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A STUDY ON THE GEOTHERMAL ENVIRONMENT OF NEW BRITAIN

by

L.G.M. Baas Becking, G.A. Taylor and W. Thomas

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1. SUMMARY

Over 100 samples of geothermal waters at the N-coast of New Britain were studied. The samples showed a wide range of pH and potentials, similar to those established for the geothermal environment of Rotarua by Kaplan The region is one of declining volcanic activity and the typical "volcanic" constituents were met with at concentrations much lower than those found at Rotarua or at Yellowstone. Evidence has been presented to show that the original, juvenile, steam does not contain sulphate, and that this sulphate is entirely formed by the oxidation of sulphides. Of particular interest is the mixing of the acid volcanic water with seawater, in which we could confirm the observations of Zelenov (1958). In some oxidized samples hydrogen peroxide, perchlorate and nitrate could be found. X-ray spectrograms showed a high arsenic content of mud spring samples from Rabaul. The biological observations on algae, thiobacteria and iron organisms showed the presence of marine diatoms up to 52°C, marine bluegreens up to 79°C, while an Actinomycete developed in waters the temperature of which was $91^{\circ}\mathrm{C}$ at collection. For the first time iron organisms were found in the geothermal environment. A plea is made for a more systematic study of the various oxidation stages of several elements occurring in volcanic waters. iological study should also be systematized and extended.

2. TOPOGRAPHY OF LOCALITIES STUDIED.

The Talasea region was visited by N.H. Fisher and L.C. Noakes in 1938 (Fisher, 1939). A further description. establishing international nomenclature of the sites, was given by Fisher in 1957. M.A. Reynolds visited Talasea in 1953 (Reynolds, 1954). Most localities were explored after the war by G.A. Taylor (unpublished). The material for this report was obtained from volcanoes in the solfatara stage and their emanations, from hot springs, solfataras, mudsprings A Geyser-solfatara field was studied and special attention was given to the mixture of hotsprings with seawater. The localities studied are marked on a sketch map (Figure 1).) characterizes the environment further. Table 1 (Page On the whole, activity has remained about at the same level since 1938, with a few exceptions. The temperature of the solfatara field at Pangalu is slightly lower, the silica content of the geyser water must have decreased, as there was active silicification in 1938, which has almost stopped. The solfatara in Garbuna crater are now lower in temperature

and the gaseous emanation is confined to H_2S where, in 1938, SO_2 was observed. A number of springs, halfway between Kilu Village and Garbuna are mentioned, in 1939, to be hot (Dewa). Their temperature is now $27^{\circ}C$. Only in one instance there seems to be evidence for an increase in activity. Since 1938 a hot lake has been formed at the Walo solfatara field, and while in 1938 the highest temperature observed there was $96^{\circ}C$, there is now, in some localities, superheated steam. Moreover SO_2 is present in the emanations, which was not reported twenty years ago. The above changes, however, appear comparatively insignificant.

In Rabaul, most localities could almost be reached by car or by launch; the western localities were visited on board the M.V. "Mangana", to the master of which, Mr. A. Savage, we tender our thanks for his hospitality and for the interest he showed in our work.

Figure 1.

TABLE I ..

LOCALITIES, GEOTHERMAL ENVIRONMENT, NEW BRITAIN.

Locality	International Nomenclature	Co-ordinates	Date visited	no obs.	Symbol used	Elevation	Character	Max.temp. (taken 1938)	Temp.range 1959	Emanations 1939	Emanations 1959	3 Activity
Pangalu, Willaumez Peninsula, N.Garua Harbour.	5, 2-6 ^a	5 ⁰ 16'10" S 150 ⁰ 05'15"玉	13.8.59	14	Pa	Sea level	Geysers, solfataras, mudsprings	101 ⁰ C	Geyser II 101°C Geyser I 96°C (T)92 -101°C		SO ₂ (1315)	decr?
Talasea, Willaumez Pen. S.Garua Hbr.	5, 2-6 ^b	5 ⁰ 16'20"3 150 ⁰ 03'15"E	12.8.59 13.8.59	10	Т0	Sea level	hotsprings near beach	104 ⁰ C	96-101 ⁰ C	H ₂ S, CO ₂	H ₂ S	same
Same locality, uphill.				б	TU	50-100 feet	Solfataras mudpots	104 [°] C	49° - 99°C			decr?
Garbuna. Strat Volcano, S. Willaumez	o 5, 2-7 ^a	5 ⁰ 27'00"S 150 ⁰ 02'00"E	14.8.59	10	GV ·	1850 feet	fumarolic solfataric	101 ⁰ C	89 - 99 ^o c	H ₂ S, SO ₂ CO ₂ HCl	H ₂ S	decr?
Dewa. 14KM.S of Talasea	5, 2-8 ^a		14.8.59	,4 ;*	GD	200 fe et?	cold acid springs, Dewa,	"hot springs"	27-29 [°] C	н ₂ S	H ₂ S	decr?
Walo, Planet Bay	5, 2-9	5 [°] 32'00"S 150 [°] 54'00"E	15.8.59	7	Wa.	50 deet	solfatara field	96°C	56-101 ⁰ C	H ₂ S,CO ₂	SO ₂ , hot lake formed	incr?
Lolobau	5,2-13	4 ⁰ 55'40"S 151 ⁰ 10'15"E	16.8.59	б	Ī. o	3060 feet	gases			H ₂ S		
Vulcan	5,2-14 ⁸	4 ⁰ 16'15"S 152 ⁰ 10'00"E	30.7.59	3	RO	740 feet	hot		65-67°C			
Rabaul Tawurwur	5,2-14 ^b	4 ⁰ 14'15"S 152 ⁰ 12'50"E	30.7.59	12	RO	sealevel	hot seawater					
(Matupi) Rabaul			6.8.59 8.8.59	6	RV	750 feet	fumaroles solfataras	100°C	37-71°C		H ₂ S	same
Rabaul Sulphur Creek	5,2-14 ^d	4 ⁰ 13	4.8.59	S	RSC	80 feet	hotsprings	45°C	26.5-50°C			same
Tawurwur	5,2-14 ^b		30.7.59	3	Rab	0-5 feet	hotsprings, abnormally acid		85-91 [°] C			decr?
Rabalanakaia	5,2-14 [°]	4 ⁰ 13	7.8.59	1	RV	396 feet	solfataras	100°C	100 ⁰ C	Parlimon Marine de M		same

3. METHODS USED.

Samples were collected directly or, in the case of gaseous emanations, the steam was condensed in a zinc chimney pipe or in a glass funnel. Temperatures were read, but the instrument at our disposal did not allow us to differentiate temperatures of superheated water or steam. Superheated steam is indicated as 101°C. The samples were collected in 30 ml, sterile phials with plastic tops. we had to use phials with metal screw tops. The samples were numbered beginning with the date of collection (30.7.59 Before the further properties of the samples to 16.8.59). were determined, there was a time lapse from 15 minutes to several hours after which we determined pH and electrode potential of the cooled water. The electrometer used was constructed by Jones, Melbourne. This rugged instrument will stand transportation under adverse conditions and while the potentials are less accurate (plus or minus 5 mV) than those of laboratory instruments, the readings were steady and reliable. Malachite Green paper was used to establish the presence of SO2, lead acetate paper to detect H2S. tested for free chlorine by the red colour developed on erythrosin bromide paper.

The samples collected in or near Rabaul were examined under the microscope the same day. At Canberra, several weeks later, the pH and electrode potential (Eh) of the, now oxidized, samples was redetermined. The size of the sample did not allow for a direct determination of Resistivity was determined on a Philips instrument instead. As the waters contain variable, and sometimes large, quantities of chloride and sulphate, the results were not satisfactory. Chloride was determined titrimetrically, sulphate by comparison of the optical density of the barium sulphate precipitate. Total Iron was determined by means of thiocyanate in sulphuric acid solution, Silica by means of ammonium molybdate (Harvey, 1945, Brujewicz, Ammonia was determined by means of Nessler's reagent, nitrate was estimated using Na-diphenylamine-sulphonate. The water was further tested for H_2O_2 (lead sulphide paper), for Boron (turmeric paper), for heavy metals (Cu, Ni, Co, Zn, Mn & Pb) by chromatography, and for phosphate (molybdate). Perchlorate was detected by various colour reactions on a chromatogram. Tests for polythionic acids were carried out chromatographically.

Cultures were made on both seawater and freshwater

media of algae, thiobacteria and iron bacteria.

X-ray spectrograms were obtained from solid samples. We have to thank, at this place, Mr. W.M.B. Roberts for the preparation and the interpretation of the spectrograms.

4. GENERAL CHARACTERISTICS OF THE ENVIRONMENT.

The geothermal waters of New Britain occur as solfataras, hot springs, mud springs, steam vents and geysers. An acid hot spring at Dewa, now cooled down to air temperature, is included in this assemblage because of its close affinity in composition to thermal waters at Talasea, 14 KM to the North (Table 3). The waters and emanations show a very wide range in pH, oxido-reduction state, in chemical properties The large range in pH and in electrode and in temperature. potentials was first established by Kaplan (1956) for the thermal district of Rotarua, N.Z. Figure 2 shows the electrode potential and the pH limits for the New Britain environment, for the Rotarua environment and for the probable pH range of the global geothermal environment including the characteristics of saturated solutions of ferric chloride and of sodium carbonate, both substances recorded as occurring in the volcanic milieu. The full set of data is given at the end of the paper in Table A-C. It might be said that the geothermal environment presents a unique chance, to the hydrologist and to the hydrobiologist, to study, in a small area, the influence of widely diverging conditions, both physical and The present paper is highly preliminary in character, but we wish to point out the necessity of a further systematic study of this environment.

Table 2 shows the range of various characteristics. The lowest pH value is probably due to a mixture of sulphate, hydrosulphate and sulphuric acid. It was found in a hot spring (95°C) in the geyser region of Pangalu. The highest pH values were obtained from environments highly influenced by seawater, and are mostly due to photosynthesis. .contention of Barth(1950) that the acidity of emanations is proportional to the activity does not apply to the waters of New Britain. The lowest \mathbb{E}_{h} was found in the solfatara field of Walo, in a mudspring (101°C) containing SO2. The highest potential was found in a highly oxidized mudspring water from Talasea (Temperature at collection 99°C). The lowest chlorine and the lowest sulphate content was found in volcanic condensates from Rabaul and Garbuna craters, the highest chloride and sulphate were found in the abnormally acid, concentrated seawater from certain Rabaul hot springs.

This environment contained also the largest amount of iron and of silica met with in New Britain. Ammonia was highest in the geyser water, nitrate in the mudsprings (temperature 97° - 101° C) of the solfatara field at Walo.

Figure 2: Electrode potential and pH, New Britain. Rotarua and for the global geothermal environment.

TABLE 2. Limits pH, Eh and substances present in New Britain geothermal waters.

рН	Eh	Cl-	so ₄ =	tot Fe	SiO ₂ *
+.85 Pa.	-73 Wa	(ppm) 5 RV	(ppm) 30 GV	(ppm) O Sev	(ppm) O Sev
8.70 RSC	+797 Tu	29,800 Rab	3100 Rab	100 Rab	13.5 Rab

NH ₄ +	NO3	В	H ₂ O ₂	C10 ₄	Polythionates
(ppm) O Sev 10 Wa	(ppm) O Sev 10 Wa	O Sev ++ Wa	O Sev ++ Tu	O Sev Ro +++ Wa	O mat + Rab + RV

^{*} unreliable, probably too low.

Substances present in small amounts will be described in Section 13 of this paper.

At 25°C or 298°A the expression for the electrode potential of a reaction as a function of pH is:

 $E_h = E_0 - .0591$ a/n pH volt

in which <u>a</u> represents the number of hydrogen ions, and <u>n</u> the number of electrons involved. Both E_0 and the numerical factor .0591 are derived from the electrochemical equivalent for RT. This means that, at 1000° C, the value for the E_0 will become 4.25 times the value at room temperature, while the slope of the line will become 4.25 times greater. For a reaction like:

 $2Fe^{++} + 3H_2O \implies Fe_2O_3 + 6H^+ + 2e^-,$

 $E_h=725-177\ pH$ mV. at $25^{o}\text{C}.$ This will be $E_h=3140-774\ pH$ mV at $1000^{o}\text{C}.$ Moreover, at hydrothermal temperatures the processes are non adiabatic, and as RT equals PV, we obtain, for an isothermal correction, the same value. This means that, at higher temperatures both the E_h and pH will become indeterminate. We have to judge, however, the thermal processes at 25^{o}C which is a serious disadvantage, especially when we want to use the potential values to interpret certain reactions. We have to content ouselves, therefore to use these values as characteristics of the samples.

5. CLASSIFICATION OF THE ENVIRONMENTS STUDIED.

Volcanic gas vents with temperatures appreciably exceeding 100°C were not encountered in the eastern part of New Britain. The areas visited are characterized by solfataric activity and dormant volcanic conditions. 84 samples for which we have complete data, only 5 showed, at collection, temperatures of more than 100°C. As we shall see later, the amounts of compounds, indicative of volcanic activity is much lower than in other parts of the world. Our chief aim, however, was to study the effect of seawater on volcanic emanations (Zelenov, 1958). Blanche Bay and the beaches at Talasea, Pangalu, near Kilu village and at Walo are particularly suited for this study. The values obtained were compared with the characteristics of purely volcanic emanations and with "uncontaminated" seawater. For this we used average values obtained from Harvey (1945) and from data obtained at the Division of Fisheries and Oceanography, C.S.I.R.O., Cronulla, N.S.W. We classified the samples as follows:

TABLE 3

AVERAGE VALUES FOR VARIOUS ENVIRONMENTS

(the SiO₂ values are probably too low)

			When collecte	After ed 1 month	After n 4 months		parts p	oer mi	llion				qual	Litativ	е					
Group	Symbol	No.	pH Eh	gH El	areas and a subspecificated which the parties of the parties of the subspecific states of	Cl	SO ₄ =	Рe	SiO ₂	NH/+	NO3	В	H ₂ O ₂	${ m CLO}_4$	CL ₂	H ₂ S	S0 ₂	Poly thionic	HCl	ТОС
Seawater	Se	3	გ.20+380			19, 600	2260	nil	(1.25	<. 1	<. 5	+		++			_	_	_	26.5
Rabaul,oceanic	RO	12	5.83+317	6.87+466	7.46+481	20,990	1700	1.0	8.2	.8	0	+	MACY	++-		+	_	-		69.0
Rabaul aberrant	Rab	3	3.42+450	3.11+577	2.98+697	22,600	2500	67.0	10.5	• 7	0	+	***	+++	tr	eco	=	ŧr	-	87.1
Rabaul, volcanic	RV	5	3.61+328	4.86+449	2.99+605	3.	3 110	2.6	• 5	3.9	0		++	÷	_	+	aliene	tr	+	100
Rabaul,freshwater	RF	2	7.57+412	6.39+383	7.85+473	370	150	0	5.5	0	25	-	_	tr	MCAO	Mass	=	www		26.5
Rabaul, Sulphur Ck.	RSC	7	6.34+412	6.92+452	8.02+448	5,710	600	0	4.8	.6	0	+	+	+	A119-	et in	_		_	47.5
Pangalu, Walo oceanic	00	4	5.99+146	6.16+413	6.41+479	11,750	1900	0	3.0	2.0	0	tr		+	M/CR		wa.	ne.	-	86.0
Talasea, near the ocean	TO	10	5.03+368	4.41+491	3.71+696	10,810) 710	2.5	4.7	2.9	O	tr	++	+		t r	and the	-	_	98.6
Talasea,50-100 ft. elev.	TU	6	2.88+434	2.74+ 586	3.23+663	20	1250	5.0	5.4	3.0	0	mrs.	+	+	-	_		. September 1	_	79.0
Pangalu	Pa	12	2.28+394	2.58+622	3.02+670	3,450	1100	• 4 _F	1.0	3.7	0	_	+	+	-		tr	_	_	98.3
Garbuna,volcanic	GV	9	2.96-258	4.02+496	2 . 19+686	22	2 320	1.9	4.0	1.0	0	-	<u>+</u> .	+			-		+	97.6
Garbuna,Dewa	GD	4	2.47-132	2.69+502	1.50+717	1(1160	5.2	5.3	O	1.3			post		+	_	_	_	27.2
Walu	W a	7	6.66+147	6.08+442	6.23+488	1,850	740	1.6	7.2	2.3	4.0	+	+ -	+	-	•••	+		-	90.5
		84																		

84

Symbol No. of

	Oceanic	S	3	
Oceanic -	· Volcanic	RO	12	Rabaul, beach Vulcan, Matupi; Rapindi
		TO	10	Talasea, near the beach
		RSC	7	Rabaul, Sulphur Creek
		00	4	Beach Pangalu, Kilu and Walo
		Rab	3	Tawurwur, highly concentrated; acid springs.
	Volcanic	RV	5	Rabaul, vents and condensates
		GV	9	Garbuna, vents and condensates
Cold wate	er from			
рс	res	RF	2	Two bores S of Rabaul
Decadent	solfataric	TU	6	Talasea, 50-100 ft. above sea-1:
11	H	GD	4	Dewa, acid springs, between Garbuna and Kilu
Unce	rtain,			
probably		Pa	12	Geysers & Solfatara, Pangalu
	Volcanic	Wa.	7	Walo, Planet Bay.

Table 3 shows the further characterisation of these groups,

6. CHLORIDE AND SULPHATE.

The geothermal waters of New Britain contain from 5 to 30,000 ppm chloride and from 30 to 3100 ppm sulphate. If we want to represent this graphically (Figure 3. Page 12) the logarithms of the concentrations have to be The waters are mixtures of volcanic waters, groundwater In this paper we will (plus meteoric water) and seawater. assume that, in the original volcanic water, all compounds are in the reduced state (see Section 13) and that these waters contain no sulphate (Allen, 1935). Two sulphate containing minerals, hauynite and noselite are described as igneous but they belong to the younger, effusive eruptives and, moreover, they are decomposed at temperatures above 700°C (Morazewicz, cited by Clarke, 1916). The changes are. therefore, that these minerals are formed in the oxidative In steam from a vent at White Island (N.Z.) Wilson (1953) found a large quantity of chloride (.91%) while Kimuru (1953) mentions even higher chlorinity in water from drillholes at Arima, Japan. In both cases no sulphate could be detected. We will extend the range of chlorinity in Figure 3, in the volcanic waters from 3000 to 100,000 ppm. Values of $\langle 1 \text{ ppm of Cl}^- \text{ or SO}_{\Lambda} = \text{determine the lower limit.}$

Juvenile steam (called V in this paper) is present in nearly all waters investigated. Foshag (1950) is of the opinion that only a small part of the volcanic emanation is truly volcanic, but that groundwater is, as it were, sucked in when the lava recedes in the crater pipe. Unfortunately there are no chemical analyses, either of juvenile steam or of groundwater, to support his claim. There are, however, other reasons to make us support Foshag's hypothesis, for a great many geothermal waters show very low chlorinities which could only be accounted for by either a juvenile steam of very low chlorinity (which is most unlikely) or by the mixture of volcanic water and groundwater (plus meteoric water). Groundwater (symbol G) is limited by a region $log (SO_4 =)$ ppm 1-2 and log (Cl) ppm lower than 2. These figures are based upon the average of the great number of analyses given The region in which the influence of the by Clarke (1916). volcanic water is still felt is called GV.

Seawater is of fairly constant global composition, the chlorinity between 18,500 and 20,000 ppm. sulphate 2200-2300 ppm. A seawater containing 19,600 ppm Cl and 2260 ppm SO_4^- is represented in the figure by a black circle. Seawater (Symbol S) might mix directly with volcanic steam (SV). Furthermore, seawater may be concentrated by evaporation or it may be diluted with groundwater or by meteoric water (broken line in Figure 3). The symbol used for these waters is SC. The highly diluted mixture of volcanic steam and groundwater, containing reduced sulphur compounds, oxidizes at the air and, dependent upon the original sulphide content, will generate a variable amount of sulphate. This oxidation is indicated in Figure 3 by vertical lines (symbol GVO). The SV mixtures may also undergo oxidation (SVO). At this place we want to mention the evidence obtained by Sakai (1957) from the proportion of sulphur isotopes in various environments. This author is of the opinion that the sulphate in seawater is of magmatic origin. In our nomenclature the process The oxidized volcanic emissions could be described as SVO. may mingle again with seawater, SGVO. In these compound waters the groundwater or (and) the seawater component may be oxidized to a different degree . From Figure 3 we may derive an inkling as to the nature of various geothermal waters. will be seen later (section 13) that the influence of seawater may be traced by other means, as in seawater and diluted seawater a definite pH-LE $_{
m h}$ relation is set up (the E $_{
m h}$ between pH 2- 6 not rising above +500 mV) which shows a great difference with waters of the GVO type, which attain much higher \mathbf{E}_h values upon oxidation. A preliminary classification of the geothermal waters on the basis of chloride and sulphate content is given in the next table (Table 4).

TABLE 4.
Classification of Geothermal waters on chloride & sulphate content.

	S	SV	SVO	SVG	SVGO	GV	GVO	Ocean	Mixt.	volc.
RO	3	6	1	· · · · · · · · · · · · · · · · · · ·				+	+	
Rab.				4						
RSC		1			4		,		+	
RF				· 2					+	
RV					·· , · · <u>·</u> _ · · · · · · · ·	4	1			+
TO		4	· · · · · · · · · · · · · · · · · · ·		2				+	
TU			···········			1	4			+
Pa			2			4	5		+	+
Pa0	1		1						+	
GV						1	2			+
GD							2			+
GO					1				+	
Wa		3			1	1			+	+
Wa0			2			•			+	
	3	14	6	6	8	11	14	3	34	25

From the foregoing it appears that, apart from the volcanic exhalations from Tawurwur, Garbuna, the solfatara field at Talasea (uphill) and the acid springs at Dewa, all localities probably contained seawater. It is interesting to note that the waters from both geysers at Pangalu belong Curiously enough, condensates from vents to this class. between the geysers show the characteristics of a mixture of groundwater and juvenile water. Data from the literature are also represented in Figure 3. From these data it would appear that both the waters from the Taal volcano (Philippines) and from the Idjen volcano (Java) are, in some way, related These young tertiary volcanoes, rising from to seawater. the seabottom, could still contain fossil seawater in their Geysers from Yellowstone, Iceland and from the Rotarua district (N.Z.) do not contain a marine element, Moreover, they are at a low oxidation level. The legend to

Figure 3.

Index to Figure 3.

Logarithmic relation between chloride and sulphate in various waters.

Mixtures between two waters are represented, in this diagram, by logarithmic lines.

If no author is mentioned, the data are taken from Clarke (1916).

G groundwater, V volcanic water, S seawater, O oxidized. The New Britain waters are further described in the text.

1110 11011 1111 110111 1101011		
Acid volcanic waters	(1) Solfatara, Puzzuoli, Naples	GVO
	(2) Sulphur Bank, California	GVO
	(3) Sulphur Deposits, Cove Creek, Utah	GVO
	(4) Paramo de Ruiz, hotspring, Columbia	GVO
	(5) Cameron's Bath, Rotarua (N.Z.)	GVO
	(6) Rio Vinagre, Columbia	GVO
	(7) Bitter River, Idjen, Java	SGVO
	(8) Hot Spring, Taal, Philippines	SGVO
	(9) Green Lake, Taal, Philippines	SVCO
	(10) White Island (N.Z.) Hotspring	SVCO
	(10 ^a)As (10), Wilson (1953)	SVCO
Siliceous Geyser Water	G.	
biliceous deyser mater	s a) Coral Springs, Yellowstone	GV
	b) Echinus Springs, Norris Basin	GVO
	c) Old Faithful, Yellowstone	GV
	d) Great Geyser, Iceland	GV
	e) Te Tarate, Rotarua (N.Z.)	GV
	f) Excelsior Geyser, Yellowstone	GV
Miscellaneous	β) Norris 33, Yellowstone, White (1953)) GVO
	3) Steam, White Island (N.Z.) Wilson	V
	¿) Arima Hotsprings, Japan, Kimura (195	3) V
	Average freshwater, Clarke 1916	G
	-	

TABLE A - RABAUL

Place	Locality	. Environment	Remarks		At	After		After				· · · · · · · · · · · · · · · · · · ·								-0"-1"-1"-1"-1"-1"-1"-1"-1"-1"-1"-1"-1"-1"					
				No. TOC	collection pH Eh	1 mo. pH Eh	Hq	4 mo. Eh	-	parts	per milli	on			acid			Qualit	ative te	ests					i : :
Rahaul	Fear Vulcan	sea			8.25 +267	*	~ · · • · ·		C1-	S0 ₄ =	fot Fe	Si) ₂	NH ₄ +	NO3	10 ⁻³	H ₂ S	S0 ₂	polythi	Cl_2	010,	В	H ₂ O ₂	Type	No.	Oxidizab
nasaur	Walaur, Vulcan	sea		301 26.0		7 04 ±4	82			2600		0	——————————————————————————————————————						ζ	4		<u> </u>	S	300	ility
	Vulcan	sea near beach	steaming, brown, turbid	302 67	6.95 +349	7.13 +4		10 : 105	- 18,600		0	0								4			S	301	
	11	sea near beach	steaming, brown, turbid	303 65	7.03 +333	7.31 ÷4				1100	0	10.9	1							3	2		SV	302	+86
	Tawurwur	sea near beach	steaming, faint H ₂ S	304 49	5.90 +345	5.37 +5			21,000		0	10.9	0	5						3			SV	303	+83
	li li		steaming, brown, turbid	305 72	6.27 +257	4.88 +4				2200	O	5.7	1							3	2		SVO	304	• +69
	11	ii	steaming	306 85	4.41 +500			29 +745		2800	10	13.5	1							0			SCO	305	+268
		!!	II II	307 87	2.90 +435			69 +726	22,600	2200	100	11.5	1							4			SCO	306	+245
		ii ii	ıı	308 91	2.95 +415			98 +610		2800	100	10.0	0						tr					307	+291
		sea near beach	cool, brown, turbid	309 31	7.00 +320		00 2,)O +010			100	10.0	1						tr	4	1			308	+195
		ii	steaming	3010 79			o .	16 ,510)0	• 5	1							3				309	
	Tawurwur-	sea near beach			5.80 +295			16 ÷518		1100	0	10.7	1					tr		4	2		SV	3010	+223
, 4 1	Rapindik		steaming, greenish	3012 52	5.38 +330	7.00 +4	43 1.0	33 +513	21,400	1000		6.9	1							3			SV	3012	+183
!	11	spring near beach		3013 80	E 45 .240	C 50	00 7 7	70 .545	19 100	1700	0	40 =												3013	
	Noon Ponindila		steaming, clear	3014 80	5.45 +340						0	10.5	1							2			SV	3014	+205
į	Near Rapindik Former junction	sea	cool, clear	3015 37	4.85 +305	7.14 +4			12,000		0	10.0	1			- • •				3	tr		SV	3015	+131
	Matupi	sea	steamy, turbid	3016 71	5.80 +285			42 +482	1 050		0	10.0	1								1	4		3016	+197
	Sulphur Creek	N-E side, water		41 49		6.97 +4			1,950	220	0	5.1	1		• • •					1	tr			41	+64
•	11			42 45	6.50 +425				17,600		0	3.8	0							3	tr	tr		42	+88
:	" "	Rear craterlets		44 50	6.81 +329				1 600	560	U	5 . 0	1						-	3	1		SVGO	44	+56
-	11 11	SW side		45 44	7.71 +372	₹. 27 +4	06 6.	17 +428		560 	0	5 . 2	1						3	7	tr	tr	SV	45	
		S -W side		46 45	6.50 +430					700	Û		0		• • •								37G0	46	
	11 11	approaching ocean			6.38 +425					700													SVGO	47	
	Dept.Civil	11 11			7.11 +485	_			1,730								-						SVGO	48	
	Aviation	bore			7.12 +435					160	0	5.7	0	5					2	2			SD	61	+40
	New Guinea Club	11			8.22 +390	5.73 +3	79 7.6	56 +417	120	140	.01	5.2	0	0;					1	1			SDO	62	+27
	Tawurwur Crater	solfatara		63 100							. 1	5.8	С	0					1	1				63	
	" " Rabalanakaia	"		64 100																				64	•
	crater	condensate		71 100	4.79 ÷405	3.60 +5	30			250	10	0	8	0					1	1			GVO	71	
•	Tawurwur crater	· ·		81 100	3.20 +1 75	4.75 +4	50 2.8	38 +625	5	50	1	0	3	0 ::		1			C)			GV	81	+450
	11 (1	11		82 100	3.70 +455	5.65 +4	11 2.9)0 +605	75	80	1	0	2	0 .		1		tr	1	1.		. • .1	GV	82	+150
	11 11	11		83 100	3.15 +300	4.56 +4	63 3.0)5 +597	70	80	. 0	0				tr	-	tr	1	1		2	GV	83	+297
	11 11	11		84 100	3.20 +305	5.76 +3	92 3.	19 +577		90	.1	0	2	0		1			2	2			GV	84	+272

Figure 3 gives our interpretation of the origin of the other volcanic waters, using the same symbols. The Tables A-C at the end of this paper, also give our interpretation as to the origin of every sample.

7. IRON.

The total iron in volcanic waters varies from zero to over 1% (11,400 ppm, White Island, (N.Z.), Wilson, 1953). The iron content is, in the first place, a function of pH as, above pH 6-7, the iron content cannot be ascertained by ordinary analytical means. A thorough filtration of the sample is necessary prior to analysis. Statements in the literature of soluble iron present in alkaline solutions may be due to the use of turbid solutions.

Meteoric waters draining through fresh nuce deposits, when it emerges, leaves a bright yellow-brown precipitate in its channel. This has been noted at Mount Lamington and Manam. Perhaps increasing dilution and a rising pH also supplies an explanation of this phenomenom.

Our own determinations and those from the literature (Zelenov, 1957, White et al. 1953, Wilson, 1953) yielded the following relation between total iron and pH:

RELATION BETWEEN PH AND IRON CONTENT OF VOLCANIC WATERS.

pH 0 - 1 1 - 2 2 - 3 3 - 4 4 - 5 5 - 6 6 - 7 7 - 8 8 - 9

Fe 11,400 298 17.1 23.5 3.2 2.4. trace 0 0 (76 samples)

From this it follows that the mixing of acid volcanic waters and the alkaline seawater (pH 7.5-8.5) will cause a precipitation of iron. The precipitate may be iron oxide or hydrated Zelenov (1957) describes this phenomenon in the ocean near Paramushir Island in the Kurile island group, where the volcano Ebeko produces iron-rich acid spring water which flows into the Okhotsk Sea and causes a brownish-yellow turbidity which may be traced for miles. On a smaller scale. this phenomenon may be observed in the sea near the beach East of Matupi, Rabaul and also near the beach at Talasea and in the sea around Tuluman and Bam volcanoes. The geothermal waters of New Britain contain from 0 to 100 ppm total iron-The highest concentrations (100 ppm) were found in coastal springs at Rabaul, near Tawurwur Volcano. These springs (symbol Rab) had a high concentration in both Cl and SO4, they were more acid than the other mixtures of seawater and volcanic effluent and they contained, moreover, the highest

values for silica recorded in New Britain. These samples probably represent a secondary oxidation of partially evaporated seawater in a material rich in iron. Apart from three samples the iron is correlated with pH by the following expression (least squares): Total Iron = 9 - 1.3 pH ppm. Inasmuch as there is a correlation, in the volcanic waters, between pH and sulphate-content, there is a positive correlation between total iron and sulphate which may be expressed by:

Log (Fe) = $-7.9 + 2.9 \log (SO_4^=)$ ppm. Both Zelenov (1957) and Wilson (1953) state the content of ferrous and of ferric iron. The fact that we encountered, in oxidized volcanic waters, electrode potentials of almost +800 mV shows that most of the ferrous iron may disappear in the oxidation and that the characteristics of the final oxidation products are very much like those obtained in the oxidation of pyrite, via ferrous sulphate, to ferric sulphate (unpublished).

The iron my be carried by water or by the steam and may be a direct product of the magmatic sulphides or, as there is a great deal of admixture with groundwater and with soil, it may be not directly volcanic in origin.

8. SILICA.

The two components of the geothermal environment in New Britain, seawater and volcanic water, contain variable quantities of silica. Our knowledge of the silica content of seawater has been extended by Brujewicz (1955). He found that the surface values of less than 1 ppm SiO₂ were not representative of the water mass, as the SiO₂ increased to values of almost 7 ppm in the bottom (Pacific) water.

Moreover, sediment-solutions would yield values as high as 52 ppm. (Caspian). In the volcanic environment, especially near travertine deposits, values as high as 509 ppm SiO₂ have been recorded (Wilson, 1953).

The silica content of the New Britain waters has been found to be very low, varying from 0 to 13.5 ppm. The highest values of over 10 ppm were found in acid, concentrated scawater near the volcano Tawurwur. This water has apparently been in contact with iron-rich sediments (see section 7). In the solfatara and Geyser field of Pangalu, north of Garua Harbour, active silicification of wood was observed by Fisher and Noakes in 1938 (Fisher, 1939). At the present time these geyser waters contain only 1.0 to

1.3 ppm SiO₂. However, slight concentration of these waters by heat will cause a milky opaqueness to develop. The method used was that described by Harvey (1945) using molybdate and comparing the yellow colour with picric acid standards with a correction for the chlorinity of the sample. The same method was used by Brujcwicz (1955). It may be that this method is unsuitable for these waters and that the absolute values should be checked.

The comparative values show that the silica content of the samples does not correlate with other chemical properties of the water, except with sulphate. In oxidizing water the silica increases with the sulphate. The highest silica values were noted at temperatures of the waters between 75° and 80°C; the values dropped at lower and at higher temperatures. The whole topic needs reinvestigation using recently collected samples because of the fact that samples four months old did not contain appreciable amounts of silica. The figures given are obtained from 1 month old samples. Most of the silica might have precipitated before that.

Go Okamoto Takeshi Okuro and Katsumi Goto (Faculty of Eng. Hokkaido Univ. Sappuro Japan) encountered similar trouble and have reported their findings in Geochimica et Cosmochimica Acta Vol. 12 Nos 1&2, 1957.

They used the silicomolybdate complex method for determining "molecularly dispersed silica". They report that trivalent cations have a profound effect upon the solubility of Si, small amounts of which will precipitate large quantities in relatively concentrated 'solutions' of silica.

The problem is complicated by the difficulty of determining silica in the following states; solution, colloidal suspension, adsorbed, and complexed.

9. AMMONIUM AND NITRATE.

The origin of the volcanic ammonium is still controversial. Goldschmidt (1953, p.443) claims that it originates from the biosphere. The very high values found by Wilson (1953) for New Zealand hot springs (705 ppm NH₄+ in Waihi) and by White et al. (1953) in the United States (up to 543 ppm at Sulphur Bank) are never encountered in the biosphere. Sewage contains maximally 50 ppm. Moreover, Wilson (1953) mentions 200 ppm ammonium ion in steam of "the Geysers", California.

In comparison with the high values found in the literature, the New Britain geothermal environment shows very low values for ammonium ion in its waters. These values range from 0 to 10 ppm, with an average of 2.47 ppm. In seawater values higher than .1 ppm are rare. Values higher than average are found in the New Britain environment in volcanic vents and Geysers. Of the twelve high values the average is 5.6 ppm while the average pH of the waters at collection was 4.0, temperature 97°C. Low temperature waters, in which biological activity occurred, were free (or almost free) of ammonia.

While the global evidence for the magmatic origin of the ammonia is overwhelming it must be granted that the values observed by us are within the biological range. However, the exclusive occurrence at high temperatures and it a volcanic environment support the contention that the origin The low values obtained may be due to declining is volcanic. volcanic activity. As far as we are aware, no determinations have been carried out on the nitrate content of volcanic In the New Britain waters we found nitrate only in 4 cases, from 5 to 10 ppm: One of them could be ascribed to nitrification, a freshwater bore near Rabaul pH 7.05, at 26.5°C. A hot seawater sample, pH 7.31, at 65°C developed nitrate two months after collection. Possibly, if the result is not due to air infection, there may have been a thermotolerant phase in the life history of the causative bacterium. Nitrification also occurred in a sample from an acid spring, pH 2.62 at 29° C. It may be that there exists an acid resistant strain of nitrifying bacteria. Two samples collect at Walo, pH 4.99 and 7.95 at 1000 to 1010C showed the most copious formation of nitrate.

thigh temperature sample contained a little (1 ppm) ammonium ion, the other was entirely free of ammonium. It may be that, in an inorganic, sterile, environment, nitrification can take place, at 100°C, perhaps with a suitable catalyst. The results are highly preliminary and further observations on nitrification in the geothermal environment should be undertaken.

10. BASE AND ACID

If the pH of a natural water is higher than ca. 5.0 traces of bound carbon dioxide may be present. In seawater, with a pH above 8, this bound carbon dioxide is almost entirely present as bicarbonate. The titration value of seawater, with .001 n HCl, to pH 5.0 is called the Total Base.

and if the water is in equilibrium with the atmospher, it would be possible to calculate the value for the Total Base (ca. 2.5x10⁻³) for seawater) for any solution containing bound CO₂. One of us (Baas Becking, 1956) has shown that equilibrium conditions hardly ever prevail and that there is a wide variation of Total Base values at the same pH, dependent, chiefly, upon biological activity. We can say a little more about acid waters, where the titration value is a function of the concentration of ions and un-ionized acids present.

For a number of geothermal waters of low pH, listed in Tables A to C, there appears (1) a relation between pH and titration value, (2) a relation between pH and sulphate content of the water and (3) a relation between titration values and sulphate content. This shows that, at least in part, the acidity is caused by acid sulphate ion and by undissociated sulphuric acid. As the pH changes rather rapidly during the oxidation of the sample, the relation between total acid and sulphate remains the most reliable of the three. (see Figure 4.).

Figure 4. Relation between pH and sulphate content and between "titration values and sulphate content of geothermal waters.

11. SUBSTANCES PRESENT IN SMALL QUANTITIES.

- (a) BORON is present as borate or boric acid. Quantities larger than those in seawater were found in the hot lake and the hot springs of Walo. This environment, at 50 feet elevation above sealevel is, as stated above, highly influenced by seawater. The other environments that yielded boron (in quantities comparable with those of seawater, or less) were all influenced by the marine environment (RO, Rab, RSC, TO). No boron reaction could be obtained with waters of (presumably) volcanic-groundwater origin (RV, TU, GV, GD). Its absence in the waters of the Geyser region (Pa) which waters are apparently influenced by seawater, is striking. Again, comparison with other volcanic environments show tlat the New Britain values must be very low. The values for seawater are 3-5 ppm B, while 525 ppm has been recorded by White et al. (1953) for the waters of Sulphur Bank, California.
- (b) HYDROGEN PEROXIDE (tested on oxidized samples). The solubilization of lead sulphide has been used as a test. Seawater, RO, Rab, and GD yielded negative tests. The most convincing reaction was given by sample 127, TO. No correlations with any other property of the water was found, except for the fact that the waters containing hydrogen peroxide showed a high electrode potential (see section 13).
- (c) Baas Becking et al. (1959) reported upon the occurrence of PERCHLORATE in seawater. Usually it is present in concentrations of ca. 50 to 200 ppm. A reliable quantitative method does not exist. For testing (oxidized) samples we used paper chromatography in an alcoholic alkaline Various compounds were used to test for perchlorate. The amount of perchlorate seems to be a function of the chloride content of the water. The presence of $\mathrm{H}_2\mathrm{S}$ of SO_2 seems to be incompatible with the occurrence of perchlorate. In sample 71 a condensate from the volcano Rabalanakaia, a faint positive test was obtained with a water containing 10 ppm chloride. A condensate from Garbuna volcano (sample 149), 13 ppm chloride, showed a fair amount of perchlorate. It may be that the electrode potential of the environment is a codeterminant. Low perchlorate at high salinities was met with in some volcanic waters issuing near the ocean beach (141, Kilu village 2850 ppm chloride, 1216, Talasea beach, 13,300 ppm chloride and 1315, Pangalu beach, 8900 ppm chloride).

Anaerobic decomposition of perchlorate has been shown to occur. When a reliable quantitative determination of perchlorate is available, the work should be repeated.

- (d) FREE CHLORINE. Papers were soaked in a solution containing erythrosin and KBr on which a red spot is formed by free chlorine. The test was carried out in the field. Positive reactions were obtained with the "abnormal" hotsprings at Rabaul (Rab), with two samples from Talasea beach and with one sample collected near Pangalu beach. The search for free chlorine has to continue, preferably with quantitative methods.
- (e) HYDROCHLORIC ACID. In waters of pH 4.5 (outside the carbon dioxide range) a sudden increase of pH after collection is most probably due to the presence of fair quantities of HCl, as, from a weak solution, no HCl is given off. The indications are that both the volcanic condensates of Tawurwur and Garbur contain HCl.
- (f) HYDROGEN SULPHIDE. While the nose can detect 10^{-6} n H₂S (17 microgram per litre of air) the sensitivity. of chemical reactions in a liquid milieu is limited to quantities larger than 10^{-4} to 10^{-5} n. A superficial inspection of the region shows that, as compared to the Rotarua region, the quantity of H2S is small. We detected H2S (be smell) in or near the vents of Tawurwur, but we could not obtain a positive chemical test, except in one The volcanic environment of Rabaul yielded four sample. samples containing H2S. Talasea beach, where the inhabitants used to complain about the smell, only showed weak tests. Hot springs in Garbuna crater contained H2S and also the cold acid springs at Dewa. Here the HoS cannot be formed by sulphate reducing bacteria, as the pH (2.22 - 3.21 at collection) is too low for their development. Comparing our experiences with those obtained by Fisher and Noakes in 1938 (Fisher, 1939) we get the impression that there is less hydrogen sulphide in the goothermal environment than before. The relation between the occurrence of H2S and the electrode potential will be treated in Section 13.
- (g) SULPHUR DIOXIDE. Traces of SO₂ were found in sample 1315, Pangalu Beach, while appreciable quantities must have been present, at the time of collection in a vent and in mud springs at Walo. This occurrence is not mentioned by Fisher (1939). On the other hand, the vents in the Garbuna crater, which showed the presence of SO₂ in 1938, did not contain this substance in 1959 (see also Section 13).

(h) POLYTHIONIC ACIDS. Polythionates, discovered by Maclaurin in 1911, have been repeatedly found since (S.H. Wilson, 1941, 1953). Large amounts were encountered in vents of Langila Volcano at the west point of New Britain by Taylor and co-workers (1955). It was found that by using chromatography from an alcohol-acetone solution the polythionates could be detected by means of silver nitrate. Unfortunata : the polythionates oxidize, finally yielding sulphate and as the samples at our disposal were several months old, no significant results could be expected. Still, traces of polythionates were present in the "aberrant" hotsprings in the Matupi region, Rabaul and also in condensates obtained from Tawurwur. In our future program, fresh samples should be used.

We failed to detect, in any of the samples, polysulphides, phosphates or heavy metal other than iron. Traces of heavy metal were found by X-ray spectroscopy (Section 12).

Hydrogen peroxide, nitrate and perchlorate were detected in volcanic waters for the first time. As compared with other volcanic regions, the New Britain geothermal environment is poor in the compounds enumerated in this section. It would be worth while to extend the investigation to regions which have been more recently active, such as Langila volcano. New Britain.

12. X-RXY SPECTROGRAMS

From five localities solids were investigated by X-ray spectrography by Mr. W. Roberts. Table 5 shows the The assemblage is indicative of a basic lava, in confirmation of the results of analyses mentioned by Fisher Both samples from Rabaul contained percentage quantities of arsenic, which element is known to occur in the geothermal environment (Clarke, 1916, p. 14). occurs only in traces in the more western environments of Lolobau, Pangalu and Talasea. Cerium, Chromium, Manganese, Samarium, Strontium and Copper are found in all samples, while Titanium, Zirconium, and Vanadium are more abundant in Bromine was found only in material from Lolobau. Lolobau contains, moreover, traces of 10 elements, amongst which are some rare earths. It is interesting to note that two localities, only a few miles apart (Talasea and Pangalu) while yielding similar spectra, still show differences in composition. The two samples collected at Rabaul, also a

TABLE 5 X-RAY SPECTROGRAMS

	As	Fe	Ti	Ce	Cr	Mn	Zr	Sa	Sr	Cu	Re	V	Co	Ni	Br	Eu	Dy	Hf	Zn	Pb	Au	Bi	Sb	Sn	Мо	Υt	U	Cd	Tr	Ga	Th	Ba
a)	5	5	2.72	3	3	3		2	2	2		e et s	_		-	1	1	1	w	_		•	-	_	_	_			_	_		
b)	5	5	2	3	3	3	=	2	2	2			-	. 2	ve	•	-			_	-	en	_	•••		-	_	-	-	_		
c)	1	5	3	3	3		1	2	1	2	1	3	2	2	-	-	-		1	-		1	_	-	_	1	_	-	1	1	1	-
d)	1	5	4	-	1	1	2	3	2	2	_	3	1	1	-	-	-	- 1	1	-	-	***		-	-	-		-	_	-	-	1
e)	1	5	4	3	2	3	3	3	2	2	2		***	-	3	-	-	-	1	1	1	1	1	1`	1	1	1	1	-	-	-	-

- (a) Beach near Tawurwur, Rabaul.
- (b) Be .ch 2 miles North of Tawurwur, Rabaul.
- (c) Mud spring, Talasea, Uphill.
- (d) Mud spring, Pangalu, between geysers.
- (e) Lolobau, sulphur concretion in crater.

few miles apart, show a greater similarity, with a few exceptions (Ti, Ni) and traces, in one sample, of Europium, Dysprosium and Hafnium.

13. OXIDO-REDUCTION SYSTEMS

As stated above, the geothermal environment has, among the natural aqueous milieux, the greatest range in hydrogen-ion concentration and in electrode potential. This is doubtless due to the oxidation of the reduced compounds in the juvenile water or steam. As the natural occurrence of reduced compounds depends upon the pH-Eh relations in the environment, we might expect these compounds, and also the highly oxidized compounds, to occur in definite pH and Eh ranges. Figure 5 illustrates this for various reduced and oxidized compounds.

It is true that sulphur dioxide occurs in apparently juvenile steam. However, as the electode potentials of water containing SO₂ as observed by us were high, in harmony with the equilibrium potential calculated for the reactions:

$$H_2S + 2 H_2O = SO_2 + 6H^+ + 6e^-$$

and $S + 2H_2O = SO_2 + 4H^+ + 4e^-$

it follows that at lower potentials only the highest oxidation stage of the sulphur will be stable.

For a future programme of work on the hydrochemistry of the geothermal environment we need to know what substances may be expected to occur. Table 6 shows the oxidation states of eighteen elements occurring in the volcanic environment. the deepest plutonic environment it is reasonable to suppose that the elements are present at their highest reduction state. Methane and ammonia are known from such environments, but phosphine (or phosphide) is only known to occur in meteorites. This environment should also be investigated for the presence of hydrides of arsenic, antimony, bismuth, iron, boron and Of the elements themselves several have been recorded in the native state. Phosphorous seems too active a substance to occur in elemental form, but free fluorine has been claimed to occur inside crystals of fluorspar (Goldschmidt, 1954) and there is some evidence to show that certain algae prepare native bromine, while native iodine has been isolated from decaying algae.

Contrary to expectation, most of the iodine in seawater occurs as iodate (Sugawara, 1955) and iodates, and also bromates have

Figure 5: Characteristics of samples containing oxidized and reduced substances.

been reported to occur in Chili saltpetre. Recently the presence of hypochlorite in certain peroxydase systems was discovered in the human body (Agner, in litteris). Nitrous oxide was discovered in the atmosphere and later in garden soil. Hydrogen peroxide is a product of different lactic acid bacteria and in plants it is formed by oxidation of oxabic acid. It is claimed to occur in rain. This will serve to illustrate that our approach to the study of the geothermal environment has been anecdotical

TABLE 6.

rather than systematic and it is hoped that a more systematic approach will be made in the near future. This also pertains to the microbial life in this environment which has been confined, thusfar, chiefly to algae and certain selected groups of bacteria.

Since we know that the environments of many bacteria are delimited by both pH and electrode potentials, a further study of the geothermal microbes seems indicated.

Figure 5 shows the pH- \mathbb{E}_h characteristics of samples containing SO₂, H₂S, H₂O₂ and NO₃⁻. More determinations, especially from fresh samples, will be needed.

Figure 6: Changes in pH and Eh in the environments studied.

Figure 6 shows the changes in pH and in electrode potential of the environments studied. The samples were measured at the time of collection (or soon after), again after one month and finally four months after collection. It is apparent from the figure that there are two groups of oxidation curves, one, initially more acid, shows a tendency to increase the acidity still more, while the other, already starting at a higher pH, becomes progressively more alkaline. The waters of the alkaline group are highly influenced by seawater, except for the two freshwater samples (RF) which, however, in view of their location near the ocean, could contain some seawater.

The acid group of environments contains two volcanic condensates, RV and GV. The initial increase in pH may be due to HCl, either escaping or reacting with the walls of the vessel. Apart from traces in Rab and RV, polythicnic acids have disappeared from these samples. The increase in E_h seems to consist entirely of an oxidation of ferrous to ferric iron. In this acid group of environments there are three which seem to be influenced by seawater: Rab, Pa and TO. However, volcanic influence caused an acidity sufficient for ferrous ion to go into solution. The oxidation of the iron, in the presence of sulphate, is the cause of the final characteristics. The fate of the polythionates remains to be investigated.

While working at the Division of Fisheries and Oceanography, C.S.I.R.O., the first author and Mr. D. Izard studied the electrode potential of seawater over a wide range of pH conditions, brought about by bubbling, at 20°C, carbon dioxide, nitrogen or HCl gas through the seawater. drawn line in Figure 7 represents the average of 150 samples of seawater treated in this way. It was found that in the pH range 2-6 the electrode potential stayed constant at +500 mV while, at higher pH the potential dropped ca. 60 mV per pH unit. By bubbling nitrogen through the water, a pH of 9.4 could be obtained. If seawater is an important component of a geothermal water this water will yield, on oxidation, values close to those observed for pure seawater. From Figure 7 it appears that those waters observed to have close contact with seawater show the seawater characteristics on oxidation.

Figure 7: Eh and pH for geothermal waters compared to seawater.

14. THE ORIGIN OF GEOTHERMAL WATERS.

In the preceeding sections evidence has been adduced to show that the magmatic steam, rich in chlorides and hydrochloric acid, sulphide sulphur, ammonia, hydrogen and methane, will be greatly diluted by groundwater, seawater On dilution with groundwater or with and meteoric water. meteoric water the chloride content will decrease while the sulphate will be the end product of a chain of oxidation products of sulphide: polysulphide (?), sulphur, sulphur dioxide, thiosulphate and sulphite, and polythionic acids. The ammonia will be oxidized to nitrate, some of the water to hydrogen peroxide. It may be that, as Sakai (1957) assumes, the sulphate in seawater represents an oxidation product of the reduced sulphur compounds of the magma. Seawater may mix directly with deep volcanic water and so form solutions with properties intermediate between the magmatic steam and seawater. There may be a mixing of

seawater and oxidized volcanic water and, there may be a concentration or dilution of seawater with concomitant acidification by volcanic influence. Finally, the seawater may be diluted with the diluted magmatic water.

At this place we want to point out that the completely reduced juvenile steam approaches, in its composition, that of the atmospheres of the Jovian planets. Hydrogen, methane and ammonia are apparently the chief constituents of the atmospheres of Jupiter, Saturn, Uranus, Neptune and of the Saturnian satellite Titan. The oxidized compounds in our atmosphere are typically terrestrial (Kuiper, 1951).

15. ORGANISMS.

Samples examined in the field yielded, for the heated seawater near Rabaul, bluegreen algae (Lyngbya) and the diatom Melosira (52°C at pH 5. 38). The acid springs at Dewa showed the development of the bluegreen alga Aphanocapsa (27°C at pH 1.90 - 2.11). This genus is known to occur in acid bogwater together with Desmids (Smith, 1933). Later, algal development occurred in several tubes after a month in the light, yielding the following forms:

<u>Sample</u>	T ^O at collection	pH at collection	Forms observed after a month in the light.
3012	52 ⁰	5.38	Melosira, Fragilaria, Stauroneis (Diatoms).
42	- 45 ⁰	6.50	н п
1214	49 ⁰	2.55	Aphanocapsa, cells 2-3 micron diameter
303	65 ⁰	7,13	Hyphae, perhaps an Actinomycete
307	87°	2.90	и и и п
308	910	2.95	и и и и
306	85°	4.41	и и и и
63	100?	?	Synechocystis (Bluegreen)
71	100?	4.79	Short, twisted hyphae, 1 micron wide.

From the last two samples the actual temperature could have been lower.

Cultures were made using artificial seawater and freshwater to which ammonium magnesium phosphate was added. After 2 months we observed:

No.	Medium	T ^o at collection	pH at collection	Forms observed
1413A	fresh- water	27°	1,90	Aphanocapsa, 2 species, 3 and 8 micron diam.
1414	H	270	2.11	и и и
11214	u .	49°	2.55	" 2-3 micron diameter
301	seaw.	270	8,65	Melosira sp.
3010	n	79 ⁰	5.80	Synechocystis ? 2 micron diam.
3015	11	· 37°	4.85	Melosira sp.
3016	"	71°	5.80	small bluegreen (Chroococcales)

Thiobacteria were cultured on liquid media containing 1% thiosulphate. Only sample 1212, to at collection 80°C, pH 2.61, yielded Thiobacilli. The samples may have been kept too long before attempts were made at isolation, as Kaplan (1956) reports the common occurrence of Thiobacteria in the geothermal environment of Rotarua.

Agar plates, containing ammonium-magnesium phosphate and 1% FeSO₄ were infected with a great number of freshwater samples. Only one sample, 1210, taken at the bridge crossing of the creek near the A.D.O's Office at Talasea yielded positive results. Unfortunately, the temperature and pH readings of this locality got lost. The organism obtained is a rather constant companion of the iron bacteria which develop during the oxidation of pyrite; a small <u>Torulopsis</u> - like yeast (unpublished).

Apart from the results obtained from samples 63 and 71 the data check well with those of Copeland (1936), Velasquez and Soriano (1953), and Kaplan (1956). Diatoms were found from samples the temperatures of which, when collected, ranged from 27° to 52°C. Blue green algae occur from 27° to 79°C, while the Synechocystic from sample 63 might have occurred at higher temperatures. Copeland gives for the upper thermal limit of Cyanophyceae 85°C. The Actinomycete occurred in samples with an original temperature of 65° to 91°C. We did not attempt to culture this form further. Chemo-autotrophs, needing oxygen for their

development, may be influenced by the low oxygen tension in water near the boiling point.

It should be remarked, however, that the oxidation of sulphide and sulphur to sulphate in the New Britain environment is chiefly abiological, furthered by the high temperature. This follows from the sulphate content and of the pH of condensates which, in cases, were obtained from superheated steam. A further investigation of the environment is needed to see whether the influence of organisms, as indicated by Copeland (1936) and Kaplan (1956) may be important at lower temperatures.

16. CONCLUDING REMARKS.

In this preliminary paper we have tried to sketch briefly possibilities in the chemical and biological study of the geothermal environment. We have tried to avoid, as much as possible, generalizations based upon the region studied, which is one of declining volcanic activity. In some of the foregoing sections we have already outlined a programme of study based, for the chemical work, upon the compounds known to occur (partly as laboratory products) in the oxidation series of various elements while the microbiological study should investigate the acid-tolerant and thermo-tolerant Thusfar, both the chemical and biological autotrophs. characterization of the geothermal environment contain arbitrary elements. For a wider scope, future field work should include regions in which volcanic activity is greater than what we found on the north coast of New Britain, between Blanche Bay and the Willaumez Peninsula. The region around Langila, at the west point of New Britain, suggests itself as a suitable area.

REFERENCES

- ALLEN, E.T., 1935 Geyser Basins and Igneous Emanations. Econ. Geol. 30, 1-13.
- ALLEN, E.T. and DAY, A.L., 1934 Hot Springs of the Yellow-stone National Park. Proc. Pacif. Sci. Cong. V, 3, 2275-2283.
- BAAS BECKING, L.G.M., 1956 Observations on Total Base. Roy. Neth. Ac. Sc. B 59, 408-420.
- BAAS BECKING, L.G.M., HALDANE, A.D., and IZARD, D., (1958)Perchlorate, an important Constituent of
 Seawater. Nature 182, 645-647.
- BAAS BECKING, L.G.M., KAPLAN, I.R., and MOORE, D., 1960 The Limits of the Natural Aqueous
 Environment. J. Geol., in press.
- BARTH, T.F., 1950 Volcanic geology Hot Springs and Geysers of Iceland. <u>Carnegie Inst. of Washington Publ.</u> 587, p. 174.
- BRUJEWICZ, S.W., 1955 On certain Chemical Features of Waters and Sediments in the N.W. Pacific.

 Proc. Unesco Symposium on Physical
 Oceanography, Tokyo, p. 277-292.
- CLARKE, F.W. 1916 The Data of Geochemistry, <u>U.S. Geol. Survey</u>
 <u>Bull.</u> 616, Washington, 821 pp.
- COPELAND, J.J., 1936 Yellowstone Thermal Myxophyceae. Ann. New York. Ac. Sc. 6, 1-232.
- DAY, A.L., and ALLEN, E.T., 1925 The Volcanic Activity and Hot Springs of Lassen Peak. Publ. Carnegie Inst. Washington.
- FISHER, N.H., 1939 Report on the Volcanoes of the Territory of New Guinea. <u>Territory of New Guinea</u>
 <u>Geol. Bull. No.2. Govt. Printer,</u>
 Canberra, 23 pp.
- FISHER, N.H., 1957 Catalogue of the Active Volcanoes of the World, including Solfatara Fields. Part V. Melanesia. <u>Intern. Volcan. Assoc.</u>
 Naples. 105 pp.
- FOSHAG, W.F., 1950 The Aqueous Emanations from Paracutin Volcano. Am. Mineral. p. 749-755.
- GOLDSCHMIDT, V.M., 1954 Geochemistry. Oxford, Clarendon Press, 730 pp.
- HARVEY, H.W., 1945 Recent Advances in the Chemistry and Biology of Seawater. Cambridge, Univ. Press, 164 pp.
- KAPLIN, I.R., 1956 Evidence of Microbiological Activity in some of the Geothermal Regions of New Zealand.

 N.Z. Journal of Science and Technology, 37, 639-662.

RAFERENCES CONTINUED:

- KIMURA, K., 1953 On the Utilization of Hot Springs in Japan. Proc. Pacif. Sci. Cong. VII. Vol. II Wellington, H.H. Tombs Ltd., p. 500-505.
- KUIPER, G.P., 1951 The Atmospheres of the Earth and Planets. Univ. of Chicago Press. 434 pp.
- MACLAURIN, J.S., 1911 Occurrence of Pentathionic Acid in Natural Waters. Proc. Chem. Soc. 27, 380-390.
 - REYNOLDS, M.A., 1954 An Examination of Thermal Areas at Garua Harbour, New Britain. Bur. Min. Resour. Aust. Records 1954/63 2pp. 3 maps.
 - REYNOLDS, M.A., and BEST, J.G., 1957 The Tuluman Volcano, St. Andrew Strait, Admiralty Islands. Bur. Min. Resour. Aust. Report No.33, 38 pp.
 - SAKAI, H., 1957 Fractionation of Sulphur Isotopes in Nature.

 Geoch. et Cosmoch. Acta 12, 150-169.
 - SMITH, G.M., 1933 The Fresh-Water Algae of the United States McGraw-Hill, New York 716 pp.
 - SUGAWARA, K., 1955 The Distribution of some Minor Bio-Elements in the W. Pacific Waters. <u>Froc.</u> Unesco Symposium on Physical Oceanography, Tokyo, p. 168-174.
 - VELASQUEZ, G.T., and SORIANO, D., 1953 The Ecology of the Phillipines, p. 202-203.
 - TAYLOR, G.A., BEST, J.G., and REYNOLDS, M.A., 1957 Eruptive Activity and Associated Phenomena, Langila Volcano, New Britain. Bur. Min. Resour. Aust. Report No. 26, 53 pp.
 - WARING, G.A., 1953 The Occurrence and Distribution of Thermal. Springs. Proc. Pacif. Sci. Cong. VII, Vol. II. Wellington, H.H. Tombs Ltd., p. 439-448.
 - WHITE, D.E. SANDBERG, C.H., and BRANNOCK, W.V., 1953 Geochem. and Geophys. Approaches to the Problem of Utilization of Hot Spring Water and Heat. Proc. Pacif. Sci. Cong. VII, Vol. II Wellington, H.H. Tombs Ltd., p.496-500.
 - WILSON, S.H., 1941 Natural Occurrence of Polythionic Acids.

 Nature 148, 502-503.
 - WILSON, S.H., 1953 The Chemical Investigation of the Hot Springs of the N.Z. thermal Region. Prof. Pacif. Sci. Cong. VII, Vol. II, Wellington, H.H. Tombs Ltd., p. 449-459.
- ZELENOV, K.K., 1958 On Iron in Solution carried into the Okhotsk Sea by the Hotsprings of Ebeko Volcano. (Russian). Rep. Ac. Sc. U.S.S.Z., 120, 1089-1094.

Place Locality		Environment	Remarks			At collection		Afte on 1 mc			After 4 mo.	((parts per million) Acid									***************************************				
					T ^O C	Hq	Eh	рН	Eh	рН	Eh	Cl-	so ₄ =	Tot. F	e SiO ₂	NH ₄ +	NO ₃ -	10 ⁻³	H ₂ S	SO ₂ polythi Cl ₂ onic acids	C10 ₄	В	H ₂ O ₂	T ype	No.	Oxidiz-
Talasea Near	, . 	hot spring near beach	steaming	121	99	4.11	+530	3.49	+568	3.45	+716	7,600	260		2.2	2				tr			·····			ability
A.D.C.		11 11	"	122	97	3.50	+516	3.91	+584	3.23	+739	6,500	220		2.2	2				31					121	+186
Office		11 11	17	123	101	4.58	+87			5.71	+655	14,000	440		6.1	3									122	+223
	Between wharf	11 11	slightly turbid	124	95	6.47	+420	5.18	+405	3.00	+774	17,300	2600		6.8	2							tr		123	+568
	and	11 11	11 11	125	100	5.1 8	+405	5.08	+514	3.28	+775	11,400	550	.01	6.4	8									124	+354
	mouth of Creek (N).	11 11	11	126	100	6.35	+315	5.55	+478	3.83	+741	10,400	70	0	5.7	8							tr	SV	125	+370
		H H	11 11	127	100	4.99	+395	4.95	+462	3.61	+727	11,900	1100	.01	.6	2				•				SV	126	+426
		11 11	11 11	128	97	5.95	+357	6.10	+452	5.01	+603	10,600	800		5.9	0				ł		1	3	SV	127	+332
		hot spring in the surf	steamy	129	100	4.80	+370	5.22	+463	2.49	+766	4,900	550		5.3	2								SV	128	+246
	E. of wharf	hot spring near beach		1216	96	4.36	+280	4.59	+496	3.82	+461	13,600	170	10	6 .1	0								SVGO	129	+396
	uphill	hot spring		1211	71	2.20	+457	2.12	+648			56	2800	10	5 . 2			17						SV 12	216	+181
	11	11		1212	80	2.61	+515	2.68	+750			10	300	5	5.2	4		5				tr		GVO 12	211	
	11	11		1213	85	2.70	+365	2.92	+660	2.40	+668	20	300	5	5.2	2		<i>J</i>						GVO 12	212	
· -	n	11	cool	1214	49	2.55	+595	3.60	+465			5	2800			_		4+					1	GVO 12	213	+303
	near A.F.O.	mud spring		1215	99	3.60	+465			2.85	+796													GVO 12	114	
	H	condensate from hot		1217	100	3.61	+135	5.38	+408	4.45	+525	15	40	.01		Λ								12	15	+331
Pangulu	near beach	spring hot spring near beach		132	92	2.46	+349	2.36	+604	2.81	+731	520	700	1.0	1.2	2		r-						GV 12	17	+390
	H	li li		133	92	2.22	+565	2.77	+540	2.86	+766	580	7 00		1.2	2		5		tr	3			GVO 1	32	+382
i :	Geyser field	Geyser No.1		134	96	2.24	+460	2.28	+658	2.35	+753		008		4 0	6)			3	tr		GVO 1	33	+201
		Geyser No.1		135	96	1.40	+460	2.28	+680	2.41	+738	10,400	1500			10					2		tr	SVO 1	34	+298
		Geyser No.II		· 136	101	3.42	+170	3.80	+578	3 . 89	+678	18,500	110		1.2	2					3			SV 1	35	+278
		Geyser No.II		137	101	3.41	+256	4.30	+455	4.07	+625		170		1.3	<u>د</u> ۸					3		tr	SV 1	36	+508
		hot spring ,S.E.of æyse	ers	138	100	• 95	+593	1.82	+686			340	2100 1		1.2	4		5.0			3		tr	SVO 1	37	+369
		" "		139	100	1.60							2800 1		1.0	4		52			1		tr	GVO 13	38	
		11 11		1310	95				+652	1.80	+601		3100		1 • U	(62			1			GVO 13	39 -	÷154
		11 11		1311					+454	3.14		25				b O		57			2			GVO 131	0 -	+312
		mudspring S.of geysers	į			2.62				- '		-		• '		2					1			GV 131	1	
~		hotspring between deyser	1	1313				5.42	+566	3.89	+505	100	80 .0)1	0	0								131	2	
-	mear beach	hot spring		1314	-				+392	7.00	+503		3000 .0		0	2					0			G V 131	3 +	-186
		"		1315	92	6.60	+160		+397	6.70	+504		2200 o) 	1.0	1					4			SVO 131		-258
		I							・ファー an in	J• 1 U	· / / · · · · · · · · · · · · · · · · ·			-	5.8	2			1		1			SVO 131		

TABLE C - GARBUNA WALO.

Place Locali	Locality	Environment	Remarks	At collection		ion	After 1 mo.		After 4 mo.		(parts per millio		ion)	on)				Qualitative tests							
				No.T ^O C			рН		рН	Eh	Cl_	$SO_A =$	Tot. Fe	si0 ₂	NH ₄ +	NO_3^{-1}	10 ⁻³	H ₂ S	\$02 polythi Cl			H ₂ O ₂	T ype	No.	Oxidi:
Garbuna	Kilu village	hot spring near beach	steaming, turbid	141 67	6.21	+295	6.39	+353	6.11	+453	2.85	0 2200	0	0	2	· · · · · · · · ·		-	oni: acids			<i>د</i> د			abilit
	Dewa	acid spring	cool	142 29	2.22	+100	2,62	+486					5.0				1]		2	. 1		SVGO	141	+158
	11	11	11	143 26					1.50	+717			10.0	10.1	0	<u>5</u>		1		0			GVO	142	Paramananan ()
	tt	11	11	144 27								1900	· · · · · · · · · · · · · · · · · · ·	1.0	0		8	2		1			GVO	143	+617
	Garbuna crater	vents, condensates		145 99					2 31	±605				5.0	0		9	2		1	tr			144	
	11	!!		146 99							-	·····	1.0		·									145	+420
	11	II .		147 98									1.0	5.0	2	-	: :			1			GVO	146	+432
	11	II .		148 98							<u> </u>	5 400	.1	5.0	2		1			1			GVO		
	11		<u> </u>	· · · · · · · · · · · · · · · · · · ·							2() 440	. 1	5.0	1					1			···		+428
	II .	li li	1	149 99							13	30	0	0	2		:	1		2			GV		+550
	11	hot apping is another	1	1410 99							18	3	0	0	2		39	1		0					
	11	hot spring in crater	1	1411 98			1.80	+646	1.70	+755	40	2500	5.0	5.1	0					1	····				+265
			<u>.</u>	1412 99				····					5.0	5.4	0		:				4		GVO		+502
	TI .	"		1413 89	2.11	+385			1.32	+665	20	560	5.0	5.2	0		27	······································		! 	tr			1412	
	Dewa.	acid spring	cool	1414 27			·					220			2						tr	tr	··-·	1413	+280
alo			steaming, turbid	151 56	6.83	+373	6.82	+453			6,500	100	1	······································	2		:			<u> </u>	·		GVO	1414	
	11	muddy hot spring		152 100	6.53	+345	6.38	+462			7,400	80	·	5.5	- 					4	2	-	SV	151	
	21	!!		153 97	6.60	+33	4.99	+477			220	100	10	10 4		40	£ ^{3,575}			3	3	· · · · · · · · · · · · · · · · · · ·	SVGO	152	
	11	mudspring		154 101	7.95	- 73							1 ()	10.4		10				Û			Ğ.V	153	-
	14	mudspring			6.92	+175	6.70	+328					+		1	10		1		С				- 154	
	Planet Bay	hot spring near beach	steaming	156 92	5.15	+26	6.03	+489			17 700	1500	tr.	6.6	· · · · · · · · · · · · · · · · · · ·			1		0	tr			155	
	11	11 11	"	157			· · · · ·	1403	7 1 4	: 467	17,100	1500	.07	·						4	tr		SV	<u>156</u>	7.7
			!		···				7.14	+40/		1900	.01			0				1			UTT	4 = = =	-