Experimental hot water–rock interactions and their significance to natural hydrothermal systems in New Zealand

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Abstract—A study has been made of the interaction of a New Zealand greywacke and hot water at temperatures up to 500°C. Comparisons are drawn between the trace element content of the reaction solutions and the composition of New Zealand thermal waters with particular reference to the Broadlands geothermal field.

The experiments have demonstrated that hot water can extract significant quantities of As, Sb, Se and S at temperatures below the maximum temperatures recorded for the major geothermal fields in New Zealand.

The amount of Tl and Co leached up to 500°C was below the limits of detection and data could not be obtained for Au, Ag, Te and Bi.

INTRODUCTION

ELLIS and MAHON (1964, 1967). ELLIS (1968) and MAHON (1967) investigated the compositions of solutions obtained from hot water–rock interactions. They described experiments in which volcanic and sedimentary rocks common to the Taupo Volcanic Zone in the North Island of New Zealand, were reacted with water at temperatures varying from 100 to 600°C and pressures ranging from 500 to 1500 bars. They demonstrated that appreciable quantities of constituents such as K, Na, Li, Rb, Ca, Mg, SiO_2, Cl, F, B and NH_3 were readily taken into solution along with trace amounts of Fe, Mn, Cu and Pb. Their studies indicated that the compositions of waters in natural hydrothermal systems could be approached by the interaction of hot water and rock, without requiring a contribution from a magmatic fluid rich in these elements. CRAIG (1965) concluded from isotopic investigations that geothermal waters are generally meteoric and in this regard New Zealand geothermal waters appear to be no exception (GIGGENBACH, 1971; GRINDLEY, 1965).

In the present study, a series of hot water–rock leaching, experiments were undertaken to ascertain whether trace elements not previously investigated were readily available for solution at temperatures and pressures likely to be encountered in natural hydrothermal systems.

EXPERIMENTAL TECHNIQUES

(a) Procedure

All reactions were conducted in sealed, high purity silica ampoules at temperatures up to 500°C. The rock fragments (0.4–0.7 mm, about 210 mg) were contained in a perforated

gold capsule crimped almost closed at each end. The charge was loaded into a silica tube (10 mm o.d., 7 mm i.d.) sealed at one end and a slight constriction was made about 4 cm from that end. After streaming high purity dry N_2 through the tube for 15 min to expel as much air as possible, 1.4 ml of distilled water (previously boiled to remove dissolved CO_2) were pipetted into the tube and the streaming of N_2 was continued. After the contents of the tube had been frozen in a dry ice–alcohol bath, the tube was then sealed about 4 cm above the constriction to give an 8 cm long ampoule.

The ampoule was loaded into a stainless steel pressure vessel which was suspended vertically inside a tube furnace. Water was added to the pressure vessel to balance the pressures generated within the ampoule. Pressure vessel temperatures were measured twice daily using chromel–alumel thermocouples connected to a potentiometer. Variations were controlled within ±3°C.

The volume of liquid contained in each ampoule was sufficient to maintain a two-phase system up to the critical point of water (374°C). Hence pressures could be accurately determined from tables of the vapour pressure of water. Above the critical point (to 500°C) pressures were calculated less accurately using the Law of Corresponding States (KAUZMANN, 1966).

On the completion of an experiment, the furnace was tilted and the pressure vessel and its contents withdrawn in an inverted position. In the process the solution ran through the constriction, thus becoming isolated from the rock fragments, preventing any back reaction during cooling. The ampoule was removed and its contents frozen with a dry ice–alcohol bath prior to being broken open. The gold capsule and its contents were recovered and the solution retained for analysis if required. The gold capsule was forced open at each end and the rock fragments were flushed on to a watch glass with distilled water. After several washings, the fragments were air dried and retained for analysis.

(b) Analytical methods

Analyses were carried out using neutron activation analysis. A flow chart outlining the procedure used to determine As, Sb, Tl, Bi, Se, Te and Co is given in Fig. 1. The Bi and Tl methods were developed by HUGHES (1976), while the Se and Te methods were adapted from

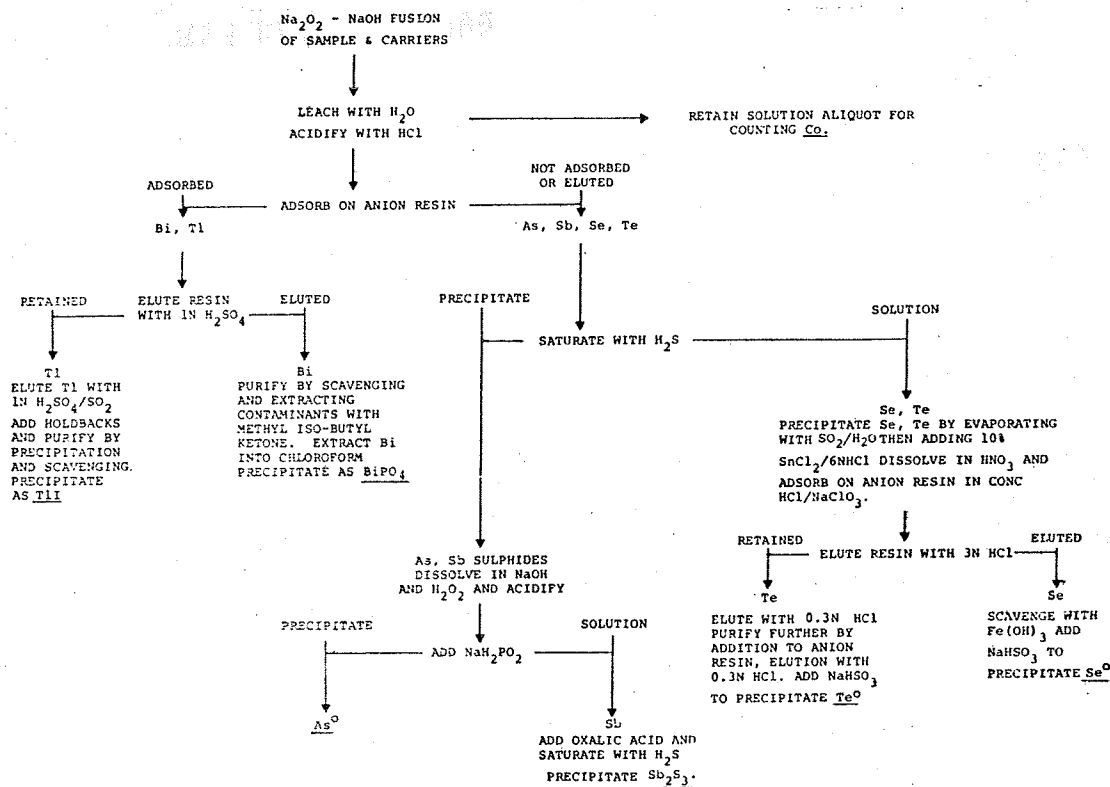* Present address: Bureau of Mineral Resources, P.O. Box 378, Canberra City, A.C.T. 2601, Australia.

Na$_2$O$_2$ - NaOH FUSION
OF SAMPLE & CARRIERS

LEACH WITH H$_2$O
ACIDIFY WITH HCl → RETAIN SOLUTION ALIQUOT FOR COUNTING Co.

ADSORBED — ADSORB ON ANION RESIN — NOT ADSORBED OR ELUTED

Bi, Tl   As, Sb, Se, Te

RETAINED — ELUTE RESIN WITH 1N H$_2$SO$_4$ — ELUTED   PRECIPITATE

Tl
ELUTE Tl WITH 1N H$_2$SO$_4$/SO$_2$ ADD HOLDBACKS AND PURIFY BY PRECIPITATION AND SCAVENGING. PRECIPITATE AS Tl$_2$I

Bi
PURIFY BY SCAVENGING AND EXTRACTING CONTAMINANTS WITH METHYL ISO-BUTYL KETONE. EXTRACT Bi INTO CHLOROFORM PRECIPITATE AS BiPO$_4$

SATURATE WITH H$_2$S → SOLUTION

Se, Te
PRECIPITATE Se, Te BY EVAPORATING WITH SO$_2$/H$_2$O THEN ADDING 10% SnCl$_2$/6NHCl DISSOLVE IN HNO$_3$ AND ADSORB ON ANION RESIN IN CONC HCl/NaClO$_3$.

RETAINED — ELUTE RESIN WITH 3N HCl — ELUTED

Te
ELUTE WITH 0.3N HCl PURIFY FURTHER BY ADDITION TO ANION RESIN, ELUTION WITH 0.3N HCl. ADD NaHSO$_3$ TO PRECIPITATE Te^0

Se
SCAVENGE WITH Fe(OH)$_3$ ADD NaHSO$_3$ TO PRECIPITATE Se^0

As, Sb SULPHIDES DISSOLVE IN NaOH AND H$_2$O$_2$ AND ACIDIFY

PRECIPITATE — ADD NaH$_2$PO$_2$ — SOLUTION

As^0 Sb
ADD OXALIC ACID AND SATURATE WITH H$_2$S PRECIPITATE Sb$_2$S$_3$.

Fig. 1. Flow chart of analytical scheme used for As, Sb, Se, Te, Bi, Tl and Co.

those of MORRIS and KILLICK (1963). The methods used for As and Sb draw substantially from the work of FOUCHÉ and SMALES (1967) and HAMAGUCHI et al. (1969). Au and Ag were determined by a procedure modified after that of Keays et al. (1974). Samples and standards were irradiated for 6 days in a thermal neutron flux of 6×10^{12} neutrons/cm^2/sec and cooled for 3 days before processing. Bi and Tl were counted on a Beckman Widebeta detector and the remaining elements were γ-counted on a 45 cm^3 Canberra Industries Ge(Li) detector. Sulphur determinations were made with a Leco automatic sulphur titrator (model 532).

Table 1. Analyses for U.S.G.S. standards, DTS-1 and BCR-1

ELEMENT	DTS-1	BCR-1
Ag (ppm)	0.043, 0.059	0.031, 0.032
As (ppm)	0.036, 0.026	0.55, 0.53
Au (ppb)	0.75, 0.73	0.66
Bi (ppm)	< 0.010, < 0.010	0.050, 0.048
Co (ppm)	159, 153 154, 147	41.8, 41.1 40.5, 38.9
Sb (ppm)	0.64, 0.53	0.76, 0.76
Se (ppm)	< 0.005, <0.005	0.082, 0.084
Te (ppm)	< 0.05, < 0.05	≤ 0.05, ≤ 0.05
Tl (ppm)	0.003, 0.002	0.285, 0.280

The analytical methods have been assessed by analysing the U.S.G.S. standards BCR-I and DTS-I. The values obtained are quoted in Table 1 and are consistent with the published data in FLANAGAN (1969) and LAUL et al. (1970a, b, c).

Analyses were made on the rock fragments before and after leaching rather than the leaching solutions for several reasons. It was considered that with the anticipated low trace element concentrations in the solutions, the presence of some fine suspended material might have contributed significantly to these values giving erroneous results. It was also not possible to irradiate liquids in the reactor HIFAR and the risks of losses through volatilization and contamination when evaporating the liquid on to powdered silica for irradiation were considered to be too great. The rock fragments recovered from each experiment were divided into two approximately equal portions for duplicate analyses.

SELECTION OF ROCK TYPE

For the following reasons, a greywacke was chosen as the most suitable starting material. First, Mesozoic greywackes and argillites are likely source rocks for metals found in New Zealand geothermal waters since they flank both sides of the Taupo Volcanic Zone and are thought to underlie it extensively. Second, analyses for a selection of greywackes, argillites and acid volcanics (seemingly unaffected by hydrothermal fluids and collected from various localities in the North Island of New Zealand) indicated that those elements being considered were more abundant in the sediments (EWERS, 1975). Although the greywackes

Table 2. Analyses for unaltered greywacke, P 23556

	As (ppm)	Sb (ppb)	Tl (ppb)	Bi (ppb)	Se (ppb)	Te (ppb)	Au (ppb)	Ag (ppb)	Co (ppm)	S (ppm)
	8.02	320	395	170	66	n.f.	1.97	< 20	5.99	490
	10.54	300	420	190	66	n.f.	2.46	22	7.26	510
	9.95	280	380	220	74	n.f.	–	–	7.17	480
	9.85	330	420	130	72	n.f.	1.63	< 20	6.10	500
AVERAGE	9.59	310	405	177	70	–	2.02	< 20	6.63	495
STANDARD DEVIATION	1.09	22	20	66	4	–	0.42	–	0.68	13
% STANDARD DEVIATION	11.4%	7.1%	4.9%	37.3%	5.7%	–	20.8%	–	10.3%	2.6%

n.f. = not found.

and argillites in the North Island have been divided into three distinct lithological groups, depending upon their provenance (EWART and STIPP, 1968), the trace element concentrations were similar in the two types most intimately associated with the geothermal areas (i.e. greywackes of andesitic and granitic derivation).

The greywacke selected (P 23556) came from an outcrop about 70 km south of Lake Taupo and according to EWART and STIPP (1968) was derived from a granitic plutonic terraine. It was a coherent, fine-grained rock with a uniform texture and was composed of angular to sub-rounded quartz fragments, acidic plagioclase, alkali feldspar, muscovite, iron oxides, minor biotite and some secondary chlorite. Calcite veining was also quite common. In polished thin section, a number of small rounded pyrite grains were found to be randomly distributed throughout the rock.

RESULTS

To establish the elemental concentrations in P 23556 with more precision, the rock fragments used in the leaching experiments were analysed in quadruplicate and the results are presented in Table 2. Included in the table are average concentrations, standard deviations and percentage standard deviations for each element. While the As, Sb, Tl, Se, S and Co analyses for each sample deviate little from the mean, the Bi and Au analyses have a wider spread and consequently much larger standard deviations. The Ag and Te contents are generally below the limits of detection. Since leaching was anticipated to be minor for low temperature experiments, the standard deviations for Bi and Au were considered to be too large and might have obscured whether leaching had in fact occurred. For these reasons only the elements As, Sb, Tl, Se, Co and S are dealt with further.

Table 3. Experimental and analytical data for hydrothermally leached greywacke, P 23556

RUN NUMBER	TIME (hours)	TEMPERATURE (°C)	PRESSURE (bars)	H₂S ODOUR	As (ppm)	Sb (ppb)	Tl (ppb)	Se (ppb)	Co (ppm)
1	53	467	770 ± 100	STRONG	3.49 / 3.27	120 / 115	430 / 460	53 / 56	5.17 / 6.86
2	23	152	6.5 ± 0.5	–	9.35 / 8.12	170 / 185	450 / 390	66 / 62	n.d.
3	48	153	6.5 ± 0.5	–	9.35 / 9.68	190 / 200	420 / 440	71 / 73	n.d.
4	95	151	6.5 ± 0.5	–	8.38 / 7.40	160 / 180	410 / 415	74 / 61	n.d.
5	449	151	6.5 ± 0.5	–	7.92 / 9.99	180 / 205	470 / 460	60 / 69	n.d. / 7.28
6	24	343	154 ± 2	SLIGHT	7.00 / 7.12	115 / 115	400 / 440	51 / 61	5.97
7	42	342	152 ± 2	SLIGHT	7.05 / 7.16	110 / 140	395 / 450	58 / 71	6.59 / 5.80
8	114	347	162 ± 2	SLIGHT	6.02 / 8.70	90 / 95	395 / 405	69 / 63	7.68 / 9.13
9	278	346	160 ± 2	SLIGHT	6.61 / 6.63	90 / 105	410 / 400	64 / 59	7.63 / 7.67
10	72	106	2.5 ± 0.5	–	10.31 / 9.00	230 / 260	435 / 380	61 / 68	7.06 / 6.31
11	72	196	16 ± 0.5	–	8.32 / 9.99	185 / 190	350 / 395	71 / 59	6.28 / 6.88
12	72	288	74 ± 1	SLIGHT	7.12 / 6.78	140 / 130	390 / 395	60 / 58	5.63 / 6.34
13	72	387	440 ± 80	STRONG	4.38 / 6.21	115 / 85	400 / 345	56 / 52	6.20 / 6.93
14	72	484	780 ± 100	STRONG	3.15 / 2.41	100 / 120	360 / 390	30 / 40	6.83 / 5.98
AVERAGE CONCENTRATION IN UNREACTED GREYWACKE					9.59	310	405	70	6.63

n.d. = not determined.

Table 4. Experimental data and sulphur analyses for hydrothermally leached, greywacke, P 23556

RUN NUMBER	TIME (hours)	TEMPERATURE (°C)	PRESSURE (bars)	H₂S ODOUR	S (ppm)
15	48	142	5.5 ± 0.5	–	370 460
16	48	295	82 ± 1	SLIGHT	230 340
17	48	510	830 ± 100	STRONG	110 210

Table 3 summarizes the run data and analytical results for As, Sb, Tl, Se and Co after leaching for periods of up to 449 hr and temperatures in the range 100–484°C. Since only small quantities of the rock fragments could be leached at one time, there was insufficient sample to analyse for these elements and S simultaneously. Consequently, a number of experiments were repeated for the S determinations, the results of which are given in Table 4.

Having ascertained in the first run that hot water at a temperature of 467°C was capable of leaching at least some of the elements (i.e. As, Sb and Se) within 53 hr, a series of runs was conducted at constant temperatures to establish the minimum time for optimum leaching. The first series of runs (nos. 2–5) was carried out at about 150°C with times varying from 23 to 449 hr and indicated that Sb was the only element to be significantly leached. For each run, the concentration of Sb in the rock fragments was consistently depleted by about 130 ppb (approximately 40%). The results of a second series of experiments at about 350°C (run nos. 6–9), where the duration of each run varied from 24 to 278 hr, have been presented diagrammatically in Fig. 2. Although As, Sb and possibly Se (percentage leaching generally <10%) were the only elements leached at this temperature, it would appear that they were substantially taken into solution in less than 24 hr.

In the remaining experiments (run nos. 10–14) the duration of each run was kept constant at 72 hr while the temperatures were increased from 100 to 500°C in 100°C intervals. The results of these experiments have been summarized in Fig. 3. Also included in this diagram are the results for S determinations on the leached rock fragments from a series of 48 hr experiments (run nos. 15–17). The data indicates that while As, Sb, Se and S are appreciably leached at temperatures up to 500°C, there is no perceptible depletion in the Tl or Co contents of the rock fragments.

Examination of polished thin sections of rock fragments that had been leached showed there were no signs of alteration at temperatures up to 200°C. However, above 200°C, it was evident that the fragments were more heavily stained with iron oxides, due probably to slight oxidation of the matrix and the breakdown of pyrite. On breaking open the ampoules used in experiments above 200°C, the smell of H₂S was noticeable.

It was noted that the solutions recovered after leaching in the higher temperature experiments (>200°C) developed a gelatinous white precipitate on standing. This was later identified as amorphous silica. Since the silica ampoules showed signs of having been etched (especially at high temperatures), it was concluded that this was the main source of silica with some also being derived from the quartz in the greywacke. From data on the solubility of amorphous silica and quartz in water (KENNEDY, 1950), concentrations of up to 2000 ppm could be anticipated in the reaction solutions at 300°C.
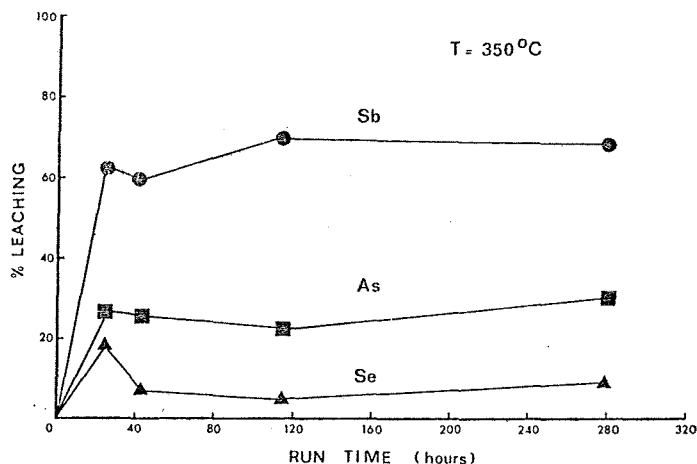

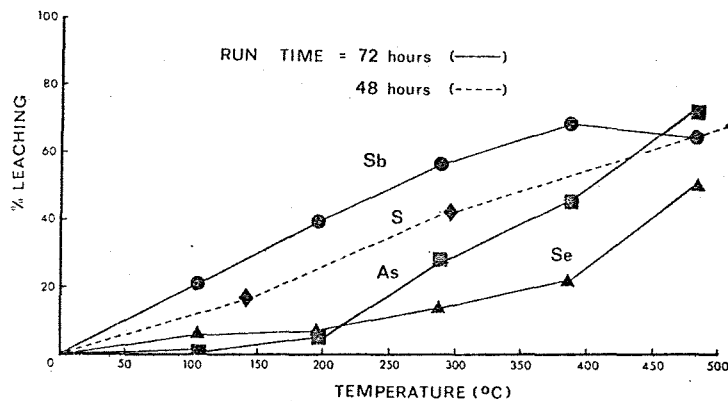Fig. 2. Variation with time in the percentage of constituents leached from greywacke, P 23556.

Fig. 3. Variation with temperature in the percentage of constituents leached from greywacke, P 23556.

Although no pH measurements were made on the reaction solutions, measurements by MAHON (1967) for solutions recovered after leaching greywackes with hot water indicate that they should be near neutral to slightly acid.

DISCUSSION

(a) General considerations

While the experimental data demonstrate that appreciable quantities of some elements were readily leached from the greywacke, the exact amounts are not of great significance. The ratios of rock to water in natural hydrothermal systems would be much higher than the 0.14 ratio used in the present experiments. ELLIS and MAHON (1964) have concluded from porosity measurements that ratios of ten to twelve appear reasonable for recent volcanic areas and these may be higher in sedimentary or metamorphic rocks. It follows that elemental concentrations in geothermal waters could be at least a factor of 70 higher than in the experimental solutions providing concentrations are not held at lower levels by solubility product relationships involving any of the elements. There is also the possibility that since the trace elements considered are not all extracted with the same ease (e.g. As and Sb in Fig. 3), then the trace element content of geothermal waters would probably show variations over the lifetime of the hydrothermal system. Although estimates have been made of the duration of hydrothermal activity in some New Zealand geothermal fields (GRINDLEY, 1965), there are no reliable estimates for the total volume of water which has passed through a given system or its rate of turnover. It could be expected that as the water in the system is recharged and recirculated, those rocks already leached would tend to release progressively lower amounts of the trace elements for solution. On the other hand, trace element concentrations could be maintained if fracturing (through fault movement) exposed fresh rocks for leaching, while pre-existing channelways were closed by mineral deposition.

It should also be emphasized that the reaction times for the experiments were very short in comparison to those available in natural systems. While significant concentrations of As, Sb, Se and S were released to the solutions in 72 hr at 300°C (Fig. 3), it is doubtful whether chemical equilibrium was established. With much longer reaction times and the opportunity for greater hydrothermal alteration an increased portion of those elements bound up in silicate and sulphide structures would probably be liberated.

(b) Individual constituents

Arsenic. It is evident from Fig. 3 that appreciable quantities of As were leached from the greywacke at temperatures greater than 250°C and that at about 480°C more than 70% or 7 ppm of the As was liberated to the solution. It is also apparent that the As was taken into solution rapidly (Fig. 2). These results supplement the data obtained by ELLIS and MAHON (1964), who observed that hot water contained trace amounts of As (<1 ppm) after leaching acid volcanics for up to 480 hr at 300–350°C.

The results indicate that the source of As found in geothermal waters need not be magmatic as ONISHI and SANDELL (1955) have proposed. If the assumptions are made that (1) the As contents of natural waters are not depressed by either solubility product relationships or adsorption on to the surface of minerals (such as clays) and (2) the rock to water ratio is ten, then concentrations of 25–30 ppm As in the fluid phase could be anticipated for solutions at 300°C in contact with a greywacke (such as P 23556) containing 10 ppm As. Applying the same boundary conditions, ELLIS and MAHON (1964) have concluded that concentrations of at least 6–8 ppm As could be expected in thermal waters percolating through andesites or rhyolitic pumice. Since the drillhole waters in many New Zealand geothermal fields attain maximum temperatures approaching 300°C at depth and generally contain less than 6 ppm As (ELLIS and MAHON, 1964), the volcanics and sediments of the

Taupo Volcanic Zone may act as source materials.

The fact that appreciable quantities of As were not readily available for solution at <200°C may indicate that it is mainly contained within mineral lattices rather than being held adsorbed on to mineral surfaces within the greywacke. The leaching profiles for As and S (Fig. 3) indicate that the As is possibly being liberated from pyrite as it breaks down to release S.

Antimony. The form of the Sb leaching profile differs significantly from that of As (Fig. 3). At 100°C, about 20% of the Sb was in solution and at 200°C, 40% had been leached. In contrast, the As content of the greywacke had been depleted by less than 10% at 200°C. In addition to this, the percentage of Sb leached between 350 and 500°C remained reasonably constant, while the depletion of As over the same temperature interval almost doubled.

The explanation of these differences may lie in the availability of each element for extraction by water. Although it is likely that pyrite in the greywacke would contain Sb, it is also possible that some Sb may be present either in other submicroscopic sulphide phases (e.g. stibnite, tetrahedrite) or adsorbed on to crystal surfaces and the walls of microfissures. Low temperature leaching experiments of short duration would probably produce negligible hydrothermal alteration and liberate very little Sb from the pyrite. However, these reaction times and temperatures may be sufficient to readily dissolve more soluble Sb-bearing sulphides and/or any adsorbed Sb. Ellis and Mahon have concluded from their experimental studies that a proportion of constituents such as chloride, boric acid and ammonia is held adsorbed on surfaces in rocks and is readily available for solution by water. The importance of adsorption phenomena has also been verified by GONI and GUILLEMIN (1968) for a wide range of trace elements.

Calculations of the likely Sb contents of thermal waters, using the experimental leaching data and applying the same assumptions made for As, suggest that at 300°C the solutions in contact with the greywacke P 23556 would contain up to 2 ppm Sb. Higher Sb concentrations in solution could be anticipated, as some greywackes and acid volcanics analysed contained greater Sb concentrations than P 23556. However, since the rate at which Sb would be liberated from a rock depends on the way in which the Sb is held and the rate of reaction between the rock and the solution, no quantitative estimates can be made. It would appear though from the above calculation that with the Sb concentrations of the Broadlands waters no more than 2 ppm (WEISSBERG, 1969; BROWNE, 1971) and the Sb contents of New Zealand thermal waters generally less than 0.3 ppm (RITCHIE, 1961), the elements may originate from the sediments and acid volcanics of the Taupo Volcanic Zone through leaching.

Selenium. Only traces of Se were leached from the rock fragments up to 300°C. In view of the ability Se has to substitute for S in sulphides, there is a strong possibility that it is mainly contained in pyrite and that as the pyrite dissociates, Se is liberated to the solution.

Extrapolating the experimental data as before, it can be calculated that in a natural hydrothermal system at least 100 ppb Se could be released to a solution at 300°C in contact with this greywacke. Unfortunately, there are no data for the Se concentrations in thermal waters from which comparisons can be made. However, if Se is to be derived by leaching, the argillites and greywackes are more likely source rocks than the acid volcanics which generally contain less than 10 ppb Se (EWERS, 1975).

Sulphur. Insufficient S determinations were made on the leached samples to enable many conclusions to be drawn. Analyses for the New Zealand greywackes and argillites indicate that S concentrations are typically in the range 500–2500 ppm. GIGGENBACH (in preparation) has shown that this sulphur is a mixture of sulphide and sulphate, though it is present mainly as pyrite. The efficient extraction of S from P 23556 by hot water as leaching temperatures were increased (see Fig. 3), illustrates the potential for these sediments to act as source material.

ELLIS and MAHON (1964) have stated that sulphides in contact with hot water containing oxygen would hydrolyse to H_2S and then the latter would partly oxidize to sulphate. Although the present experiments were carried out in a nitrogen atmosphere and the distilled water was boiled, it is probable that some air trapped between rock fragments and along microfractures produced appreciable quantities of sulphate. This may explain why H_2S was not detected at 150°C even though almost 20% of the S in the greywacke had been leached.

Of further significance is the fact that the greywacke is a suitable source rock for As and Sb as well as S. Since it is known that As and Sb form very stable thio complexes (WEISSBERG et al., 1966; BROOKINS, 1972; NORTON, 1964), the availability of S in a reduced form could play an important role in their transport.

Thallium. The fact that large amounts of Tl were not readily liberated on leaching suggests that Tl is incorporated into silicate lattices (substituting for K in K-feldspars and K-micas). With prolonged leaching (such as in natural hydrothermal systems) these silicates would alter and small quantities of Tl would be released for solution. However, under the experimental conditions, reaction times were too short for silicate alteration to take place. If Tl were in the pyrite or adsorbed on to crystal surfaces, some leaching should have occurred below 500°C as was the case for As, Sb, Se and S.

Although the data suggest that Tl was not leached to a significant extent from the greywacke up to 500°C, it would be inappropriate to assume that some other source must therefore be invoked. Analyses for Broadlands drillhole waters indicate that Tl concen-

trations are less than 10 ppb (WEISSBERG, 1969; BROWNE, 1971). For these concentrations to be obtained by the interaction of greywacke P 23556 with hot water (assuming a rock to water ratio of ten) less than 1% leaching would be required. Obviously, at such low levels of leaching, the precision of the analytical technique and variations in the Tl content of the starting materials would make it difficult to establish whether leaching had occurred.

Cobalt. The absence of significant Co leaching was perhaps surprising in view of the probable high Co content of the pyrite in the greywacke. It might be expected that as the pyrite breaks down, Co would be released to the solution. The fact that this was not the case suggests that most of the Co is either incorporated in the lattices of the new hydrothermal minerals (e.g. iron oxides) or retained in the unaltered Fe-bearing silicates (such as biotite) and is not readily available for solution.

Gold, silver, bismuth and tellurium. For reasons already stated, leaching data was not obtained for these elements. However, for a rock to water ratio of ten, only minor leaching would be necessary to produce the low concentrations of these elements found in the Broadlands waters [Au 0.1–1 ppb, Ag 2 ppb and Bi 0.3 ppb, according to BROWNE (1969)]. WEISSBERG (1969) has shown that waters from the Broadlands drillhole, BR 2 contain only 0.04 ppb Au and 0.6 ppb Ag, even though discharge precipitates with 55 ppm Au and 200 ppm Ag are forming from them. Data collected by GOTTFRIED et al. (1972) have indicated that the thermal waters of Yellowstone National Park generally contain 0.004–0.04 ppb Au, though the sinters deposited from them contain up to 5 ppm Au. They have concluded that above average Au concentrations in the country rocks are not required for them to serve as a possible source for the Au.

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