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BORON IN SOIL OVER NAIKE AND WHITFORD LOW-ENTHALPY GEOTHERMAL FIELDS, NEW ZEALAND

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Mercury, arsenic, bismuth, antimony and boron soil surveys were conducted over two low-enthalpy, sedimentary-hosted, geothexmal fields, Naike and Whitford, in New Zealand. Analysis was by ICPAES following a 1M HCl leach. Appreciable amounts of boron (0.13 to 4.25 mg/kg) were found at both Whitford and Naike; As, Hg, Bi and Sb were not detected. A positive strong boron anomaly (>2 mg/kg) exists in the warm spring area of Naike. This was probably created by boron transported in water phase, a conclusion supported by the relatively high concentration of Na Mg and Li in soils of the same area. Weaker anomalies (1.1 to 2 mg/kg) were found at Naike and Whitford. These are problems caused by boron transported in the vapour phase and indicated more permeable areas and possible upflow zones. Boron in soils can be used as a pathfinder for low-enthalpy geothermal system and as a guide to upflow areas.

INTRODUCTION

Soil surveys in geothermal exploration have been developed over the last two decades since a mercury survey was first employed at the Long Valley USA (Matlick and Buseck, 1976) and proved that strong positive anomalies exist over regions of geothermal activity. One area, Summer Lake, a low-temperature system (up to 47^0C in well), contained up to 100 ppb of mercury in the soil. The single-element mercury method was popular in United States during the late 1970s to the early 1980s (eg. Klusmen and Landres (1978) in Long Valley, Phelps and Buseck (1980) in Yellowstone and Varekamp and Buseck (1983) in Lassen and Breitenbusch). However since 1983, multiple volatile-element soil surveys have been gradually introduced: Hg, As and Sb in Roosevelt (Moor et al, 1983); As, B and Hg in Onikobe of Japan (Shiikaua 1983); Hg and As in Meagre Greek, British Columbia, Canada (Openshaw, 1983) and Hg, As, Bi, Sb and B in Yangbajing, Tengchong and Xiaotangshan, China (Zhu et al, 1986, 1989). However, most of these studies have been conducted on high temperature systems where volcanic gas. hot water and vapour contain those volatile element in a great quantities, and there are very few example of soil surveys over low-temperature systems. However, at Beijing Xiaotansnen mercury and boron concentrations of up to 200 ppb and 50 ppm respectively were found, and a strong positive ammonia anomaly, which probably indicated an upflow area, was found at Naike (Aredes and Nicholson, 1990).

The major purpose of this study was to determine how Hg, As, Sb, Bi and B in soil behave over two low-enthalpy areas, Naike and Whitford of New Zealand, and the effectivities of these elements in geothermal exploration for low enthalpy resources.

NAIKE AND WHITFORD GEOTHERMAL FIELDS

Naike

The Naike geothermal field is located 96 km south of Auckland at latitude $S37^0$ 29' 00" and longitude E1740 55' to 174^0 57' 30" (Fig.1). It is characterized by steep hills and flood plains with an elevation range of 10 to 260 meters above sea level. The local stratigraphy (Fig.4) consists of alluvium and swamp deposits (pa; up to 6 meters thick), Glen Murry sandstone (kg; up to 90 meters thick), Ellyood limestone (kge; up to 20 meters thick) and Pongawakatiki siltstone (and greywacke np; up to 12000 meters thick) (Siswojo, 1985). As shown in Fig.4, the greywacke siltstone are exposed in the southwest of the survey area, but are covered by Tertiary siltstone and limestone to the north and east. The fractured greywacke is considered to be the thermal water aquifer, with a subsurface flow along the NE fault. Four warm springs are exposed on the bank of Te Maire stream and have a total flow rate of 29 l/s (Siswojo 1985). Spring temperatures of 58^0C to 64^0C have been measured (Petty, 1972; DSIR, 1967; Sulasdi, 1983; Liu, 1988). The stream and spring water chemistry are listed in Table 1. According to geophysical surveys, the greywacke occurs at a depth of less than 20 meters and characteristicly shows high apparent resistivity values up to 78 m (Simandjuntak, 1983).

Whitford

The Whitford field is located 24 km SE of Auckland, at latitude $S36^0$ 57' 30" and longitude $E174^0$ 59' 40" (Fig.7). The topography is characterized by steep and rolling hills with

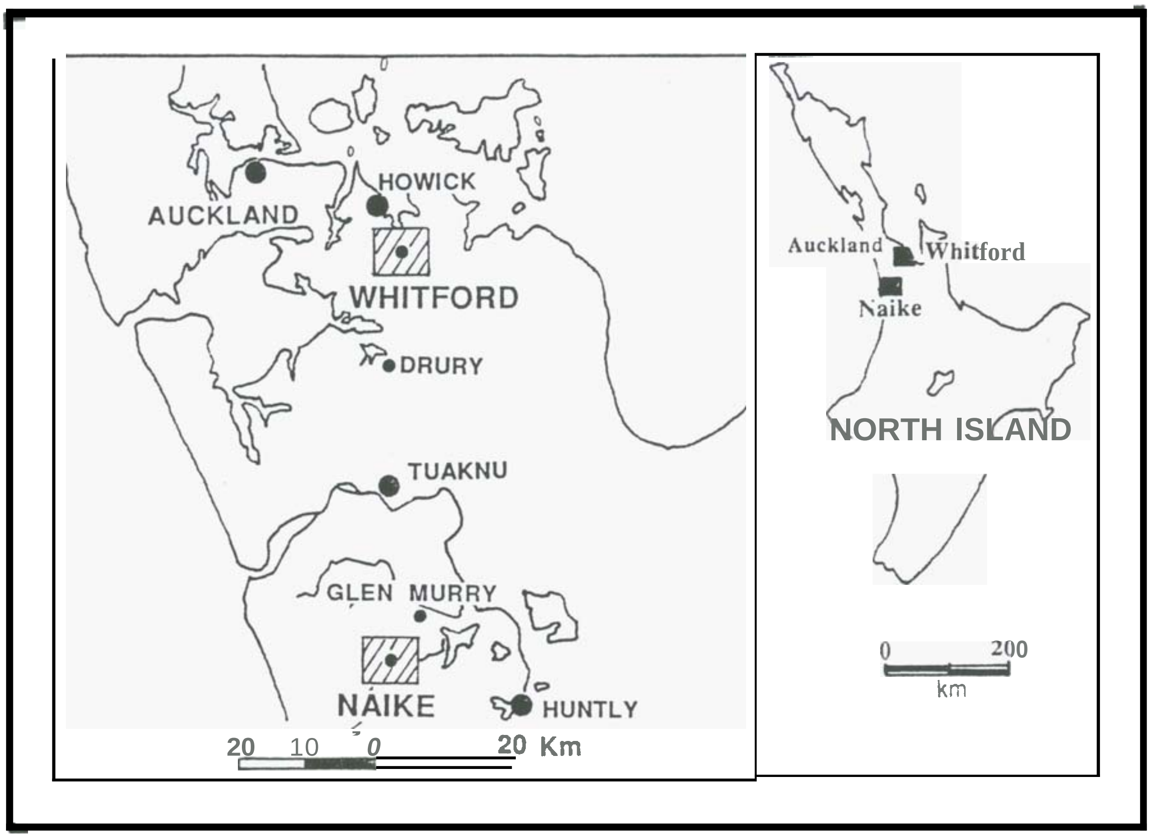


FIG 1 . LOCATION MAP OF SURVEY AREA (NAIKE AND WHITFORD)

an elevation range from 20 to 120 meters above the sea level. The geology of the area is shown in the Fig.9. The Tertiary Waitemata group, with a thickness of about 70 m is composed of thick bedded sandstone, minor thin sandstones and a basal conglomerate, with localized thin, impure limestones up to 3 meter thick. The Jurasic Waiheke group underlies Waitemata Group and mainly consist of interbeded, dark-coloured mudstone (argillite) and graded sandstone (greywacke) with total thickness excessing 7000 m. The main structures are NNW and NE trending basement faults (Fig.9) (Schofield, 1967, 1974 and 1979; GCNZ, 1987). There are no thermal manifestations reported around the Whitford area, but five drillholes with depths of more than 80 meters have revealed the existence of a warm geothermal system with temperatures of 32 to 54^{0}C within a greywacke aquifer (GCNZ, 1987). The water chemistry of the well discharge is presented in Table 1:

TABLE 1: Chemical analysis of geothermal water from Naike and Whitford

date year	location	type	T °C	pH	Na mg/l	Li mg/l	K mg/l	Ca mg/l	Mg mg/l	B mg/l	Cl mg/l	SO_4 mg/l
1983	Naike	spring1	64	9.7	155	0.2	2.1	5.2	0.01	12.3	160	5.0
1983	Naike	spring2	60	9.7	150	0.2	2.2	4.7	0.02	12.8	163	7.0
1983	Naike	spring4	59	9.7	145	0.2	2.1	4.5	0.01	12.4	153	8.0
1988	Naike	stream	19	6.5	14.7	0.13	-	12.52	2.14	0.16	18.3	-
1987	Whitford	Maltby1	-	9.3	77.6	-	0.6	2.2	0.1	16.3	39	20
1987	Whitford	Maltby2	48	9.3	99.4	0.14	1.3	1.2	0.3	14.3	46	21

Data sources: Sulasdi (1983), Liu. (1988). GCNZ, (1987). -= no data
Maltby1=drillhole in Whitford

GEOTHERMAL SOIL SURVEY PROGRAMME

The sampling and analytical procedure followed this survey are summarized in Fig.:!

Sampling

Samples at the Naike are3 were collected at four different dates: April, August and December. 1988 and June, 1990. The majority of the Whitford samples were collected in May, 1990 except for 19 samples which were collected from shallow drillholes in 1989. Samples were collected from both the A and B soil horizons for a comparison of best substrate (organic matter or clay respectively) for optimum anomaly recognition.

Sample Preparation

The samples were subdivided in the laboratory. The subsamples were then dried in an oven at <30^{0}C for 48 or 72 hours until no further weight loss occurred. A mortar and pestle were employed for disaggragation, and the c1 mm size fraction was retained. This was then quartered, and 10g taken for extraction. A total HF-HCl-HNO_3 extraction method was used, but this method introduced significant errors, was time consuming and expensive, and therefore not suitable for routine use. Instead, partial extraction methods using 1M HCI, HNO_3, NH_4 oxalate at ambient temperature

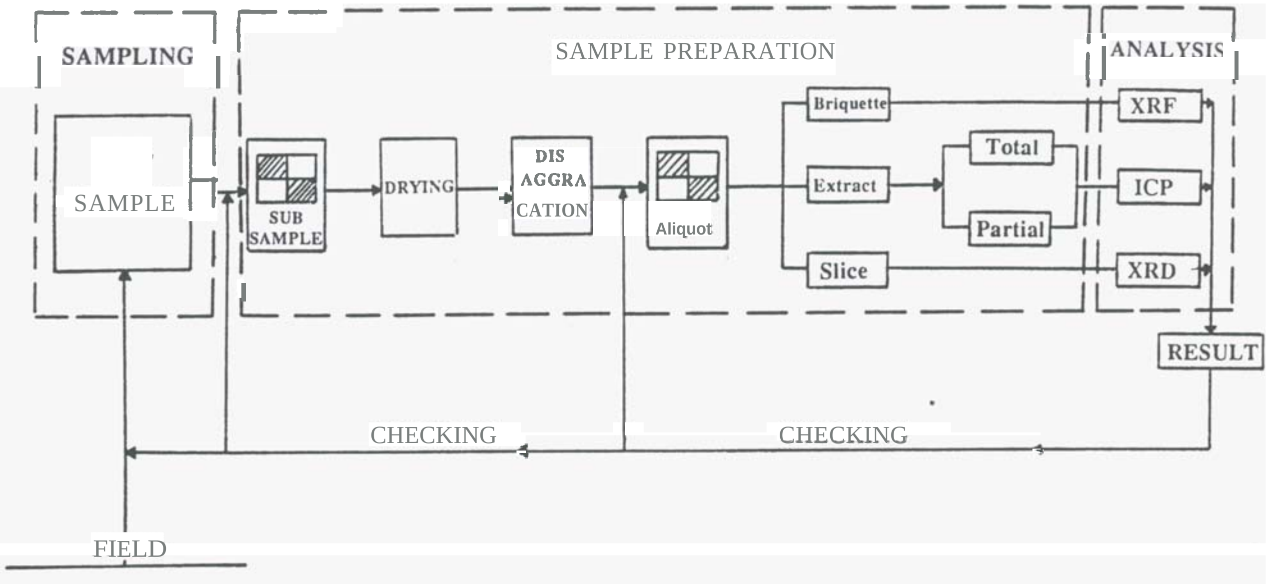


Fig 2. SOIL SURUEY PROCEDURE

and hot water were examined. These were found to be simple, effective and reliable methods; details are presented in Table 2. The HCl-leach was employed through this study. Trace element in soils were also determined by XRF, while mineralogical determination in the soils were performed by XRD.

TABLE 2: Extraction procedure

Reagent	Temp.of Extract.	Mass of Sample	Mass of Reagent	Leaching Time
1M HCL	20℃	10g	100g	1hr
1M HNO_3	20℃	10g	100g	1hr
0.25M NH_4 Oxalate.	20℃	100	1009	1hr
HOT WATER	70k	5g	50g	8hr

Sample Analysis

The resultant leachate was analysed using inductively coupled plasma atomic emission spectroscopy (ICP-AES), model ARL 3410. The arsenic, antimony, bismuth and mercury were not detected in any sample and will not be discussed further. Detection limits are listed in Table 3.

TABLE 3. ICP-AES detection limits

ELEMENT	DETECTION LIMITS (mg/kg)
B	0.013
As	0.076
Hg	0.006
Bi	0.046
Sb	0.060

At 5 mgkg B, the determination have a relative standard deviation of 2.234 % at the 95% confidence interval , which translates to an error of only ±0.07 mg/kg B. The instrument condition for boron analysis were:

Reference wavelength	355.431
PMT setting	10
Range for wavelength scan	0.04
integration time	0.5 second
Boron wavelength	249.678
PMT setting	14
Integration time	1 Second

Each sample were flushed for 30 second to equilibrate the spray chamber before measurement.

RESULTS AND DISCUSSION

Naike

Boron concentrations of 0.3 to 4.25 mgkg were found in the A soil horizon. More than three individual populations can be distinguished from the whole data set by using a probability plot (Fig.3). Threshold concentration were calculated according to three inflection points on Fig.3: 0.58 mg/kg indicates a regional background threshold encompassing 12% of samples; an anomaly threshold occurs at 1.1 mgkg. The concentrations higher than this value are considered anomalous and these can be divided into three grades: weak anomaly 1.1 to 1.5 mg/kg; intermediate anomaly 1.5 to 2 mgkg; strong anomaly > 2 mgkg. The anomaly contour map (Fig.4) shows:

(1). A strong positive anomaly appears over the warm spring area

(2). Two intermediate anomalies exist in the southern and northern region

(3). Both the A and B horizons show a similar anomaly pattern, but the concentration in the B horizon are slightly lower than A horizon (Fig.7).

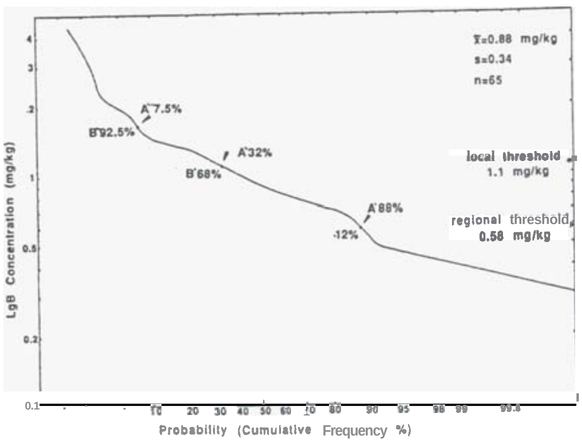


Fig 3 . Diagram of Probability Analysis (Naike A Horizon)

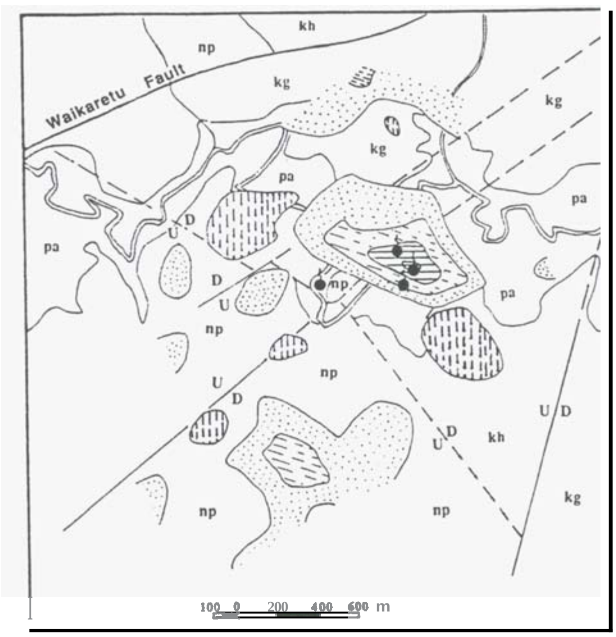
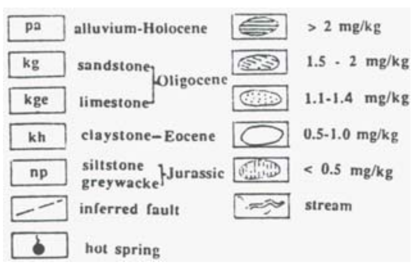


Fig 4 . Geology and Boron Distribution Map of Naike (A Horizon)



The ammonia soil survey (Aredes and Nicholson **1990)** pattern does not to exactly **be** match that **of** the boron soil survey, although there is some agreement with the anomaly pattern in the **SW of** the area. The reason could be because ammonia is **more** volatile than baron.

Factors influencing boron distribution in soils

Organic matter: Davies **(1980)** reported that the greater concentration **of boron** in the near surface soil, compared to **those** at depth, is due to the high level **of** organic matter in the upper **horizons.** This distribution is present at Naike; as shown in Fig.5, the upper layers contain the highest concentration **of** boron. It comparison with Fig.6, shows a concentration between B and organic matter (determined by LOI at **950⁰C).** This strong association between **B** and organic matters is important since it prevent B being leached from the soil by meteoric water (Davies, **1980).**

BORON CONCENTRATIOS (mg/kg)

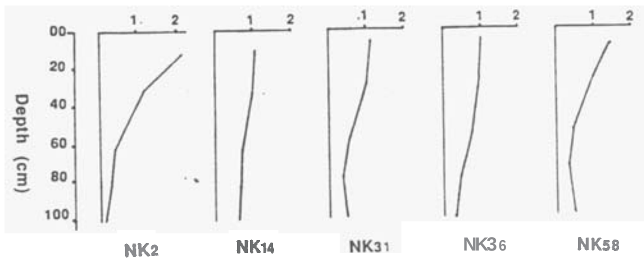


FIG 5 . BORON IN SOIL PROFILE

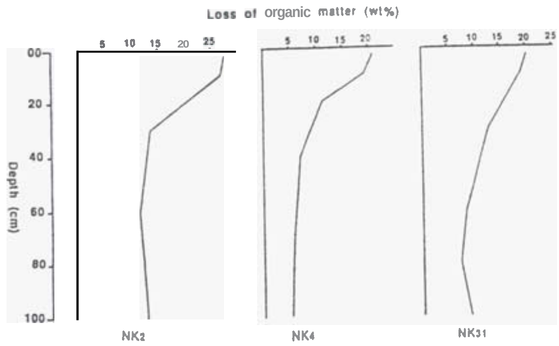


FIG 6 . ORGANIC MATTER IN SOIL PROFILE

Topography: Fig.7 shows that the distribution **of** B concentration in both the A and B horizons **are** independent of topography. **A** topographic control does not therefore have to **be** considered when interpreting the anomaly pattern.

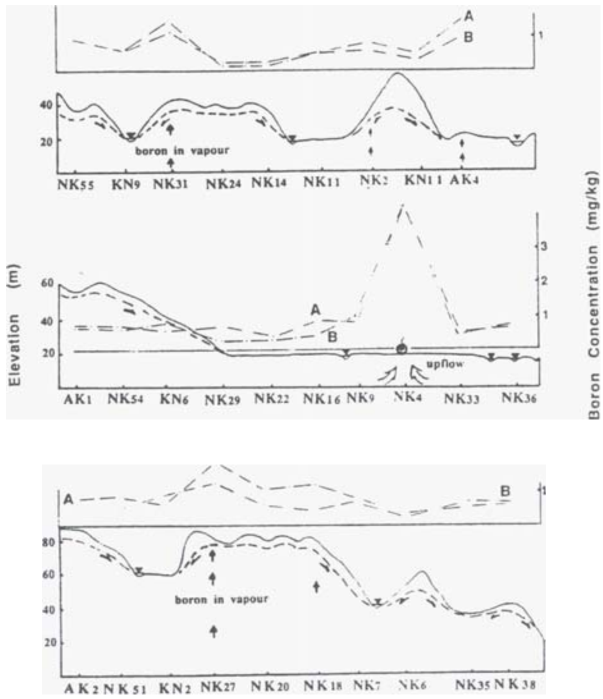


Fig.7 Relationship Among Ground Water ,Topography and Boron

Geology: **As** anomalies are not aerially restricted to a given lithology (Fig.4), then the bedrock geology does not influence distribution of boron. The anomaly pattern may indicate an unknown structure line with a NNE trend through the southern anomaly, the warm springs and the northern anomaly area. However, some negative anomalies along the centre **NE** trending fault appear to indicate that fault might not only lead to positive anomalies.

Whitford

Boron concentrations in the soil from **0.54** mgkg to **1.89 mg/kg** were found in the **A** horizon. The thirty five sample population show a mean value of 1.15 mgkg (Fig.8), which is slightly higher than value from Naike of 0.88 mg/kg. Probability plots show the regional background to be designated by a threshold of **0.72 mg/kg** and the local anomaly threshold occurs at **1.35 mg/kg**. The anomaly

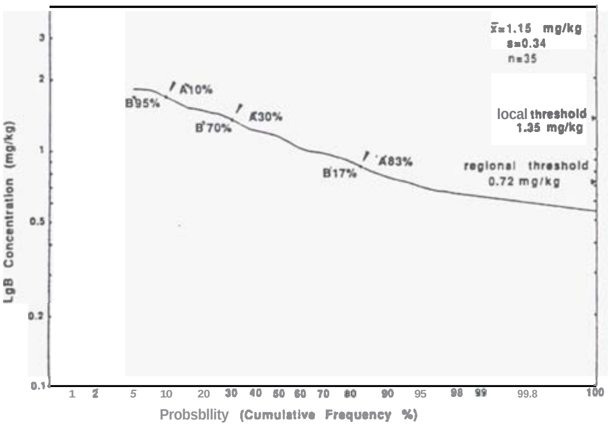
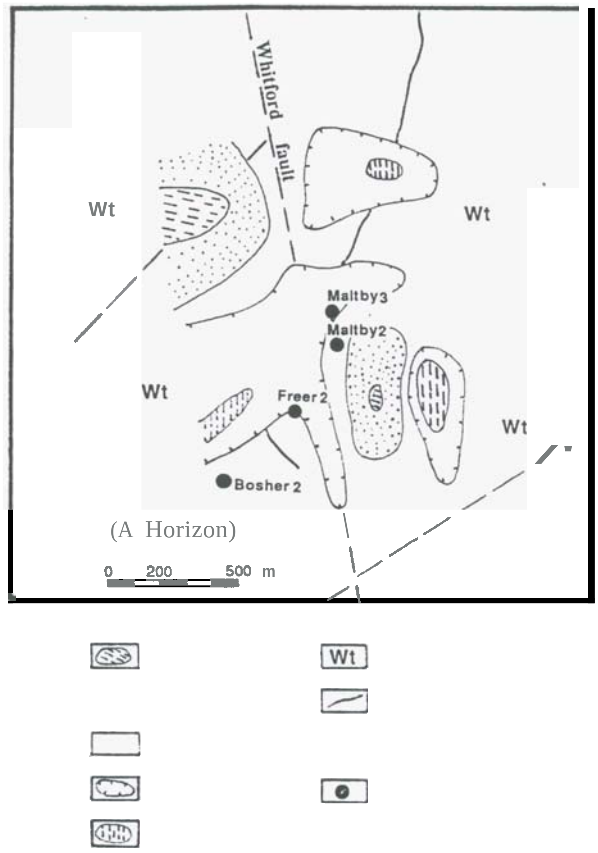


Fig.8. Diagram of **probability analysis (Whitford A horizon)**

pattern is **summarized** in Fig.9. Two positive anomaly regions occur at the northwest and southeast of the survey **area,** either side of, and **200** meters away from the Whitford fault. The location of north anomalies is close to the intersection of the **NE** trend faults with the Whitford Fault. This **may** indicate that the positive anomalies are related **to** an high permeabilities fracture controlled by the **NE** trend faults. It is interesting that negative boron anomalies occur over the hot water drillhole area (Fig.9) where the geothermal resources with high boron content up to 18.3 mg/kg and temperatures up to **54°C (GCNZ** 1987) have been revealed. The large negative anomalies seems to reflect the trend and location of the Whitford Fault. This pattern is not easily explained but could be due to the existence of some impermeable lithologies over the greywacke thermal reservoir, whereas in the positive anomalies are related to leakage of the boron vapour from more permeable fault zones.

The analyses are undoubtaly reliable because the patterns of both the **A** and B horizons are very similar, with the high positive and the low negative anomaly occurring at the same position. The B soil horizon values are slightly lower than the **A** soil horizon, which is probably due to the relative



abundance of organic matter in the upper horizon (davies, 1980).

CONCLUSIONS

(1). **A** boron soil survey has been successfully used in the Naike area, where geothermal water discharges at the surface, the caprock is very thin and a permeable NE-trending fault exists in the greywacke rocks. The survey in the Whitford area could not be as readily explained as that in the Naike area, possibly because of the presence of a thick caprock, which is impermeable **to** geothermal vapour.

(2). Boron can be considered **as** a pathfinder over a low enthalpy area, but the anomaly created by vapour-born B is of poorer-contrast to that developed on **high** temperature systems and ***can*** be influenced by anomalies created by water-born B.

(3). The boron pattern over Naike is different to the ammonia pattern possibly because ammonia has **a** higher volatility **than** B. There is, however, some agreement in the anomaly pattern in the **SW** of the area : the proposed upflow zone.

(4). Organic matter strongly absorbs appreciable levels of boron and prevents natural leaching.

(5). Hg, **As,** Sb and Bi in soils were not detected by ICP-AES at both Naike and Whitford and may therefore **be** of **limited** use in low-enthalpy resource exploration.

(6). Partial soil boron extraction using HCl, HNO_3, NH_4

oxalate and hot water as leaching agents is recommended but not total extraction method using aqua-regia and HF-HCl-HNO_3.

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