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GEOTHERMAL SINTER CHEMISTRY: TOWARDS A DIAGNOSTIC SIGNATURE AND A SINTER GEOTHERMOMETER

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ABSTRACT

Sinter samples from Atiamuri, Ohaaki, Waiotapu and Tokaanu geothermal fields in the Taupo Volcanic Zone, New Zealand were subjected to major and trace element analysis by X-ray fluorescence spectrometry. Silica and water are the major components, with CaO assuming importance in sinters from Ohaaki, which are composed of an intimate mixture of calcite and silica. Most of the trace elements examined (As, Ba, Cr, Cu, La, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn, Zr) are often present in concentrations of <10mg/kg. Arsenic, however, is commonly enriched (up to 246mg/kg), while Sr shows a dramatic increase in concentration (up to 684mg/kg) when calcite is present in the sinter. The As-Sb-TI-Hg association may be diagnostic and discriminate sinters from other siliceous lithologies. Although sinters are heterogeneous deposits, ratios of constituents in sinters across a field are reasonably consistent. A linear relationship exists between the Na/K ratio in the water and that in the sinter. This was used to develop a $Na/K_{(sinter)}$ geothermometer, which has the equation:

$$t\,^{o}C = \frac{1390}{1.750 + \log\,[4\ (Na/K)_{sinter} + 5.5]} - 273.15$$

This should only be applied to sinters with $SiO_2 \geq 80$ wt% as the relationship breaks down at lower concentrations.

INTRODUCTION

Remnants of geothermal deposits preserved in ancient terrain are valuable guides to locating exploration targets for epithermal mineralisation (eg. Nicholson, 1988; 1989). In this respect mineralogical alteration sequences diagnostic of a given fluid type, and criteria to recognise hydrothermal eruption breccia have both been well defined (eg. Henneberger and Browne, 1987; Hedenquist and Henley, 1985). However, similar criteria to enable the discrimination of ancient sinters from other siliceous lithologies still await definition. Textural and petrographic features which enable the recognition of some, but not all, sinters have been recently described by Nicholson and Aquino (1989) and White et al. (1989). However, if a sinter-diagnostic geochemistry could be defined, then the relative simplicity of such a signature would be of obvious value to mineral exploration programmes.

This paper reports the initial results of a geochemical survey of sinter deposits in New Zealand. The objectives of this research are two-fold: to define a sinter-diagnostic geochemical signature, and to determine whether sinter chemistry can be related back to the composition of the depositional fluid.

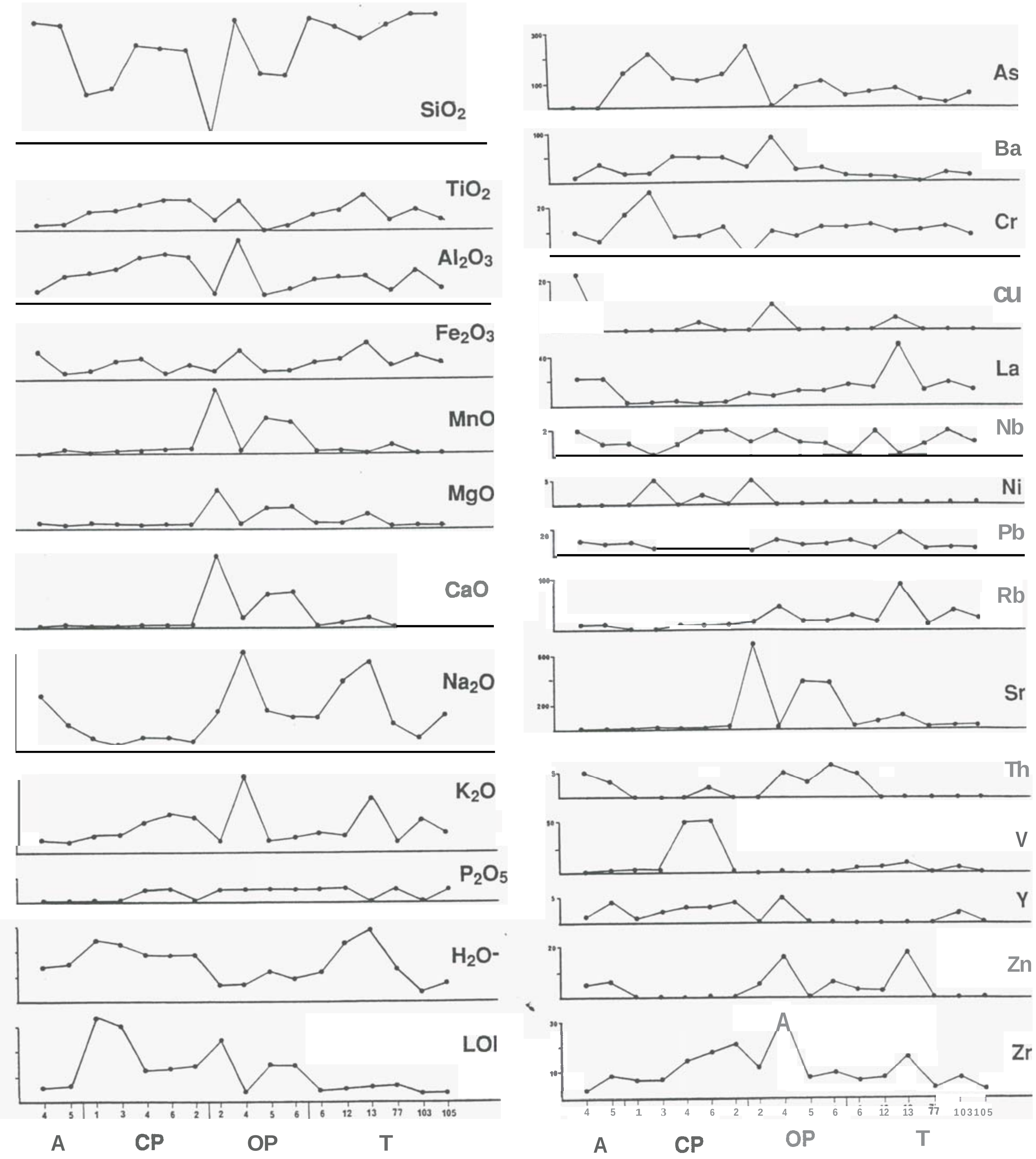
SAMPLING AND ANALYTICAL PROGRAMMES

Sinter was collected from Atiamuri, Ohaaki, Waiotapu and Tokaanu geothermal fields in the Taupo Volcanic Zone of the North Island, New Zealand. The sinter-depositing hot pools or springs in these fields were selected to include a range of fluid chemismes in the survey (Table 1). Historical data illustrates that the water chemistry of hot springs can vary with time (eg. Robinson and Sheppard, 1986) consequently, several samples were collected from around each pool to evaluate the chemical variability of the sinter. As the Tokaanu field contains the only remaining extensive set of chloride hot pools, several of these were sampled to determine the variability of sinter composition over a field.

The sinters were analysed by X-ray fluorescence spectrometry. H_2O^- represents adsorbed water lost at 105°C, LOI represents combined water, organic matter and other volatiles lost at 950°C.

SINTER CHEMISTRY

The chemistry of the sinters is presented in Table 2, and the relative changes in concentration of a constituent between samples is illustrated in the spider plots of Figure 1. Two observations are immediately apparent: silica, adsobed water and LOI are usually the major components of the sample; there are significant chemical differences between sinters from different fields, with the Ohaaki Pool sinter being most distinct. Moreover, elements often do not show consistent sympathetic or antipathetic behaviour with respect to the silica content of the sinter; the observed trends differing between fields. Alumina, for example, might be expected to show a positive association with silica as Al^{3+} commonly substitutes for Si^{4+}. Such a trend is generally seen in samples from Ohaaki and Tokaanu, but the alumina concentration in sinters deposited from the Champagne Pool does not mirror the variations in silica content (Fig. 1). Similar variable behaviour is observed for TiO_2, Fe_2O_3 Na_2O and K_2O;



gure 1. Variations in sinter chemistry between and within geothermal fields. Concentrations in (wt %) for the major constituents and in (mg/kg) for the trace ements. A = Atiamuri; CP = Champagne Pool, Waiotapu; OP = Ohaaki Pool, Ohaaki; T = Tokaanu springs.

TABLE 1
Chemistry of sinter-depositing spring waters

	CP	OP	T6	T13	T103	T105
t°C	75	98	96	100	88	82
$pH_{20^{\circ}C}$	5.6	7.0	7.3	7.8	7.7	7.5
SiO_2	445	338	305	262	317	189
Li	8.3	7.4	22.3	24.3	24.2	nd
Na	1102	860	1750	1871	1892	1840
K	151	82	165	161	161	172
Ca	35.1	8.5	36	31	37	58
Mg	0.05	0.22	0.5	0.8	0.7	0.31
Cl	1898	1040	3064	3052	3062	3121
SO_4	53	100	65	64	66	69
HCO_3	346	680	nd	29	38	nd
B	25.4	32.1	92	99	97	95

All concentrations in mg/kg; nd = not determined; CP = Champagne Pool, Waiotapu: OP = Ohaaki Pool, Ohaaki; T = Tokaanu springs.
Data sources: Mahon and Klyen, 1968; Mahon and Finlayson, 1972; Robinson and Sheppard, 1986; Wang, 1987; Hedenquist and Browne, 1989.

concentrations of these elements generally reflect variations in silica content although the relationship is not consistent over all sinters. Alternatively, CaO, MgO, MnO and LOI all show increases in concentration at the expense of silica, notably in the Ohaaki samples. Subsequent petrographic study of the Ohaaki sinter revealed the presence of calcite intermixed with silica, and this mineral exercises the dominant control over the above elements and Sr. Considering the other trace elements, few show consistent associations across all sinters. However, Ba Rb, Zr with possibly V and Zn generally follow sympathetic trends with silica content, whereas As shows a negative silica association.

A SINTER-DIAGNOSTIC GEOCHEMICAL SIGNATURE

To enable sinters to be distinguished on the basis of their chemistry, elements forming a diagnostic association must be consistently present in sinters at levels clearly anomalous compared to other siliceous lithologies. Elements can become incorporated into silica sinter through adsorption, substitution or as part of a co-precipitated phase included within the sinter. As most metals will be complexed by the various ligands available in a geothermal fluid (eg. chloride, sulphide, hydroxyl) most will be transported as an anionic species. The iso-elecmc point of amorphous silica occurs at about pH2, consequently at the near-neutral pH of chloride waters silica will be negatively charged and adsorption is not therefore likely to be a major process in the incorporation of metals into sinter. Substitution of Si^{4+} by Al^{3+} is probably a common process, as indicated by the consistent presence of alumina in sinters: although as shown in Fig. 1 this positive trend is not always displayed. In any case, aluminium and other major-element, substitution in silica is widespread, and would not be diagnostic of geothermal deposits. Considering the trace constituents, only Ba is consistently present and shows a positive association with silica: it therefore offers potential as a sinter-discriminating element. However, a literature search showed that Ba is also present, and often at higher levels, in other siliceous lithologies (Iijima et al., 1983; Hein, 1987; Hein and Obradovic, 1989) negating its value in this respect.

Elements within phases co-precipitated with silica, and subsequently incorporated into the deposit, may therefore offer the best opportunity to distinguish sinters; such elements would show a negative correlation with silica. It is clear that only As is consistently antipathetic with silica and, despite some variations, is consistently present at high, easily detectable levels (Table 2; Fig. 1). The presence of arsenic in sinters is discussed in greater detail by Parker and Nicholson (1990). The possibility that As may be a sinter discriminating species, together with the suggestion that Sb also had potential in this respect (Nicholson, 1988; Nicholson and Parker, 1990), and the regular deposition of amorphous As-Sb-Tl-Hg-sulphides in geothermal well and spring discharges (Weissberg, 1969; Browne and Lloyd, 1986), implies that this suite of metals could be sinter-diagnostic. Note however, that only enrichments in this assemblage can be interpreted, since the absence of an As-Sb-Tl-Hg enrichment does not preclude a geothermal origin (eg. Atiamuri, Table 2).

The amorphous sulphide precipitates mentioned above can accumulate gold and silver to ore-grade levels (Weissberg, 1969). It is probably these deposits which account for the presence of precious metals in sinters, rather than the direct incorporation of gold into silica (which is unlikely to occur anyway, given the negative surface charge on silica and that gold is transported as an anionic sulphide complex). Since both arsenic and antimony are present at greater concentrations than gold or silver, then these elements are less likely to be diluted beyond detection by silica. The As-Sb-TI-Hg sinter-association is therefore probably more widely applicable as a pathfinder to mineralisation than analysis of the sinter precious-metal-content alone.

TABLE 2

Geochemistry of sinters from the Taupo Volcanic Zone, New Zealand

	A4	A5	CP1	CP3	CP4	CP6	CP8	OP2	OP4	OP5	OP6	T11	T12	T13/2	T77/1	T103/1	T105/1
wt%																	
SiO_2	89.16	88.82	60.27	63.19	80.85	79.60	78.69	43.75	90.06	68.77	67.06	91.87	87.18	83.12	89.42	92.96	92.58
TiO_2	0.01	0.01	0.04	0.04	0.05	0.06	0.06	0.02	0.06	<0.01	0.01	0.03	0.04	0.07	0.02	0.04	0.02
Al_2O_3	0.53	1.14	1.26	1.42	1.91	2.00	1.97	0.41	2.52	0.38	0.54	1.00	1.18	1.94	0.60	1.36	0.67
Fe_2O_3	0.55	0.14	0.18	0.34	0.39	0.11	0.30	0.14	0.55	0.14	0.18	0.34	0.39	0.71	0.30	0.46	0.31
MnO	<0.01	0.02	<0.01	0.01	0.01	0.02	0.02	0.26	< 0.01	0.14	0.13	0.01	0.01	0.01	0.04	<0.01	<0.01
MgO	0.11	0.08	0.10	0.06	0.08	0.10	0.08	0.75	0.10	0.38	0.39	0.12	0.11	0.26	0.06	0.09	0.04
CaO	0.11	0.11	0.04	0.04	0.06	0.06	0.06	28.08	0.33	13.37	14.46	0.12	0.21	0.42	0.09	0.09	0.10
Na_2O	0.46	0.23	0.12	0.07	0.12	0.12	0.09	0.34	0.80	0.34	0.29	0.27	0.57	0.72	0.21	0.11	0.29
K_2O	0.10	0.08	0.13	0.14	0.24	0.31	0.28	0.09	0.61	0.10	0.12	0.16	0.14	0.43	0.08	0.25	0.15
P_2O_5	<0.01	<0.01	<0.01	<0.01	0.01	0.01	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	<0.01	0.01	<0.01	0.01
H_2O-	2.64	2.99	4.94	4.44	3.61	3.68	3.61	1.22	1.24	2.31	1.98	2.18	4.54	5.81	2.72	1.35	1.77
LOI	5.94	6.24	33.00	30.00	12.35	13.40	14.35	24.41	3.96	13.97	14.33	4.23	4.91	5.96	6.28	3.65	3.76
Total	99.19	99.88	100.00	99.52	99.41	99.47	99.33	99.47	100.24	99.90	99.49	100.34	99.30	99.44	99.83	100.34	99.68
ppm																	
As	<1	<1	147	214	128	115	134	246	5	86	110	49	60	76	33	26	55
Ba	12	39	17	19	51	51	50	30	91	26	30	13	13	12	<1	20	15
Cr	10	6	17	26	8	8	12	<1	10	8	12	12	13	10	11	12	9
Cu	23	<1	<1	<1	<1	3	<1	<1	10	<1	<1	<1	<1	5	<1	<1	<1
La	22	22	3	3	4	3	3	10	8	11	12	17	15	48	13	19	14
Nb	2	1	1	<1	1	2	2	1	2	1	1	<1	2	<1	1	2	1
Ni	<1	<1	<1	5	<1	2	<1	5	<1	<1	<1	<1	<1	<1	<1	<1	<1
Pb	11	8	11	6	7	6	5	4	12	9	9	12	6	18	6	7	6
Rb	14	12	5	3	10	11	10	16	47	18	19	30	16	86	12	39	23
Sr	7	9	5	5	11	9	11	684	34	386	385	28	64	118	25	34	28
Th	5	3	<1	<1	<1	2	<1	<1	5	3	6	5	<1	<1	<1	<1	<1
V	<1	5	<1	6	51	51	4	<1	5	<1	<1	10	10	16	<1	9	<1
Y	1	4	1	2	3	3	4	<1	5	<1	<1	<1	<1	<1	<1	2	<1
Zn	5	6	<1	<1	<1	<1	<1	5	16	<1	6	3	3	18	<1	<1	<1
Zr	3	9	7	7	15	18	21	12	33	8	10	7	8	16	4	8	3

A - Atiamuri; CP = Champagne Pool, Waiotapu; OP = Ohaaki Pool, Ohaaki; T = Tokaanu springs

A SINTER GEOTHERMOMETER

It is notable that several elements show a common pattern throughout the sinter samples; eg. Al_2O_3-TiO_2 and Na_2O-K_2O (Fig. 1). Of these, sodium and potassium are major cations in geothermal fluids, and form the basis of the Na/K solute geothermometer. If the Na and K content of sinters is related to that in the depositional fluid, then this could form the basis of an empirical Na/K-sinter-based geothermometer. Recognition of ancient sinter not only locates the palaeo-surface, but also indicates subsurface temperatures were in excess of ~180°C. A geothermometer based on sinter composition would yield more precise information on the deep-temperature than this general guide, and would provide an interesting comparison with any available fluid inclusion temperatures obtained from core samples.

The Na/K ratio of the sinters analysed in this study, and their corresponding spring water were plotted (Fig. 2) together with data from Lloyd (1975), Rimstidt and Cole (1983) and Yokoyama et al. (1987). To eliminate samples with significant quantities of phases other than silica, only sinters with $SiO_2 \geqslant 80$ wt % were employed in the construction of this figure. As already noted, the water chemistry of the pools varies over time; furthermore, and possibly as a consequence of this variation in water chemistry, the sinters themselves are not homogeneous. To overcome these variations and still obtain a meaningful diagram, the median values of both sinter and water Na/K ratios were plotted together with the lowest and highest values.

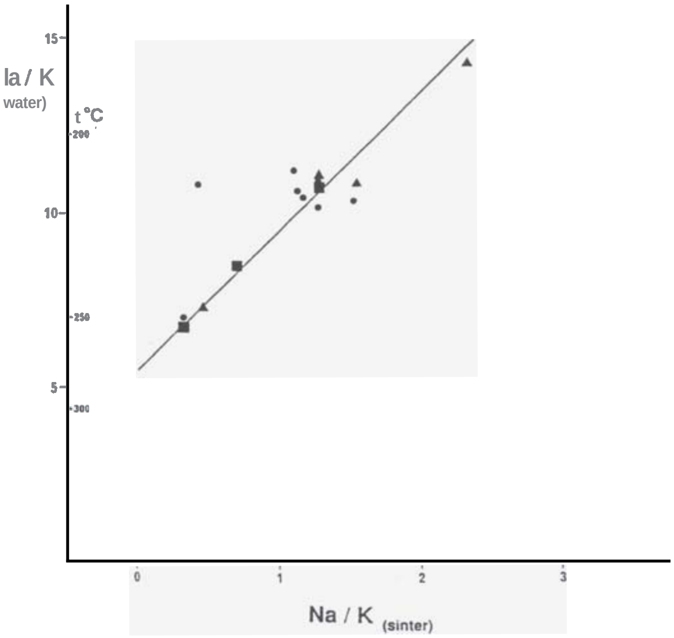


Figure 2. Sodium:potassium ratios for sinters (with SiO_2 > 80%) and the corresponding depositional geothermal water. Key: dots = median values; squares = lowest ratio; mangles = highest ratio. Data sources: This work (Table 2); Lloyd, 1975; Rimstid and Cole, 1983: Yokoyama et al., 1987.

The resultant plot shows a clear, linear relationship between the sinter and water Na/K ratio which is remarkably distinct given the limited data currently available. The clustering of points at $Na/K_{(water)}$ –10.5, $Na/K_{(sinter)}$ ~ 1.3 is particularly encouraging since if a relationship did not exist then a more random distribution would be expected. The equation for the linear relationship shown is $y = 4x + 5.5$; this can be substituted into an expression for the Na/K solute geothermometer (that of Giggenbach (1988) is used here) to obtain the Na/K-sinter geothermometer:

$$t\,^{o}C = \frac{1390}{1.750 + \log\,[4\ (Na/K)_{sinter} + 5.5]} - 273.15$$

Although the constants within the equation will no doubt be modified as more data becomes available, the basic form will remain the same. Unlike the solute geothermometer, water temperature will not directly limit the application of the sinter geothermometer, since sinters are unlikely to be deposited from waters derived from low-temperature reservoirs (–120-150 °C) where the Na/K geothermometer breaks down. However, the $Na/K_{(sinter)}$ geothermometer should only be applied to sinters with $SiO_2 > 80$ wt %, since at lower silica levels Na and K in the sinter are conmbuted by other phases and the defined relationship does not hold.

CONCLUSIONS

Sinters are heterogeneous deposits and should be sampled accordingly, since even examples from the same pool can show significant variations in composition. Across a field sinter composition is relatively uniform; while absolute concentrations may vary, ratios of components are reasonably consistent.

Fluid chemistry does influence sinter composition, with calcite being incorporated into sinters deposited by the bicarbonate-rich waters of the Ohaaki Pool. Arsenic, is invariably present in sinters. It may occur as submicron colloidal amorphous sulphide precipitates incorporated within the sinter and, with other relatively volatile metals of the gold-pathfinder sequence (Sb, Tl, Hg), is a potential sinter-discriminating species.

Palaeo-subsurface temperatures of extinct geothermal systems can be determined from the ratio of the Na and K concentrations in the sinter by the relationship:
$t\,^{o}C = \{1390/(1.750 + \log[4\,(Na/K)_{sinter} + 5.5])\} - 273.15$
This equation should only be applied to sinters with Si02 concentrations equal to, or in excess of, 80 wt%.

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