THE USE OF NOBLE GASES AND STABLE ISOTOPES TO INDICATE TEMPERATURES AND MECHANISMS OF SUBSURFACE BOILING AND (LESS CERTAINLY) RESERVOIR DEPLETION IN GEOTHERMAL SYSTEMS

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Salts are essentially insoluble in the low pressure steam produced from vapor-dominated systems. Hence, the normal chemical constituents used in studying hot-water geothermal systems prove ineffective in the study of subsurface conditions of vapor dominated systems. However, noble gases and stable isotopes of water may be used to fill this gap and may, in addition, provide a means of estimating the degree of reservoir depletion.

Although steam alone is produced from wells and natural vents in vapor-dominated systems, it is generally accepted that liquid water exists at depth. During exploitation this water boils in response to pressure decrease to produce steam which feeds the wells (Truesdell and White, 1973). As the liquid boils, gases and isotopes of hydrogen and oxygen fractionate between steam and remaining liquid. Oxygen-18 is fractionated preferentially into the liquid phase at all temperatures below the critical point of water while deuterium is preferentially fractionated into liquid water below 221°C. Above 221°C deuterium is preferentially fractionated into the vapor with a maximum fractionation occurring at 280°C. There is no fractionation of deuterium at 221°C and fractionation of both oxygen-18 and deuterium is zero at the critical point where the distinction between liquid and vapor disappears (Truesdell, et al., 1977).

Gases also exhibit temperature-sensitive fractionation between liquid and vapor, and their contents may be used to interpret subsurface boiling processes. The contents of the major gases of geothermal systems (CO_2, H_2S, H_2, etc.) are, however, also affected by chemical reactions and cannot be simply interpreted in terms of subsurface boiling. This limitation does not apply to the atmospheric noble gases (Ne, Kr, Xe, and most Ar) which are not reactive and originate only from solution of air in recharge waters (Mazor, 1976).

The solubilities of the noble gases, He, Ne, Ar, Kr, and Xe, have recently been determined up to the critical point of water (Potter and Clynne, 1977). The solubility in the liquid phase decreases steadily at temperatures greater than 0°C, then

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passes through a minimum (He = 25°C, Ne = 70°C, Ar = 100°C, Kr and Xe = 125°C) and finally increases steadily up to the critical point. The solubilities of the noble gases and nitrogen (which is also inert in most systems) are shown in figure 1 as Henry's law constants equal to the ratio of the partial pressure of the gas to its mole fraction in the liquid. Larger Henry's law constants indicate relatively liquid-insoluble gases, smaller constants relatively soluble gases.

The initial noble gas compositions of the recharge water can be estimated from the mean temperature of the recharge area, the noble gas composition of air and the experimental solubilities. Since the intake compositions can be estimated, it is possible to calculate the temperature of boiling from the noble gas contents of the steam. The assumptions involved in this calculation are that (1) the liquid water at depth has the same noble gas contents as the recharge water, (2) that the quantity of steam boiled off is small compared to the quantity of water remaining, and (3) that the water at depth is well mixed.

Instead of using absolute concentrations of the noble gases, it proves more reliable to use ratios of the various gases. Since He has a major non-atmospheric source we cannot use it in estimating boiling temperatures. The other noble gases are essentially all atmospheric and their original concentrations in the liquid phase can be estimated. Neon is the least soluble of the noble gases (Fig. 1) and ratios of neon with other gases are most useful in indicating boiling processes. Unfortunately, the Xe/Ne ratio changes little with temperatures above 80°C and therefore large uncertainties in the calculated boiling temperature result from analytical errors. The Ar/Ne versus T curve also has difficulties in that it goes through a maximum at about 230°C to 250°C and then decreases. The Kr/Ne curve is, however, a smoothly increasing function of temperature with a moderate slope and is satisfactory for boiling temperature estimation. In figures 2 and 3 these ratios are shown for steam samples from a geochemical section across the Larderello geothermal field (Table 1 and Mazor, 1977) with boiling temperatures calculated using an estimated recharge temperature of 10°C. The noble gas ratios appear to indicate slightly higher temperatures than those measured at the wellhead during flow. This is not unexpected as temperature decreases occur in the well due to adiabatic expansion.

The differences may however result from depletion of liquid water in the reservoir. It is reasonable to assume that the production of steam from a well may be modelled as a Rayleigh distillation process. Figure 4 is a Kr/Ne versus T plot on which contours for various fractions of water removed from the reservoir

by conversion to steam have been plotted. Data from the Pineta well did not plot near the established ratio curves in figures 2 and 3; however, figure 4 suggests that this is due to a high degree of depletion of the recharge fluid. This observation is in agreement with Pineta's history as well as its lower production temperature. In Figure 4 it can be noted that the ratio for Columbaia lies on the zero depletion curve. This observation agrees with the observation that it is the only well of this group which contains tritium, hence indicating active recharge of the system.

If samples of both the liquid and steam phase are available, the fractionation patterns of the stable isotopes will allow the temperature of boiling to be calculated. The isotopic data may also be used to set constraints on possible models of steam separation. Combined with noble gas data, models for subsurface steam separation in a geothermal system can be established. These models can be improved and more complete knowledge obtained of boiling mechanisms and of the volume and situation of liquid and vapor in steam-producing geothermal systems through long-term monitoring of stable isotopes and noble gases.

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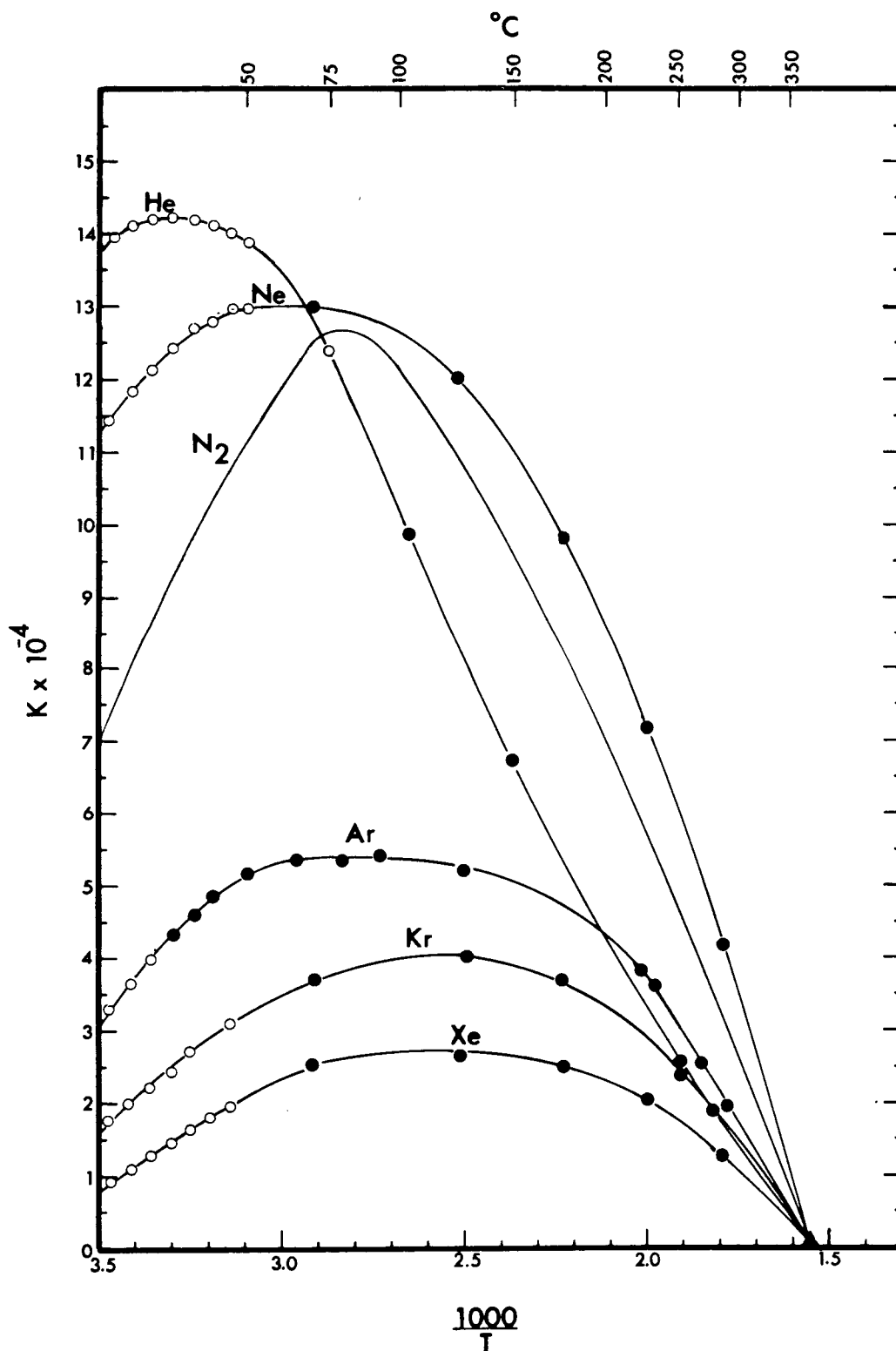
Figure 1. Solubilities of the noble gases He, Ne, Ar, Kr, and Xe
and of nitrogen from 0 to 374°C expressed as Henry's law constants
equal to the partial pressure of the gas in atmospheres divided
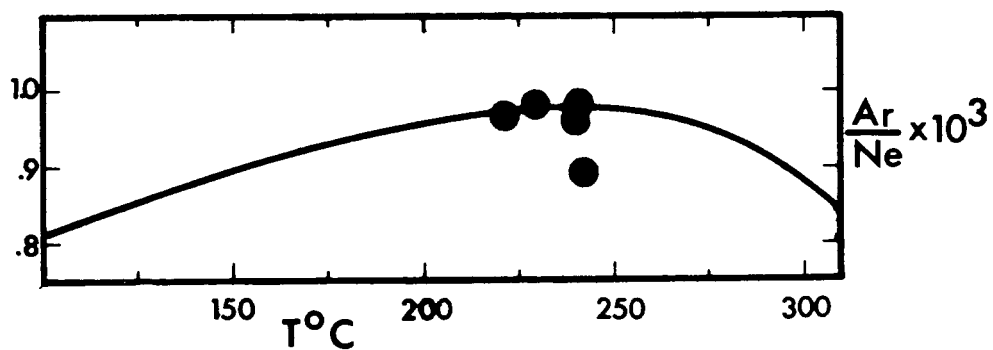by its mole fraction in the solution.

Figure 2. The ratios of Ar/Ne in steam samples from Larderello wells compared with calculated ratios for the first steam separated at various temperatures from a large well mixed body of water originally equilibrated with air at 10°C.
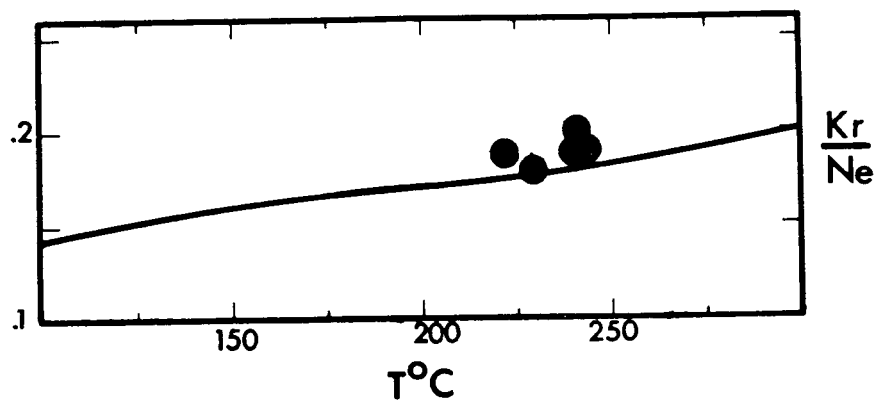

Figure 3. The Kr/Ne ratios calculated as in figure 2 compared with observed Larderello steam values.
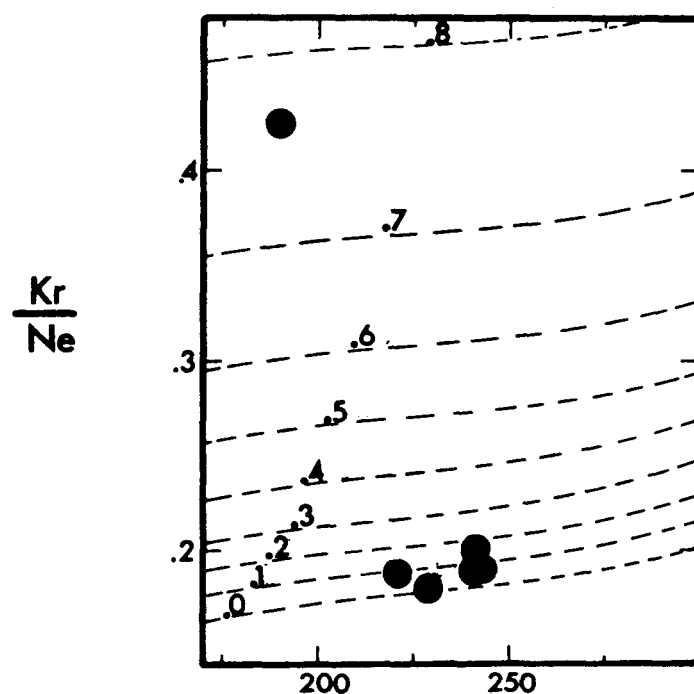
Figure 4. The ratios of Kr/Ne calculated for various temperatures and amounts of boiling (expressed as the fraction of steam boiled off) of a well mixed water body and the observed ratios of the Larderello steam samples.

Table 1. Characteristics of wells sampled.

Well	Date drilled	Depth m.	Production t./hr.	WHT* °C	WHP* kg/cm²	Gas/steam l./kg STP
				In August 1975		
Columbaia	?	470	9.1	229	2.4	3.25
La Pineta	1942	316	11.1	200	4.3	17.5
Lard.57	∿1951	486	10.7	241	4.3	46.1
Lard.155	∿1961	844	15.3	222	4.9	33.9
Gabbro 6	1964	771	52.2	242	7.7	69.3
Gabbro 1	1962	853	44	240	7.4	54.2

*Well head temperature and pressure during flow