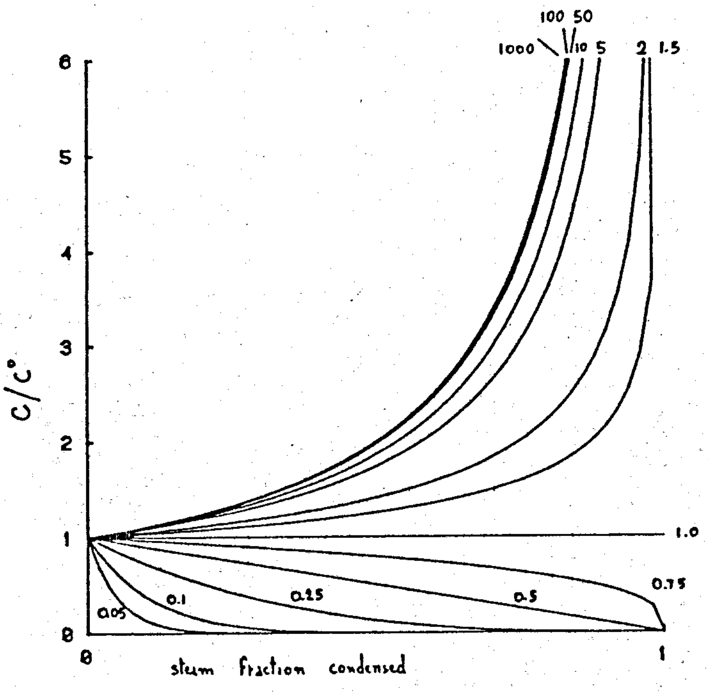


Figure 5. Results obtained from the Raleigh condensation equation for $K = 0.05$ to 1000.

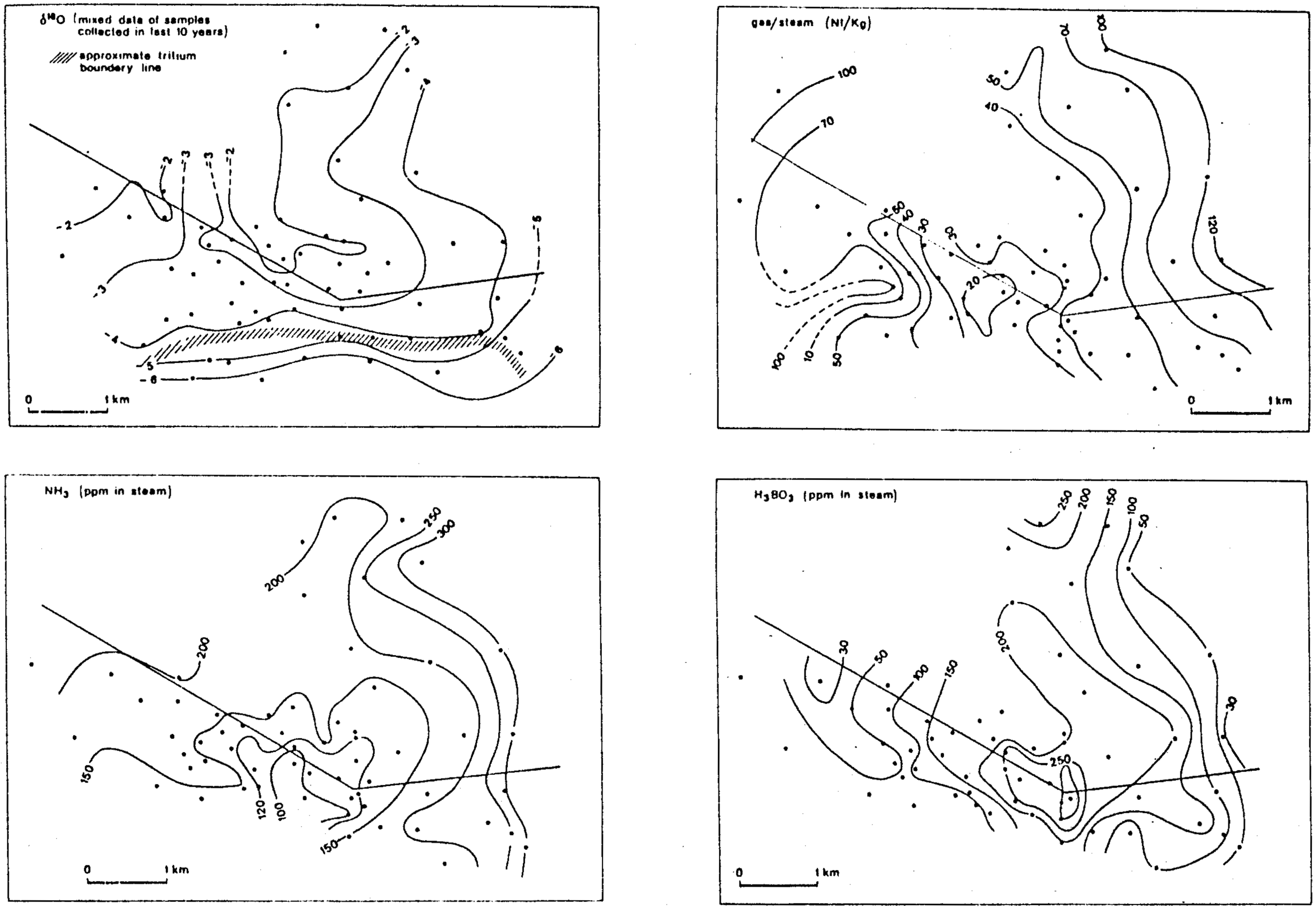


Figure 6. Detailed patterns of $\delta^{18}O$, gas/steam, NH_3 and H_3BO_3 in the northern part of the larderello geothermal field and the line of the profiles shown in figure 7.

Using detailed concentration data, profiles of gas/steam, NH_3, H_3BO_3, Cl and $\delta^{18}O$ were taken across the northeast zone of Larderello along what was considered to be a steam path. This path was somewhat arbitrarily chosen to cross a maximum range in each variable and to avoid the area of Castelnuovo where recent recharge was indicated by the presence of tritium. The detailed concentration patterns for ^{18}O, gas/steam, NH_3, and H_3BO_3, and the line of the profiles are shown in figure 6. The concentration pattern of Cl is similar to that of H_3BO_3 but rapidly decreases to zero within 2 km of the center. The resulting concentration profiles are shown in figure 7.

To apply the Raleigh model to the field data, we made a search of the literature for experimental distribution coefficients of the gases and slightly volatile solutes found in Larderello steam. In figure 8 calculated profiles are shown for substances found in Larderello steam (CO_2, NH_3, H_3BO_3, and Cl) based on experimental distribution coefficients for 240°C (a reasonable average temperature for Larderello). Experimental data for gas solubilities appear to be quite reliable, but data for boric acid are limited and data for chloride are nonexistent. The calculated curves are therefore highly approximate for boric acid and chloride. Also shown in figure 8 is a curve for $\delta^{18}O$ calculated from a form of the Raleigh condensation equation appropriate to the standard notation for isotope concentrations:

$$\delta - \delta_o = 1000[(m/m_o)^{(\alpha-1)} - 1]$$

where α is the fractionation factor between water and steam.

The calculated profiles in figure 8 have been scaled for direct comparison with the observed profiles in figure 7. The coincidence of calculated and observed concentrations from the center to the east is nearly exact for ^{18}O and NH_3 and satisfactory for gas/steam. With a shift of the center about 1 km, the observed concentration profiles of H_3BO_3 and Cl match those calculated although the correspondence is less significant because the experimental distribution coefficients for these species are uncertain.

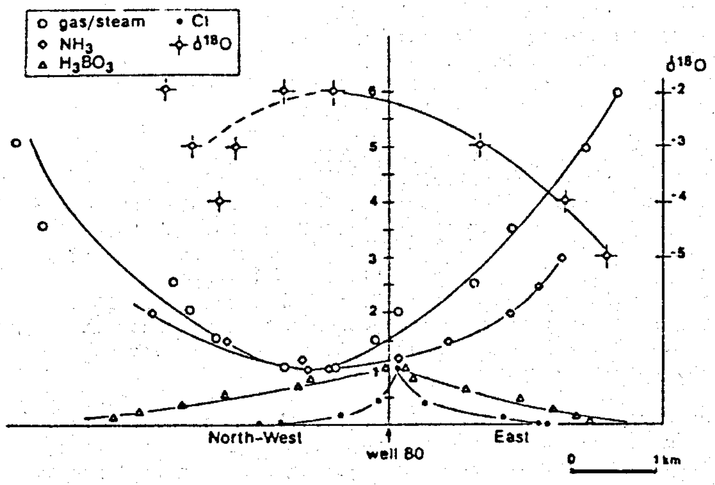


Figure 7. Observed concentration profiles of substances in steam along a line through northern Larderello shown on figure 5.

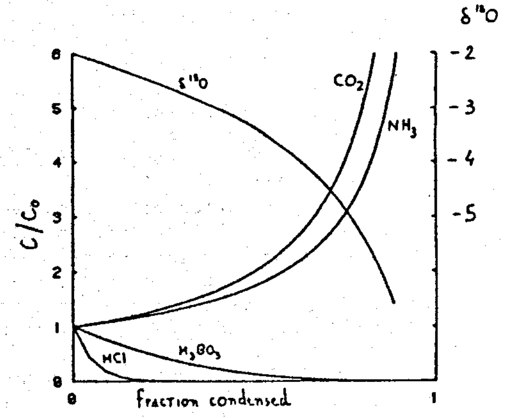


Figure 8. Concentration profiles calculated from the Raleigh equation for comparison with figure 6.

Limited data from The Geysers (made available by Union Oil Co.) show that the Raleigh condensation model also explains the major patterns of steam composition in this field. Figure 9 shows a profile of CO_2 contents from the center to the edge of the producing field (crosses) and a theoretical line for CO_2 in steam condensing by the Raleigh model.

The agreement of the observed and calculated profiles (figures 7-9) demonstrates the operation of a Raleigh condensation process along the steam flow path of the sections. For this process to operate in a chosen section, certain special conditions must have occurred:

(1) the chosen section must be along a steam flow line;

(2) condensation must occur along this line probably as a result of conductive heat flow to the surface; and

(3) the rate of condensation (and thus of heat flow) must be uniform so that the fraction condensed increases uniformly from zero to one along the section.

Although we have illustrated the Raleigh condensation process from study of changes along sections of Larderello and The Geysers, the general distribution of ^{18}O, gas/steam, NH_3 and other species indicates that Raleigh condensation controls patterns in steam composition over most of the Larderello reservoir. We believe that the process also determines the distribution of ^{18}O and gases in The Geysers steam although supporting data are more limited. In the northern part of Larderello, steam from the edges of the field is generally higher than the center in gas/steam by 5 times, in NH_3 by 3 times, and lower in $\delta^{18}O$ by 3°/°°. The magnitudes of these changes are close to those predicted by the model for 80 percent condensation of the original steam -- 5 times increase in gas/steam, 3.6 times increase in NH_3, and 3.2°/°° decrease in $\delta^{18}O$. These figures suggest that at Larderello the boundary of the productive field is defined by 80 percent condensation of steam. Beyond this boundary the accumulation of noncondensable gases is so great and the amount of steam flow so limited that wells are not productive. At The Geysers, the +17X change in CO_2 concentrations (figure 9) and the -7°/°° change in $\delta^{18}O$ (Truesdell et al. 1977) suggest that productivity in this field extends to 95 percent condensation. This difference may result from the much lower gas concentrations in steam from The Geysers.

PRESERVATION OF CHEMICAL GRADIENTS DURING EXPLOITATION

Up to this point we have discussed the composition of the steam phase in the reservoir and assumed that the chemical gradients predicted by the model for reservoir steam will be those observed in steam produced by the wells. To some extent this simple assumption is true; reservoir steam is produced by wells, but calculations have shown that steam contained in the reservoir as vapor is insufficient to provide the large quantities of steam produced by these systems (James, 1968; White et al., 1971; Nathenson, 1975). All reasonable models for these systems assume that most of the steam is produced from vaporization of liquid water (Truesdell and White, 1973). If this is the case, how is it possible that chemical patterns calculated for the vapor in the reservoir can be observed in steam that originates from reservoir liquid? The patterns of for ^{18}O and NH_3, which are reasonably soluble in both vapor and liquid, are not hard to explain . Figure 10 shows the calculated ^{18}O compositions of both steam and condensate for the condensation process. The isotopic difference between the phases is constant and the condensate shows the same gradient as the steam. Thus steam produced from complete vaporization of condensate would exhibit the same ^{18}O gradient as the steam, merely displaced to about 2°/°° higher values of $\delta^{18}O$, and any mixture of original steam and steam from vaporization of condensate would show approximately the same changes. It is also quite reasonable to expect that NH_3 in steam from vaporized condensate would show the calculated gradient because condensate at 250°C will contain about 25 percent as much NH_3 as steam. CO_2 and other gases, however, present a greater problem.

At equilibrium, condensate contains less than 1 percent of the dissolved gas concentration of steam so if most steam originates from vaporized condensate, relatively minor variations in the amount of steam from original vapor would greatly affect the gas/steam pattern. Since the observed gas/steam ratios are in good agreement with the model (figures 7, 8, and 9), we must suppose that a significant and nearly constant proportion of the steam of Larderello and The Geysers comes from original vapor in the reservoir. The changes with time of the gas/steam ratio discussed in the first section of this report suggest that, even after 40 years of production, a substantial proportion of the steam came from original vapor and that the gas/steam ratio varied by a factor of less than two after the first 10 years of production.

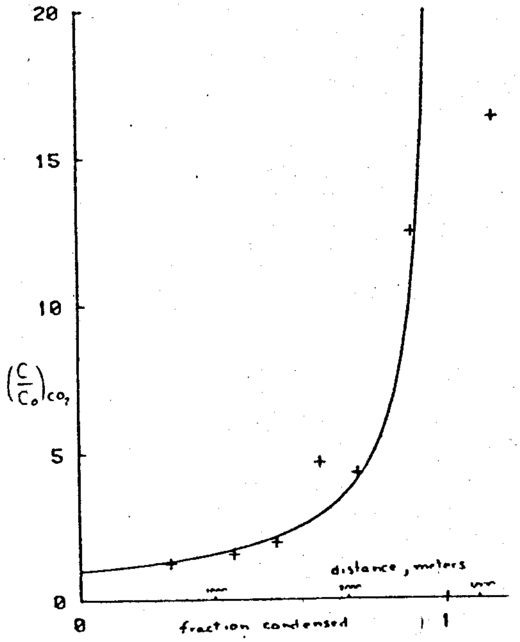


Figure 9. A CO_2 profile across part of The Geysers (+) compared with the calculated profile for CO_2.

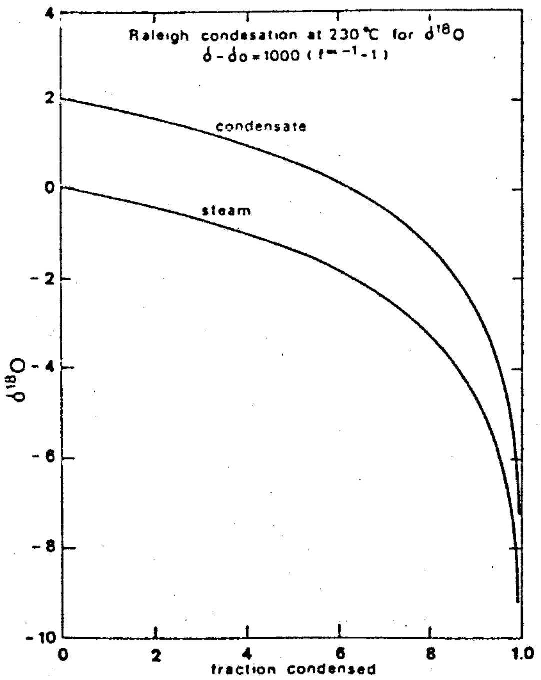


Figure 10. Calculated profiles for ^{18}O in steam and condensate ($f = m/m_o$).

These solubility considerations suggest that ^{18}O contents may be the most reliable indicator of the position of a well in the condensation sequence. Unfortunately, reliable records of ^{18}O contents of single wells spanning any considerable time period are too few to test this assumption.

OTHER PROCESSES POSSIBLY AFFECTING STEAM COMPOSITIONS

Oxygen-18 patterns at Larderello were considered by Panichi et al. (1974) and Celati et al. (1973) to be due to exploitation-induced marginal recharge by less-exchanged ^{18}O-poor water. This hypothesis is supported by the presence of significant amounts of tritium in steam from wells near areas where the reservoir complex crops out (Castelnuovo, Monterotondo, Lago and Lagoni Rossi; Celati et al., 1973) and by hydrologic balances that indicate substantial recharge to the Larderello system (Petracco and Squarci, 1976). Steep oxygen isotope gradients, however, also occur in areas without obvious recharge pathways or detectable tritium (northeastern Larderello, Serrazzano and all of The Geysers), and recharge cannot explain the ^{18}O patterns (much less the gas and ammonia patterns) in these areas.

The recharge model requires steam at the edges of the system to be out of isotopic equilibrium with the reservoir rock, but it appears very unlikely that lateral recharge could be rapid enough to prevent this equilibration. Steam without detectable tritium has probably been at temperatures near 240°C for more than 20 years and should have equilibrated isotopically with rock minerals. Even steam containing tritium is probably a few years old and should at least be in isotopic equilibrium with calcite, which is a major mineral in the Larderello reservoir. Experimental equilibration of ^{18}O between calcite and water takes 15 days at 240°C (O'Neil et al., 1969), and feldspar-water equilibrium at this temperature may be estimated to occur in a few years (equilibrium at 350°C was demonstrated in 20 to 40 days by O'Neil and Taylor, 1967).

The condensation model does not have this problem. Lateral steam circulation and condensation must have operated for many thousands of years before the field was exploited. This is sufficient time for the isotopic compositions of minerals in the flow pathways of steam and condensate to have equilibrated with the fluid compositions and achieved a stable gradient. Recharge cannot produce a stable gradient unless the intermediate mixtures are removed as they are formed. This is conceivable for the present heavily-exploited field but cannot have operated in the past when only a few vents existed.

Recharge also cannot be the cause of the increase of gas and NH_3 toward the system margins because recharge water contains little gas or NH_3. If recharge controls the chemical gradients of gas at the margins of the system, then the observed tritium contents should correlate with the observed increase in the gas/steam ratio. The correlation is in fact negative, and steam from parts of the field with high tritium shows abnormally low gas/steam ratios as well as low concentrations of other species (NH_3) originating in the geothermal system.

We believe that recharge in the Larderello system is local to areas of outcrop of the reservoir rock and has occurred recently in response to reservoir pressure declines caused by exploitation. The areas showing effects of recharge are thus limited to areas where steam contains tritium, and we have avoided data from these areas in developing our model.

It has been suggested (D. E. White, oral communication, 1979) that the observed gradients in gases and ^{18}O could be explained by the existence of vent areas where gas escapes (reducing gas/steam ratios) and boiling is intensified, producing steam from deeper, more oxygen-isotope-shifted water. This suggestion deserves consideration because vent areas in northern Larderello and The "Big" Geysers (but not in southern Larderello or the Lakoma Fame area of The Geysers) are centrally located close to the source areas postulated by the present theory. However, like the recharge theory, this theory does not explain how it is possible for steam and water to remain at 240°C in contact with rock without a shift of oxygen isotope composition. This theory also requires a steeper gradient in gas and ^{18}O near the vent (where the effect of pressure reduction is greatest) rather than at the edges as required by the condensation theory and as observed in Larderello and The Geysers. By this model, the different patterns in gas concentrations would result from different diffusion rates, and the isotope patterns would result from different degrees of water-rock reaction. It seems highly unlikely that these unrelated processes could produce by coincidence the magnitudes of change required to fit the Raleigh model for each steam constituent. The venting of gases that would otherwise accumulate to produce gas-rich systems such as those at Monte Amiata is undoubtedly important to the evolution of Larderello and The Geysers, but we do not believe that this process is as important as condensation in producing the chemical patterns in the steam.

The sequence of exploitation must also have some effect on the patterns of steam chemistry but cannot be the dominant influence. The exploitation of Larderello proceeded from zones of natural discharge where the reservoir could be tapped at shallow depths toward other zones where the reservoir was deeper and no surface vents existed. In the southern part of the field (Lagoni Rossi, Lago, Monterotondo, Sasso, and Castelnuovo), this early exploited zone corresponds to the edge of the field where steam ^{18}O and boron concentrations are relatively low and chloride is absent (here gas and ammonia contents have been reduced by mixture with recharge waters); in northern Larderello, early exploitation took place near the center of upflow where steam now has high ^{18}O, boron, and chloride and low total gas and ammonia concentrations. The correlation of steam chemistry with sequence of exploitation is thus opposite in these parts of the field and must be discounted as the source of the patterns. Furthermore, steam chemistry of The Geysers shows similar patterns in unexploited and exploited zones.

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