PRELIMINARY RESULTS OF PRECIOUS METAL ANALYSES OF DOWNHOLE SAMPLES FROM KAWERAU AND NGAWHA GEOTHERMAL SYSTEMS

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Summary – We report analyses for precious and related metals on deep waters obtained from Kawerau and Ngawha geothermal systems with a purpose-built titanium sampler. Solutions were analysed by ICP-MS. Lab testing using blank solutions shows minimal sources of contamination from materials used in the construction and sampling procedure (i.e. titanium, MilliQ water and aqua regia). At Kawerau, samples were obtained from deep wells at ≥1000 m depth at temperatures of **260** to **295°** C, while at Ngawha samples were taken from > **800 m** depth at temperatures of 225° to >235° **C.** Gold, silver and thallium are at ppb levels, while arsenic, antimony and copper range from hundreds to thousands ppb. Comparing these results with calculated solubilities of gold, silver and acanthite, suggests deep waters are undersaturated in gold but close to saturation in silver, These results are preliminary in the absence of, blank samples subject to downhole conditions and sampling procedures.

1.0 INTRODUCTION

The precious metal concentrations of deep geothermal waters have been difficult to determine because waters ascending wells undergo gas loss which causes metal deposition (Brown, **1986).** Thus, downhole sampling remains the only means by which a deep sample can be obtained and analysed for trace metals. Unfortunately, sampling devices made of steel contribute significant sources of contamination. In an earlier attempt to overcome contamination a ceramic lining was applied to the interior of the steel vessel with promising results (Brown et al., **1996).**

In this paper, we report analytical results for precious and related metals on deep waters collected from Kawerau and Ngawha geothermal systems with a purpose built titanium sampler. This work is part of a larger investigation assessing the transport and deposition of metals in modern epithermal environments in New Zealand.

2.0 TITANIUM SAMPLER

The sampler used in this project was built for sampling waters subject to trace metal analysis. It is a modified version of the Klyen sampler. All but the release mechanism, which is constructed of 316 stainless steel, is constructed of titanium with a one litre sampling volume. A titanium non-return valve is incorporated into the design, so the only other materials to make fluid contact are the stainless steel shim, which prevents fluid entry to the sampler until pierced by an inertial spring mechanism at the sampling depth, and the VITON O-rings that seal the top and bottom of the sampler and the non-return valve.

To assess any trace metal contamination from the titanium sampler, oil free titanium turnings from waste during fabrication were subject to three solution tests: I) add **200** ml MilliQ water (laboratory water reagent grade 111; >18 MΩ) to plastic sample bottle forming the deionised water blank; 11) add **40** ml of aqua regia **(30** ml of BDH Aristar HCL and 10 ml of BDH Aristar HNO_3) to **120** ml of MilliQ water forming the aqua regia blank; and 111) place acid washed titanium turnings into a plastic bottle and add **40** ml of aqua regia, shake for 1 minute and then dilute with 120 ml of MilliQ water forming the titanium blank. All plastic sample bottles were soaked for at least **5** hours in **10%** nitric acid then washed six times with MilliQ water.

These blank solutions and the sample solutions described below were analysed quantitatively for Au, Ag, Cu, Sb, Tl and As by ICP MS at CSIRO, Centre for Advanced Analytical Chemistry, Lucas Heights, NSW, Australia. The blank results are given in Table 1.

Table 1. Analytical results for Blanks I, II and III reported in µg/L.

	Ag	As	Au	Cu	Sb	Tl
I	<.01	<.05	<.01	<.05	<.01	<.01
II	.19	<3.0	.09	.09	0.09	<.01
III	.04	<3.0	.02	.89	0.05	<.01

Table 2. Results of trace metal analyses on downhole samples of geothermal waters from Kawerau (KA) and Ngawha (Ng) wells. All data given in µg/L except for chloride which is given in **mg/L**. DF=Dilution factor. "X" and "Y" refer to two different wells at Kawerau; "M" indicates sample analysed for major cations and anions.

	sample vol mls	Ag	As	Au	Cu	Sb	Tl	DF	Cl ppm
KA Y (4)	650	10.20	1220	0.64	1210	380	4.30	1.369	
KA Y (5)	680	1.40	540	0.03	490	125	3.00	1.147	
KA Y M	700								717
KA X (1)	600	31.50	4860	2.10	2360	540	4.60	1.400	
KA X (2)	800	14.30	3120	0.70	770	480	7.50	1.300	
KA X M	750								1204
NG 4A	780	0.40	170	1.00	750	470	1.8	1.205	
NG 4B	780	7.00	430	0.50	4700	1690	3.8	1.205	
NG 4 M	?								1249
NG 13A	730	10.10	380	0.70	1050	470	1.4	1.219	
NG 13B	650	19.10	770	0.50	1770	2080	4.7	1.246	
NG 13M	730								1242

The small amounts of Ag, **Au** and Sb contamination in Blanks **II** and **III** likely sourced from the Aristar HCl used to make the aqua regia. In blank **III,** the titanium turnings account for the Cu concentration analysed.

Given that earlier estimates of metal contents of deep fluids exceed **1 µg/L** (Brown, **1986),** these results show minimal contamination **from** the solutions and materials used in sampling deep geothermal waters.

3.0 METHODOLOGY

Kawerau and Ngawha high temperature geothermal fields (Christenson, **1987;** Skinner, **1981;** Sheppard and Giggenbach, **1984)** were chosen for trial testing of the sampler. At both fields, downhole sampling was undertaken on deep vertical wells used for monitoring; i.e. these wells are not used for production. At Kawerau, samples were taken from ≥1000 **m** depth at temperatures of **260** to **295°** C in wells in the middle of the production reservoir. At Ngawha, samples were taken from **1300** m and >**235°** C in Ng 13 in the middle of the reservoir and from **800** m and >**225°** C in Ng **4** on the periphery of the reservoir.

Sampling methods employed follow. Before sampling, all trace metal sampling bottles **(1** litre HDPE) were soaked overnight in **~5%** HNO_3 (lab grade) and then rinsed with MilliQ water. While sampling, surgical gloves were worn to prevent contamination of the sample as well **as** to provide skin protection from aqua regia. The titanium sampling equipment was initially cleaned with **40 ml** of **BDH** aqua regia, followed by **40** ml of MilliQ water, followed by **40** ml of aqua regia, followed by a further 40 ml of MilliQ water. This cleaning routine replicates the post sampling procedure that is used to dissolve any precipitates that may have deposited in the sampler upon cooling and **gas** loss when the sampler is brought to the surface and opened. These post-sampling rinses were added to the sample in order to preserve the deep metal concentrations **as** best as possible. For each sample collected, the sampler was fitted with new VITON O-rings and evacuated with a hand pump. The release mechanism was attached, and the sampler was run down the well to the required depth. By pulling on the wire line, the sampler was triggered, piercing. the stainless steel shim, so that well bore fluid could enter the sampler. At the surface, the sampler was opened. The volume of the liquid sample **was** measured with a volumetric cylinder and transferred to the sample bottle. The sampler was subsequently washed with aqua regia and MilliQ water as described above adding 160 ml of solution to the sample. Black precipitates formed in both samples from Ngawha and so these waters were filtered **(0.45µm)** before analysis.

4.0 RESULTS

The results of the analyses reported in Table **2** **are** corrected for addition of aqua regia and MilliQ water. For reference the dilution factors reflecting the amount of aqua regia and MilliQ water for rinsing are also reported. Note that at Kawerau, 80 ml of aqua regia plus 80 ml of MilliQ water were added to samples 1, **2** and **4** in the first two rinses of the sampler so that dilution factors reported in Table **2** are somewhat higher than for Ngawha. Having depleted the supply of acid in the field, 50 ml of aqua regia plus 50 ml of MilliQ water total were added to Kawerau sample **5** and the dilution factor reflects this. Unfortunately, no blank samples in which MilliQ water **is** placed into the sampler then run down to depth, returned to the surface, and acid washed were run due to time and expense. Accordingly, the results need to be considered as preliminary indications of deep trace metal concentrations. We also obtained waters for major element analysis and only the chloride concentrations for these are reported in Table **2.** These chloride concentrations are similar to those calculated for the respective reservoirs and demonstrate that representative waters of the deep geothermal system were indeed sampled.

5.0 DISCUSSION

The results (Table 2) show gross trends that are consistent with earlier determinations of deep trace metal contents at Broadlands Ohaaki (Brown, 1986; Brown et al., 1996). Accordingly, gold and silver concentrations of deep geothermal waters are at ppb concentrations with most Ag/Au ratios ranging from 10 to 20. Thallium also occurs at ppb level. By contrast, copper, arsenic and antimony range from hundreds to thousands of ppb. Arsenic is five to ten times more concentrated than antimony at Kawerau, while antimony is about two to four times more concentrated than arsenic at Ngawha. Given the stibnite deposition in the heat exchangers at Ngawha (Dorrington and Brown, 2000), this difference is not so surprising.

At finer scale of examination, the results in Table 2 show considerable variation that likely reflects the vagaries of sampling and analysis for trace metals. For example, all replicate samples show greater than a two times difference in gold concentration except for the two samples from Ng 13. In these same two samples, however, silver concentrations are different by almost two times. Dark precipitates only formed in the Ng 13 samples so while they might account for metal variations here, they cannot account for the metal variations in the other samples. In the absence of a downhole sample blanks, we reserve detailed discussion of trace metal variations to subsequent reports.

5.1 Gold and Silver Solubilities

Taking the known reservoir fluid compositions and temperatures (based on water and gas samples from production wells) it is possible to assess the maximum concentrations of gold and silver in solution assuming that the following equilibria are attained:

$$Au + H_2S + HS^- = Au(HS)_2^- M.5 H_2$$

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

$$Ag_2S + H_2S + 2 HS^- = 2 Ag(HS)_2^-$$

Data for gold solubility are from Shenberger and Barnes (1989), and the data for silver solubility are from Gammons and Barnes (1989). Major ion speciation was calculated with program software SOLVEQ and CHILLER (Reed, 1982; Spycher and Reed, 1989).

Table 3. Calculated aqueous concentrations (ppb) of gold and silver in deep reservoir waters assuming equilibria with gold, silver or acanthite (Ag_2S).

	Kawerau	Ngawha
Au	36.3	6.0
Ag	30.7	7.9
Ag_2S	23.7	5.9

Comparing the calculated solubilities with the results in Table 2 suggests that the deep waters at both Kawerau and Ngawha are undersaturated in gold, consistent with earlier findings (Brown, 1986). By contrast, the silver contents of deep waters are much closer to saturation.

5.2 Future Work

We have also obtained downhole samples from Mokai and Rotokawa at temperatures greater than 300° C beyond the working limits of the VITON seals. The results from these efforts were mixed and difficult to assess, though we learned that sample blanks need to be incorporated into the survey procedure. These two fields will be revisited in future sampling. Currently, we are waiting for results from sampling at Wairakei and Broadlands-Ohaaki, where sample blanks were obtained, which will be the subject of a future report.

6.0 ACKNOWLEDGEMENTS

We thank the Ministry of Commerce and Top Energy for access to geothermal wells for sampling. We also thank Century Resources for their assistance in obtaining downhole samples. Peter Dorrington (Top Energy) and Tricia Scott (NZ Environmental Ltd) deserve special mention for their assistance and cooperation with the sampling at Ngawha. This work was funded by a PGSF-FRST contract.

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