

TRACE METALS IN DEEP GEOTHERMAL WATER, PALINPINON GEOTHERMAL FIELD, SOUTHERN NEGROS, PHILIPPINES

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SUMMARY—The purpose of the study is to gain insights into metals transport in geothermal fluids, leading to an understanding of the processes for ore deposition in porphyry/epithermal environments. Deep waters from 2 wells located in different hydrological settings, at the Palinpinon geothermal field, Philippines were analysed for trace metals. Chemical variability between waters, the influence of contamination and lack of data from other wells hinders interpretation of the results with regard to chemical differences and differences of hydrological setting. Gold shows no apparent effects of contamination. The Au concentrations for both wells range 1-4ppb; analogous to measured Au concentrations from other geothermal fields (Ohaaki, Cerro Prieto). For Palinpinon waters at reservoir conditions, AuHS⁰ is the dominant Au-bearing complex. The Au solubility is calculated to be 1-5ppb which is comparable to measured Au concentrations. This result implies Palinpinon waters are saturated with respect to gold and hence are potential ore-forming solutions.

1 INTRODUCTION

Deep geothermal water samples from Palinpinon Geothermal Field, Southern Negros, Philippines, were collected and analysed for trace metals. This has been done to gain insights into metals transport in geothermal fluids, leading to an understanding of the mechanisms and processes for ore deposition. Understanding the transport of metals in the geothermal environment is of particular interest as it has possible implications for our understanding of the formation of epithermal deposits.

In a previous study, Au, Ag, Cu and PGE contents of deep geothermal waters were analysed from downhole water samples from two wells at Ohaaki geothermal field, N.Z. (BR9, BR20; Brown et al., 1996). The downhole sampler used in that study was specifically designed for the collection of deep geothermal water for trace metal analysis. The same sampling tool has been used in the current study.

2 METHODS

2.1 Sampling Preparation

Prior to sampling, washing and weighing of the sample bottles and preparation of fresh aqua regia (AR) and analytical blanks was carried out in the PNOC Energy Development Corp. (PNOC EDC) geochemistry laboratory at Palinpinon. Acids used for the AR were Merck, suprapur[®] grade, HCl and HNO₃.

New Nalgene[®] sample bottles were washed in concentrated HNO₃, ('analaR', BDH) and then left

to soak overnight in 5N HNO₃, ('analaR', BDH). They were then rinsed with distilled and deionised water (DDI) and allowed to air dry. To preserve the chemistry of water samples, 20ml conc. HNO₃, (suprapur[®], Merck) was added to water sample bottles.

Analytical blanks were prepared:

- **DBI:** DDI water from the Palinpinon geochemistry laboratory.
- **d/hDDI acid:** a downhole DDI blank consists of 500ml of DDI placed in the sampling chamber and lowered down well PN14 to sampling depths (2299m). The tool was left unopened for 2 minutes before returning to the surface and the water collected. This was acidified with 20ml conc. HNO₃, (suprapur[®], Merck).
- **pure AR:** a 100ml AR blank consists of 50% AR and 50% DDI.
- **ARwash:** the pre-cleaned sampling chamber was rinsed with 80ml AR followed by 80ml DDI. These were combined and kept as a wash blank (**ARwash1**). The procedure was repeated and a second wash blank collected (**ARwash2**).

2.2 Well Selection

Ideally, geothermal wells used for deep water sampling should have a wide geographical distribution across the hydrothermal system. This is so that a range of waters, from different physicochemical environments in the hydrothermal reservoir, can be collected. Wells in the hydrological upflow and outflow regions should be sampled including wells with different water chemistry (e.g. acid sulphate, neutral chloride waters), wells with

mineralised drillcore, wells with sulphide scale blockages. These are the main criteria used for selecting appropriate geothermal wells for deep water sampling.

The realities of an active geothermal field utilised for power production, place severe constraints on well selection. These are as follows:

- A deviated well cannot be used. Jerking of the suspension wire, which activates the inertia mechanism to open the valve and allow fluid entry into the sampling chamber, is more effective if the well is vertical. This also minimises the danger of losing the tool down the well; the suspension wire could easily get caught on the well lining and sever. Unfortunately most geothermal wells collared in steep terrains, such as at Palinpinon, are deviated.
- The well had to be off-line, i.e. not supplying power to a power station. If this was not the case, an alternative well, that could maintain an equivalent energy output, needed to be brought on-line whilst the selected well was sampled.
- The well had to have a water-dominant fluid. High vapour pressures will allow steam to pass preferentially into the sampling chamber and subsequently, any water returned to the surface will be mostly steam condensate.
- The well could not have any blockages, such as

mineral scales or damaged well lining, that would hinder passage of the sampling tool.

- The well had to show minimal effects of geothermal power exploitation (e.g. waste water reinjection returns; pressure drawdown of shallow, cooler fluids).
- The well water chemistry could not be too severe on sampling equipment. Highly acidic waters can damage the sampling tool and the suspension wire.
- The well had to be able to be opened. Many of the earliest drilled wells at Palinpinon are abandoned and plugged with cement.

23. Well Sampling

Sampling water from geothermal wells for trace metal analysis is not easy. After sample collection, but whilst the tool is returning to the surface, the reduction in temperature and associated gas loss results in some elements (importantly, Au and Ag) precipitating on the inside walls of the sampling chamber. To capture these elements, it is necessary after each sampling run to rinse out the chamber with aqua regia (AR); a chemical reactive enough to dissolve any precipitates coating the interior walls. The sampling tool has been designed to withstand the reactive qualities of AR (Brown et al., 1996). After sampling, the trace metal concentrations of the

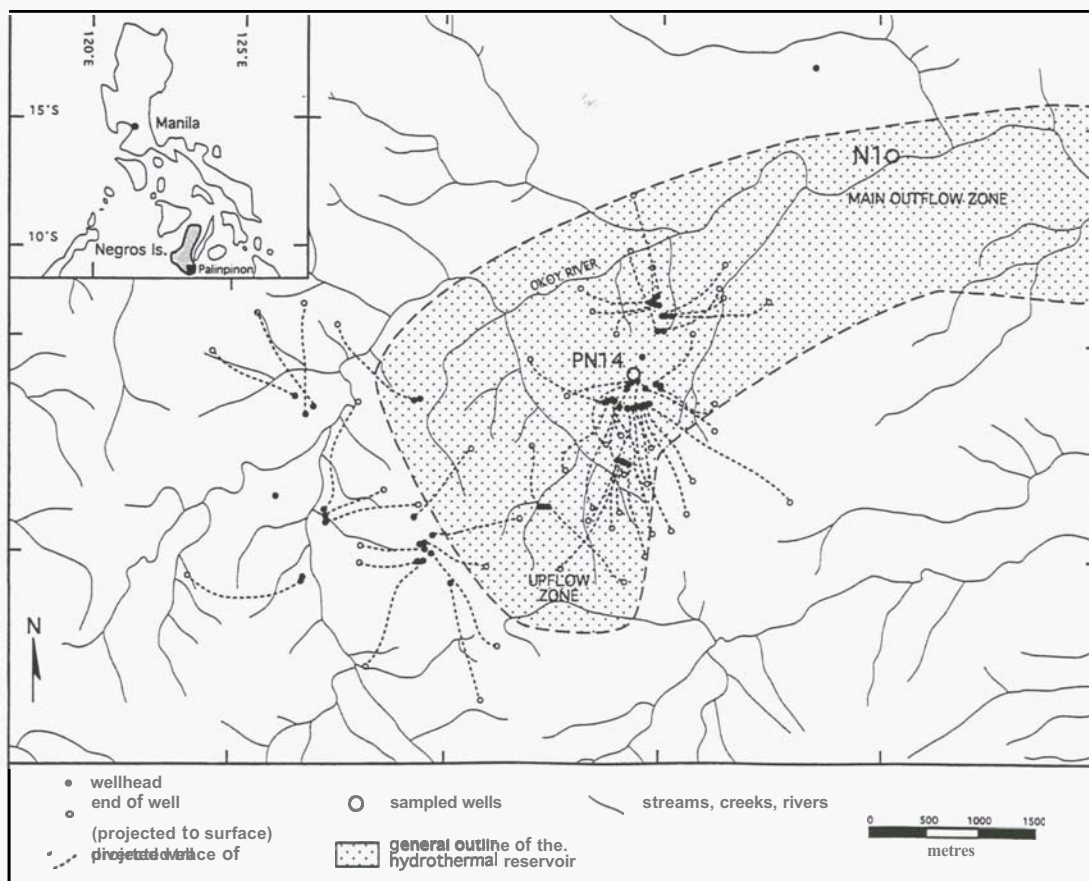


Figure 1: Location of sampled geothermal wells, Palinpinon geothermal field

Table 1: Characteristics of sampled wells

Well	N1	PN14
Status (as of 12/97)	shut	shut
Total depth (m)	603.3	3077.7
Water level (m)	400-450	1200
Wellhead pressure (MPa)	2.2	0.9
Main feed zone (m)	450	2600-2800
Blockage depth (m)	500	2900
Max. temp. (as of 09/97) (°C)	206	261
Max. temp. depth (m)	300	2900

Table 2: Volumes of sampled water and their sample depths

Well & Sample No.	Sample Vol (ml)	Sample Depth (m)
N1 #2	600	501
N1 #3	410	500
PN14 #1	525	2300
PN14 #2	550	2306

geothermal water and the **AR** rinse are analysed by ICP-MS. The total metal content of the deep geothermal water is therefore the **sum** of the trace metals in the water and in the **AR** rinse.

Two wells at Palinpinon geothermal field were sampled successfully (N1, PN14); Figure 1. The key characteristics of each well are summarised in Table 1.

Well N1 is located at lower elevations (300.7m) in the Okoy Valley (Figure 1). The well is shut, and is not a steam supplier. N1 intersects the outflow zone of the hydrothermal reservoir. The well **has** a total depth of 603.3m with a water level located approximately at **400-450m**, and a main hydrological feed zone at **450m** depth. The maximum downhole temperature measured in September 1997 was 206°C at 300m depth; above the water level. A well blockage is located at 500m depth.

Three sampling runs were attempted at N1 with a target depth of 500m. The sampling tool was left at these depths for 15 **minutes**. The first run collected only 150ml of water. The steel shim above the non-return valve was unbroken, suggesting that the water contents represented steam condensate that had leaked into the sampling chamber. The second run to 501m depth collected 600ml of water; the third to 500m collected **410ml**. Only results from the second and third sampling runs are reported here.

Well PN14 is located closer to the hydrological upflow zone at 710.5m elevation (Figure 1). It is currently shut, and is not supplying steam to the power station. PN14 **has** a depth of 3077.7m with the water level located **1200m** below the surface. The main feed zone is situated between 2600 and 2800m. A maximum temperature of 261°C was measured in September 1997 at 2900m. There is **a** well blockage at **this** depth.

Two sampling runs were made at PN14. The first to 2300m depth, returned 525ml of water. The second, at 2306m, collected 550ml of water. A third run down this well was to obtain a downhole **DDI** blank.

3. ANALYTICAL RESULTS

Four water samples were collected from wells N1 and PN14. Table 2 summarises respective volumes and sample depths. The water samples, **AR** washes and blanks have been quantitatively analysed for 15 trace elements using the ICP-MS facility at the University of Tasmania. Elements analysed are: Co, Cu, Zn, Mo, Ag, Cd, **Sn**, Sb, Te, W, Au, Hg, Tl, Pb and **Bi**. Results for the blanks, sampled waters and respective **AR** washes are presented in Tables 3a and 3b.

Analyses of blank samples must be **used** to negate the effects of contamination. The most likely source for contamination is the sample tool, especially the **AR** rinse leaching metals from the sample chamber walls. The concentration of trace metals in the blanks are assumed to be background levels; metal concentrations in the blanks, d/hDDI acid and **AR** wash2, are subtracted from the water and **AR** wash analyses, respectively. Comparing analyses of the pure **AR** with the **AR** washes (Table 3a), shows that most elements are significantly higher in the **AR** washes, especially Co, Cu, Zn and Mo. It implies that **AR** is leaching metals from the ceramic surface coating the sampling chamber. Elements least affected by contamination are Au, Tl and Te.

The total trace metal concentrations of the downhole water have been calculated by combining analyses of the waters with their respective **AR** washes and taking into account blank analyses and the volumes of water collected. The recalculated metal concentrations for the deep waters from both wells are presented in Table 4. Some metals are present in high concentrations. Waters from N1, located in the

Table 3a: Results of trace metal analysis of blanks (ppb)

	Blank DDI	Blank d/hDDIacid	Blank pureAR	Blank ARwash1	Blank ARwash2
Co	0.07	18.04	0.32	5484.21	4653.64
Cu	0.48	82.24	8.83	15046.88	4944.75
Zn	1.52	74.75	9.76	3984.83	3500.06
Mo	0.07	54.81	0.29	415.89	355.04
Ag	0.01	0.03	0.27	48.25	7.29
Cd	0.01	0.20	0.08	4.23	2.32
Sn	0.09	1.01	1.50	147.74	109.57
Sb	0.02	20.99	0.78	47.38	28.30
Te	0.02	0.09	0.08	0.93	0.81
W	0.20	11.72	0.82	22.13	16.22
Au	0.01	0.02	0.04	0.63	0.16
Hg	0.24	0.50	1.12	53.72	2.60
Tl	0.00	1.42	0.73	1.00	0.68
Pb	0.11	1.65	1.58	105.99	94.81
Bi	0.02	0.08	0.10	1.58	1.15

Table 3b: Results of trace metal analysis of waters and AR washes (ppb)

	N1 #2 water	N1 #2 AR	N1 #3 water	N1 #3 AR	PN14 #1 water	PN14 #1 AR	PN14 #2 water	PN14 #2 AR
Co	2.44	6680.01	63.74	4450.48	9.14	2382.30	3.80	2151.73
Cu	100.38	14057.08	1229.21	9246.26	694.32	5384.00	121.87	3865.89
Zn	237.36	6140.47	960.49	4698.66	116.85	2333.16	85.93	1683.46
Mo	32.91	515.74	89.60	985.86	241.40	615.25	235.60	1105.29
Ag	0.56	17.33	3.51	8.90	6.87	52.06	0.75	8.03
Cd	0.36	6.31	0.81	3.89	0.98	3.13	0.56	2.43
Sn	0.71	154.61	2.53	303.98	1.93	271.41	0.59	324.50
Sb	114.85	2473.34	514.18	1420.74	171.49	315.43	119.92	211.42
Te	0.62	1.82	0.51	1.26	0.26	0.68	0.62	0.56
W	4.39	48.10	10.18	34.08	23.72	14.83	16.13	30.77
Au	0.13	3.18	0.94	1.95	0.74	4.49	0.10	0.67
Hg	1.39	23.64	7.92	12.02	0.62	0.98	0.45	0.59
Tl	25.88	596.17	133.81	308.57	22.72	69.12	27.09	63.27
Pb	3.31	171.81	21.35	113.90	17.15	139.43	4.20	49.72
Bi	0.08	2.10	0.09	1.39	0.08	0.84	0.08	0.50

hydrological outflow zone, have 5-6ppm Cu and 2ppm Zn and Sb. Generally however, the trace metal concentrations are variable; not only between waters from different wells, but also between waters from the same well (e.g. PN14: 40-950ppb Cu, 1-41ppb Ag, 3-50ppb Pb; N1: 50-1350ppb Co, 110-650ppb Mo, 30-190ppb Sn). Despite the variability, the N1 waters (outflow zone) appear to have higher concentrations of Co, Cu, Zn, Sb, Hg and Tl than PN14 waters (upflow zone) (Table 4).

It is useful to compare these results with the trace metal contents of waters from other geothermal areas. Precious and base metal concentrations in waters from Ohaaki, N.Z., Cerro Prieto, Mexico and Salton Sea, U.S.A. are presented in Table 5. The Cl⁻ concentrations provide a comparison of water salinities. With a salinity range of 6800-8600ppm

Cl⁻, the Palinpinon waters are much more saline than Ohaaki, but less than the Cerro Prieto waters and a few orders of magnitude less than the brines from the Salton Sea geothermal field.

The Au concentrations of Palinpinon waters (1-4ppb) are comparable with the Au contents at Ohaaki, N.Z. (<2ppb; Brown, 1986; Brown et al., 1996) and Cerro Prieto, Mexico (4ppb; Weissberg et al., 1979). A wide range of Au concentrations are reported for the Salton Sea brines from <0.1ppb to as high as 80ppb (McKibben et al., 1990; Gallup, 1998). The Ag contents of the Palinpinon waters (1-41ppb) are also comparable with Ohaaki and Cerro Prieto geothermal areas. However, 41ppb in Palinpinon PN14#1 (Table 4) is very high for low salinity geothermal waters; it is more comparable to the Salton Sea brines. This result is possibly due to analytical/sampling error.

Table 4: Recalculated trace metal content of downhole waters (ppb)

	Outflow Zone		Upflow Zone	
	N1 #2	N1 #3	PN14 #1	PN14 #2
Co	1351	46	0	0
Cu	6093	5347	947	40
Zn	1923	2055	42	11
Mo	107	650	385	726
Ag	7	5	41	1
Cd	3	2	1	0
Sn	30	191	124	156
Sb	1724	1852	369	232
Te	1	1	0	1
W	21	17	12	15
Au	2	3	4	1
Hg	15	17	0	0
Tl	421	433	73	71
Pb	53	38	50	3
Bi	1	0	0	0

Table 5: Trace metal contents in geothermal waters (ppb unless specified otherwise)

	Au	Ag	Cu	Pb	Zn	Cl ⁻ (ppm)
Palinpinon						
N1	2-3	5-7	5,350-6,100	38-53	1,900-2,060	6,800-7,050
PN14	1-4	1-41	50-950	3-50	11-42	8,500-8,600
Ohaaki, N.Z.						
BR9 ^{a,b}	0.9-1.0	13-19	23,000-70,000	-		
BR20 ^{a,b}	0.5-1.2	6-12	39,000-65,000	-		
BR22 ^c	15	8	9	2.3	1	1,188
Cerro Prieto, Mexico ^{d,e}	4	4	5	4.6	6	13,800
Salton Sea, USA ^{f,g}	0.02-80	45-1,400	4,000-8,000	7x10 ⁴ -9x10 ⁴	28x10 ⁴ -79x10 ⁴	15.1x10 ⁴

^a Brown et al. (1996) ; ^b Hedenquist (1990) ; ^c Brown (1986) ; ^d Weissberg et al. (1979) ; ^e Henley et al. (1984) ;

^f McKibben et al. (1990) ; ^g Gallup (1998)

The Cu values in Palinpinon and Ohaaki (BR9, BR20) waters (Table 5) are very high; analogous to, and well above that of the Salton Sea. It is probably due to contamination from the sampling tool. The Pb and Zn contents at Palinpinon are higher than those at Ohaaki (BR22) and Cerro Prieto but considerably less than the Salton Sea Pb and Zn concentrations. Without a large source of published data to draw on, it is difficult to ascertain the degree of contamination affecting the Palinpinon Pb and Zn values.

4. DISCUSSION—IMPLICATIONS FOR GOLD DEPOSITION

Gold appears to be one of the few metals least affected by contamination. This has allowed for some conclusions to be made with regard to Au solubility and the possibilities for gold deposition in an epithermal environment. The analysed gold contents of Palinpinon waters are comparable to the gold values analysed in other relatively dilute, chloride waters (i.e. Ohaaki, Cerro Prieto). With values ranging between <1-4ppb, these waters are not

especially enriched with respect to gold. Concentrations of this magnitude are the expected average background levels for volcanic and plutonic rocks in areas of plate convergence (Crocket, 1993) and 3-4 orders of magnitude lower than ore grade Au in epithermal and porphyry deposits in volcanic terranes. Whether these concentrations are to be expected for epithermal ore forming solutions is an important point that needs addressing. Crucial to this, is the estimation of the dominant Au-bearing complex at reservoir temperatures and pH.

For Palinpinon waters, the reservoir pH and temperature for wells N1 and PN14 are calculated to be 5.3, 210°C and 5.5, 240°C, respectively. Using data from Benning and Seward (1996), and under the conditions specified for each well, the dominant Au-bearing species for both waters is calculated to be AuHS°. Varying the pH from 2 to 5.5 does not change the dominant Au-bearing species and implies that ΣS and salinity for both waters are too low for Au(HS)₂⁻ and AuCl₂⁻ complexes to be stabilised respectively. The Au solubility for Palinpinon waters calculated as AuHS°, are 2.3-3.5ppb for N1 and 1.2-4.6ppb for PN14. These values are the same as the

measured Au concentrations for the deep water. It implies that the Au concentrations in the Palinpinon geothermal waters are at saturation and these waters are potential ore forming solutions. Only minor changes in the activity of reduced sulphur (i.e. loss of H_2S due to boiling, or H_2S oxidation via fluid mixing) will result in gold deposition.

5. CONCLUSIONS

Accurate analysis of downhole waters for trace metal concentrations is made difficult by contamination from the sampling equipment. This is most obviously seen in the very high Cu values for the Palinpinon waters, and also the Ohaaki (BR9, BR20) waters which were sampled using the same equipment.

An apparent difference in trace metal chemistry exists between the sampled Palinpinon wells. The well located in the outflow zone (N1) has significantly higher concentrations of Co, Cu, Zn, Sb, Hg and Tl than the well located closer to the upflow zone (PN14). However, the Palinpinon trace metal chemistry is variable. The concentrations of some metals have up to 2-3 orders of magnitude difference between waters from different wells, and also between waters from the same well. This variability may be an inherent quality of trace metal geothermal water chemistry. With contamination having a dominant influence on analytical results, and without data from other Palinpinon wells, it is difficult to know whether or not the apparent chemical differences are related to differences of hydrological setting.

The measured Au concentrations from Palinpinon and other geothermal fields show that Au concentrations of only a few ppb (<1-4ppb) can be expected for dilute chloride geothermal waters. Whether or not these waters are potentially ore-forming solutions is dependent on the dominant Au-bearing species. The treatment of gold solubility in terms of $Au(HS)_2^-$ by previous workers (Brown, 1986; Krupp and Seward, 1987; Brown et al., 1996) has resulted in an order of magnitude difference between calculated gold solubilities and measured estimated Au concentrations of the deep reservoir. Thus the conclusion that dilute geothermal waters are undersaturated with respect to gold has required an efficient and effective trapping mechanism for any gold deposition.

The Benning and Seward (1996) experimental data has required a re-evaluation of chemical models for

Au transport and deposition. For geothermal waters with low ΣS , salinity and weakly acidic pH, $AuHS^0$ will be predominant. As a result, Au solubilities will be of the same order of magnitude as the measured Au concentrations. It implies that geothermal waters such as Palinpinon, with Au concentrations <4ppb and $AuHS^0$ the dominant Au-bearing complex, are potentially ore-forming solutions and the requirement for a trapping mechanism for gold deposition is no longer required.

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