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ORIGIN OF RARE GASES IN THE PALINPINON GEOTHERMAL FLUID AS TRACED FROM ISOTOPIC AND ELEMENTAL COMPOSITIONS

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ABSTRACT

Except for very high $^3He/^4He$ ratios (R/Ra = 6.5-8), noble gas isotopic ratios determined for eleven (11) well samples in Palinpinon approximate those of air. The He ratios are typical for island-arc settings, indicating a definite mantle He source for the Palinpinon geothermal fluid. The close to atmospheric ratios of the other noble gases (Ar, Ne, Kr, Xe), on the other hand, suggest that these are derived mainly from air or air-saturated water.

Re-calculated bulk compositions of Palinpinon noble gases can be explained by simple single and multi step boiling models. Dry well samples fit separated steam single step boiling lines, while 2-phase and liquid-dominated well fluids fall on multi-step boiling separated steam curves. There is, however, a systematic increase in Kr and Xe concentrations and normalized ratios, F(X) with decreasing Ne and Ar. This "behaviour" cannot be explained by boiling models, and it is construed that this is due to mixing between three (3) end-members - air saturated water (ASW), the geothermal parent fluid, and reinjection water.

1.0 INTRODUCTION

The use of noble gas isotopes to study geothermal fluids as an aid in reservoir management is a relatively new and unexplored field of noble gas geochemistry. Most of the work done on noble gas geochemistry (e.g., Ballantine & Barfod, 2000; Ozima, 1994; Burnard et al., 1997; Moreira et al., 1998, among others) deal with origins and compositions of mantle rare gases relative to atmospheric, cosmic and other noble gas reservoirs. Others workers (e.g., Kennedy et al., 1997; Sorey et al., 1993/1998; Hiyagon and Kennedy, 1992; Clark and Hudson, 2001; Magro and Pennisi, 1991; Torgersen and Kennedy, 1999, among others) use noble gas isotopes to monitor and interpret changes in volcanic areas and natural gas fields, as well as establish the origin of these gases. Work on noble gas isotope applications to geothermal geoscience have been done by only a limited number of researchers (e.g., Kennedy et al., 1991/2000; Hulston and Lupton, 1996; Christenson et al., 2002; Sano et al., 1985; Mazor and Truesdell, 1982; Welhan et al. 1988, Magro et al., in prep; Poreda and Arnorsson, 1992; Torgersen and Jenkins, 1982, among others). Very few of these studies, however, actually tackle the effects of field exploitation on rare gas compositions and isotopic ratios. Kennedy and Shuster (2000) demonstrated the role of returning reinjected water on the noble gas isotopic composition of the Dixie Valley geothermal fluid, but there have been very few other researches along this specific line of investigation.

This study was conceptualized to investigate the possible effects of reservoir processes on the noble gas isotopic and elemental compositions in the Palinpinon geothermal fluid (Fig. 1), along the same line as the work done in Dixie Valley. This study is part of a two-year technical co-operation project funded by the International Atomic Energy Agency (TC PHI/8/023). In this paper, analytical results will be presented and discussed. The interpreted origins of Palinpinon noble gases are derived from isotopic ratios, while effects of reservoir processes are correlated with rare gas elemental compositions.

2.0 THE PALINPINON GEOTHERMAL SYSTEM

Andesitic extrusive rocks of the Quaternary Cuernos Volcanics (CV) form the youngest stratigraphic unit in Palinpinon (Aniceto-Villarosa

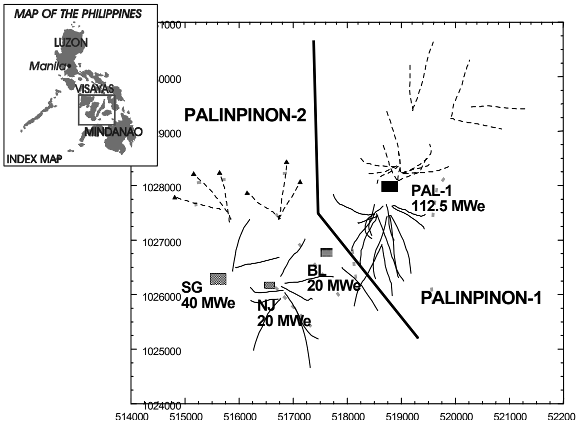

Figure 1. Location map of Palinpinon geothermal field.

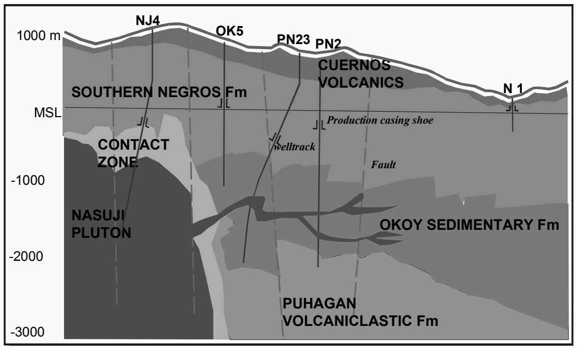

Figure 2. Conceptual subsurface stratigraphy of the Palinpinon geothermal field (horizontal axis not drawn to scale).

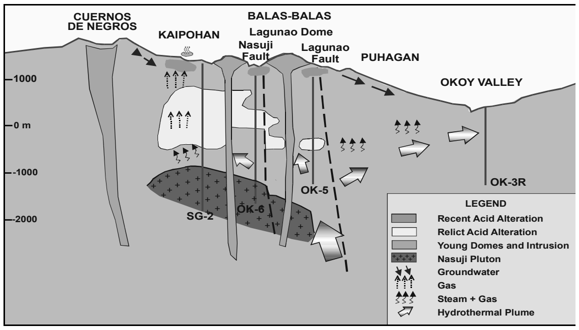

Figure 3. Conceptual Hydrothermal flow model, Palinpinon geothermal system (horizontal axis not drawn to scale).

et al., 1988; Fig. 2). These are underlain by hydrothermally-altered tuffs and lahars of the Pliocene-Pleistocene Southern Negros Formation (SNF). In the northeastern portion of the geothermal field, the SNF is underlain by a thick sequence of interbedded calcareous sedimentary rocks and volcanic breccias belonging to the Early Pliocene Okoy Sedimentary Formation (OSF). This is in turn underlain by the Puhagan Volcaniclastic Formation (PVF) made up of altered andesitic breccias of possible Middle Miocene age. Towards the northwest, the OSF is absent. In its place is a Late Miocene quartz monzodiorite body called the Nasuji Pluton (NP), enveloped by a contact metamorphic aureole (Contact Zone).

The center of the Palinpinon geothermal system lies near the Lagunao dome where upwelling geothermal fluids have temperatures greater than 300°C (Hermoso & Mejorada, 1997; Fig. 3). The parent fluid typically contains 4,000 mg/kg Cl. Northwest and northeast trending faults channel the upwelling brine to Nasuji and Sogongon in the northwest, and Puhagan in the northeast. In Nasuji-Sogongon, the brine has a temperature range of 260-280°C and Cl content of about 3,400 mg/kg due to dilution with meteoric water. In Puhagan, on the other hand, Cl concentration is higher (4,200-5,000 mg/kg) while fluid temperature is lower (<260°C) because of boiling. Stable isotope (^{2}H, ^{18}O) data indicate that the parent fluid in Palinpinon is composed of 80% meteoric and 20% "andesitic" water. The stable isotope trend conforms with meteoric water dilution in Nasuji-Sogongon (depleted) and boiling in Puhagan (enriched). Alteration assemblage in the whole field is neutral and progradational, in agreement with the current hydrothermal regime. There are sporadic occurrences of acid alteration assemblage, but these are mostly confined to the shallow portions of drilled wells.

The two major reservoir processes in the Palinpinon geothermal system in response to field exploitation are rapid reinjection fluid returns and boiling due to fluid extraction. The primary effect of the former is to reduce fluid temperature, increase fluid mineralization, and reduce gas levels. The latter process, meanwhile, has the same temperature and mineralization effect as the former but the gas concentrations increase significantly. Both processes are being controlled through proper production and injection well utilization.

3.0 WELL SELECTION FOR THIS STUDY

A total of eleven (11) geothermal wells were sampled for noble gas isotope analyses, namely

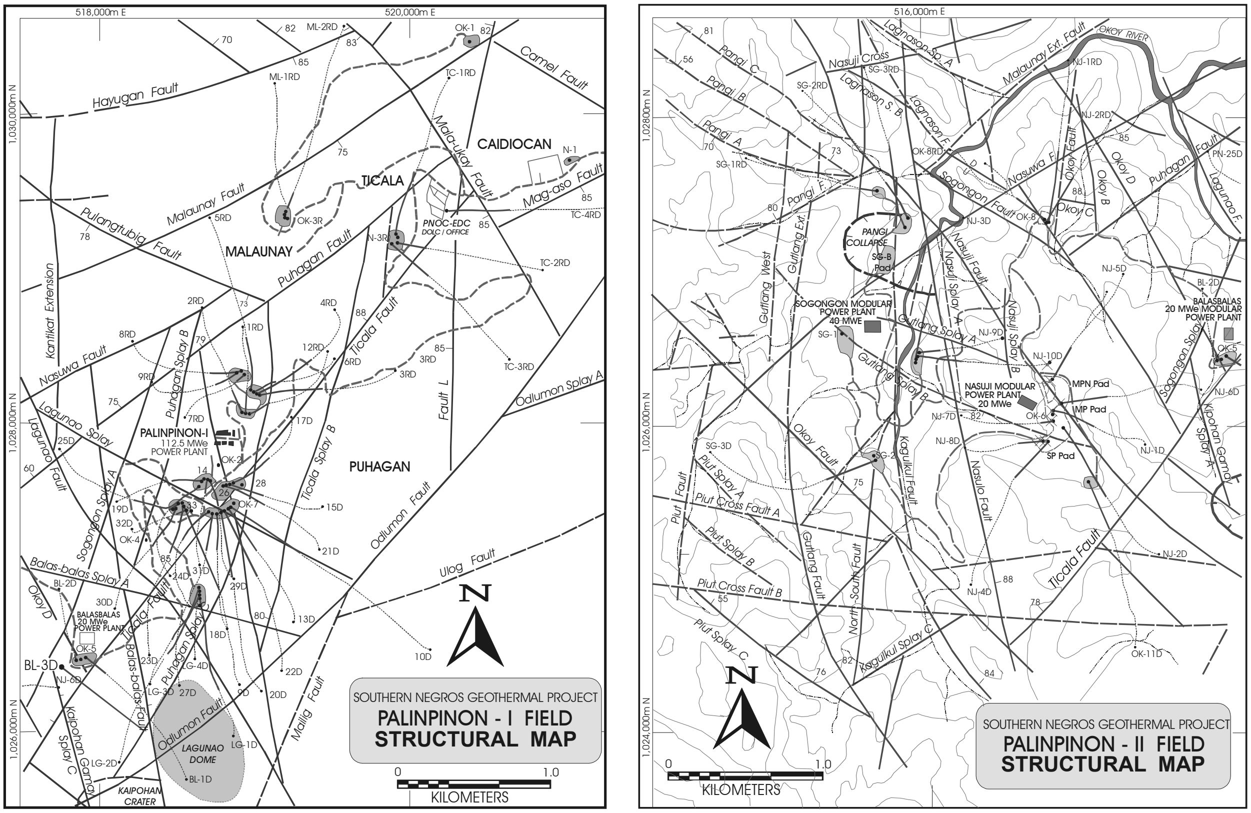

Figure 4. Palinpinon-I and -II structural and welltrack map.

LG-3D, OK-2, PN-15D, PN-22D and OK-9D from Palinpinon-I, and OK-5, BL-3D, NJ-5D, NJ-8D, SG-2 and SG-3D from Palinpinon-II (Fig. 4). All wells sampled were producers, carefully selected to obtain a representative spectrum of well fluids in Palinpinon.

The postulated upflow zone of the geothermal system is represented by fluids from wells OK-5, OK-9D, BL-3D and LG-3D. OK-2, PN-15D and PN-22D probe the Puhagan sector. Wells NJ-5D, NJ-8D, SG-2 and SG-3D, on the other hand, account for the Nasuji-Sogongon sectors. Well SG-3D also represents the western periphery of the field. With a large portion of the field being characterized by the presence of an expanded upper steam zone, four (4) wells - BL-3D, OK-2, SG-2 and PN-15D - were dry during the time of sampling. NJ-5D is a well that has been infected with reinjection fluid return, and this well was picked for this study to determine the effect, if any, of reinjection fluid on rare gas compositions and isotopic ratios.

Water and gas samples for complete chemical analyses were collected in tandem with noble gas samples for all wells. Complete water and gas analyses were analyzed in the Palinpinon chemistry laboratory, and results are given in Table 1.

4.0 RESULTS OF ANALYSES

The samples were analyzed for noble gas isotopic compositions at the noble gas laboratory of the Institute of Geochronology and Georesources (IGG), Council for National Research (CNR) in Pisa, Italy. The noble gases were separated from the other gases present in the sample in a high-vacuum all-metal line using a series of cold and hot traps. He, Ne, Kr and Xe isotopic ratios were measured by a magnetic mass spectrometer for rare gases (Map 215-50), while Ar isotope ratios were analyzed using a quadrupole mass spectrometer (Spectralab 200VG-Micromass). Elemental compositions were measured by comparison of the peak height with known amounts of air standard. The elemental compositions and isotopic ratios are summarized in Table 2.

Table 1. Water and gas chemistry of selected Palinpinon wells.

A) Water

	DATE	WHP	H	SP	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3	B	NH3	SiO_2	H_2S	CO_2T
SG3D	*5/22/01*	*0.87*	*1952*	*0.79*	*6.26*	*2871*	*649*	*57.3*	*0.29*	*917*	*20*	*17.6*	*85.7*	*1.37*	*706*	*3.2*	*2.5*
OK5	*5/23/01*	*0.92*	*2440*	*0.87*	*6.82*	*2554*	*382*	*81.8*	*0.04*	*4162*	*81*	*26.4*	*103*	*2.5*	*666*	*4.19*	*25.1*
OK9D	*5/23/01*	*0.88*	*1462*	*0.76*	*6.94*	*4359*	*71*	*282*	*0.24*	*7526*	*23*	*17.8*	*111*	*7*	*640*	*3.34*	*16.1*
PN22D	*5/23/01*	*0.70*	*1982*	*0.67*	*6.48*	*5327*	*823*	*418*	*0.32*	*9369*	*37*	*24.3*	*137*	*9.52*	*578*	*5.35*	*35.6*
NJ5D	*5/24/01*	*0.81*	*1358*	*0.76*	*6.85*	*3074*	*512*	*139*	*0.04*	*5253*	*14*	*18.1*	*81.6*	*1.53*	*658*	*3.41*	*20.2*
NJ8D	*5/24/01*	*1.26*	*1507*	*1.23*	*6.89*	*2513*	*475*	*38.6*	*0.02*	*4124*	*25*	*25*	*65.3*	*2.02*	*671*	*3.27*	*24.6*
LG3D	*5/21/01*	*0.72*	*2706*	*0.70*	*4.67*	*769*	*154*	*18.2*	*2.38*	*1113*	*352*	*0*	*58.9*	*25.4*	*708*	*1.43*	*0*

Units: Pressure (WHP, SP) in MPaa, Enthalpy (H) in J/g, chemical species in mg/kg

B) Gas

	DATE	WHP	H	SP	CO_2	H_2S	NH_3	He	H_2	Ar	N_2	CH_4
SG3D	*5/22/01*	*0.87*	*1952*	*0.79*	*456*	*22.73*	*0.6*	*0.003*	*1.247*	*0.06*	*6.55*	*0.461*
OK5	*5/23/01*	*0.92*	*2440*	*0.87*	*385*	*22.27*	*1.6*	*0.002*	*3.264*	*0.073*	*2.408*	*0.583*
OK9D	*5/23/01*	*0.88*	*1462*	*0.76*	*287*	*23.55*	*3.47*	*0.002*	*2.167*	*0.132*	*9.916*	*2.796*
PN22D	*5/23/01*	*0.70*	*1982*	*0.67*	*760*	*57.52*	*3.38*	*0.004*	*8.485*	*0.02*	*2.171*	*3.343*
NJ5D	*5/24/01*	*0.81*	*1358*	*0.76*	*219*	*16.73*	*0.81*	*0.001*	*1.102*	*0.022*	*1.38*	*0.326*
NJ8D	*5/24/01*	*1.26*	*1507*	*1.23*	*260*	*16.74*	*1.1*	*0.002*	*0.45*	*0.027*	*2.438*	*0.187*
LG3D	*5/21/01*	*0.72*	*2706*	*0.70*	*532*	*29.88*	*2.38*	*0.003*	*4.227*	*0.025*	*1.8*	*0.586*
BL3D	*5/23/01*	*0.96*	*2697*	*0.93*	*227*	*24.46*	*1.27*	*0.001*	*2.321*	*0.017*	*2.257*	*0.138*
OK2	*5/21/01*	*0.89*	*2700*	*0.84*	*537*	*44.36*	*4.66*	*0.006*	*2.494*	*1.928*	*194.8*	*2.455*
PN15D	*5/22/01*	*1.13*	*2685*	*0.68*	*724*	*47.83*	*4.56*	*0.004*	*8.356*	*0.199*	*20.09*	*3.568*
SG2	*5/22/01*	*0.77*	*1952*	*0.74*	*293*	*22.18*	*0.5*	*0.002*	*1.17*	*0.034*	*2.233*	*0.159*

Units: Pressure (WHP, SP) in MPaa, Enthalpy (H) in J/g, gas species in mmoles/100 moles steam

Table 2. Isotopic ratios and elemental composition of Palinpinon rare gases.

WELL	**R/Ra**	**(+/-)**	**$^{20}Ne/^{22}Ne$**	**$^{40}Ar/^{36}Ar$**	**$^{84}Kr/^{86}Kr$**	**$^{129}Xe/^{132}Xe$**	**$F(^4He)$**	**$F(^{20}Ne)$**	**$F(^{84}Kr)$**
SG3D	6.92	0.19	13.99		3.58	0.987			
OK5	7.69	0.24	12.01	300.4	3.29	0.988	94.52	0.54	3.95
OK9D	7.8	0.16	9.66	335.8	3.44	0.989	18.27	0.81	1.45
PN22D	7.27	0.23	10.31	313.3	3.32	1.106	90.48	0.79	1.42
NJ5D	7.63	0.16	10.69	311.6	3.24	0.99	27.45	0.56	5.85
NJ8D	7.5	0.22	10.37	282.30	3.61	1.006	54.51	0.53	5.59
LG3D	8.2	1.36	11.58	310.1	3.3	0.984	144.90	0.53	13.97
BL3D	7.4	0.23	10.6	295	3.35	0.987	39.04	0.53	3.05
OK2	7.54	0.11	9.65	319.4	3.35	0.99	1.74	0.98	1.09
PN15D	7.51	0.17	9.83	330.9	3.3	0.988	16.73	0.87	1.09
SG2	7.02	0.88	9.62	274.7	3.32	0.983	60.87	0.35	3.37
+/- (%)			***3.1***	***1.2***	***5.13***	***2.1***			
Air	**1**		**10.3**	**296**	**3.28**	**0.98**			

$*F(^aX)$ = relative abundance of X

$= (^aX/^{36}Ar)sample/(^aX/^{36}Ar)air$

WELL	*He, ppmv*	*Ne, ppmv*	*Ar, ppmv*	*Kr, ppmv*	*Xe, ppmv*	*He res, ppmv*	*Ar res, ppmv*	*Ne res, ppmv*	*Kr res, ppmv*	*Xe res, ppmv*
SG3D	7.60	0.045	232.0	0.102	0.0079	0.012323	0.362	2.63E-04	1.38E-04	1.06E-05
OK5	5.92	0.050	118.2	0.069	0.0097	0.007229	0.139	1.43E-04	6.66E-05	9.93E-06
OK9D	5.96	0.335	688.0	0.117	0.0194	0.005662	0.629	8.74E-04	9.89E-05	1.74E-05
PN22D	3.80	0.044	82.7	0.017	0.0028	0.009390	0.196	2.84E-04	3.20E-05	4.58E-06
NJ5D	4.27	0.112	257.0	0.132	0.0293	0.002962	0.204	2.09E-04	1.39E-04	3.68E-05
NJ8D	6.11	0.085	198.8	0.167	0.0279	0.005071	0.159	1.73E-04	1.14E-04	1.70E-05
LG3D	3.57	0.018	48.0	0.089	0.0106	0.006281	0.081	7.87E-05	1.32E-04	1.59E-05
BL3D	2.82	0.055	134.0	0.067	0.0097	0.006552	0.300	3.11E-04	1.13E-04	1.66E-05
OK2	4.15	3.251	4036.4	0.433	0.0536	0.029093	32.196	5.69E-02	3.98E-03	5.72E-04
PN15D	3.84	0.293	477.7	0.069	0.0139	0.011059	1.325	2.00E-03	1.57E-04	3.23E-05
SG2	6.47	0.051	183.4	0.106	0.0118	0.051206	1.395	1.01E-03	6.22E-04	7.34E-05

Degree of error of the $^3He/^4He$ analysis (represented as R/Ra in Table 2) is 2.5% on the average, except for LG-3D and SG-2 where the standard deviation is 16.6% and 12.5%, respectively. Ne, Ar, Kr and Xe isotopic measurements, on the other hand, all fall between 1.2% and 5.1% standard deviation. Since bulk concentrations are calculated values, no error bands are associated with these figures. Reservoir concentrations of noble gases were derived from equilibrium solubility equations given in Potter and Clynne (1978).

A short program written in QuickBasic was created to: (1) calculate the theoretical noble gas concentration at any given temperature based on Henry's constants as defined in Potter and Clynne (1978), and (2) determine separated steam and residual liquid noble gas composition (i.e., from this theoretical source fluid) with single-step boiling, multi-step boiling and Reyleigh distillation processes. Critical inputs in the program include the deep fluid temperature of the system (i.e., 300°C) and surface recharge temperature (i.e., 20°C). Program output runs were used to generate theoretical curves representing residual vapour and liquid, which were then compared with the generated Palinpinon data set. Interpretations were based mainly on comparison of theoretical and actual noble gas compositions.

Although the solubility equations include He, elemental He concentration was not included in the computation for all Palinpinon deep well fluids. It is normal to exclude He as there is commonly excess He in the fluid, coming from either mantle or radiogenic inputs. In this case, the excess is most probably due to mantle contribution.

5.0 DISCUSSION

5.1 Isotopic Ratios

As shown in Table 2, most of the isotopic ratios of the Palinpinon samples are close to those of air, except for He where excesses in all samples are very evident. The ^{20}Ne/^{22}Ne ratios, for instance, are within 10% of the air ratio in seven (7) of eleven (11) measurements. For ^{40}Ar/^{36}Ar and ^{84}Kr/^{86}Kr ratios, eight (8) of ten (10) samples are likewise within 10% of air ratios. The difference is much smaller for ^{129}Xe/^{132}Xe, wherein only well PN-22D is beyond 3% of air ratio (13%). These results strongly imply that Ne, Ar, Kr and Xe in Palinpinon geothermal well waters are derived from air, or are modified atmospheric noble gases. Air is a significant noble gas reservoir primarily because this is a major source of recharge fluid for most terrestrial systems. For instance, studies of gases from volcanic/hydrothermal, hydrocarbon and groundwater systems yield results indicating a major contribution of atmospheric noble gases to the rare gas inventories of these systems. In most cases, noble gas isotopic ratios in fluid samples reflect atmospheric ratios, and deviations can be readily explained by invoking processes commonly occurring in the systems under study. This is not true for He, however, as R/Ra in the Palinpinon geothermal fluids are consistently in the range of 6.5-8 as against the air ratio of 1. He enrichment in the samples is not surprising considering the young volcanic setting of the geothermal system. The R/Ra range of Palinpinon samples is very close to the widely accepted ratio of 8 for island arc volcanic systems. Other isotopic data (i.e., ^{18}O, ^{2}H, ^{34}S) also indicate a magmatic fluid contribution to, or origin of, some chemical components of the well fluids.

Although the ratios are similar to air, there are evident differences between atmospheric noble gases and gases from the Palinpinon geothermal fluid. In order to see these differences better, ratios are commonly normalized to F(^{a}X) (where F(^{a}X) = (^{a}X/^{36}Ar)$_{sample}$ / (^{a}X/^{36}Ar)$_{air}$; ^{a}X is a specific isotope such as ^{20}Ne). With this normalization, F(X) in air is equal to 1, and enrichment or depletion of noble gases compared with air are clearer. With the earlier discussion on He, this will not be included here as there is already a clear deviation in He of the Palinpinon well fluids. Nonetheless, the other noble gases also exhibit deviations from air ratios as tabulated in Table 2 and show graphically in Figure 5. It appears that there is a systematic depletion in ^{20}Ne accompanied by increases in ^{84}Kr and ^{132}Xe in the ^{20}Ne vs. ^{84}Kr and ^{20}Ne vs. ^{132}Xe cross plots (Fig. 5, a&b).

Some Palinpinon samples may be interpreted to fall on a mixing line between air and air saturated water (if other data are considered outliers) as outlined by the straight dashed lines in Figure 5 a&b. As such, noble gases from these well fluids may be thought of as mixing products of these 2 end members. Some, but

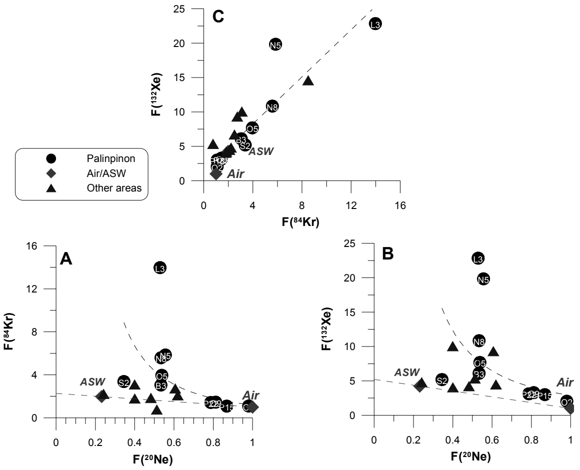

Figure 5. Normalized isotope ratio cross plots.

not all, of the fluids from volcanic and geothermal areas around the world (e.g., Japan, Italy, Honduras) also fall on this possible air-ASW mixing line. If the previously considered outliers are taken into account, however, a separate mixing line between air and another end-member (dashed curves in Fig. 5 a&b) enriched in heavy noble gases (Kr and Xe) relative to Ar and Ne can be invoked. Reinjected water could be that end-member, since in theory degassed fluids are depleted in light noble gases and enriched in heavy rare gases. The ^{84}Kr vs. ^{132}Xe cross plot (Fig. 5c) seems to favour the second interpretation, as the data reflect a steady enrichment in Kr with increase in Xe (dashed line). Although air and ASW fall along this linear trend, both are towards the lower end of the spectrum. This particular plot would appear to favour mixing between air and a heavy-noble-gas-enriched end-member distinct from ASW. It is worthy to note that ^{84}Kr and ^{132}Xe in other geothermal and volcanic areas plot along the same general trend as the Palinpinon samples. Curiously, the most enriched sample from the other areas worldwide is from a natural gas well in China (the only non-geothermal/volcanic sample plotted).

Noble gases in well OK-2, which essentially mimics the normalized composition of air, are most probably purely atmospheric. The isotopic ratios of well NJ-5D, meanwhile, are in the same cluster as the other well fluids with no evident reinjected water component. This would imply that reinjection fluid, at least in this particular well, is not significant as to alter the rare gas isotopic ratios of the original well reservoir fluid.

5.2 Elemental Composition

Table 3. Noble gas elemental compositions* Palinpinon well fluids.

well	*Ne*	*Ar*	*Kr*	*Xe*
SG3D	1.46E-08	2.01E-05	7.68E-09	5.88E-10
OK5	7.97E-09	7.74E-06	3.71E-09	5.53E-10
OK9D	4.87E-08	3.50E-05	5.50E-09	9.71E-10
PN22D	1.58E-08	1.09E-05	1.78E-09	2.55E-10
NJ5D	1.16E-08	1.14E-05	7.75E-09	2.05E-09
NJ8D	9.63E-09	8.86E-06	6.37E-09	9.47E-10
LG3D	4.38E-09	4.49E-06	7.35E-09	8.87E-10
BL3D**	**1.73E-08**	**1.67E-05**	**6.27E-09**	**9.24E-10**
OK2**	**3.16E-06**	**1.79E-03**	**2.21E-07**	**3.18E-08**
SG2**	**2.22E-08**	**3.07E-05**	**1.37E-08**	**1.63E-09**
PN15D**	**2.80E-07**	**1.85E-04**	**2.19E-08**	**4.48E-09**

Theoretical noble gas concentration of recharge fluid

Temp, °C	*Ne*	*Ar*	*Kr*	*Xe*
20	1.05E-08	1.35E-05	3.03E-09	4.06E-10

**composition units in moles gas/kg water*

***steam-dominated well fluid*

Elemental noble gas compositions for all Palinpinon samples are shown in Table 3. Also given is the theoretical composition of the recharge water to the hydrothermal system, using solubility data and equations from Potter and Clynne (1978). Helium is again excluded here because of the excess of helium in the geothermal fluid. Using simple boiling models, the bulk concentrations of the samples were evaluated in relation to possible sources and effects of reservoir processes. The boiling models assume that the recharge fluid, at a given initial temperature (i.e., 20, 80, 160°C), are heated to the temperature of the geothermal parent water (~300°C). The accompanying temperature-dependent equilibration are also assumed to take place, thus slightly modifying the noble gas compositions. The geothermal parent water is then flashed, the composition of separated steam and residual liquid at the different flash temperatures determined based on solubility and partitioning equations (Potter and Clynne, 1978), and the boiling curves matched with the data set.

The cross plots shown (Fig. 6) lump the Palinpinon data set with theoretical concentrations of separated steam for single and multi-step boiling processes. The assumed recharge water temperatures here are 20°C, 80°C and 160°C, and the deep geothermal fluid at 300°C. The recharge/parent combination of 20/300°C is probably the most realistic and likely approximates actual conditions in the reservoir. The two other recharge temperatures are included in the plots, however, as the data set shows some degree of correlation with these recharge temperatures. In all plots of Figure 6, the most enriched sample is well OK-2, which discharges two-phase steam-dominated fluid.

For Ar vs. Ne (Fig. 6a), almost all data points, especially the liquid-dominated wells, fall on either single step or multi-step boiling curves of the deep fluid from an original recharge temperature of either 80°C and 160°C. The steam-dominated wells almost exactly fit the single-step separated steam lines save for well SG-2. This particular well falls on either the 80°C-recharge water multi-step separated steam curve or the 20°C-recharge water single-step

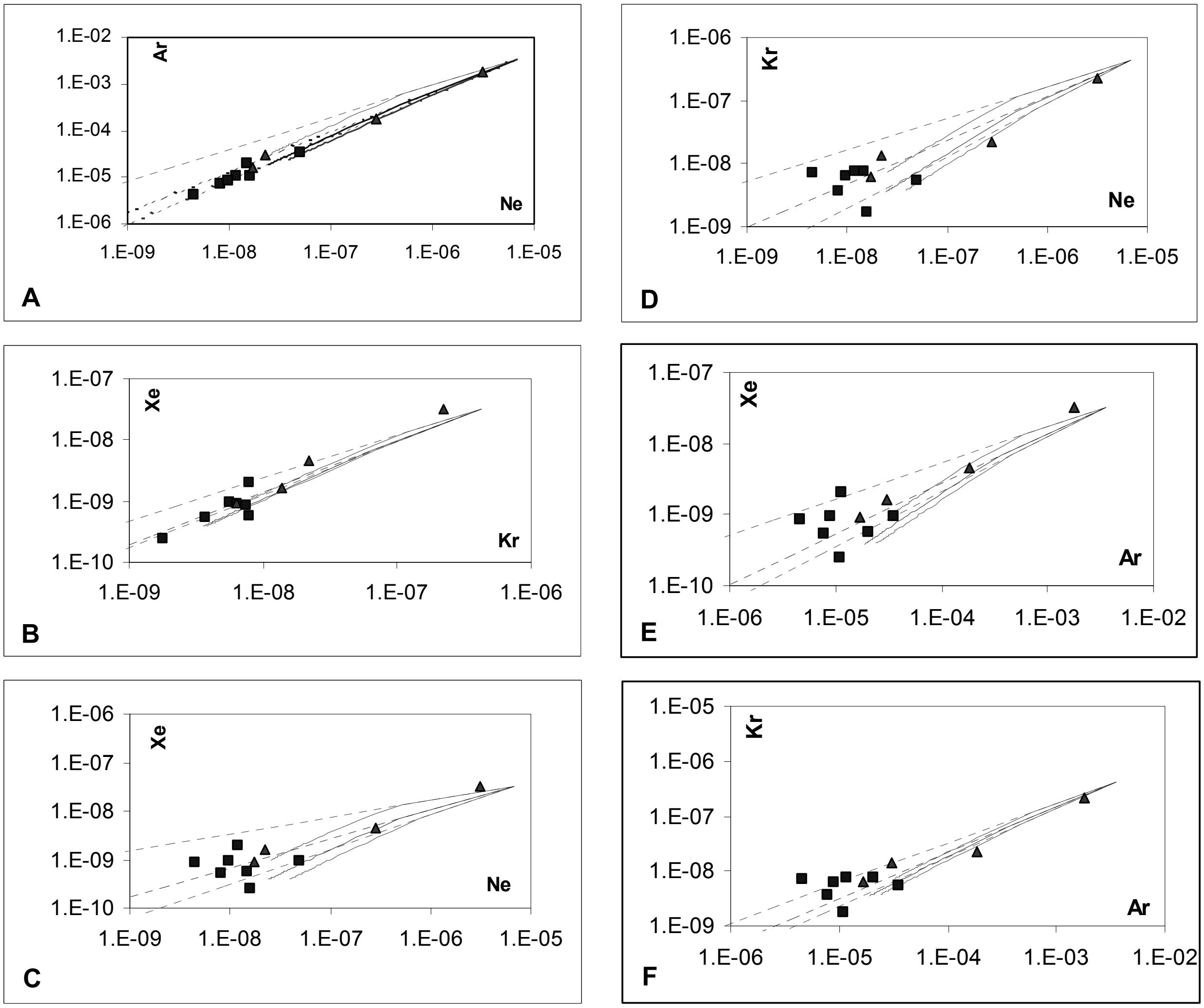

Figure 6. Cross plots of noble gas compositions

Legend: blue squares - Palinpinon liquid-dominated wells; red triangles - Palinpinon steam-dominated wells; red lines - separated steam after boiling, recharge fluid = 160°C; blue lines - separated steam after boiling, recharge temperature = 80°C; grey lines - separated steam after boiling, recharge fluid = 20°C; solid lines represent single step steam separation, broken lines depict multi step steam separation; deep geothermal fluid temperature (before boiling) = 300°C; all compositions in moles gas/kg water

separated steam line. In the Kr vs. Xe plot (Fig. 6b), meanwhile, only three data points (SG-2, PN-15D, NJ-5D) fall off the 80°C and 160°C boiling curves. Wells NJ-5D and PN-15D fit the 20°C-recharge water multi-step curve, while SG-2 is somewhat off this line.

There are inconsistencies in the cross plots of Ne vs. Kr or Xe and Ar vs. Kr or Xe (Fig. 6, c-f). In these diagrams, the data points are scattered between multi-step separated steam curves defining the full range of recharge water temperature. Wells NJ-5D, NJ-8D and LG-3D consistently approach the 20°C-recharge water multi-step curves in all four (4) cross plots. The other data points, meanwhile, tend to fit multi-step curves for 80°C and 160°C recharge fluids. Moreover, a trend of increasing Xe and Kr with decreasing Ne and Ar for liquid-dominated wells is discernible in the diagrams. This trend duplicates those observed in the normalized isotope ratio pots (see Section 5.1).

Although there are ambiguities, the plots of Figure 6 and the observations above tend to suggest that noble gas concentrations in Palinpinon may be largely controlled by multi-step boiling of the deep geothermal fluid (assumed at 300°C). Noble gases in steam-dominated well fluids may be derived from single step boiling processes, but can also been seen as products of multi-step boiling. It is puzzling, though, that the implied recharge temperatures are 80°C and 160°C instead of 20°C which is closer to the true groundwater recharge temperature of the system. The 160°C temperature may be taken to represent reinjected water (with a temperature of 165°C at the separator); this implies that wells falling on the 160°C curves have reinjected water component in the discharges. Standard geochemistry monitoring tools, though, show no such presence in these particular wells. On the other hand, NJ-5D is a well that is positive for reinjection water component, yet it does not plot on the 160°C curves but rather on the 20°C lines.

The scatter of data points may also be taken to denote 3-point mixing rather than simple multi-step boiling. The inferred end-members here are the deep geothermal fluid, groundwater (natural recharge water) and possibly reinjected water. Although this theory is consistent with the F(X) plots, there is no compelling evidence to validate this hypothesis. What is clear at this point is that (multi-step) boiling in the reservoir has some influence on the noble gas composition of the geothermal fluid. Whether boiling is the major process controlling noble gas concentrations or not remains debatable. The effect of mixing is not obvious, but the scatter in the data may be an indication that the isotope data somehow reflects this process.

An unequivocal explanation for the Kr and Xe enrichment cannot be offered at this point. A number of hypotheses for quite similar conditions have been presented elsewhere. In a study made in the Elk Hills oil field in California (Torgersen & Kennedy, 1999 and references therein), for instance, the hydrocarbons are enriched in Kr and especially Xe relative to Ar and Ne. Two possible explanations were forwarded here. One is that the heavy noble gas enrichment is due to mixing of the original hydrocarbon fluid with a distinct gas reservoir during migration and storage, with carbon being the heavy noble gas carrier. This distinct gas reservoir somehow preferentially absorbed Kr and Xe, thus the enrichment in heavy noble gases in the "mixed" Elk Hills samples. Another explanation is based on what is referred to as the Bosch and Mazor model (in Torgensen and Kennedy, 1999) where noble gas abundance patterns in hydrocarbon systems are determined by equilibrium solubility partitioning between ASW, oil and gas. Partitioning of this nature results in enrichment in heavy noble gases. Although the first interpretation is possible for Palinpinon, there are stark differences in geologic setting and overall geologic structure between the two (2) areas which may make a direct correlation questionable. The linear alignment of the Palinpinon data set in the F(^{132}Xe) vs. F(^{84}Kr) diagram (Fig. 5c) may appear to be consistent with the second hypothesis. The problem, though, is that the Palinpinon system is not a hydrocarbon system, and there is no oil present here. The 3-point mixing theory may still be occurring in Palinpinon, however the end-members are air, ASW and reinjection water. The enrichment in heavy rare gases in this case may simply be due to the component or input of reinjected water, which are known to be depleted in light noble gases and enriched in heavy ones.

6.0 CONCLUSIONS

Noble gases in the Palinpinon geothermal fluid are derived mainly from atmospheric noble gases. This is evidenced by the isotopic ratios of Ne (20/22), Ar (40/36), Kr (84/86) and Xe (129/132), which are all very similar to ratios in air. Based on bulk concentrations of rare gases, a multi-step boiling process in the geothermal reservoir can be invoked.

There are notable enrichments in Kr and Xe accompanied by declines in Ne and Ar as seen from the normalized isotope plots (F(X)) and concentration cross plots. Simple reservoir boiling models cannot account for the Kr and Xe enrichment, and it is possible that 3-point mixing between air/ASW, the deep geothermal reservoir and reinjected fluids is responsible for the heavy noble gas enrichments.

There is obvious excess of He in all Palinpinon samples, with a corresponding R/Ra of between 6.5 and 8. The R/Ra ratios unequivocally point to a mantle source for the He in the hydrothermal system, and are typical of island arc volcanic systems. This is consistent with findings of magmatic inputs into the geothermal system from other isotopic studies done previously.

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