# PRECIOUS METAL SAMPLING AT THE OHAAKI GEOTHERMAL FIELD

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**SUMMARY -** A special downhole sampler has been built to sample for precious metals in deep geothermal reservoirs. During the February **1996** shutdown period, samples were collected from two wells at the Ohaaki geothermal field. The fluids were analyzed by quantitative ICP-MS. In the deep geothermal reservoir, gold concentrations of 0.5 - **1.16** ppb and silver concentrations of 5.7 -**18.0** ppb were found. These results agree with previous approximate estimates of the gold and silver concentrations from surface derived measurements.

## 1. INTRODUCTION

The link between epithermal ore deposits and geothermal systems has been well proven now for some time. (eg Henley and Ellis **1983,** Brown **1986).** In particular, the analysis of orifice plates from Br22 and Br27 showed the presence of significant gold and silver concentrations at the Ohaaki geothermal field. (Brown, **1986).** The presence of these precious metals in geothermal discharges had not been previously recognised because the majority of the gold and silver is deposited at higher pressures upstream of the weirboxes, and most trace metal sampling had been carried out on weirbox water samples, which have very low gold concentrations (<0.02ppb).

Gold and silver are transported in geothermal fluids primarily as the bisulphide complex - $Au(HS)_2^-$. The bisulphide ligand relies on the presence of $H_2S$ gas dissolved in the geothermal liquid. After pressure reduction at an orifice plate for instance, most of the $H_2S$ that was previously dissolved in the geothermal liquid, becomes distributed into the vapour phase. Consequently, the gold can no longer remain in the liquid fraction of the geothermal fluid, because the binding ligand (bisulphide) is no longer present. Thus the gold is deposited at this point.

Pilot plant extraction of gold and silver was attempted at the Kawerau and Rotokawa geothermal fields (Brown and Roberts, **1988).** In these experiments, a number of gauzes were placed in a vessel at the point of pressure reduction. After a time interval, the gauzes were removed and the gold that had been deposited was analyzed. Recovery rates were of the order of **1 -** 2 ppb which is 1-2 **gms** for every **1000** tonnes of geothermal fluid. These concentrations are very similar to that calculated **(1.5** ppb) from deposition on *to* an orifice plate at the surface (Brown, **1986).**

Thermodynamic calculations for the formation reaction of the bisulphide complex:

$$Au + H_2S + HS^- = Au(HS)_2^- + 0.5\,H_2$$

have shown that the expected solubility of gold due to the formation of this bisulphide complex under the conditions at Kawerau and Rotokawa was about **10** ppb. Consequently, it would appear that the amount recovered was an order of magnitude less than that theoretically available in the geothermal fluid. This discrepancy could be due to:

a) the gold actually not being present at the calculated concentrations in the geothermal fluid at depth, or

b) the gold being deposited in the well casing or at points other than in the pilot plant vessel, or

c) the thermodynamic calculations being based on erroneous data.

The order of magnitude difference between the recovery of gold in the pilot plant and the calculated amount in the deep geothermal reservoir has a large impact on the economic viability of any gold extraction process. Consequently, it became imperative to measure as accurately as possible, the gold concentration in the deep geothermal reservoir.

Such a measurement is fraught with difficulty. Normal downhole chemical samplers for sampling geothermal fluid at depth in a geothermal well are fabricated from stainless steel which can contain significant impurities of gold and silver - remembering that these elements are present in trace concentrations only. As well, when the sampler is brought to the surface, the temperature reduction and the loss of the occluded gases force the gold and silver out of solution and deposits it on the sides of the sampler.

We approached this problem by redesigning and constructing a downhole sampler specifically to measure precious metal concentrations in deep geothermal wells. The sampler was based on the principles of the Klyen sampler and was constructed in a number of different sections. The main body of the sampler was a stainless steel tube. However, the sections of this tube that were exposed to the deep water, were coated with a ceramic lining. The valve assemblies at either end of the sampler were constructed of titanium which is much more inert than the stainless steel. The normal stainless steel non-return valve assembly was replaced with a synthetic elastomer washer which would be gas tight. The idea was to collect a sample in the normal manner and then bring it back to the surface, collecting the water sample in the normal manner for analysis. The sampler would then be rinsed with aqua regia which would dissolve any of the gold that had been plated on to the walls of the sampler during cooling and gas loss. Both the original geothermal fluid and the aqua regia would then be analyzed for precious metals and the total gold and silver concentration of the deep geothermal fluid could thus be measured by adding the metals analyzed fiom the aqua regia wash back into the downhole sample.

With the shutdown of the Ohaaki geothermal field in Feb 1996, an opportunity arose to sample the deep wells at Ohaaki in order to test the sampler and to attempt to resolve the question of the deep concentrations of gold and silver at Ohaaki.

## 2. EXPERIMENTAL METHOD.

### 2.1 Well Selection

An investigation of the feed depths and chloride concentrations of the Ohaaki wells was carried out in order to determine appropriate wells for sampling. The strictest criterion was the availability of deep geothermal waters without dilution by surface derived waters. As well, a purely liquid feed was required in the well - both to give a good downhole sample, and to ensure that the deep fluid was not diluted with condensed steam. On the basis of previous chemical analyses and well discharge enthalpy measurements, two wells were chosen - Br20 and Br9. Both of these wells were on the West bank of the Ohaaki geothermal field.

### 2.2 Chemical Preparation

Aqua regia was fieshly prepared in the laboratory, and a preliminary washing of the sampler was carried out with both DDI (distilled and deionised) water and then aqua regia (AR). The first aqua regia wash was discarded and then two AR washes of 60ml each, followed by 60ml each time of DDI water were kept as an AR sampler blank (sample G1). All sample bottles were Nalgene and were prepared by washing in concentrated nitric acid, followed by overnight soaking in 5N nitric acid, followed by washing with DDI water. 500ml flasks were prepared for the untreated sampler contents and 1000ml flasks were prepared for the AR washings in this manner. Sample bottles for the untreated downhole sampler contents had 20 ml of "Aristar" conc nitric acid added to preserve the sample. A sample of 625ml DDI water + 20 ml Aristar nitric acid was placed into a sample bottle, and the lid opened at the BR9 field site for ten minutes in a light breeze. This sample then became the field blank (Sample G2).

New viton seals were placed in the ceramic lined sampler and the sampler then assembled. The sampler was fitted with a high temperature EDPM washer in the non-return valve in order to collect any gas fiom the sampler. The actuator mechanism for the sampler is a stainless steel inertial spike that pierces a mild steel shim at the top end of the sample chamber in the sampler. It was anticipated that these would not contaminate the sample with any significant gold or silver.

### 2.3 Well Sampling.

The WHP at BR9 was approximately 4.5Bg and the well had been shut for a few days. The main feed in this well is at 760m CHF and all samples were collected at this depth. On lowering the sampler and on discharge of the well during the sampling, it was noticed that the water level was very low in this well, and it was assumed that there was probably a gas cap at the top of the casing.

The first attempt at sampling was aborted because the ceramic sampler was slightly too large in diameter to fit through the recovery tube. At this stage, a normal downhole sample (sample G4) was collected in a stainless steel sampler, which was of slightly lesser external diameter and could just fit through the recovery tube valve. A small separate sample of 50ml was taken fiom the downhole sample for arsenic analysis. The remainder of this downhole sample was analyzed for major ions.

A larger recovery tube was located and fitted to the Br9 wellhead. The ceramic sampler was assembled again and run down to 760m without problems. Due to time constraints, the gas was not collected when the sampler was returned to the surface. The sampler was cooled and the sampler water contents were transferred to a Nalgene measuring cylinder that had previously been washed with AR and DDI water. Exactly 500ml of downhole water was recovered. This was named sample G6 (sampler). It was found that the viton seals on the upper and lower compartments had fiactured on disassembling the sampler and, consequently, small pieces of these O-rings were included in the sample.

After the deep reservoir water sample was recovered, the sampler was dis-assembled to reveal the bottle compartment without the non-return valve mechanism. This compartment was then washed as thoroughly as possible with 100ml of AR followed by 100ml of DDI water and then a further 100ml AR followed by 100ml of DDI water. The 400 ml of combined water and AR washings were collected into a 1000ml Nalgene bottle for analysis as sample G6(washings). Two further attempts at collecting samples proved unsuccessful before a third attempt succeeded again at Br9. In this case, the ceramic sampler was used and it was evacuated in order to collect a gas sample as well as the water sample. In addition, the viton O-rings were coated with petroleum jelly, to try to stop them fracturing when the sampler was dis-assembled. On descent, there was a jolt in the Wire line at ~470m CHF depth - presumably the water level. On return, there was only a small amount of gas in the sampler, but a good water sample of 570ml was obtained (sample GS (sampler)). The ceramically lined bottle was then washed as before with consecutive AR, DDI water, AR and DDI water, and these were collected (Sample G8(washings)). It was found that the petroleum jelly had made a slight difference to the ease of extracting the viton O-rings, but the sample still contained pieces of o-ring.

Attention now shifted to sampling Br20, the other likely prospect for a deep, uncontaminated sample of the gold bearing fluid. The WHP at this well was 14.0Bg, and the water level was at the top of the well when sampled. The middle of the large feed zone at 965m CHF was chosen as the sampling site.

The sampling regime for G9 was the same as for G6, with collection of the downhole water (sample G9 (sampler)) followed by collection of the AR +DDI washings (sample G9(washings)). Once again, a 50ml sample of the acidified 310ml sample was taken for arsenic analysis.

Sample G10 was collected with the same conditions as G9. In this case, however, the sampler was evacuated first. The sampler was lowered to 965m CHF and then triggered. On return, it was found that there was no gas present, and only a 325ml water sample was collected. All of this sample was saved for analysis. It was noticed that the bottom seal on the bottle was punctured, and this may be why the sample volume was smaller than previous samples.

At this stage, the wells were required for production, and further sampling was not possible.

### 2.4 Surface samples.

Surface samples were collected from both Br9 and Br20, using a Webre separator. In both wells, a full set of simultaneous water and gas samples were collected. These samples were analyzed for major ions.

### 2.5 Sample preparation and analytical methods.

Aqua regia samples are not received kindly by the postal system, therefore, approximately 150ml aliquots for ICP-MS analysis were transferred to pre- acid washed 175ml Nalgene containers. The solutions were then evaporated to dryness on a water bath over 2-3 days. The dry containers were sealed and sent to CSIRO in Lucas Heights Australia, for analysis. The samples were analyzed by quantitative ICP-MS for Au, Ag, Cu and PGE's and semiquantitative analysis for a general sweep of most other elements available by ICP-MS. The major ion samples were analyzed in the Wairakei laboratories of IGNS by AAS and wet chemistry. The gas samples from both the downhole sampling and the Webre sampling were analyzed by wet chemistry and gas chromatography. Arsenic concentrations were determined by HG - AAS.

## 3. RESULTS

The samples sent to CSIRO were reconstituted and made up to 100ml in AR and analyzed. No problems were observed in dissolving the solutions, and ammonia was added to dissolve the silver chloride.

### 3.1 Platinum Group Elements

The concentrations of the platinum group elements (PGEs) in all samples analyzed were below detection limits. Detection limits in the reconstituted samples were:

| | | | |
|---|---|---|---|
| Ruthenium | Ru | 1.0 | ppb (µg/L) |
| Rhodium | Rh | 0.5 | " |
| Palladium | Pd | 10.0 | " |
| Iridium | Ir | 0.2 | " |
| Platinum | Pt | 0.5 | " |

Since the evaporated solutions were made up to 100ml for analysis at CSIRO and these generally contained between 180 - 220 gm of sample, the true detection limits were:

| | | | |
|---|---|---|---|
| Ruthenium | Ru | 0.52 - 0.65 | ppb (µg/L) |
| Rhodium | Rh | 0.26 - 0.32 | " |
| Palladium | Pd | 5.2 - 6.5 | " |
| Iridium | Ir | 0.10 - 0.13 | " |
| Platinum | Pt | 0.26 - 0.32 | " |

Therefore, the opportunity for extraction of PGE's from geothermal waters - at least from Ohaaki waters - would appear to be very limited and almost certainly non-economic.

### 3.2 Precious metals - Au, Ag, Cu

The analytical results for the precious metals, corrected for the evaporation in the analytical procedure, are as follows (analyses in ppb):

| Sample | Gold | Silver | Copper |
|---|---|---|---|
| AR Blank G1 | 0.30 | 0.63 | 6550 |
| Field Blank G2 | 0.11 | 1.5 | 3.1 |
| Br9 Sampler G6 | 0.08 | 5.5 | 210 |
| Br9 AR wash G6 | 1.63 | 19.0 | 93000 |
| Br9 Sampler G8 | 0.54 | 7.3 | 310 |
| Br9 AR wash G8 | 0.90 | 10.4 | 39000 |
| Br20 Sampler G9 | 0.19 | 2.1 | 68 |
| Br20 AR wash G9 | 0.80 | 6.9 | 53000 |
| Br20 Sampler G10 | 0.72 | 5.8 | 330 |
| Br20 AR wash G10 | 0.75 | 7.0 | 59000 |

These results show that the deep Ohaaki fluids definitely contain significant concentrations of silver. There is, however, a very large scatter in all of the data. The analyses for gold are somewhat equivocal. In the G6 and G9 sampler samples, the gold concentration is barely above background, although the AR wash data for these samples indicate significant concentrations of gold. For the G8 and G10 sampler samples, the gold concentrations are definitely above background, although there is considerable scatter in the results. The copper concentrations in the sampler analyses are well above background indicating significant copper concentrations in the deep geothermal fluid.

### 3 3 Major component data

The three samples especially collected for major element analyses were analyzed at the Wairakei laboratories of IGNS. These were one downhole sample (from Br9 - 760m), and webre water and steam samples from both Br9 and Br20. The webre steam and water samples were combined to provide total flow concentrations.

### 3.4 Arsenic concentmtions

Separate samples were taken for arsenic analysis. Because the ICP-MS arsenic analysis is seriously affected by interference from large chloride concentrations, the arsenic samples were analyzed by hydride generation AAS. The downhole sample from Br9 had an arsenic concentration of 4.12 ppm, while the downhole sample from Br20 had an arsenic concentration of 1.77 ppm.

## 4. DISCUSSION

### 4.1 Deep fluid concentmtions.

The analytical data for the sampler contents, plus the analytical data for the aqua regia washings, together with the data for the field blank and the AR wash of the sampler can be combined to calculate the aquifer concentrations of the precious metals. It is pleasing to note that the field blank concentrations of gold and silver are comparable to the aqua regia blank concentrations of these metals. This implies that there is little contamination of the calculated aquifer concentrations of these metals by the aqua regia, or an aqua regia rinsing of the ceramic surfaces. This confirms earlier analyses conducted at the USGS in 1993, prior to selection of the ceramic coating. Unfortunately, there is significant contamination of copper from the aqua regia washings. This could be due to the copper washers required for sealing the sampler, although these should not have been in direct contact with the aqua regia, or it could be due to the ceramic coating itself.

The aquifer concentrations were calculated by taking the analyzed sampler concentrations, subtracting the field blank concentration, and adding into the downhole sample volume the absolute amount of metal calculated fiom the aqua regia washings with the aqua regia blank subtracted. Using this algorithm, the following aquifer concentrations (µg/L) have been obtained for the 4 downhole samples obtained with the ceramic lined downhole sampler:

| | Gold | Silver | Copper | Ag/Au ratio |
|---|---|---|---|---|
| G6 (Br 9) | 1.03 | 18.9 | 69800 | 18.3 |
| G8 (Br 9) | 0.86 | 12.7 | 23100 | 14.8 |
| G9 (Br 20) | 0.50 | 5.74 | 38600 | 11.6 |
| G10 (Br 20) | 1.16 | 12.15 | 65000 | 10.5 |

The gold concentrations measured in this work are in remarkable agreement with the very approximate value calculated in Brown (1986) for Br 22. It seems that the gold concentration in the deep geothermal fluid at Ohaaki is in the order of 1 ppb. *On* the other hand, the silver concentrations seem to be slightly higher than that previously estimated (8.0 ppb) for Br22. The Ag/Au ratios are reasonably consistent for samples from the same well, which would indicate that the downhole samples were being diluted in runs G8 and G9. This is supported by chloride concentrations for the downhole samples collected in the G4, G6, G8 and G9 runs which suggested that the runs at Br9 were sampling a fluid diluted with respect to the fluid sampled later by the Webre sampling, while those at Br20 appeared to be only slightly diluted with respect to the later Webre samples.

In summary, within the scatter of the data, there seems to be little difference in the measured gold concentrations between wells Br9 and Br20, but possible differences in the silver concentrations and these are reflected in the different Ag/Au ratios for the two wells.

### 4.2 Thermodynamic considemtions

Only analytical data fiom the Webre steam and water samples is suitable for the thermodynamic calculations. This is due to the difficulty of reliably sampling gas concentrations fiom downhole samples. Using the analytical data fiom the concentrations for the major species measured in the Webre samples, it is possible to calculate the $H_2S$ species concentrations, the partial pressure of hydrogen in the reservoir, the ionic strength, and activity co-efficients of all of the species present. From all of these data, and the measured equilibrium constants (Seward 1973, Shenberger and Barnes, 1989) for the reaction: .

$$Au(c)+H_2S(aq) + HS^-(aq) = Au(HS)_2^-(aq) + 0.5H_2(g)$$

it is possible to calculate an equilibrium concentration of gold.

Such a calculation for the measured Webre data is only rigourous for Br20 for which a liquid feed zone is indicated. The measured discharge enthalpy of Br9 indicates that it has a two-phase feed and consequently the thermodynamic calculations for the reservoir waters are much less reliable in this case. With this caveat, the gold solubility, calculated as $Au(HS)_2^-$, in the deep geothermal waters is 32.5 (14.2) ppb for Br 9 and 10.5 (4.5) ppb for Br20. These figures are calculated fiom data fiom Seward, 1973; the figures in parentheses are those calculated from the later data of Shenberger and Barnes, 1989. These calculated results are about an order of magnitude greater than the measured values for the more reliable calculations of Br20, indicating that the gold concentrations are less than the equilibrium solubility. The data of Shenberger and Barnes, however, more closely approximates the measured concentrations. This tends to confirm earlier approximate calculations at Br22 (Brown, 1986). The values for Br9 are more equivocal, but indicate a greater divergence fiom equilibrium solubility.

Under these reservoir fluid conditions, it is likely that gold is transported as the bisulphide complex. However, cyanide complexes of gold are very strong, and if there were cyanide ions present in the reservoir fluid, they may easily account for the gold concentration. Therefore, we have analyzed a sample of the Broadlands/Ohaaki fluid for cyanide. The concentration found in this sample was below the detection limit of 0.01ppm. The only data for cyanide complexing of gold was measured at 25°C (Vlassopoulos and Wood, 1990 and Skibsted and Bjerrum, 1977). Thermodynamic calculations comparing the formation constants of $Au(HS)_2^-$ and $Au(CN)_2^-$ show that at 25°C, only 1/200th the concentration of $CN^-$ compared to $HS^-$ is required to obtain the same gold concentration in solution. Assuming that the temperature dependence of the formation constants is similar, then a concentration of only ~0.02 ppm of $CN^-$ is required to provide the same gold solubility as is found at Ohaaki. Although the measured $CN^-$ concentration is < 0.01, this minimum value is very similar to the amount required. Thus cyanide complexing cannot be ruled out on these grounds. Furthermore, the data of Skibsted and Bjerrum (1977) requires an order of magnitude less $CN^-$ to provide equivalent gold concentrations, and if these data are more accurate, then the measured gold concentrations could easily be accounted for by cyanide complexing.

At the chemical conditions of the deep Ohaaki fluid, the predominant dissolved silver species present will probably be the $Ag(HS)_2^-$ complex. Thermodynamic data for the equilibrium reaction with acanthite ($Ag_2S$):

$$0.5\ Ag_2S + 0.5H_2S + HS^- = Ag(HS)_2^-$$

have been measured (Gammons and Barnes, 1989). Calculation of silver solubilities using these data yields silver concentrations of 2.9 ppb and 3.2 ppb for Br20 and Br9 respectively. The $Ag(HS)_2^-$ complex could also be considered to be in equilibrium with native silver and a reaction similar to that for gold solubility can be written:

$$Ag(c)+H_2S(aq) + HS^-(aq) = Ag(HS)_2^-(aq) + 0.5H_2(g)$$

Gammons and Barnes (1989) also derived data for this reaction, and the appropriate substitution yields silver concentrations of 3.9ppb and 12.0ppb for Br20 and Br9 respectively.

Equilibrium with either $Ag_2S$ or native silver does not seem to account satisfactorily for the silver concentrations measured. Thermodynamic data at 260°C (Seward, 1976) are also available for the silver chloride complexes formed in the reactions:

$$Ag_2S(s) + 2H^+ + 2Cl^- = 2AgCl^\circ + H_2S$$

and

$$Ag_2S(s) + 2H^+ + 4Cl^- = 2AgCl_2^- + H_2S$$

Using this data, the calculated silver concentration due to silver chloride complexes is 0.09ppb for Br20 and 0.01ppb for Br9. Consequently, chloride complexing is not an important transport mechanism at Ohaaki.

The silver/gold ratio calculated from the thermodynamic data is much lower than the reservoir measurements. For both Br20 and Br9, the Ag/Au ratio is <1, compared with measured ratios of >10.

Copper analyses seem to be way too large to be real and probably represent contamination fiom either the aqua regia, or momentary contact of the aqua regia on to the bottom copper seal through a ruptured viton seal.

## 5. CONCLUSIONS

The disappointingly low gold concentrations derived from the ceramic sampler runs mean that extraction of gold is almost certainly not economically viable at the Ohaaki geothermal field. Even if all of the gold could be extracted at say lppb concentration, and assuming that *all* Ohaaki wells contained this concentration, then the available gold would be only 24gms per 24 hours assuming a total field flow of 1000 tonnes/hour. This is slightly less than 1 oz per 24hour period with a current value of around US$375. Although silver seems to be present at a higher concentration, the very much lower value of silver would also make its extraction economically not viable.

The platinum group elements were not observed at concentrations above the detection limit of the ICPMS. Consequently, the extraction of these elements will also not be economically viable.

On a more optimistic note, the sampler seemed to have performed as expected. Trace metal analyses for elements other than copper, silver, gold and PGE's have been recorded.

## 6. ACKNOWLEDGEMENTS

I would like to thank Contact Energy (formerly ECNZ Geothermal) - especially Ian Thain - for financial support, the opportunity to take these samples, and permission to publish the data. I thank Chris Moms for fitting the sampling into the busy Ohaaki shutdown schedule, Tom Gould for help above and beyond the call of duty in running the winch late into the evening, Lew Klyen for performing the acrobatic ballet necessary to trigger the sampler and the lab at Wairakei, IGNS for putting up with two days of aqua regia pong. I thank Kerry Webster of ESR Environmental for the arsenic analyses. Part of this work was funded by Contract CO 5508 from FRST.

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