72/71

Internal Use Only

COMMONWEALTH OF AUSTRALIA

DEPARTMENT OF
NATIONAL DEVELOPMENT

BUREAU OF MINERAL
RESOURCES, GEOLOGY
AND GEOPHYSICS

Record 1972/71

Not for loan outside B.M.R.
or to be shown to Outsiders

IRON SULPHIDE FORMATION IN A THERMAL POOL ENVIRONMENT, TALASEA, NEW BRITAIN, P.N.G.

by

J. Ferguson,[1] I.B. Lambert,[2] and H.E. Jones[2].

1. Bureau of Mineral Resources, Geology and Geophysics;
2. Division of Mineralogy, C.S.I.R.O.

Record 1972/71

IRON SULPHIDE FORMATION IN A THERMAL POOL ENVIRONMENT, TALASEA, NEW BRITAIN, P.N.G.

J. Ferguson,[1] I.B. Lambert,[2] and H.E. Jones[2].

1. Bureau of Mineral Resources, Geology and Geophysics;

2. Division of Mineralogy, C.S.I.R.O.

ABSTRACT. Concentrations of iron sulphide minerals have been located in sediments within and adjacent to a small thermal pool near Talasea township.

A thermal spring is discharging at a moderate rate into the bottom of the pool. The reducing sediments in the pool are enriched in black, amorphous hydrotroilite (approximately FeS) and do not contain much pyrite. In contrast, the more oxidizing sediments of the pool banks contain considerable amounts of pyrite and marcasite; the marcasite appears to be replacing its dimorph.

Geochemical, mineralogical and bacteriological studies have been undertaken to investigate details of the origin, distribution and morphology of the various iron sulphide minerals in this miniature volcano-exhalative-sedimentary environment.

INTRODUCTION

Talasea township is situated on the Talasea (or Willaumez) Peninsula, on the island of New Britain, P.N.G. This peninsula is characterized by a number of thermal fields, which are vestiges of Quaternary volcanism (Fisher, 1939; Reynolds, 1954; Heming and Smith, 1969).

We have discovered abundant iron sulphides in sediments within and around a small intertidal thermal pool on the Talasea foreshore, 380 metres west-southwest of the sub-district office. The pool appears to provide, on a small scale, the main features of a volcano-exhalative-sedimentary environment.

In this paper we discuss the results of geochemical, mineralogical and bacteriological studies which were undertaken to determine the nature, origin, distribution and morphology of these iron sulphide minerals.

THERMAL POOL AND ENVIRONS

The Talasea thermal field includes a thin coastal strip, some 800 metres long, where hot waters and vapours rise through altered andesite lava that is overlain in most places by beach or marsh deposits. The iron sulphide bearing thermal pool is towards the western end of this area.

Figures 1A and 1B show plan and section views of the thermal pool. It is located on salt marsh flats at the landward end of a tidal inlet which extends for a distance of about 20 metres inland from high tide mark on the adjacent beach. At high tide the inlet is flooded by seawater but at low tide the exposed pool is about 4 square metres in area and a maximum of 0.7 metre deep. The pool is fed mainly by a moderately flowing (about 100 l/hour) thermal spring which discharges below the low tide level. A small tributary stream whose source is exposed at low tide also flows into the pool.

The uppermost sediments within the pool consist of several centimetres of greyish brown silty muds containing a small proportion of sand-sized grains. Under this layer is a loosely compacted black mud which persists to at least 20 cm, the maximum depth sampled. The colour of this sediment changed

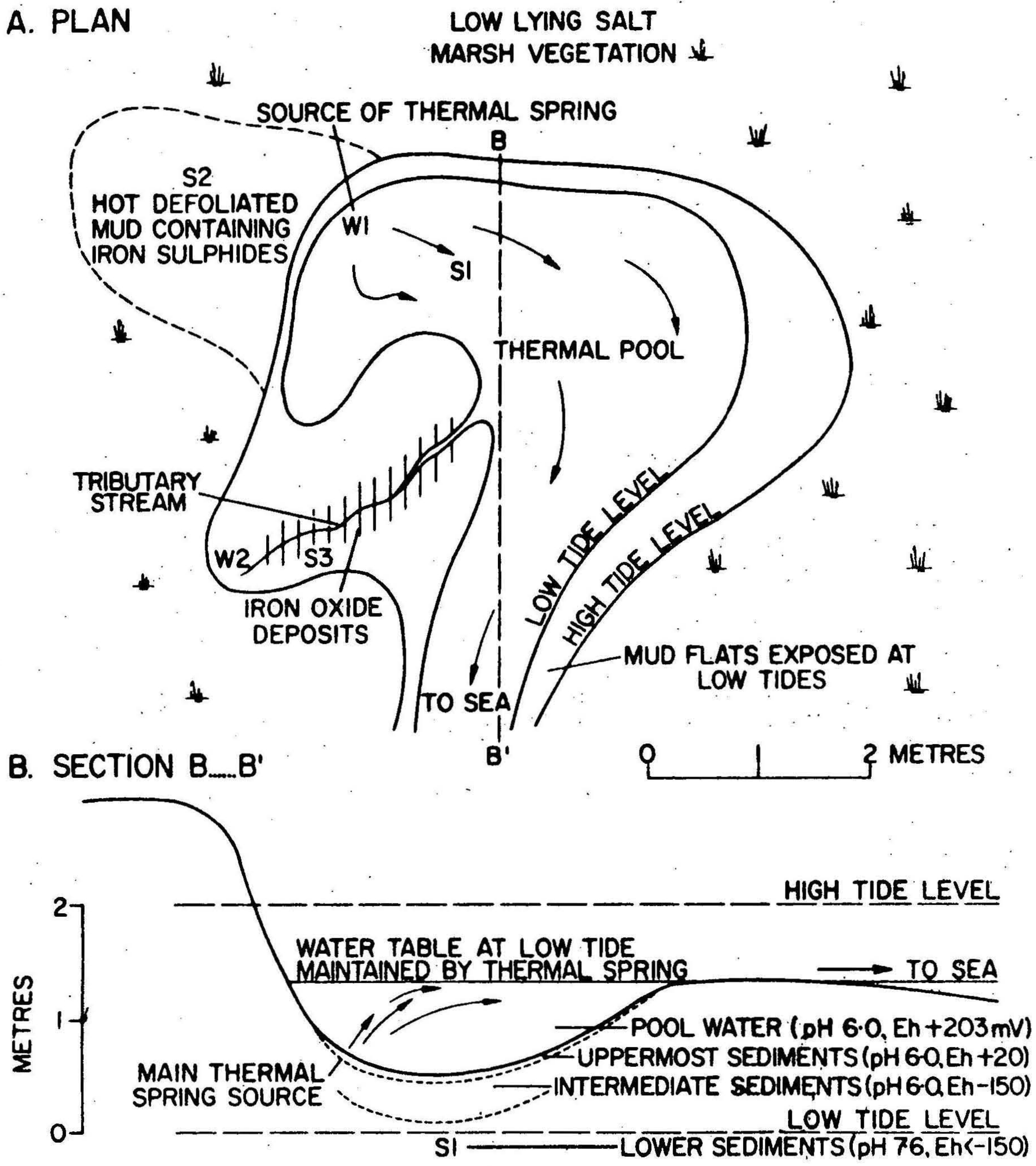


FIGURE I. PLAN AND SECTION VIEWS OF THE IRON SULPHIDE-BEARING THERMAL POOL AT TALASEA

To Accompany Record 1972/71 *P/A/371*

rapidly to reddish-brown on exposure to the air. Sediments in the tidal inlet downstream from the pool are less flocculant and consist of a thin surface layer of red-brown silt underlain by grey or dark-grey bands of sand and silt.

The pool banks are heavily vegetated on two sides and the third is a hot, defoliated area of grey mud superficially discoloured by iron oxide stains. This mud contains, in some places, abundant pyrite and marcasite which is present mainly in horizontal bands, but also occurs in cross-cutting bands and as dispersed grains.

Small deposits of iron oxides occur on the banks of the tributary stream but elsewhere surface iron oxides are minor.

SAMPLING

Collection of water and sediment samples and *in situ* measurements of temperature, pH, and Eh were carried out at low tide at the locations shown in Fig. 1A.

Samples of water (W1) and black sediment (S1) were collected from the thermal pool and a 28 cm-long core (C3) from the bed of the tidal inlet, 10 metres downstream. Sample S1 separated into mud and supernatant water after collection. Water (W2) and iron oxides (S3) were obtained from the tributary stream and a sample of sulphide-rich mud, containing a portion of a horizontal band, from the pool banks (S2).

Additional water and sediment samples were collected at locations W1 and S1 and tested for the presence of sulphate-reducing bacteria.

RESULTS

1. *pH, Eh and Temperature of Waters and Sediments (Table 1)*

Waters in the thermal pool and tributary stream are warm, slightly acid, and oxidized. Post-collection increases in Eh of the samples indicate they are not in equilibrium with atmospheric oxygen.

The top 3 cm of sediments in the thermal pool are also slightly acid but are less oxidized than the overlying waters. Beneath this (down to at least 7 cm) conditions remain slightly acid but are reducing. Sample S1, which was collected from greater than 10 cm deep in the pool sediments, is reducing but its pH is close to that of normal seawater.

Mud from the pool banks (S2) was strongly acid 2-3 weeks after collection.

2. *Chemical Compositions of Thermal Waters (Table 2)*

The thermal spring and tributary stream waters have salinities approximately one third and one quarter respectively, that of normal seawater. Their Br/Cl ratios and, to a lesser extent, B/Cl, K/Cl, and Na/Cl ratios are similar to those of normal seawater, but other ion ratios are markedly different. So_4/Cl ratios are <u>low</u> relative to seawater.

Pool and tributary stream waters are, in general, similar in chemical composition. Their K/Cl, Mg/Cl, Br/Cl, B/Cl and K/Na ratios differ by less than 10% and their Na/Cl, SO_4/Cl, Ca/Na and Mg/Ca ratios differ by factors of two or less. In contrast, although the Mn contents of the two waters are similar, the Fe/Mn ratio of the thermal spring waters is less than one tenth that of water from the tributary stream. Both water samples contain trace quantities of zinc, copper and lead.

Supernatant water from the pool sediment sample S1 has a specific conductance of 45,800 micromho.cm^{-1}, which is similar to that of normal seawater.

3. *General Chemical Compositions and Mineralogies of Sediments (Tables 3 and 4).*

Sand and silt samples from non-thermal areas of the foreshore near Talasea are essentially reworked volcanic fragments of average intermediate composition.

Sediment from the bottom of the thermal pool has generally similar major element chemistry to sediments from the pool banks. Compared with the beach sediments from outside the thermal field, both have much higher losses on ignition at 900°C (mainly sulphide, water and organic matter), higher Fe, and lower Ca and Mn contents.

Organic carbon contents of sediments from the thermal pool (3.6%) and downstream (0.43 - 1.51%) are high, due mainly to introduction of plant debris, but sample S2 from the hot defoliated area of the pool bank contains only 0.3%.

Sediments remote from thermal activity contain pyroxenes feldspar, and quartz, with lesser amounts of calcite, magnetite and glass shards, but sediments associated with the thermal pool banks consist mainly of clays (predominantly montmorillonite), quartz, amorphous shards, and iron sulphides or oxides.

4. *Iron and Sulphur Species of Sediments (Table 4)*

a) Thermal Pool

The pool sediments contain 1-2% pyrite which is present mainly as small spheroids and framboids typically with diameters in the range a few microns to about 20 microns. A minor proportion of the grains have poorly defined crystal faces.

Treatment of the black mud S1 with cold 1N HCl changed its colour to brown, H_2S was evolved, and Fe, equimolar to the acid soluble sulphide liberated by boiling the sample with 1N HCl, was taken into solution. This strongly suggests that the black colour of the sediments is due to the presence of hydrotroilite which is shown by analysis to make up about 5% by weight of the dry sediment. Neither mackinawite or greigite could be detected by X-ray diffraction.

Most of the remaining Fe is present in the clay minerals. Treatment of a cold 1N HCl-leached portion of the sediment with hot 1N HCl and then with boiling 12N HCl separates this Fe into a "hot 1N HCl" fraction and a "boiling 12N HCl" fraction of 1.9% and 1.6% respectively.

Total dissolved sulphide concentrations in the sample of thermal pool mud and supernatant water were 16 and 4 ppm respectively when measured 2-3 weeks after collection. However, data given in Table 1 are consistent with the formation of sulphide in the sample after collection and these values are unlikely to be reliable guides to total dissolved sulphide concentrations *in situ*.

The small amount (0.026%) of elemental sulphur detected in a hot 1N HCl-leached portion of the sample may have been released from sulphur-bearing organic matter during preliminary acid treatment (see Methods).

Experimental diagenesis of sample S1 (Table 5). To define the factors controlling the relative proportions of the various iron sulphide minerals in the pool sediments, the reactions of sample S1 with a limited supply of air, excess elemental sulphur, and excess H_2S were examined. The conditions chosen (see Methods section) approximate those used in experimental studies of iron sulphide formation (Berner, 1970a; Rickard, 1969; Roberts, Walker, and Buchanan, 1969).

The amounts and types of iron sulphide minerals in sample S1 remained essentially unchanged after heating a portion of the sample in the presence of seawater in a nitrogen atmosphere for 17 days at 65°C.

In the presence of excess elemental sulphur, and in a nitrogen atmosphere, the hydrotroilite content of the sample was reduced almost to zero and its pyrite content increased markedly. Also, the "boiling 12N HCl" Fe fraction in the clay minerals decreased from 1.6% to zero.

Heating the sample at 65°C for 17 days in the presence of seawater and a limited supply of air converted the hydrotroilite to ferric oxides and pyrite, the amount of pyrite being considerably less than formed in the presence of excess elemental sulphur. Marcasite and elemental sulphur were not detected, but may also have been present in small amounts. The amounts of Fe in the HCl-soluble Fe fractions associated with the clay minerals remained essentially unchanged.

A hydrotroilite-free portion of the sample, prepared by shaking it with cold 1N HCl, was heated at 55°C for 30 minutes in the presence of excess H_2S. Under these conditions 1.9% Fe in the clay minerals was converted to hydrotroilite.

b) Thermal Pool Banks (S2)

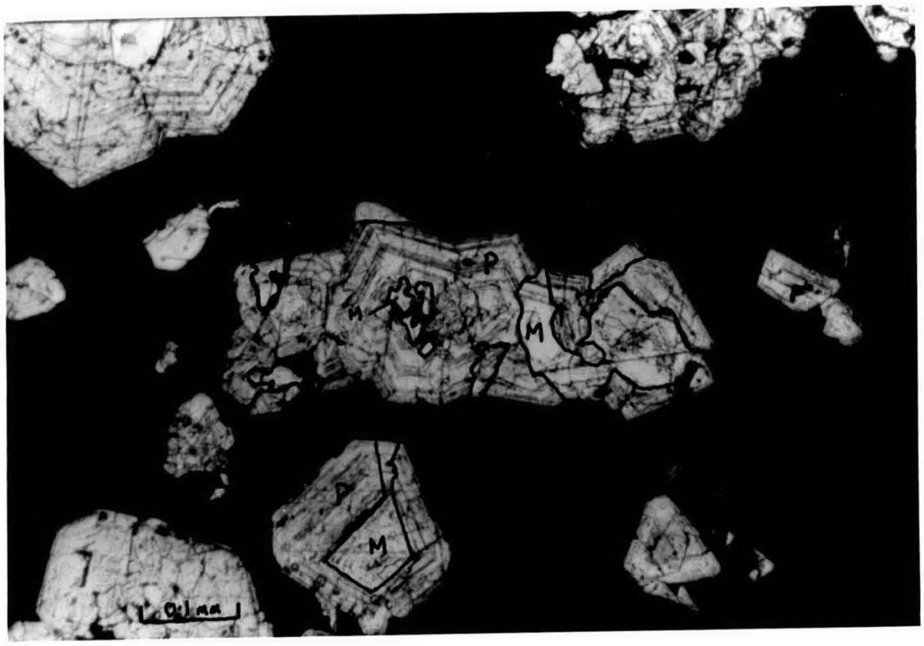
Pyrite and marcasite are the dominant iron minerals on the pool banks where they occur in concentrations of 5-10% overall.

Most of the pyrite is slightly anisotropic. It usually has good crystal outlines, displaying in most cases pyritohedral faces. Simple cubic crystals are rare. The maximum grain size is about 0.75 mm and the mean is about 0.2 mm. Etching with 1:1 HNO_3 reveals numerous concentric zones within the pyrite crystals, and many of the larger grains are shown to consist of coalescing smaller grains (Plate 1).

Patches of marcasite are common within the pyrite grains and in some cases marcasite has completely replaced pyrite. The marcasite, which constitutes about 40% of iron disulphides in the pool banks, is mostly twinned but not usually zoned. It generally cuts across pyrite zoning (Plate 1).

Insufficient sample was available for an acid soluble sulphide determination, but the value of 0.56% Fe extracted by cold 1N HCl places an upper limit of about 1% on its hydrotroilite content. It is likely that the actual hydrotroilite content is much less as there was no significant colour change or evolution of H_2S when cold 1N HCl was added to the sample.

Plate 1 Composite, zoned pyrite crystal containing unzoned, cross-cutting marcasite. P = pyrite. M = marcasite. Etched with 1:1 HNO_3 for 1 minute.



Microscopic examination indicates that significantly greater amounts of iron oxides are present in sample S2 than are present in sediments within the thermal pool. The 0.56% Fe leached from the bank sediments by cold 1N HCl is probably derived from these oxides.

The elemental sulphur content of the pool bank sediments (0.27%) is at least ten times that of sediments in the thermal pool itself. Also, it is noteworthy that the mole ratio of cold 1N HCl-soluble Fe to elemental sulphur in the pool banks is approximately 1:1.

The "hot 1N HCl" and "boiling 12N HCl" Fe fractions of 1.6 and 0.2%, respectively, are comparable to those of the pool sediment sample S1 after reaction with elemental sulphur.

c) Iron oxide Deposit from the Tributary Stream (S3)

Sample S3 contains 14.6% Fe, mainly as amorphous iron oxides. A significant amount of elemental sulphur and a trace of pyrite were found, but hydrotroilite was not detected.

d) Downstream From Thermal Pool (C3)

The total Fe contents of the 0.3-13 cm and 17-28 cm layers of sediments 10 metres downstream are considerably lower than those of sediments from within the thermal pool and adjacent banks, and are similar to those of sediments from non-thermal areas. The intermediate (13-17 cm) layer has a significantly higher total Fe content.

About 0.5% pyrite is present in the 17-28 cm layer but the two upper layers contain only traces of sulphide. There is no evidence of hydrotroilite in any of the layers.

Microscopic examination indicated that the iron oxide contents of all three layers are higher than those of sediments from within the thermal pool. This is reflected by their relatively high cold 1N HCl-soluble Fe contents.

5. *Bacteriological Studies*

Five media were used per sample. Medium 1 was the complete growth medium for sulphate-reducing bacteria and contained K_2HPO_4, 0.5 g; NH_4Cl, 1 g; Na_2SO_4, 1 g; $MgSO_4.7H_2O$, 2g; NaCl 25g (optional - see Methods); $CaCl_2.2H_2O$, 0.1 g; sodium lactate, 3.5 g; yeast extract, 1 g; distilled water 1 litre. Medium 2 (medium 1 minus yeast extract and sodium lactate) was designed to show the ability of the sample to provide organic matter for growth of sulphate-reducing bacteria. Medium 3 (medium 1 minus the sulphate content) was designed to show if sufficient sulphate was present in the sample to support growth of sulphate reducing bacteria. Medium 4 (medium 1 minus yeast extract, sodium lactate and the sulphate content) was used to indicate if hydrogen sulphide was produced from the sample without added organic matter and sulphate. Medium 5 (medium 1 with sodium pyruvate 0.35% ($^w/_v$) instead of sodium lactate, plus 3% ($^w/_v$) agar) was used in addition to medium 1 plus 3% ($^w/_v$) agar for isolation of colonies of sulphate-reducing bacteria.

Samples W1 and S1 both showed the presence of H_2S when incubated for 1 month at 30°C with (media 1 and 3) and without (media 2 and 4) added organic matter. Further sub-culturing of the samples in medium 1 (the complete medium) resulted in a positive reaction for H_2S up to at least the third sub-culture, thus confirming that the H_2S production in these samples was a result of bacterial sulphate reduction. Additional confirmation was obtained for both samples by formation of black colonies (i.e. containing FeS) after plating out on media 1 and 5 containing ferrous ammonium sulphate.

When transferred from 30°C to 55°C, H_2S was detected after at least three sub-cultures in medium 1 and black colonies were formed on the agar media, showing that the samples contained sulphate-reducing bacteria capable of growth at 30°C or 55°C. Ideally, for isolation of bacteria capable of growth at 55°C samples should have been immediately incubated at 55°C after collection, but this was not possible at Talasea. However, despite initial unfavourable incubation temperature the samples contained sulphate-reducing bacteria which grew at 55°C. These results are similar to those found in soil samples by Butlin, Adams & Thomas (1949). Whether the 55°C cultures were strictly thermophilic or were capable of growth at 30°C was not determined. Certainly such temperature tolerance is not reported in pure cultures of sulphate-reducing bacteria, although some 30° strains have been "trained" to grow at 50° (Postgate, 1956).

The results with media 1 and 3 show that both samples contained sufficient sulphate to support the growth of sulphate-reducing bacteria.

The above results were obtained with both 5% and 95% ($^v/_v$) inocula. The smaller inoculum reduced, by about 20 times, the concentration of any materials in the sample which might have adverse effects on growth of sulphate-reducing bacteria. Conversely, the large inoculum was used to enable such effects to be apparent and also prevented dilution of any utilizable organic matter and sulphate in the sample.

DISCUSSION

1. *Thermal Waters*

The Talasea thermal pool and tributary stream waters have chemical compositions unlike those of most thermal waters (White, 1957; White, Hem and Waring, 1963). They are probably a result of complex interactions of thermal emanations with the strongly seawater-influenced coastal sediments.

Evidence for a seawater-like component is provided by the similarities of their Br/Cl, B/Cl, K/Cl and Na/Cl ratios to those of normal seawater and interstitial waters from salt-marsh and cove environments (Friedman and Gavish, 1970).

The acidity and high Fe, Mn, and trace metal contents of the thermal pool and tributary stream waters are characteristic of the "acid-sulphate"-type thermal waters which are common in inland thermal fields near Talasea (Lambert, Ferguson, and Jones, in preparation). Such waters are formed when water circulating into the volcanic pile dissolves H_2S and returns to near-surface conditions where the H_2S is being partly or completely oxidized to sulphuric acid. These waters leach the host rocks forming hot, acid waters, high in sulphate, and containing abundant Fe(II), Mn(II), and, in some cases, trace metals and dissolved sulphide.

On this basis the SO_4/Cl ratios of the Talasea thermal pool and tributary stream waters are low. Sulphate may have been removed from the waters by precipitation as calcium sulphate, or to a limited extent, by the actions of sulphate-reducing bacteria, processes which are thought to contribute to the low sulphate contents of chloride-rich brines evolved from seawater (Lerman, 1970). However, the calcium contents of the pool sediments are low and abnormally high rates of bacterial sulphate reduction would be required to account for the observed sulphate depletion. The most likely explanation is that calcium sulphate is precipitating at depths greater than those sampled.

Enrichment of the thermal pool sediments in Fe, and the presence of iron oxide deposits on the banks of the tributary stream indicate that, prior to discharge at the surface, the thermal spring waters contained considerably larger quantities of Fe than were found in the pool and stream samples. Further, the low Fe/Mn ratio of the thermal pool waters, compared to the otherwise chemically similar tributary stream waters, indicates a considerably more efficient process of precipitation in the thermal pool sediments than on the tributary stream banks, where Fe is precipitating as a result of air-oxidation of dissolved ferrous iron.

2. *Environments of Iron Sulphide Formation*

pH and Eh conditions in the pool sediments appear to be a result of the competing influences of the upwards flow of mildly acid, reducing thermal spring waters, and the seawater-like interstitial waters of the salt-marsh sediments.

Thermal spring activity is dominant in the uppermost 7 cm of the pool sediments, which are mildly acid, but at depths greater than 10 cm the pH is strongly influenced by seawater.

The Eh profile of the thermal pool sediments is similar to those of most non-thermal areas where iron sulphides are forming at the present day. However, as the thermal pool waters are not in equilibrium with atmospheric oxygen, it seems likely they are reinforcing the effects of normal oxygen-depleting bacterial metabolic processes.

Sediments on the pool banks are less directly influenced by thermal spring activity and are considerably less anaerobic than those in the thermal pool itself.

3. *Sources of Iron*

The high total Fe and low iron oxide contents of the thermal pool banks and sediments compared to sediments downstream and in non-thermal areas is evidence that a large proportion, if not all, of the Fe provided by the thermal waters is being converted to iron sulphides.

The observation that 1.9% Fe present in the clay minerals of a hydrotroilite-free sample of the pool sediments reacts with excess H_2S indicates that this Fe is a potential additional source of Fe for iron sulphide formation. Conversion of this Fe to iron sulphides has probably occurred in the pool bank sediments and in the reaction of sample S1 with elemental sulphur. In both cases the "boiling 12N HCl" Fe fraction is small.

The considerably higher "boiling 12N HCl" Fe fraction in the pool sediments, combined with the presence of excess H_2S in the pool sediment sample 3 weeks after collection, indicate that this Fe is, however, relatively inert towards H_2S under conditions in the pool sediments. This may be an effect of coatings of hydrotroilite on the clay grains.

4. *Sources of Sulphide*

Sulphate-reducing bacteria capable of growth at 55°C are present in the thermal pool waters and sediments; the latter are not in themselves toxic towards bacteria, and both contain sufficient sulphate for bacterial growth. However, there is no direct evidence that these bacteria are producing sufficient sulphide to contribute significantly to the overall rate of iron sulphide formation.

The rates of sulphide precipitation and the overall sedimentation rate (iron sulphides plus detritus) in the thermal pool can be calculated from the discharge rate and Fe content of the thermal spring waters, and the iron sulphide content of the sediments. If it is assumed that, prior to iron sulphide precipitation, the Fe/Mn ratios of the thermal pool and tributary stream waters were equal, then the initial and final concentrations of Fe in the thermal spring waters would be 0.5 and 0.04 ppm, respectively. On this basis sulphide is precipitating at the rate of 50 $g\ S\ m^{-2}\ yr^{-1}$ and the overall sedimentation rate in the thermal pool is approximately 1 cm per 5 years. This rate of sulphide production is within the range of values for bacterial sulphate reduction in natural environments quoted by Trudinger, Lambert, and Skyring (in press) but is above average (16 g S m^{-2} yr^{-1}).

Further, the organic carbon to sulphide ratio in the pool sediments ($^w/_w$) is 1.3 which is considerably lower than the value of about 3 found for the top 2 cm of sediments from the Connecticut coast. In these latter sediments the rate of pyrite formation is controlled by the rate of bacterial sulphate reduction which is, in turn, limited by the concentration of organic carbon (Berner, 1970a).

It seems unlikely, therefore, that bacterial sulphate reduction could be the sole source of sulphide in the thermal pool. Although there is no direct evidence that the thermal pool waters contain significant quantities of volcanically derived sulphide, the thermal pool lies on the fringe of the most active area of the thermal field which is characterized by the presence of boiling mud pools, small steam vents, and a strong smell of H_2S.

The above considerations suggest that volcanically derived sulphide makes the major contribution to iron sulphide formation in the thermal pool, with bacterial sulphate reduction perhaps playing a secondary role.

5. *Formation of Iron Sulphides*

Considerable information on the mechanisms of formation of iron sulphides is available from experimental studies (e.g. Berner, 1970a; Roberts, Walker, and Buchanan, 1969; Rickard, 1969) and most of the present data can be readily interpreted on this basis.

The majority of hydrotroilite in the thermal pool sediments appears to have formed by the direct reaction of ferrous ions dissolved in the thermal spring waters with dissolved sulphide of bacterial and/or volcanic origins. In the latter case hydrotroilite would be precipitated in response to higher pH and lower temperature conditions in the seawater-influenced near-surface sediments.

The high hydrotroilite to pyrite ratio in the thermal pool sediments is unlikely to be due to a rapid rate of hydrotroilite formation, as pyrite forms rapidly from hydrotroilite plus elemental sulphur at temperatures near those of thermal pool waters (Berner, 1970a). The experimental diagenesis results indicate that, in agreement with previous experimental work (Berner, 1970a; Roberts, Walker and Buchanan, 1969), the reaction is being inhibited by a scarcity of oxygen, elemental sulphur, or other oxidizing agent in the pool sediments. This is almost certainly a result of the upwards flow of anaerobic thermal spring waters which effectively minimise downwards diffusion of oxygen from the atmosphere or overlying seawater. The small amounts of pyrite which do occur in the pool sediments are probably formed by the reaction between hydrotroilite and elemental sulphur produced by oxidation of dissolved sulphide, the most readily oxidizable of the sulphide species in the pool sediments.

The pyrite (plus marcasite), minor iron oxides and elemental sulphur in the pool bank sediments seem to have formed by oxidation of hydrotroilite under more aerobic conditions than exist in the pool sediments. This is suggested by the approximately

1:1 molar ratio of cold 1N HCl-soluble Fe to elemental sulphur in the pool bank sediments, and the formation of iron oxides and additional pyrite when a sample of the pool sediments was heated in a limited supply of air.

Much of the marcasite in the pool bank sediments occurs within pyrite crystals. Its occurrence in irregular patches which cut across the concentric zones in the pyrite crystals suggests that it is replacing pyrite. Incipient formation of marcasite could possibly account for the anisotropism in the pyrite.

6. *Comparison with Other Environments of Iron Sulphide Formation*

In the Talasea thermal pool sediments it is likely that, as a result of the availability of volcanically derived sulphide, the amount of Fe supplied by the thermal springs limits the rate of iron sulphide formation. In most non-thermal areas H_2S-reactive Fe is in excess and iron sulphide formation is controlled by the rate of bacterial sulphate-reduction, which in turn can be limited by the amount of organic carbon (Berner, 1970a) or the amount of sulphate (Berner, 1970b) available in the sediments.

Iron sulphide concentrations in the Talasea thermal pool banks and sediments are significantly higher (5-10%) than those found in non-thermal sediments (1-5%; Roberts, Walker, and Buchanan, 1969) but are limited to the immediate vicinities of thermal springs. The development of much higher iron sulphide concentrations in the thermal pool appears to be inhibited by the high sedimentation rate (1 cm/5 years), a factor known to limit concentration of metals in the volcano-exhalative-sedimentary environment at Matupi Harbour (Ferguson and Lambert, 1972).

In most areas of iron sulphide formation, including euxinic basins, incomplete conversion of hydrotroilite to pyrite is relatively rare (Berner, 1970a). A notable exception is the Black Sea where a few hydrotroilite-rich bands are present in the sedimentary sequence. It has been suggested (Berner, 1970b) that they reflect a deficiency of sulphide in the environment during their formation. In the Talasea thermal pool sediments the persistence of hydrotroilite in the presence of excess sulphide appears to be a result of inhibition of normal air-oxidation of excess sulphide by the uprising thermal spring waters. "Amorphous iron sulphides" are probably present in the sulphide facies of sediments from the Atlantis (II) Deep in the Red Sea (Bischoff, 1969).

Marcasite is present in significant quantities in the thermal pool banks but has not been recorded from Recent Sediments in non-thermal areas. It is, however, present in mud samples from the Atlantis (II) and Discovery Deeps in the Red Sea where it occurs as euhedral plate or lath-shaped crystals (Stephens and Wittkopp, 1969).

Most pyrite and marcasite in the Talasea thermal pool banks occur as large euhedral crystals providing a marked textural contrast with the finer-grained framboidal pyrite found in the thermal pool sediments, and in most non-thermal areas (references in Rickard, 1970).

CONCLUSIONS

From the above discussion and results it appears that the chemical reactions responsible for iron sulphide formation in the Talasea thermal pool are basically similar to those responsible for iron sulphide formation in non-thermal sediments. However, the availability of volcanically derived Fe and sulphide, combined with the complex environment produced by interactions of thermal spring waters with the intertidal sedimentary environment has introduced several features which contrast markedly with non-thermal areas. The development of high iron sulphide concentrations is probably the most significant of these features and underlines the potential of such "volcano-exhalative-sedimentary" environments for the formation of metal sulphide ore deposits.

METHODS

1. *Geochemical and Mineralogical Investigations*

pH and Eh.

Measurements were made with a "Metrohm" Battery pH meter E250A and combination electrodes standardized immediately before use with buffer solution pH 7.0 or Zobell's (1946) solution. *In situ* measurements were made by inserting the electrodes directly into the pool waters and sediments.

Sample Collection.

Water samples were collected with an all plastic hand pump. A duplicate sample of water from the main pool was filtered hot through a Whatman No. 54 (acid-hardened) filter paper.

Sample Storage.

Facilities for on site determination of readily oxidizable sulphide species were not available and a delay of 2-3 weeks between sample collection and analysis necessarily occurred. The precautions described below were designed to minimise post-collection oxidation of the samples.

Water samples were stored in polythene containers filled right to the top and rendered air-tight by screwing down the caps over a thin layer of polythene sheeting. Significant increases in the Eh of samples W1 and W2 occurred after collection so their total dissolved sulphide and ferrous iron contents were not determined. Inspection of the samples prior to analysis showed that sample W2 and the filtered portion of sample W1 were free of precipitated ferric oxides. Trace amounts were present in the unfiltered portion of sample W1 and subsequent analysis confirmed that it was slightly depleted in dissolved Fe (but not in trace metals) compared to the filtered portion.

Black, sulphidic mud from the thermal pool (S1) was stored in a screw-top "polycarbonate" bottle sealed with adhesive tape. When opened 2-3 weeks later the sample contained detectable quantities of dissolved sulphide (Table 1) which suggests that only limited air-oxidation of the sample could have occurred.

Samples S2, S3, and C3 were sealed in plastic bags or wide-mouthed polythene jars. Inspection of the samples prior to analysis indicated that visible effects of air-oxidation were limited to near-surface layers. These layers were carefully removed and fresh materials used for analysis.

Sample Preparation.

Wet samples were used directly for pH, Eh, "total dissolved sulphide", "acid-soluble sulphide", "cold 1N HCl-soluble Fe", "hot 1N HCl-soluble Fe" and "hot 12N HCl-soluble Fe" determinations. Otherwise the samples were roughly dried by squeezing them between pads of filter papers followed by freeze-drying (sample S1) or drying in a vacuum desiccator over P_2O_5. Samples were then finely crushed with an agate pestle and mortar.

When portions of samples were removed the containers were flushed with "oxygen-free" nitrogen before being re-sealed.

Analytical Techniques.

Results of analyses are quoted as percent or parts per million in the dried starting material or in the dried (110°C) residue after extraction with HCl. None of the samples contained analytically significant amounts of carbonate so direct comparison of results is unlikely to be misleading unless large amounts of Fe were extracted from the wet samples. Where this occurred the results have been re-calculated to a non-acid leached starting material basis by assuming the Fe removed was present in the original sample as FeS (or Fe_2O_3). These values are given in brackets in Table 4.

Methods for the determination of iron and sulphur species in sediments were adapted from those reported in the literature (Berner, 1964, 1970a; Kaplan, Emery, and Rittenberg, 1963).

Iron Determinations

Total iron in dry samples was determined with an X-ray fluorescence spectrograph (Phillips P.W. 1210) using the glass-button technique of Norrish and Chappell (1966). Results are precise to ± 1% of the measured values.

Dissolved iron in water samples and solutions from acid leaching and digestion procedures was determined by direct aspiration of the sample in a Varian-Techtron Model AA-4 atomic absorption spectrometer. Precision is ± 5% for concentrations > 1 ppm and ± 10% for concentrations < 1 ppm.

Cold 1N HCl - soluble iron was determined by shaking a portion of the freshly opened sample with excess cold 1N HCl for 10 minutes. The solution was filtered, the residue dried (110°C) and weighed, and the Fe content of the filtrate measured as above.

Hot 1N HCl- soluble iron was extracted by refluxing the sample with excess 1N HCl on a steam bath for 30 minutes.

12N HCl soluble iron was extracted by boiling the sample with 12N HCl on a hot-plate for 1 minute.

Precision for the above three determinations is ± 15% of the measured value.

Acid soluble sulphide was determined on freshly opened samples. The sulphide was decomposed by boiling the sample with excess 1N HCl on a water bath for half an hour and the liberated H_2S collected as CdS (Kolthoff and Elving, 1961). Precision is ± 15% of the measured value.

Elemental sulphur was determined by extracting residues from acid soluble sulphide estimations for 3-4 hours with acetone under nitrogen in a Soxhlet apparatus. The extracted sulphur was determined colorimetrically as ferric thiocyanate (Bartlett and Skoog, 1954). Sulphur standards were prepared by extracting weighed amounts of sulphur with acetone. Precision of the colorimetric analytical technique is ± 5% of the measured value. Elemental sulphur determinations on organic-rich sediments are potentially subject to large errors (Berner, 1964).

Pyrite plus marcasite was estimated by grain-counts on polished sections of residues from hot 1N HCl extractions. Precision is about ± 25% of the reported value.

Water Analyses

pH, Eh, Ksp, (apart from those made *in situ*) Fe, Mn, Cu, Pb, and Zn determinations on water samples were carried out in B.M.R. laboratories. Other measurements were by AMDEL Laboratories, Adelaide, South Australia.

Organic Carbon

Measurements were made on cold 1N HCl-leached residues by the Australian Microanalytical Service, Melbourne, Victoria. Precision is better than ± 5% of the measured value.

Mineralogical Techniques

Phases present in the mineral assemblages were identified by optical, X-ray diffraction and electron microprobe techniques.

Experimental Diagenesis Reactions.

Effects of added seawater, elemental sulphur and air. Aliquots of sample S1 were placed in small screw-top jars, previously flushed with nitrogen and containing seawater and/or elemental sulphur. Nitrogen was bubbled through the mixture a few seconds longer or, in some experiments, air was admitted at this stage, and the bottles sealed and placed in an oven at 65°C for 2-3 weeks. At the end of this time samples were opened and analysed for iron and sulphur species by the techniques described above.

Quantities of elemental sulphur added to the sample were chosen to give a total Fe:S ratio of about 1:5. To facilitate X-ray identification of the products portions of these samples were extracted with acetone under nitrogen till a fresh portion of extractant failed to blacken bright copper foil.

Reactions with excess H_2S. 20 - 30 ml of the aqueous supernatant from sample S1 was added to a weighed amount of the cold 1N HCl-leached sample and the suspension flushed with nitrogen. H_2S gas was then bubbled through the suspension while it was heated at 55°C for 30 minutes. The suspension turned black, and was again shaken with cold 1N HCl and the amount of Fe extracted determined as above.

2. *Bacteriological Investigations*

Inoculation and Incubation of Samples.

Samples of water and sediment from locations W1 and S1 in the thermal pool were collected directly into sterile containers and inoculated on the day of collection in duplicate and at two concentrations to constitute approximately 5% ($^v/_v$) or 95% ($^v/_v$) of the inoculated medium. With the 95% inoculum, media without added NaCl were used (see below). Samples were also incubated in the absence of any medium in completely filled bottles.

McCartney bottles were filled to capacity before incubation, initially at room temperature (approximately 27 - 30°C) in Talasea for 1 to 7 days depending on the day of inoculation. Following air freight to the laboratory (7 days) incubation was continued for a further 1 to 2 weeks at 30°C.

Because one known species of sulphate-reducing bacteria prefers a growth temperature around 55°C and cannot grow at 30°C, and because the samples were above 50°C on collection, McCartney bottles were removed to 55°C after the incubation period at 30°C. After 1 week at 55°C subcultures at 55° into medium 1 + 0.5% ($^w/_v$) ferrous ammonium sulphate were made at weekly intervals.

Preparation of Media.

Media (see Results) were adjusted to pH 7.5 with NaOH before autoclaving at 121°C for 20 minutes and were used at pH 7.1 to 7.3 in 1 oz. McCartney bottles fitted with screw caps, or in Petri dishes when solidified with agar. Agar media contained ferrous ammonium sulphate which was added just before use.

Detection and Isolation of Sulphate-Reducing Bacteria.

After incubation the contents of each bottle were tested for the presence of hydrogen sulphide by addition of 0.0001 M ferric chloride solution.

The presence of hydrogen sulphide in the sample was indicated by the formation of a black precipitate; this, however, could be from other than a bacterial source. Cultures were therefore subcultured at fortnightly intervals into Medium 1 containing 0.05% $(^{w}/_{v})$ ferrous ammonium sulphate to confirm the presence of sulphate-reducing bacteria by formation of a black deposit at least after the third subculture.

In addition the samples were placed directly on medium 5 + 0.05% $(w/_{v})$ ferrous ammonium sulphate and incubated at 30° or 55° in anaerobic jars containing an atmosphere of 97% H_2 and 3% CO_2. The appearance of black colonies would be confirmation of the presence of sulphate-reducing bacteria.

ACKNOWLEDGMENTS

The Baas Becking Geobiological Laboratory is supported by the Bureau of Mineral Resources, the Commonwealth Scientific and Industrial Research Organization and the Australian

Mineral Industries Research Association. N.H. Fisher, P.A. Trudinger and W.M.B. Roberts are thanked for critical appraisal of the manuscript.

REFERENCES

Bartlett, J.K., and Skoog, D.A., 1954, Colorimetric determination of elemental sulphur in hydrocarbons; Anal. Chem. 26, p.1008.

Berner, R.A., 1964, Distribution and diagenesis of sulphur in some sediments from the Gulf of California; Marine Geol. 1, 117-140.

___________, 1970a, Sedimentary pyrite formation; Amer. Jour. Sci. 268, 1-23.

___________, 1970b, Pleistocene sea levels possibly indicated by buried black sediments in the Black Sea; Nature 227, p.700.

Bischoff, J.L., 1969, Red Sea geothermal brine deposits: their mineralogy, chemistry, and genesis in Degens, E.T., and Ross, D.A., ed., Hot Brines and Recent Heavy Metal Deposits in the Red Sea, Springer-Verlag, New York, p.368-401.

Butlin, K.R., Adams, M.E., and Thomas, M., 1949, The isolation and cultivation of sulphate-reducing bacteria; Jour. Gen. Microbiol. 3, 46-59.

Doyle, R.W., 1968, Identification and solubility of iron sulphide in anaerobic lake sediment; Amer. Jour. Sci. 226, 980-994.

Ferguson, J., and Lambert, I.B., 1972, Volcanic exhalations and metal enrichments at Matupi Harbour, New Britain, P.N.G.; Econ. Geol. 67, 25-37.

Fisher, N.H., 1939, Report on the volcanoes of the territory of New Guinea; Territory of New Guinea, Geol. Bulletin No. 2.

Friedman, G.M., and Gavish, E., 1970, Chemical changes in interstitial waters from sediments of lagoonal, deltaic, river, estuarine, and saltwater marsh and cave environments; Jour. Sed. Petrol. 40, No. 3, 930-953.

Goldberg, E.D., 1963, The oceans as a chemical system; The Sea Interscience N.Y.

Heming, R.F., and Smith, I.E., 1969, Notes on the thermal fields of Talasea, Pangalu, and Kasiloli, New Britain, TPNG; Bureau of Mineral Resources, Unpublished Record No. 1969/115.

Kaplan, I.R., Emery, K.O., and Rittenberg, S.C., 1963, The distribution and isotopic abundance of sulphur in Recent marine sediments of Southern California; Geochim. Cosmochim. Acta 27, 297-331.

Koltoff, I.M., and Elving, P.J., 1961, Treatise on analytical chemistry 7; Interscience Pub., p.109.

Lerman, A., 1970, Chemical equilibria and evaluation of chloride brines; Mineral. Soc. Amer., Spec. Paper 3, 291-306.

Norrish, K., and Chappell, B.W., 1967, X-ray fluorescence spectrography; <u>in</u> Zussman, J., <u>ed</u>., Physical Methods in Determinate Mineralogy; Acad. Press, London, p.514.

Postgate, J.R., 1956, Sulphate-reducing bacteria which are deficient in cytochrome; Journ. Gen. Microbiol. 14, p.454.

Reynolds, M.A., 1954, An examination of thermal areas at Garua Harbour, New Britain, August 1954; Bureau of Mineral Resources, Unpublished Record No. 1954/59.

Rickard, D.T., 1969, The chemistry of iron sulphide formation at low temperatures; Stockholm Contr. Geol. 20 (4), 67-95.

Rickard, D.T., 1970, The origin of framboids; Lithos 3, 269-293.

Roberts, W.M.B., Walker, A.L., and Buchanan, A.S., 1969, The chemistry of pyrite formation in aqueous solution and its relation to the depositional environment; Mineral. Deposita 4, 18-29.

Stephens, J.D., and Wittkopp, R.W., 1969, Microscopic and electron beam microprobe study of sulphide minerals in Red Sea mud samples; <u>in</u> Degens, E.T., and Ross, D.A., <u>ed</u>., Hot Brines and Recent Heavy Metal Deposits in the Red Sea, Springer-Verlag, New York, p.441-447.

Trudinger, P.A., Lambert, I.B., and Skyring, G.W., in press, Biogenic sulphide ores: a feasibility study. Econ. Geol.

White, D.E., 1957, Thermal waters of volcanic origin; Bull. Geol. Soc. Amer. 68, 1637-1658.

__________, Hem, J.D., and Waring, G.A., 1963, Chemical composition of subsurface waters; in Data of Geochemistry, U.S. Geol. Survey, Prof. Paper 440-F, p.F1-F67.

Zobell, C.E., 1946, Studies in redox potential of marine sediments; Bull. Amer. Assoc. Petrol. Geologists 30, No. 4, 477-513.

CAPTIONS FOR TABLES

Table 1.	Temperature, pH, Eh and "total dissolved sulphide" contents of thermal pool and tributary stream waters and sediments.
Table 2.	Chemical compositions and ion weight ratios of thermal waters from thermal pool and tributary stream. Concentrations in parts per million. Ion ratios are $^w/_w$.
Table 3.	Major element contents of sediments from thermal pool and pool banks. Analyses by X-ray fluorescence techniques. Concentrations are in percent of the unignited material. Na_2O not determined.
Table 4.	Iron and sulphur species and organic carbon in sediments from thermal pool and environs.
Table 5.	Iron and sulphur species in thermal pool sediment sample S1 after experimental diagenesis reactions. Samples were heated at 65°C for 17 days. Concentrations expressed as percent of acid-leached residues.

TABLE 1

Sample		T°C	pH	Eh (mV)	Total dissolved sulphide (ppm)
W1 Thermal pool water	*in situ*	55	6.0	+ 203	-
	sample 2-3 weeks old		6.6	+ 300	-
W2 Tributary stream water	*in situ*	75	5.9	+ 123	-
	sample 2-3 weeks old		5.8	+ 320	-
Thermal pool sediments	*in situ* 2.5 cm below the sediment/water interface		6.0	+ 20	-
	in situ 7 cm below the sediment/water interface		6.0	- 150	-
S1 Thermal pool sediments	sample 2-3 weeks old:				
	supernatant water		7.6	-	4
	mud		7.6	-	16
	incubated 1 week at 55°C:				
	mud			- 230	-
	incubated 2 months at 55°C:				
	supernatant water		7.6	-	22
	mud		7.6	-	3
	sample plus 0.1% magnesium sulphate and 0.2% sodium sulphate incubated at 30°C for 3 months:				
	supernatant water		7.6	-	22
	mud		7.6	-	22
S2 Compact, grey, pyritiferous mud from the pool bank	sample 2-3 weeks old		2.9	-	-
C3 Core from stream bed 10 metres downstream from S1	samples 2-3 weeks old:				
	0.3-13 cm		7.1	-	< 0.01
	13-17 cm		7.2	-	< 0.01
	17-28 cm		7.1	-	< 0.01

TABLE 2

	Ksp (micromho. cm^{-1})	Solids[1]	Fe	Mn	Cu	Pb	Zn	Al	B	Na	K	Ca	Mg	SO_4	Cl	Br	I	F	Si
Water from main hermal pool.[2] W1.	15,800	10,900	0.04	1.50	0.01	0.02	0.05	0.02	2.1	3,200	170	365	357	475	6.290	20	0.02	0.32	65
Water from small tributary stream W2.	11,200	7,840	1.13	3.25	0.01	0.02	0.06	0.05	1.5	2,050	115	462	247	215	4,590	15	0.02	0.06	60
Seawater[3]	42,500	34,360	0.01	0.002	0.003	0.00003	0.01	0.01	4.6	10,500	380	400	1,350	2,660	19,000	65	0.06	1.3	3

	SO_4/Cl	Ca/Na	Mg/Ca	K/Na	B/Cl	Br/Cl	Fe/Mn	Ca/Cl	Mg/Cl	K/Cl	Na/Cl
W1.	0.076	0.11	0.98	0.053	3.3×10^{-3}	3.2×10^{-3}	0.03	0.058	0.057	0.027	0.51
W2.	0.047	0.22	0.53	0.056	3.3×10^{-4}	3.3×10^{-3}	0.4	0.11	0.054	0.025	0.45
Seawater[3]	0.14	0.038	3.2	0.036	2.4×10^{-4}	3.4×10^{-3}	5.0	0.021	0.071	0.021	0.55

1. Total dissolved solids at 18 °C.

2. Sample filtered on collection. Unfiltered sample had Fe, 0.02; Mn, 1.18; Cu, 0.01; Pb, 0.02; and Zn, 0.04 ppm.

3. From Goldberg (1963).

TABLE 3

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	P_2O_5	Loss on ignition (900°C)
S1 Black, sulphidic mud from centre of thermal pool.	42.9	0.61	15.0	9.7	0.02	2.4	1.6	0.83	0.22	25.10
S2 Compact grey, pyritiferous mud from pool bank.	41.0	0.79	17.3	9.45	0.01	1.9	1.87	0.28	0.07	26.40
Silt from 10 cm [1] deep in a freshwater stream emerging in mud flats 50 metres west of Talasea thermal field.	56.0	0.50	17.95	7.64	0.12	3.4	7.46	0.97	0.12	3.37

[1] Typical of major element analyses of sand and silt samples from non-thermal sand and mud-flat areas near Talasea. (Lambert, Ferguson and Jones, in preparation).

TABLE 4

	pH	SULPHUR Total dissolved sulphide (ppm)	Acid soluble sulphide (%)	Elemental Sulphur (%)	Cold 1N HCl (%)	Hot 1N HCl fraction[5] (%)	IRON Boiling 12N HCl fraction[6] (%)	Total HF/HClO$_4$ digestion (%)	XRF analysis (%)	Pyrite (%)	Organi Carbon (%)
S1. Black, sulphidic mud from centre of thermal pool	6.0	(16)[1]	2.1	0.026	3.7[3] (3.5)[4]	1.9[3] (1.7)[4]	1.6[3] (1.3)[4]	6.85[2]	6.80[2]	1-2	3.58
S2. Compact, grey, pyritiferous mud from pool bank	(2.9)[1]	-	-	0.27	0.56	1.6	0.2	-	6.85[2]	5-10	0.30
S3. Iron oxide deposit from tributary stream.	-	-	-	0.6	-	-	-	14.6[2]	-	trace	-
C3. Core from stream bed 10 cm downstream from S1:											
0.3-13 cm. Dark grey silt	(7.1)[1]	-	-	-	0.99	0.3	0.0	4.1[2]	-	trace	1.51
13-17 cm. Grey sand	(7.2)[1]	-	-	-	1.21	0.1	0.3	6.0[2]	-	trace	0.43
17-28 cm Dark grey silt	(7.1)[1]	-	-	-	0.87	0.1	0.0	4.8[2]	-	0.5	0.76

1. Measured 2-3 weeks after collection (see Table 1).
2. Results expressed as percent of the original sample. Other results are percent of ppm of acid-leached residues. (see Methods Section).
3. Results are averages of at least two determinations reproducible to ± 0.3% Fe.
4. Corrected to percent of the original sample by assuming Fe was originally present as FeS (or Fe_2O_3(.
5. Hot 1N HCl fraction = Hot 1N HCl-soluble Fe - Cold 1N HCl-soluble Fe.
6. Boiling 12N HCl fraction = Boiling 12N HCl-soluble Fe - Hot 1N HCl soluble Fe.

TABLE 5

Reaction Conditions		Fe (%)				
Atmosphere	Added Components	Cold 1N HCl	Hot[1] 1N HCl fraction	Boiling[1] 12N HCl fraction	Pyrite (%)	Mineralogy
Unreacted sample		3.7	1.9	1.6	1-2	Fine-grained, framboidal pyrite; hydrotroilite.
N_2	seawater	3.6	1.8	1.9	1-2	As above.
N_2	seawater and excess elemental sulphur	0.2	1.6	0.0	5-10	Very fine-grained anhedral pyrite, minor proportion of very small spheroids. No marcasite recognized.
Air	seawater	2.0	1.5	2.1	3-4	Fine-grained partially framboidal pyrite, intimately associated with ferric oxides.

[1] See Table 4.