

GEOCHEMISTRY OF LOW TEMPERATURE GEOTHERMAL SYSTEMS IN NEW CALEDONIA

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ABSTRACT

Thermal springs in New Caledonia are overall typical of low temperature, deep circulation geothermal systems, with low flow rates and a low dissolved solids content. They appear to be associated with faulting and occur in two localities, one near the central east coast and one in the south-east of the island. Stable isotope data show the waters to be essentially of meteoric origin and to have experienced low temperature rock-water reactions. Chemical analyses also suggest some deep mixing of saline groundwater in the northern group of springs and an appreciable seawater content in the south-eastern group in Prony Bay. Chemical geothermometers suggest that a maximum subsurface equilibrium temperature of $\sim 90^\circ\text{C}$ may exist. Computer calculation of AG values shows the northern spring waters to be saturated with silica, probably chalcedony, which may be the white encrustation being deposited. The southern springs are chemically different and deposition from them is greater, consisting of subaerial terraces largely formed of CaCO_3 and submarine formations composed of $\text{Mg}(\text{OH})_2$ plus CaCO_3 .

GEOLOGICAL SUMMARY

New Caledonia is situated in the S.W. Pacific between 18°S and 22°S (see Fig. 1). It is an elongate island, 400 km in length and 40 km wide. Much of the island is mountainous with flat areas largely restricted to the west coast. The basement is formed of a variety of metamorphic and igneous rocks, ranging in age from Permian to Miocene, thrust over which are ultramafic rocks, covering one-third of the island. These ultramafic rocks, largely harzburgites with minor dunite and pyroxenites are distributed over the length of the island and are believed to represent relics of a former ultramafic sheet (Fig. 2). Their base is marked by a thick (100 - 300m) zone of strongly sheared and mylonitised serpentinites which represent a major discontinuity (Routhier, 1953; Guillon, 1975). Serpentinisation is usually moderate except for at the base of the mass and along faults (Prinzhofer et al., 1980).

The ultramafic masses and associated tholeiitic basalts are generally considered to be a composite slab of oceanic crust and upper mantle which has tectonically overridden a sialic continental edge segment (Rodgers, 1976; Prinzhofer et al., 1980).

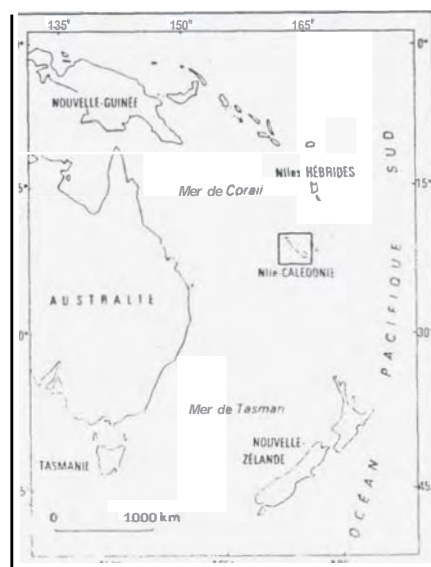


Fig. 1. Location of New Caledonia

Emplacement of the ultramafic mass onto the segment was probably by thrusting from the north-east, in a single event (Guillon, 1975). The age of the thrusting has been dated at Late Eocene on stratigraphic evidence (Paris et al., 1979), and its emplacement was followed by its intrusion (~ 35 m.y.) by granitic magma from basement faults. These intrusive felsic rocks are present in both the massifs as well as in the underlying sedimentary formations (Guillon, 1975; Rodgers, 1976).

The strike of the strata and of major fold axes generally follow the elongation of the island and strata from Permian to Eocene age are strongly folded and in places overturned and overthrust. The axial zone of the island can be basically regarded as a complex anticlinal belt formed of an "undifferentiated" group of Permian, Triassic and Jurassic greywackes and shales which have experienced low-grade metamorphism and which are associated with partly metamorphosed Cretaceous beds (Lillie and Brothers, 1969).

The north-western belt of ultramafics consists largely of peridotite masses perched on pre-Oligocene rocks; the central belt is formed of masses, or lenses, intruding the basement

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formations and ranging from several metres, to kilometres in length, and contact metamorphism is limited in development (Rodgers, 1976). In the west, the base of the ultramafic complex is horizontal, but in the central belt the base dips 10-15° NE and further to the NE, the dip progressively increases, reaching 50° on the central east coast (Guillon, 1975). Here, a positive gravity anomaly (150-170 m gal) was measured in the coastal region north-east of Canala (Crenn, 1953) and indicates the possible root, or deep-seated extension, of the eastern ultramafic belt. The south-eastern ultramafic belt is dominated by the vast Massif du Sud.

The ultramafic massifs can be divided into two parts (Routhier, 1953; Guillon, 1975): (1) The main mass, a thick pile of harzburgites, in which numerous intercalations of dunites and pyroxenites, as well as podiform lenses of chromite, are present. These rocks produce a generally well-developed layering, notably in the upper parts of the mass. Disseminated Ni and Cu sulphides and native metals occur in places in the pyroxene rich rocks and zoning within the mass produces an increase in Cu and sulphide mineralisation towards the lower part. The ultramafic rocks are depleted in Na, K and Ca. (2) The second lithological unit consists of dunite-gabbro bodies which cut through the layering of the main ultramafic mass. Magnetite and Cu-Fe sulphides are widespread in the pyroxene rich rocks of the transition zones between dunites and gabbros.

DESCRIPTIONS OF SPRING LOCATIONS

Thermal springs occur within two areas in the south-eastern half of the island: around 10 km from the east coast in the area between Thio and Canala and within Prony Bay at the south-east of the island. There are also several seepages of sulphurous, ambient temperature water within the Thio and Canala region (Fig. 2).

Springs of the Thio-Canala area

These springs are distributed over a 35 km zone which parallels the strike of the island and discharge from formations of metamorphic and associated volcanic rocks at elevations of from 20 to 55 m. The springs occur within an area through which major NW-trending structural lineations pass and with which are associated serpentinite lenses, silification and metalliferous mineralisation.

In the Thio Valley, two discharges have been described (Lozes and Yerle, 1976). The Karangue sulphurous springs on a tributary of the Kouare are seepages of cool water into a swamp, and from the bottom of a stream. Several springs discharge from Mesozoic shales near a tributary of Fanama River, about 3 km from the junction with the Thio River. The main spring has a flow of approximately 0.5 l/sec into a 2 m diameter pool, at a temperature of 32°C. Gas bubbles were observed rising from

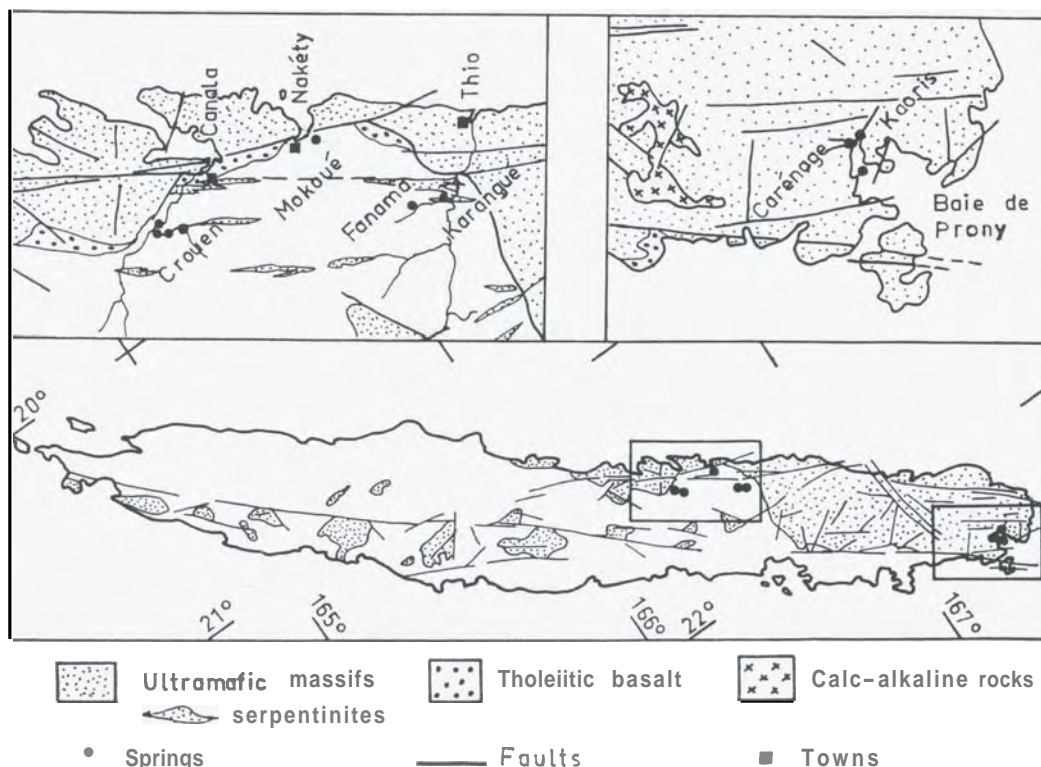


Fig. 2. Outline geology map of New Caledonia with details of areas of Thermal Springs (after Guillon, 1975).

the bottom of the pool, and there is a faint sulphurous odour; algae and a white encrustation have formed around the pool and flow-off channel. These springs appear to discharge from a NNE-trending fault. There are two seepages near Nakéty, Mokoué spring, about 3 km east of Nakéty village, is warm (~28°C) of low flow and discharges from the base of the stream bank. This spring also has a sulphurous odour and deposits a white material in flow channels (Lozes and Yerle, 1976). On Ahvia Creek, a tributary of Kopélia stream is a cool, sulphurous seepage from shales. Additional cool seepages of limited flow and with abundant algal growth have been reported to discharge from alluvial deposits of Cretaceous shales near Canala village.

The largest group of springs in New Caledonia occurs near the junction of the Crouen and Négropo Rivers, about 7 km SW of Canala. These springs can be divided into two groups; the low temperature springs near their junction, and the hotter springs of Val Pierrette 1.5 km upstream in the Crouen River. The former, consist of fourteen separate seepages beside the rivers and appear to discharge from faults which the rivers follow. The flow rates are all < 0.1 l/sec and the temperatures range from 22°C to 27°C. The spring sampled, Crouen River (EII), had a flow of 0.05 l/sec. These springs all discharge from a sequence of Permian - Triassic and Jurassic greywacke and shales with interbedded rhyolite tuffs, and emit a faint odour of H₂S. Probably the best known thermal springs in New Caledonia are those of Val Pierrette. Here are about fourteen natural discharges within a depression along a zone of weathered and sheared shales, at an elevation of 26 to 28 m. The temperatures are 40°C to 43°C and the total discharge was estimated at ~3 l/sec (Koch, 1958). Gas bubbles are abundant in the discharge pools and an odour and taste of H₂S are present. A health spa has been constructed in this group and most springs now discharge into pipes feeding thermal baths.

Pyrite and chalcopyrite are common in the numerous quartz veins and siliceous breccias which border the ultramafic formations to the north of these springs, and stibnite, chalcopyrite and scheelite occur in the Nakéty-Canala area (Guillon, 1975). Disseminated sulphides also occur in the peridotites adjacent to the Crouen-Négropo springs. Quartz veins vary from several millimetres to 0.4 m thick, many with a N-S trend, and are associated with intense mylonisation of the greywackes (Koch, 1958). Koch (1958) considers that the secondary mineralisation here may be associated with an intrusive mass of diorite and granodiorite, and notes the variety of sulphide minerals that occur both within the veins as well as the volcanics and associated sedimentary rocks. The Thio-Canala springs are peripheral to the positive gravity anomaly (Crenn, 1953), and both these springs and those of Prony Bay occur within a gravity low (~90-100 m gal) which roughly follows the axis of the island.

Springs of Prony Bay

In Prony Bay at the south-east end of the island there are three thermal spring localities. To the north-east of the bay, adjacent to the mouth of the Kaoris River, 32°C water discharges from laterites overlying the gabbro river bank and forms a travertine terrace 20 m in length. Seepages and small "stalagmite" structures occur below high tide on the adjacent beach. The total discharge is estimated at ~0.2 l/sec. In the west of Prony Bay thermal seepages are largely below the high tide level in Carénage Bay. The water is 40°C with a flow of around 0.17 l/sec, and has formed small travertine terraces. A further thermal water discharge, Roc Aiguille, occurs on the floor of Prony Bay at a depth of 38 m. Deposition from this spring has built a unique vertical structure 35 m in height, within which thermal water flows in narrow pipes, enabling continued growth. The temperature of discharge of these waters is estimated to approximate the others of Prony Bay (Launay 1981).

Greater than 80% of the region surrounding Prony Bay is covered by ultramafic rocks. These are predominantly partially serpentinised harzburgites with a dunite-chromite-gabbro core (Rodgers, 1976). The ultramafic mass here is relatively thin, 1-3 km, with generally flat lying foliation and N-S trending lineation, and the basal contact of the mass is also horizontal (Prinzhofer et al., 1980). The locations of the springs appear to be associated with the intersections between several sets of NW and NE trending faults; considering this and the chemical similarities of these springs it is likely that these faults are hydrologically connected.

CHEMISTRY OF THE WATERS

As can be seen from the analyses of spring waters (Table 1) all the thermal waters sampled are alkaline, those from the Thio-Canala area having a pH of ~8 and those from Prony Bay, a pH ~11. During sampling for this study it was not possible to sample the springs at Karangue, Mokoué and Ahvia because of their limited or nil flow. This behaviour suggests the importance of rainfall and groundwater levels for at least some of the minor seepages, especially those of ambient temperature.

The trilinear diagram (Fig. 3) shows the variations in chemical type of the waters. Most meteoric waters within the Massif du Sud are of Mg-HCO₃ type as demonstrated by shallow groundwater and (leeward) river water (12, 13). The Kaoris and Carénage River waters (10, 11) are of Mg-Na-HCO₃ type and in Fig. 3 plot near average (windward) rain (14), which is of Ca-Na-HCO₃ type. This similarity may be due to the high amount of direct precipitation in the river waters, although ionic exchange of Ca for Mg may have taken place. For all these river and groundwaters rapid dissolution of Mg from the ultramafic rocks and their weathered products is likely. No analyses of river water from the metamorphic and volcanic rocks are available, but presumably the Mg content would be lower.

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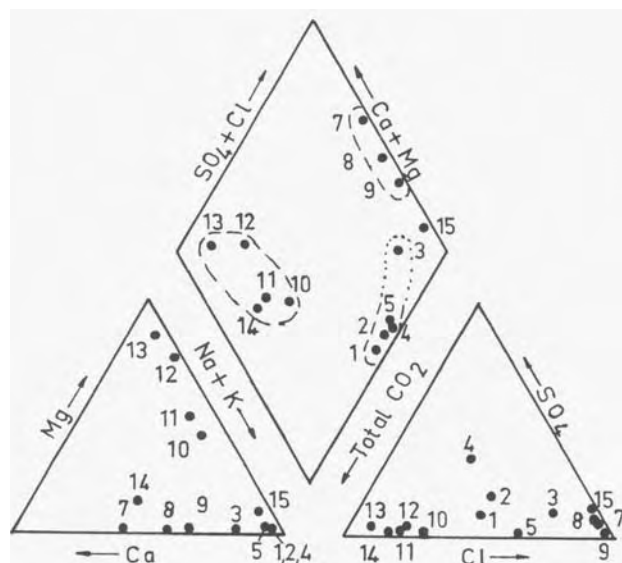


Fig. 3. Trilinear diagram showing chemical types of thermal and other waters. The top diamond demonstrates the groupings of, meteoric water, Thio-Canala and Prony Bay thermal waters. It is not known whether the 1949 analysis of #3 shows a change in water composition, or results from analytical methods.

geothermometers are shown in Table 2. These geothermometers are, however, not well suited to low temperature springs of low flow, but do provide an approximation of equilibrium temperatures. For the Crouen springs the quartz (conductive) geothermometer provides a temperature of $\sim 110^\circ\text{C}$, the chalcedony and Na/K geothermometers $\sim 80^\circ\text{C}$ and the Na/K/Ca method $\sim 90^\circ\text{C}$. A slightly lower temperature is indicated for the Fanama waters. The fact that the quartz geothermometer provides a higher temperature than the alkali geothermometers suggests that for these springs the chalcedony geothermometer may be appropriate. The theoretical free-energy calculations below, also indicate the Crouen thermal waters to be saturated with respect to chalcedony. As chalcedony has a higher solubility at lower temperature than quartz it is more likely to be the equilibrium silica mineral under the existing low temperature conditions. The cristobalite-A geothermometer gives low temperatures; the amorphous silica geothermometer gives negative values, in agreement with the

TABLE 2.

Chemical Geothermometers

No.	Location	Quartz(Conduct.)	Chalcedony	Na/K	Na/K/Ca ($\beta = \frac{4}{3}$)
1	Val Pierrette 1	106	76	73	88
2	Val Pierrette 2	106	75	74	88
3	Val Pierrette	122	94		
4	Crouen R. (E11)	111	81	86	105
5	Fanama	75	43	31	81

undersaturation of the waters with amorphous silica. None of these geothermometers are suited to the chemistry of the Prony Bay thermal waters.

DEPOSITS FROM SPRING WATERS

Many of the springs in the Thio-Canala region deposit a thin white encrustation around discharge pools, which Avias (1949) suggested may be anhydrite. Unfortunately, none of that material was sampled during this study, but assessment of the water chemistry indicates that it is unlikely to be anhydrite considering the low concentrations of Ca^{++} and SO_4^{--} in these waters. We suggest that it is probably silica, a conclusion which is reinforced by Table 3 in which the Gibbs free-energy difference (ΔG) is calculated by the computer programme SOLMNO (Kharaka and Barnes, 1973). The free energy difference between the actual and equilibrium states for a given reaction indicates the degree of saturation of the solution with respect to a specific solid and provides an indication of which mineral species may be present.

The Thio-Canala thermal waters are indicated to be supersaturated with most silica minerals, notably quartz, chalcedony and cristobalite-A, and are undersaturated with respect to amorphous silica. Also shown is that the thermal waters are well undersaturated with the CaSO_4 minerals anhydrite and gypsum. This high proportion of silica in the thermal waters is presumably due to the presence of felsic volcanic rocks and the abundant silicification within the Thio-Canala area. The low temperatures of the geothermal system and the correlation between chalcedony and alkali geothermometers suggest that silica in the form of chalcedony is the most likely mineral to deposit.

Substantial amounts of secondary minerals are being deposited by the Prony Bay springs. Typically, these springs deposit the CaCO_3 minerals calcite and aragonite under subaerial conditions, and where they discharge into seawater deposit brucite ($\text{Mg}(\text{OH})_2$), aragonite, calcite and burbankite ($\text{Q}(\text{CO}_2)$; $\text{Q}=\text{Na}, \text{Ca}, \text{Sr}, \text{Ba}, \text{REE}$) (Launay, 1981). These two processes of deposition can be observed at the Carénage and Kaoris localities, where above the high tide level (on shore at Kaoris) calcite and aragonite deposit, and below it a terrace (Carénage) and "stalagmites" of brucite are forming. The submarine structure of Roc Aiguille growing from the floor of Prony Bay is predominantly brucite with aragonite, calcite and burbankite.

The formation of subaerial CaCO_3 appears to involve absorption of atmospheric CO_2 by the CO_2 -depleted $\text{Ca}^{++}\text{OH}^-$ waters; submarine formation of $\text{Mg}(\text{OH})_2$ and CaCO_3 appears to be the result of reaction of the thermal waters with Mg^{++} and HCO_3^- in seawater, possibly accelerated by the increase in temperature. Such a process for brucite formation is suggested by the ΔG calculations for the Kaoris and Carénage spring waters which show them to be undersaturated with respect to brucite, but presumably mixing of the $\text{Ca}^{++}\text{OH}^-$ water extracts Mg^{++} ions from seawater precipitating $\text{Mg}(\text{OH})_2$.

TABLE 3
Gibbs Free Energy Difference (ΔG)

Mineral	Val Pierr- ette 1	Val Pierr- ette 2	La Crouen (El)	Fanama	Kaoris	Carenage
	(Kilocalories)					
Quartz	0.96	0.98	1.30	0.71	-0.11	-1.52
Chalced.	0.42	0.44	0.71	0.14	-0.73	-2.15
Crist.A	0.15	0.16	0.45	-0.12	-0.99	-2.41
Am.Silic.	-0.33	-0.32	-0.01	-0.59	-1.43	-2.85
Aragon.	-3.75	-3.74	-2.82	-2.81	--	--
Calcite	-3.68	-3.67	-2.76	-2.75	--	--
Anhydrit.	-6.65	-5.99	-5.42	-7.34	-4.78	-5.98
Gypsum	-6.49	-5.93	-5.13	-7.14	-4.24	-5.45
Brucite	-7.51	-9.11	-7.05	-6.50	-2.70	-1.54
Bornite	87.75	85.51	--	--	--	--
cu	7.88	7.07	--	--	--	--
Cu ₂ O	2.60	1.27	3.32	2.11	8.46	--
Cu ₂ S	30.13	29.34	--	--	--	--
CuFeS ₂	39.16	38.49	--	--	--	--
cuS	13.14	13.16	--	--	--	--
Hematite	2.76	0.57	--	--	--	--
Fe ₃ O ₄	4.87	1.45	--	--	--	--
Pyrite	40.35	40.19	--	--	--	--
Geothite	1.46	0.37	--	--	--	--
MnO ₂	60.74	59.22	--	--	--	--
PbS ₂	14.35	13.77	--	--	--	--
ZnS	12.50	12.70	--	--	--	--

-- not calculated on available data

The thermodynamic properties of the thermal waters in the Thio-Canala area indicate that they have the potential to be supersaturated with a variety of metallic minerals, notably Cu and Fe, but also Mn, Pb and Zn. (Sulphide mineral calculations are an approximation only as they use the H_2S value (2.24 mg/l) of Bontemps (1949)). This finding is compatible with the common occurrence of metalliferous mineralisation in the Thio-Canala area, and it is possible that in the depositing (?) siliceous sinters some concentration of base metals may occur. Such a situation does not, however, appear to be the case for the Prony Bay deposits, although the trace metal contents of those waters are only slightly lower than the Thio-Canala waters (Table 1). The following analyses are the means of three samples of Roc Aiguille material (in ppb): Mn=10; Fe=1178; Cu= <1; Pb=15; Zn=10 and Ni=29.

STABLE ISOTOPES

Determinations of ratios of stable isotopes of oxygen and hydrogen were made for thermal spring waters from Val Pierrette (1,2), Crouen River (4) and Fanama (5) (Fig. 4). These data confirm the spring waters as being of meteoric origin and they fall along a meteoric water line with a slope of 8 and a δD intercept of +16‰. Although no determinations were made of river water from this area, they are likely to be very similar isotopically to the thermal waters. No significant enrichment in $\delta^{18}O$ is indicated for the thermal waters, the only displacement from the meteoric water line being of $\sim 0.1\%$ for Val Pierrette (1). This, and the $\delta^{18}O/\delta D$ ratios tend to confirm the low magnitude of subsurface temperatures the waters have experienced. Although these systems are indicated to be of small throughput, the nil-low oxygen shift also suggests that it is an old system in which equilibrium between rock and migrating

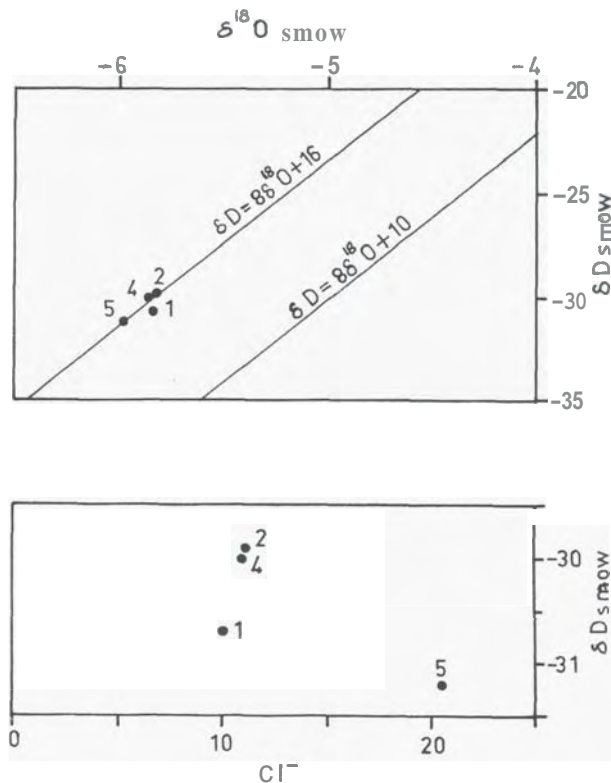


Fig. 4. Plot of stable isotope ratios $\delta^{18}O/\delta D$ and $\delta D/Cl^-$ for Crouen and Fanama thermal waters,

water has been approached.

The isotopic values for the Fanama waters are slightly different from those of Crouen; the Crouen area springs have average values of $\delta^{18}O = -5.84\%$ and $\delta D = -31.2\%$. These more depleted isotopic values for the Fanama waters are in agreement with the lower calculated geothermometer temperatures for the Fanama system, but it is somewhat anomalous that the waters have a higher Cl^- content than the Crouen springs (Fig.4). However, as the water chemistry suggests some mixing of saline groundwater, the isotopic "lightness" of the water suggests a partly different catchment area to the Crouen springs.

DISCUSSION AND CONCLUSIONS

The geochemical data indicate the thermal waters to be essentially of meteoric origin and have the characteristics of many low temperature geothermal systems. Geological data suggests that the waters migrate largely via structural permeability such as faults and shear zones, and possibly foliation permeability. It is also worth noting that many faults are steeply inclined and all springs are within topographic lows.

Little is known of the geothermal gradient in New Caledonia and consequently the circulation history of the water. However, the results of this study indicate that the water has probably experienced fairly deep circulation and rock-water exchange reactions at relatively low temperatures. Using a slightly above average crustal geothermal gradient ($35^\circ C/km$) a depth of circulation of ~ 2 km can be estimated for the Crouen springs. Assuming Ghyben-Herzberg groundwater conditions and saline groundwater underlying the basal fresh groundwater, at depth, provides an explanation of the NaCl content of the Thio-Canala springs.

The Thio-Canala thermal waters appear to circulate only within metamorphic and associated volcanic rocks, and the abundance of felsic rocks and silification is a reasonable explanation for the proportionally higher SiO_2 in these waters. The Prony Bay thermal waters probably circulate entirely within the ultramafic mass (and associated limestones) and migrate through faults from near its base to discharge at sealevel, a feasible explanation for their low SiO_2 content. Although solids deposit from thermal waters in both groups of springs, the greater abundance from the Prony Bay springs and their characteristic chemistry appear to be due to the different lithologies through which these thermal waters migrate as well as their discharge into seawater.

There are several possibilities for the source of heat to the thermal waters. The most reasonable would appear to be a slightly elevated geothermal gradient resulting from remnant heat in tectonically uplifted crustal material or from the tectonism itself. The characteristics of the New Caledonian thermal water systems suggest that they are in the waning stage. It is interesting to speculate, however, whether during geologically younger periods with a much higher geothermal gradient, if such geothermal systems could have been active in depositing

some of the quartz veins and associated base metals as seen in the Thio-Canala area.

ACKNOWLEDGEMENTS

We thank J.M. Eberle and P. Podvin (BRGM) for assistance in sample collection, C. Fraley for chemical analyses, J.R. Hulston and M.K. Stewart (INS, NZ) for isotopic determinations and G. Caldwell for computer analysis. Comments on the paper by K.A. Rodgers are appreciated. Funded in part by US Dept of Energy, while MEC was at Hawaii Institute of Geophysics.

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