Proc. 12th New Zealand Geothermal Workshop 1990

ARSENIC IN GEOTHERMAL SINTERS: DETERMINATION AND IMPLICATIONS FOR MINERAL EXPLORATION

Robin J Parker' Keith Nicholson*

'Geology Department *Geothermal Institute
University of Auckland, Private Bag, Auckland, New Zealand

ABSTRACT

The arsenic content of sinters was determined by X-ray fluorescence spectrometry using a Rh X-ray tube. Interference from Pb La, Rh Ka, Ba Ka, Ge Kβ and Ga Kβ line overlaps was minimised by careful selection of instrument settings. The samples were analysed as pressed powder briquettes, and detection limits below 3 mg/kg were achieved.

Arsenic is sinters is probably present as sub-micron-size particles of amorphous sulphides. Sinter-As is probably a reliable guide to extinct geothermal (epithermal) systems. The absence of As in a siliceous lithology does not preclude a geothermal origin, but may indicate a gold-poor system.

INTRODUCTION

Arsenic has a complex geochemistry due to its variable oxidation states (-3, 0, +3, +5) and concomitant variation in bonding and ionic size. It is widely distributed in geological materials and is notably concentrated in mineral deposits, being linked to more than 20 economically important elements (Boyle and Jonasson, 1973) including precious metals (Au, Ag, Pt) and base metals (e.g. Cu, Zn, Pb, Ni and Co). It is geochemically relatively mobile and commonly forms haloes around ore bodies; as such As is recognised as being an excellent pathfinder element in mineral exploration.

This element is significantly concentrated in geothermal waters and sinters (Onishi, 1969; Boyle and Jonasson, 1973); the sinters typically resulting from precipitation by chloride-rich hot springs considered to represent the surface expression of the deep convective waters of a hydrothermal system (Henley and Ellis, 1983; Henly, 1985). These hot spring waters are thought not to have undergone significant mixing with other fluids and they are envisaged as having reached the surface directly as a result of structural controls (Henley, 1985) such as deep fractures and/or hydrothermal breccia explosion pipes (e.g. Champagne Pool, Waiotapu). Thus sinters are considered to be precipitates from the primary hydrothermal fluid and their study should help to elucidate the nature of these fluids and their ability to transport and deposit various geochemical species.

Arsenic is one of a group of elements (As, Sb, Hg, Tl) which are typically enriched in these hot spring precipitates which also often contain ore-grade gold and silver (Weissberg, 1969). It is these amorphous sulphide precipitates which form a link between epithermal Au and Ag mineralisation and geothermal systems (Henly, 1985; Silberman and Berger, 1985). Arsenic itself has often been suspected as having a role to play in the transport and deposition of gold (Henley, 1985) although the mechanisms are not clear. Whatever the role, the work of Berger and Silberman (1985) and Silberman and Berger (1985) document the utility of As as a trace element in delineating areas of epithermal gold mineralisation. In addition, Binqui et. al. (1986) demonstrated that As can effectively delineate areas of geothermal activity.

Arsenic is potentially a toxic element and it is therefore important for environmental reasons to investigate the presence of high concentrations of As within geothermal areas.

The present study focuses on the distribution of arsenic in geothermal sinters from the Taupo Volcanic Zone and forms part of a larger investigation into sinter chemistry (Nicholson and Parker, 1990).

Geothermal geochemistry of arsenic

Aqueous speciation: The geochemistry of arsenic in geothermal fluids has been reviewed by Ballantyne and Moore (1988). Their work, together with that of Webster (1990), indicate that arsenic occurs in the reduced As(III) oxidation state in the deep reservoir fluid and is ,also present in hot spring discharges. Once all the available hydrogen sulphide has been oxidised to sulphate, then As(V) also appears in the hot spring waters along with As(III). However, the concentration of As(V) is small; Webster (1990) reports that 97-100% of the arsenic is present as As(III) in New Zealand hot-spring discharge waters. Although the speciation of arsenic is dependant upon the ligands present in solution, the neutral arseneous acid, H_3AsO_3, and arsenic acid, H_3AsO_4, complexes appear to be predominant (Ballantyne and Moore, 1988; Webster, 1990).

Sinterphase: There are few studies which include As in the suite of elements determined in sinter. The most detailed investigation is that of Takahashi et al. (1987) who examined the distribution of arsenic in silica scale. The scales were deposited from waters with As concentrations of 0.5-4.6 mg/kg and contained 6.3-284 mg/kg As. These authors used a selective leaching method to determine the fraction of the total As content in the following fractions: ion-exchangable/carbonate; iron-manganese oxide;

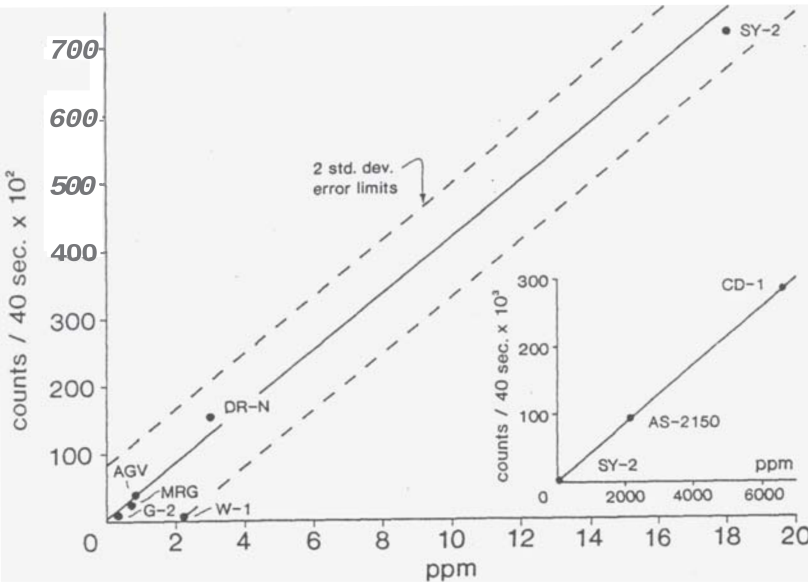

Figure 1. XRF calibration line for As; see text for instrumental settings.

sulphide and silicate-lattice. Takahashi et al. (1987) concluded that As was distributed throughout the scale in several phases with the majority of the As in the silicate-lattice fraction, but up to 60% also occurred in ion-exchangable form. In a geochemical survey, Rice and Trewin (1988) found As concentrations of <4 to 300 mg/kg in sinters deposited from one of several Devonian geothermal systems in Scotland (Nicholson, 1989). No data on the As content of other siliceous lithologies have been found in a literature search to date.

DETERMINATION OF ARSENIC IN SINTERS

Arsenic in silica scale has been previously determined by AAS-hydride generation following a perchloric-nitric-HF acid decomposition, HCI leach and removal of iron interference by ion-exchange (Takahashi et al., 1987). Similar AAS methods for the determination of As in geological materials have been used by Terashima, (1976; 1984). However, by removal of the decomposition and ion-exchange stages, X-ray fluorescence spectrometry offers a simpler option for the routine analysis of sinters. In the past, XRF has been criticised as a technique for As determination due to a lack of sensitivity (Boyle and Jonasson, 1973). However, this criticism is no longer valid since with modem instruments good sensitivity is now available.

Procedure: Analysis of As by XRF

Introduction: X-ray fluorescence spectrometry provides a straightforward technique for the analysis of As in geological materials using pressed powder briquettes. Arsenic (Z = 33) belongs to a group of elements which can be excited with good sensitivity by the Rh X-ray tube (ie. ~ 1 cps/mg kg^{-1}). Consideration of the relevant part of the X-ray spectrum shows that the As Ka line is overlapped by the Pb *La* line; other possible interferences are from Rh Ka (2nd order) and Ba Ka (3rd order). When using the Rh X-ray tube interference from Rh *Ka* is potentially serious, and this requires that effective energy discrimination be applied *to* eliminate these second order tube wavelengths. Other elements to be considered include first order Ge Kβ and Ga Kβ lines. Provided adequate energy and goniometer resolution is available all of the above interfering lines can be avoided with the exception of the first order Pb Lα line for which a correction must be made - this correction will be dependent on the amount of Pb in the sample.

Sample preparation: *8* grammes of finely ground rock powder were mixed with *6-8* drops of 2% polyvinyl alcohol followed by pressing with a boric acid backing in a hydraulic press at 12 tonne to produce 40 mm diameter briquettes. The briquettes were then dried overnight at 50°C.

Standards: Silicate arsenic standards that span a good range of concentrations are difficult to obtain. Most of the traditional international rock standards have arsenic values of < 20 mg/kg with the highest value at 18 mg/kg in SY-2 (Fig. 1). The next international standard used in the present study was CD-1 with a concentration of 6600 mg/kg(!). In order to bridge this gap a synthetic standard was prepared with an As concentration of 2150 mg/kg. This standard was prepared by spiking a silicate rock sample with a known amount of As.

Instrumental settings: Rh X-ray tube (60 kV/40 mA), vacuum, fine collimator and LiF 220 crystal; the latter settings were used to minimise the effects of line overlap from Pb and the other elements discussed above. In addition a relatively narrow pulse height window was selected to minimise second and third order reflections. Peak and background counting times were 40 seconds for As Ka and 80 seconds for Pb Lβ.

TABLE 1
Arsenic concentrations in New Zealand geothermal fluids
(mg/kg)

Fieldwell/spring	[As]
Ohaaki	
Ohaaki Pool	1.5
	39
"	1.0
spring 6	1.2
Spring 7	1.4
BR13	3.2
BR2	5.7
"	5.7
BR3	4.0
BR4	5.7
BR8	7.9
"	2.0
BR9	4 5
BR10	4.1
"	0.8
BR11	5.5
"	2.6
BR12	1.0
BR13	3.2
BR14	5.7
"	2.1
BR17	2.3
BR18	4.9
BR22	3.6
"	4.4
BR23	3.2
BR25	3.4
BR27	3.0
BR28	4.0
BR33	0.6
BR40	0.1
Tokaanu	
Taumatapuhipuhi geyser	5.6
Spring 8	6.4
Waiotapu	
Champagne Pool	2.5
"	1.3
Wairakei	
WK1	2.0
WK10	2.2
WK24	4.5
WK42	4.8
WK44	4.8
WK(av)	4.7
Spring 97	1.8
spring 190	2.8

Data sources: Ellis, 1979; Ellis & Mahon, 1977; Hedenquist & Henley, 1985; Mahon & Finlayson, 1972; Mahon & Klyen, 1968; Mann et al., 1986; MoW, 1977; Weissberg et al., 1979.

Corrections: Apart from correcting for the Pb La interference on the As Kα line (above), the raw X-ray data was also corrected for background curvature, deadtime and mass absorption effects.

Calibration: Fig. 1 shows the calibration line produced by the standards using the above instrumental settings. The calibration is largely controlled by the CD-1 and AS-2150 standards; the remaining low concentration standards serve as a test for the calibration at these lower concentrations, ie SY-2 and DR-N return average back calculated standard concentrations of 17 and 4 mg/kg respectively (versus recommended values of 18 and 3 mg/kg). Although standards G-2, MRG, W-1 and AGV-1 *are* present at concentrations too low to affect the calibration line, they nevertheless show that for 3 of the 4 standards the calibration passes through the origin with no significant positive or negative bias at these low concentrations. W-1 falls below the line but its position is still within the 2 standard deviation counting errors for these 4 standards. The calibration therefore shows an essentially linear relationship over at least three orders of magnitude (6 - 6000 mg/kg).

Back calculated standard calibration data show that the accuracy of the method is good with an overall accuracy estimated to be - 5%. The precision of the method varies with the count rate (ie concentration) of the sample and is estimated from the calibration data to be - 10% at 20 mg/kg and <5% at 100 mg/kg and higher. Detection limits will vary depending on counting times, the sample matrix and the Pb content. For typical silicate rocks with less than - 100 mg/kg Pb the 3 standard deviation detection limits vary between 3 and 4 mg/kg for the instrumental settings discussed above. Longer counting times (eg 100 seconds) will reduce the detection limits to 2-3 mg/kg. The silica rich sinters analysed in this study have detection limits of less than 3 mg/kg.

ARSENIC IN NEW ZEALAND SINTERS

Sinters were collected from the Atiamuri, Ohaaki, Tokaanu and Waiotapu geothermal fields within the Taupo Volcanic Zone, New Zealand (Nicholson and Parker, 1990). The arsenic content of waters discharged from these fields are summarised in Table 1, which also includes data from Wairakei for comparison. As can be seen, most discharge waters contain about 2-4 mg/kg As. The As content of the sinters collected in this study, together with additional data for Waiotapu deposits from Hedenquist and Henley (1985), are shown in Table 2.

Although the As content of the sinters is variable, it is at significant concentrations for most of the samples analysed. Furthermore, it is notable that for both the data set as a whole, and for data from individual fields, As is antipathetic to the silica content of the sinters (Fig. 2 and Nicholson and Parker, 1990). Since substitution within the silica lattice is unlikely, and the neutral or anionic As species will not be adsorbed onto negatively-charged silica, then this implies that As is present as a discrete phase which is incorporated into the deposit at the expense of silica. Despite a detailed examination of samples under the scanning electron microscope, by reflected microscopy and by XRD, no As-bearing phases were identified in the sinters. However, since As commonly forms colloidal amorphous sulphides, then these would not be resolved petrographically or by XRD. The frequent Occurrence of metal-rich sulphide deposits which precipitate from spring and well discharges has been noted by Weissberg (1969) and Browne and Lloyd (1986). These are currently seen to deposit and accumulate most spectacularly at Waiotapu, notably at the Champagne Pool. Furthermore, the solubility of orpiment is highly temperature dependant, and deposits as sulphide-rich geothermal discharges cool (Webster, 1990).

Following the techniques described by Nicholson and Aquino (1989), the particulate matter suspended within the waters of the Champagne Pool was examined under the scanning electron microscope; semiquantitative analyses of representative specimens are presented in Table 3. As expected, individual sulphide and silica particles were found. More significantly however, grains which were mixtures of aggregated sulphide-silica particles were also common. It is also interesting to note that Sb, but not As, was a regular constituent in the silica particles. These observations lend further support to the suggestion that As and Sb (plus those incorporated onto the sulphide precipitate: eg. Tl, Hg) are present within the sinter as a fine-grained (sub-micron) amorphous phase.

TABLE 2
Arsenic concentrations in New Zealand geothermal sinters
(mg/kg)

Field: spring	[As]
Atiamuri	
Pool	<1
- " -	<1
Ohaaki	
Ohaaki Pool	246
- " -	5
- " -	86
- " -	110
Tokaanu[1]	
Taumatapuhipuhi geyser (Spring 13)	76
Spring 6	49
spring 12	60
Spring 77	33
Spring 103	26
Spring 105	55
Waiotapu	
Champagne Pool	147
- " -	128
- " -	134
- " -	115
- " -	214
- " -[2]	12000
- " -[2]	50
Waiotapu geyser[2]	20
Lake Ngakoro Pool[2]	4500

[1] See Nicholson & Aquino (1989) for map of spring locations

[2] Data from Hedenquist and Henley (1985).

TABLE 3
Representative, semi-quantitative SEM-EDAX analyses of particulate matter from the Champagne Pool, Waiotapu.
(wt %)

	Si	S	As	Sb
1	95.2			4.8
2	82.6			9.1
3	56.5	2.8		12.4
4	53.5	1.6		5.4
5	30.8	46.3	15.3	5.1
6	6.1	51.0	39.3	3.6
7	4.4	47.9	44.0	
8	3.5	58.8	22.5	12.4
9	1.2	59.2	33.1	5.3
10		58.5		40.4

Blanks indicate concentration 4.5 wt%.

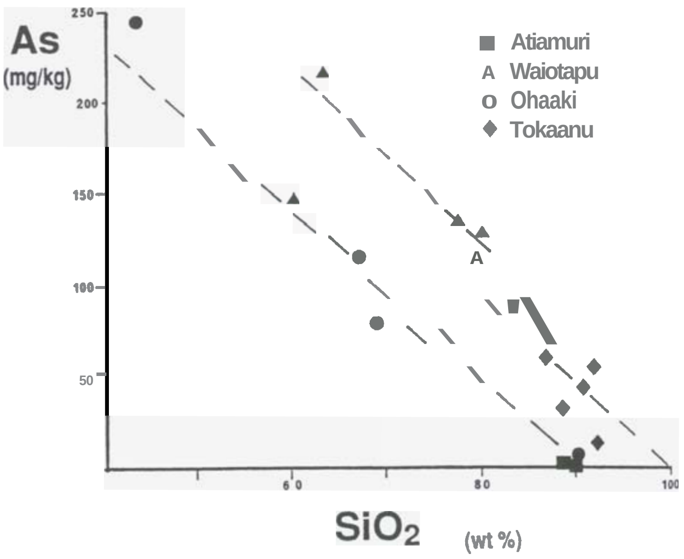

Figure 2. Silica and arsenic in sinters from Atiamuri, Ohaaki, Tokaanu and Waiotapu geothermal fields.

CONCLUSIONS

XRF spectrometry provides a simple, reliable method for routine determination of As in sinters. The arsenic is probably present as a discrete amorphous sulphide phase which deposits as sulphide-rich waters cool. The absence of As in the Atiamuri sinters may be due to the low concentration of sulphide ligands, although the lack of any data for these hot spring discharges precludes confirmation of this. Arsenic-in-sinter appears to be a reliable pathfinder for ancient geothermal (epithermal) systems. The absence of As in a siliceous lithology does not preclude a geothermal origin, though it may indicate a lack of any orpiment (or similar sulphide) precipitate which is subsequently incorporated into the sinter. This is significant in mineral exploration since the solubility of orpiment is limited by the reaction (Webster, 1990):

$$3H^+ + 3HS^{2-} + H_3AsO_3^0 = As_2S_3 + 3H_2O.$$

Gold is transported as a sulphide species, and an inadequate supply of sulphide ligands to deposit orpiment may similarly limit the mobility of gold within the system. In exploration terms: no sinter-As may also indirectly indicate no gold.

REFERENCES

BALLANTYNE, J.M. and MOORE, J.N. (1988). Arsenic geochemistry in geothermal systems. Geochim. Cosmochim. Acta, 52, 475-483.

BINQUIN, Z., JINMAO, Z., LISCIN, Z. and YASCIN, Z. (1986). Mercury, As, Sb, Bi and B as geochemical indicators for geotehrmal areas. J. Geochem. Explor., 25, 379-388.

BERGER, B.R. and SILBERMAN, M.L. (1985). Relationships of trace element patterns to geology in hot-spring type precious metal deposits. In: Berger, B.R. and Bethke, P.M. (eds), geology and geochemistry of epithemal systems. Reviews in Economic Geology, 2, 233-248.

BOYLE, R.W. and JONASSON, I.R. **(1973).** The geochemistry of arsenic and its use as an indicator element in geochemical prospecting. J. geochem. Explor., **2,251-296.**

BROWNE, P.R.L. and LLOYD, E.F. **(1986).** Water dominated geothermal systems and associated mineralisation. Tour guide, International Volcanological Congress, New Zealand, NZ. Geol. *Surv.* Record, 11, 145-212.

HEDENQUIST, J.W. and HENLEY, R.W. **(1985).** Hydrothermal eruptions in the Waiotapu geothermal system, New Zealand: Their origin, associated breccias and relation to precious metal mineralization. Econ. geol., **80,1640-1668.**

'HENLEY, R.W. **(1985).** The geothermal framework of epithermal deposits. In: Berger, B.R. and Bethke, P.M. (eds), geology and geochemistry of epithermal systems. Reviews in Economic Geology, **2, 1-24.**

HENLEY, R.W. and ELLIS, A.J. **(1983).** Geothermal systems, ancient and modem. Earth Science Reviews, **19,** 1-50.

ELLIS, A.J. **(1979).** Explored geothermal systems. In: Barnes, H.L. (ed.). Geochemistry of hydrothermal ore deposits; second edn. Wiley, New York, **632-683.**

ELLIS, A.J. and MAHON W.A.J. **(1977).** Chemistry and geothermal systems. Academic Press, New York.

MAHON W.A.J. and FINLAYSON, J.B. **(1972).** The chemistry of the Broadlands geothermal area New Zealand. Amer. J. Sci., 272, 48-68.

MAHON W.A.J. and KLYEN, L.E. **(1968)** Chemistry of the Tokaanu-Waihi hydrothermal area. N.Z. J. Sci., 11: 140-**158.**

MANN, A.W., FARDY, J.J. **and HEDENQUIST, J.W.** **(1986).** **Major and** trace element concentrations in some New Zealand geothermal waters. In: Proc. Symposium *5:* Volcanism, hydrothermal systems and related mineralisation. International Volcanological Congress, **61-**66.

MoW **(1977).** Broadlands geothermal investigation report. Ministry **of Works,** Wellington, 236pp.

NICHOLSON K., **(1989).** Early Devonian geothermal systems in northeast Scotland: Exploration targets for epithermal gold. Geology, **17,568-571.**

NICHOLSON K. and AQUINO, C.G. **(1989).** Life in geothermal systems. A key to sinter formation and recognition? In:. Browne, P.R.L. and Nicholson, K. (eds), Proc. 11th NZ Geothermal Workshop, Auckland, **143-148.**

ONISHI, H. **(1969).** Arsenic. In: Wedepohl, K.H. (ed.) Handbook of Geochemistry. Springer-Verlag, Berlin.

RICE, C.M. and **TREWIN,** N.H. **(1988).** A lower Devonian gold-bearing hot-spring system, Rhynie, Scotlamd. Trans. Instn Min. Metall. (Sectn B; Appl. earth sci.) 141-144.

SILBERMAN, M.L. and BERGER, B.R. **(1985).** Relationships of trace element patterns to alteration and morphology in epithermasl precious metal deposits. In: Berger, B.R. and Bethke, P.M. (eds), geology and geochemistry of epithermal systems. Reviews in Economic Geology, **2,203-232.**

TAKAHASHI, Y., YOKOYAMA, T. and TARUTANI, T. **(1987).** Arsenic in geotehrmal water and silica scale. Roc. NZ 9th Geothermal Workshop, **89-92.**

TERASHIMA, **S. (1976).** The determination of As in rocks, sediments and minerals by arsine generation and AAS. Anal. chim. Acta, 86, 43-51.

TERASHIMA, **S. (1984).** Determination **of** As and Sb in geologicasl materials by automated hydride generation and electrothermal AAS. Bunseki Kagaku, **29, 194-199.**

WEBSTER, J.G. **(1990).** The solubility **of** As_2S_3 and speciation of As in dilute and sulphide-bearing fluids at **25** and **90°C.** Geochim. Cosmochim. Acta, **54,1009-1017.**

WEISSBERG, B.G. **(1969).** Gold-silver ore-grade precipitates from New Zealand thermal waters. Econ. Geol., **64,** 95-**108.**

WEISSBERG, B.G., BROWNE, P.R.L. and SEWARD, T.M. **(1979).** Ore metals in active geothermal systems. In: Barnes, H.L. *(ed.).* Geochemistry of hydrothermal ore deposits; second edn. Wiley, New York, **738-780.**