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# Geological factors affecting the chemical characteristics of the thermal waters of the carbonate karstified aquifers of Northern Vietnam

C. Drogue[1], N. N. Cat[2] and J. Dazy[1]

[1]Hydrogéologie, UMR 5569 Hydrosciences, Université Montpellier 2, place Eugène Bataillon, 34095 Montpellier Cedex 5, France
[2]Institute of Geography, Vietnam National Centre for Sciences and Technology, Nghia Do, Tu Liem, Hanoi, Vietnam
e-mail for corresponding author: drogue@dstu.univ-montp2.fr

## Abstract

In northern Vietnam, exposed carbonate rock formations cover an area of more than 50,000 km$^2$. Their accumulated thickness from the Cambrian to the Triassic is in some places as much as 3000 m. Numerous thermal waters (springs and wells) occur in these strongly karstified carbonate massifs. This is the result of significant ancient and present orogenic activity, as the region demonstrates by its strong seismic activity. These karstic formations are water-bearing and strongly recharged by rainfall of between 1600 mm and 2000 mm per year in 90% of the area concerned. In view of the average annual air temperatures (17°C-25°C according to the region), 23 sample springs or wells were chosen with water temperatures of between 29°C and 68°C. Hydrochemical characteristics of these thermal waters emerging in different carbonate-rock units were examined by chemical analyses of major ions. In this large region, thermal waters are divided into four hydrochemical types: the Na-Cl type resulting from the intrusion of sea water for distances of up to several kilometres inland and depths of 1000 m, the Ca-$SO_4$ type, probably resulting from the leaching of deposits of metallic sulphides that are widely distributed in these carbonate-rock units, and finally the Ca-$HCO_3$ and Mg-$HCO_3$ types which are chemically similar to fresh karstic waters in limestones and dolostones. The occurrence of these thermal groundwaters as well as their chemical characteristics seem to indicate the existence of large-scale deepseated groundwater flow systems in the karstic aquifers.

**Keywords:** Vietnam; thermal waters; karst; hydrochemistry

## Introduction

South-East Asia is rich in thermal springs (Grimaud *et al.*, 1985; Shen Zhian *et al.*, 1989) which may flow from either eruptive or volcanic rocks or from sedimentary rocks. In the latter case, the occurrence of thermal water in carbonate rocks is of particular interest. Indeed, these rocks are often karstified, thus forming groundwater reservoirs in which flow resulting from the infiltration of rain water can be substantial. The presence of hot water means that deep thermal flows are sufficiently active not to be masked wholly at emergence by mixing with cold water. It is, therefore, possible that the hydrochemical characteristics may provide information about the modes of deep flow and, in particular, may show whether the flowpath of groundwater is related to formations other than carbonate rocks.

Northern Vietnam (north of the 17th parallel) possesses large exposed units of carbonate rocks covering a sixth of the territory, an area of nearly 50,000 km$^2$ (Fig. 1). These carbonate rocks are karstified and feed a large number of springs. They offer a resource which is exploited by wells for water supply. The water temperatures are abnormally high in some places. The intention was to identify the major chemical characteristics in a preliminary study of the karstic thermal waters. This could demonstrate the hydrochemical homogeneity or diversity at the scale of the region and the possibilities of deep flows from non-carbonate rocks.

## The geological and climatic frameworks

In northern Vietnam, the oldest carbonate formations (Proterozoïc and Lower Cambrian) are represented by marbles. However, the main carbonate rocks in the region, consisting of marble, limestone and dolomite were formed at the middle Cambrian, Ordovician, Devonian, Carbo-Permian and Triassic periods. The cumulated thickness of these carbonate formations can reach 3,000 m (Fromaget, 1941).

Northern Vietnam is an area of substantial tectonic movement due to the presence of one of the main active strike-slip faults in South-East Asia, the Red River Fault zone (Fig. 1) (Rangin *et al.*, 1995; Harrison *et al.*, 1996).

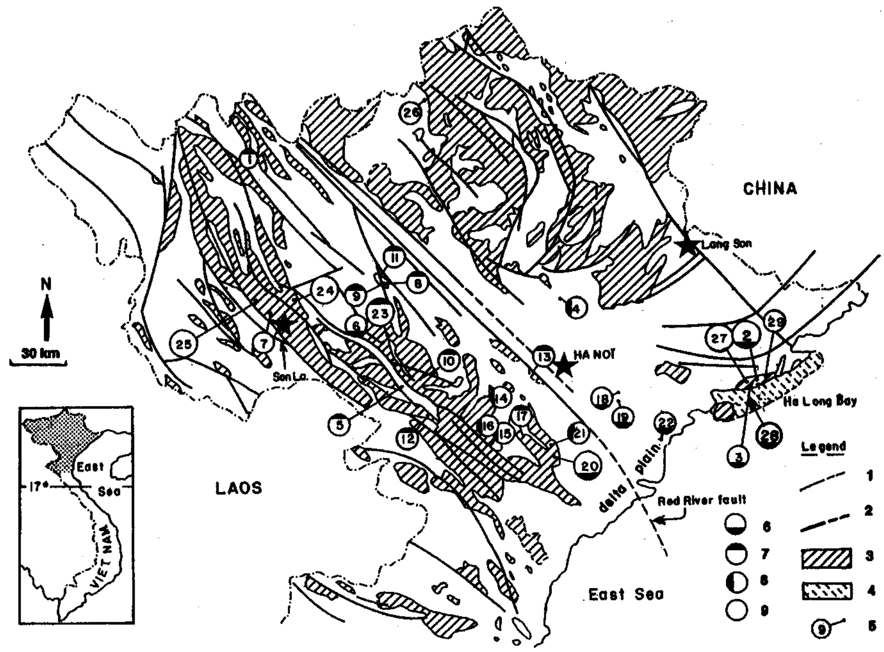


Fig. 1. *Carbonate rock outcrops in northern Vietnam (after Geological Map of Vietnam, 1986 and unpublished map of CNST-Vietnam). Location of the springs and wells studied.*

1. Observed and assumed geological boundary.
2. Observed and assumed fault.
3. Carbonate rock massifs.
4. Submerged karst in Halongbay.
5. Spring/well (the number refers to Tables 1 and 2)
6. Na-Cl typewaters,
7. Ca-$SO_4$ typewaters,
8. Ca-$HCO_3$ typewaters,
9. Non thermal waters.

This is the extension towards the south-east of the major fault separating the Indo-Australian plate from the Eurasian plate.

In addition, various tectonic phases (Huang Chu-Ching, 1978; Allen *et al.*, 1984; Leloup *et al.*, 1995) have enhanced the formation of the Red River basin in the Hanoi region with more than 3000 m of sedimentary deposits in the deepest part (Pham *et al.*, 1995). In this alluvial basin, carbonate-rock formations lie at great depth whereas karstic carbonate units outcrop widely in the northern and southern parts of the basin. The appearance of many granitic and rhyolitic intrusions (during the Jurassic and the Cretaceous) are also possible sources of thermal anomalies in the subsurface.

Tectonic movements along the major faults and the related fracturing must enhance the deep flow paths of fluids, especially as the region is the site of strong neotectonic activity. As many as 400 earthquakes have been observed annually (Can and Hoe, 1969; Xuyen, 1991). That of 1 November 1935 scored 9 on the Richter scale and caused the opening of a 50 m long crevasse and gushes of hot water. The hypocentres of the earthquakes in 1956 and 1957 were located on the Red River fault, which is thus currently active (Yem, 1986).

The intense fracturing resulting from these tectonic movements allows the infiltration of water and has enhanced karstification in the carbonate sequences of the geological series. Outcrops of the karstified sequences display different morphological forms including the spectacular tower karst and pinnacle landscape (Blondel, 1929; Glazek, 1966; Fenart *et al.*, 1999). Similar karstification has been observed at depth throughout northern Vietnam in a large number of wells drilled to extract water at depths of up to 1,000 m (wells 18 and 19 listed in Table 1).

The groundwater recharge of these aquifers depends on the climate. According to Tran Cau (1984), northern Vietnam has three types of climate, a humid tropical climate in the low-lying plains (the Red River delta), a highland sub-tropical climate at elevations of 600 to 2,500 m and a temperate climate in the mountains above 2,500 m. The average annual rainfall is between 1,600 and 2,000 mm in 90% of the region (Fig. 2). In the north-west hills, the rainfall gradients are steep and the precipitation exceeds

*Table 1.* Results of the chemical analyses of the thermal waters. The concentrations are expressed in mg $l^{-1}$. $\Sigma r^+$ and $\Sigma r^-$: Total cations and total anions (expressed in meq/I): Geology, D: Devonian, C:Carboniferous, P:Permian, T: Trias, a ? indicates uncertain determinations. The locations of the sites are indicated on the map in Fig. 1.

| N° | Location | T°C | TDS ($mg L^{-1}$) | $Ca^{++}$ ($mg L^{-1}$) | $Mg^{++}$ ($mg L^{-1}$) | $Na^+$ ($mg L^{-1}$) | $\Sigma r^+$ (meq/L) | $\Sigma r^-$ (meq/L) | $HCO_3^-$ ($mg L^{-1}$) | $Cl^-$ ($mg L^{-1}$) | $SO_4^{--}$ ($mg L^{-1}$) | Geol |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Na-Cl type waters** | | | | | | | | | | | | |
| 2 | Tam Hop | 42 | 15,941.5 | 605.50 | 390.0 | 4,868.1 | 274.00 | 275.50 | 137.2 | 8,842.1 | 1098.6 | C.P. |
| 3 | Quang Hanh | 42 | 26,602.4 | 695.90 | 812.5 | 8,104.0 | 454.00 | 462.50 | 211.5 | 14,851.3 | 1927.2 | C.P. |
| 6 | Muong Pia | 55 | 5,083.0 | 491.00 | 213.0 | 916.9 | 81.90 | 82.30 | 338.0 | 1,588.1 | 1536.0 | ? |
| 18 | Thach Khôi | 44 | 488.3 | 45.13 | 8.7 | 120.7 | 8.22 | 8.01 | 47.6 | 231.0 | 35.2 | C |
| 19 | Cam Giang | 38 | 1,122.8 | 128.80 | 28.3 | 217.7 | 18.20 | 19.10 | 49.4 | 509.4 | 189.2 | C |
| 20 | Kénh Gà | 52 | 8,871.2 | 201.80 | 30.4 | 3,206.8 | 151.90 | 152.00 | 91.5 | 5,336.7 | 4.0 | T |
| 22 | Tién Lang | 54 | 13,145.3 | 566.40 | 321.4 | 3,938.1 | 226.00 | 226.60 | 118.5 | 7,301.3 | 899.6 | T |
| **$Ca-SO_4$ type waters** | | | | | | | | | | | | |
| 1 | Vang Po | 37 | 1,002.0 | 200.4 | 60.8 | 14.0 | 15.6 | 14.2 | 219.7 | 7.1 | 500.0 | T |
| 5 | Phu Mao | 40 | 1,078.2 | 227.4 | 36.3 | 34.3 | 15.7 | 15.4 | 201.3 | 5.2 | 573.7 | ? |
| 8 | Ban Peo | 47 | 2,296.4 | 400.8 | 109.4 | 111.7 | 33.8 | 33.9 | 253.7 | 28.8 | 1392.0 | ? |
| 9 | Ban Bon | 45 | 2,444.2 | 501.2 | 94.7 | 72.0 | 36.3 | 35.7 | 308.1 | 13.6 | 1454.6 | ? |
| 10 | Nong Da | 29 | 2,259.6 | 538.1 | 82.2 | 9.0 | 34.0 | 33.1 | 195.2 | 5.1 | 1430.0 | ? |
| 11 | Ban Hôc | 53 | 2,317.8 | 517.6 | 79.7 | 52.0 | 35.1 | 33.7 | 244.1 | 6.8 | 1417.6 | ? |
| 12 | Pê Ngoài | 38 | 2,201.5 | 476.5 | 104.7 | 17.0 | 33.2 | 32.4 | 219.7 | 5.1 | 1378.5 | ? |
| 13 | Ba Vi | 33 | 1,282.3 | 292.6 | 45.0 | 7.9 | 18.8 | 18.7 | 183.1 | 7.8 | 745.9 | T |
| 17 | Suoi Am | 45 | 1,143.3 | 228.5 | 38.4 | 3.6 | 14.7 | 17.2 | 231.9 | 7.2 | 633.7 | T |
| 23 | Thanh Tan | 68 | 921.6 | 173.7 | 20.4 | 89.2 | 14.5 | 12.5 | 238.5 | 25.9 | 373.9 | D |
| **$Ca-HCO_3$ and $Mg-HCO_3$ type waters** | | | | | | | | | | | | |
| 4 | La Hien | 33 | 272.4 | 43.8 | 9.7 | 12.2 | 3.50 | 3.51 | 191.8 | 7.7 | 7.2 | D |
| 7 | Ban Mong | 39 | 420.5 | 68.1 | 13.4 | 18.7 | 5.36 | 5.40 | 311.2 | 7.1 | 2.0 | T |
| 14 | Mo Da | 34 | 427.9 | 82.6 | 15.2 | 4.7 | 5.62 | 5.85 | 232.5 | 11.7 | 81.2 | T |
| 15 | Dam Thi | 34 | 439.5 | 85.6 | 12.2 | 12.9 | 5.85 | 5.83 | 237.9 | 4.2 | 86.4 | T |
| 16 | Qui Hoa | 37 | 341.3 | 38.0 | 9.7 | 30.5 | 4.00 | 4.55 | 220.9 | 7.1 | 35.1 | T |
| 21 | Thuong Xung | 37 | 429.5 | 18.6 | 55.1 | 11.0 | 5.92 | 5.77 | 325.1 | 5.1 | 14.6 | T |
| **Sea-water** | | | 34,430.0 | 410.0 | 1,284.0 | 10,551.0 | | | 41.0 | 19,046.0 | 2,653.0 | |

4,000 mm per year at the highest summits (the highest elevation is 3,142 m in the Fan Si Pan range). As 54% of the rainfall does not evaporate (Tran Cau, 1984), the karstic aquifers benefit from ample supplies and flows are thus very active.

Average annual air temperatures are between 22°C and 26°C in the Red River delta and 15°C to 16°C in the mountains. As a result, in this study the underground water whose temperature exceeds 26°C is considered to be thermal water, for all regions.

## The chemical characteristics of the thermal waters

Thermal water is defined here as water whose temperature is higher than the average mean annual temperature on discharge at the surface. In northern Vietnam, the waters described in this paper as mineral and thermal are spring waters or well waters originating in carbonate karstic rock. Nearly all have at one time been used for medicinal or bottling purposes. Natural flows are between 0.5 l $s^{-1}$ and 14 l $s^{-1}$ for springs and between 4 l $s^{-1}$ and 15 l $s^{-1}$ for artesian wells.

### SAMPLING AND DATA ANALYSIS

Sampling of deep waters and spring waters from karstic rocks has been carried out recently. The analyses were performed by the University of Mining and Geology in Hanoï and by the Vietnam Institute of Petroleum and Gas using standard methods. The chemical analyses concern only the major ions (Ca, Mg, Na, K and Cl, $SO_4$, $HCO_3$).

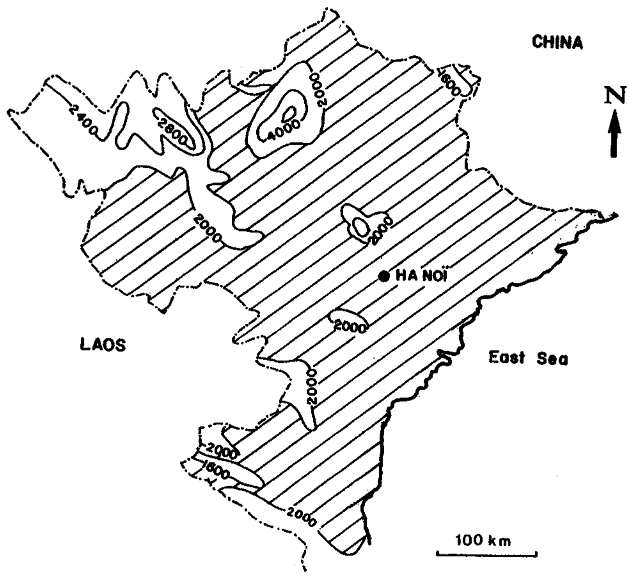


Fig. 2. *Average annual rainfall in northern Vietnam. The lines of equal rainfall are in mm. The annual rainfall depth is between 1600 mm and 2000 mm in the hatched zone.*

Minor constituents such as bromide, silica ($SiO_2$), boron and fluoride were assessed in some waters.

Detailed or partial chemical analyses are available for the majority of the 23 thermal and mineral waters examined and a representative selection of these is provided in Table 1. The temperature of these waters ranges from 29°C to 68°C (Fig. 3).

Examination of the ionic balance (concentrations expressed in meq $l^{-1}$) was used to check the acurracy of the analyses (Standard Methods, 1974). It is considered that deviation of 0.05 in 1, is acceptable in the anion/cation ratio (Domenico and Schwartz, 1990). Here, the deviation is less than $\pm$ 0.05 for 19 analyses. Analyses 1, 16, 17 and 23 for which the deviation is between 0.09 and 0.17 should therefore be suspect.

It will be seen that potassium does not appear in Table 1. Indeed, this element was only analysed in five samples (9, 11, 12, 13 and 14) for which the anion/cation ratio was similar to that of analyses with no value for potassium. The absence of $K^+$ does not therefore seem a determinant factor in the value of the anions-cations balance. However, the possibility that the imbalances in analyses 1, 16, 17 and 23 might result partly from the absence of potassium cannot be ruled out.

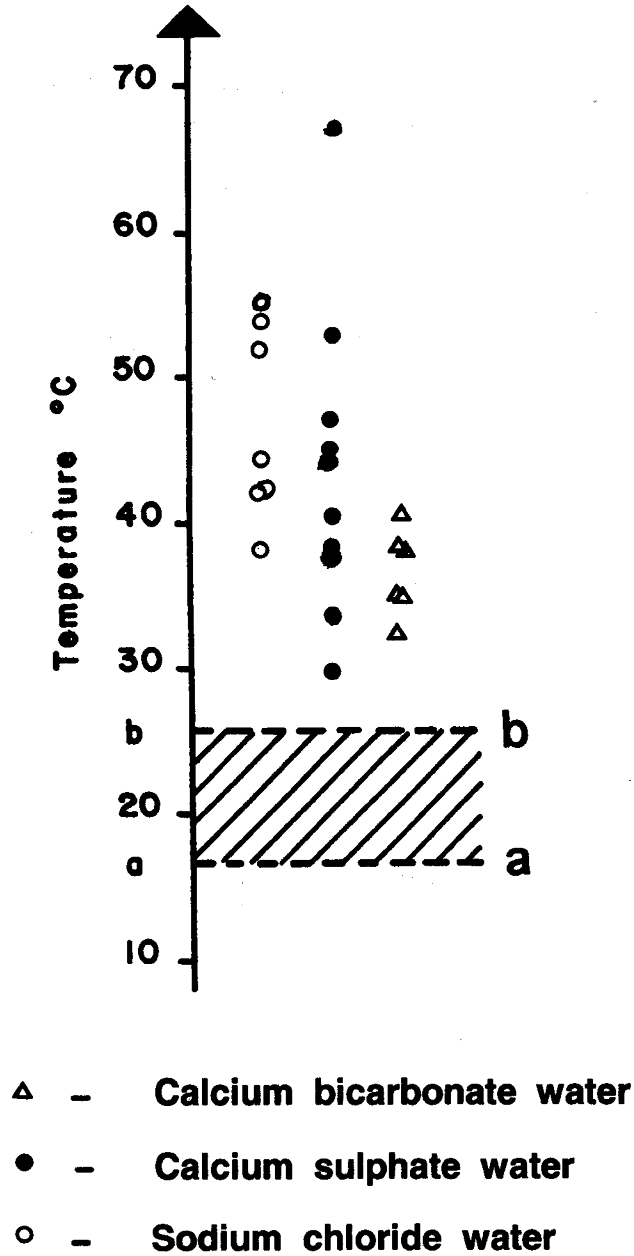


Fig. 3. *Temperature of the thermal waters studied. The hatched zone a–b represents the range of annual average air temperatures for the whole of northern Vietnam.*

## CHEMICAL CHARACTERISTICS OF THE THERMO-MINERAL WATERS

Within the diamond-shaped field of a trilinear diagram (Piper, 1944), four distinct subfields can be identified and the ionic species predominant in each are indicated in Fig. 4.

It is apparent that four types of mineral and thermal waters can be distinguished and the number of waters falling into each group is shown in brackets:

- Na-Cl type (7)
- $Ca-SO_4$ type (10)
- $Ca-HCO_3$ type (5)
- $Mg-HCO_3$ type (1)

Representation on semi-logarithmic diagrams (Schoeller, 1962) makes it possible to compare the hydrochemical types according to the concentrations in meq $l^{-1}$. (Figs. 5 and 8).

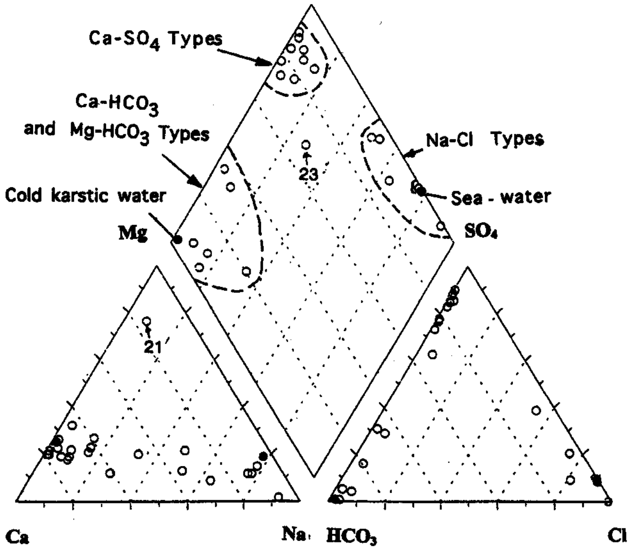


Fig. 4. *Representation of the chemical analyses of the thermal waters studied (trilinear diagram, after Piper, 1944).*

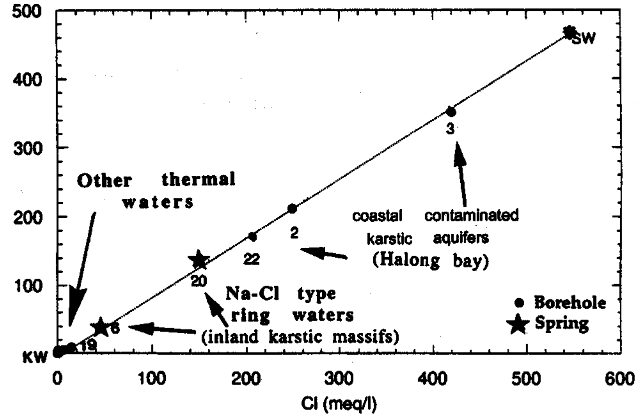


Fig. 6. *Relation betwen sodium and chloride in thermal waters. SW = Sea-water, KS = Karstic waters.*

THE NA-CL TYPE WATERS (FIG.5)

The waters belonging to this hydrochemical facies are from five wells (Fig. 5a) and two springs (Fig. 5b).

(a) Water from wells (2, 3, 18, 19 and 22)

These wells are in the Haiphong coastal region and located in two regions. Wells 2 and 22 are in karstified limestone of the coast of Halong Bay. Water is extracted at depths of between 100 m and 800 m (22). It is strongly mineralised ($13.1 < \text{TDS g l}^{-1} < 26$) and its temperature ranges from 42°C to 54°C. The chemical composition is characterised by high Na-Cl contents and rNa/Cl and $rSO_4$/Cl ratios are close to 0.85 and 0.1 respectively, identical to sea water rNa/Cl ratio and sea-water $rSO_4$/Cl ratio. Chloride and sodium concentrations are plotted in Fig. 6. The relationship observed between $Cl^-$ and $Na^+$ close indicates, to a first approximation, a mixing with sea-water.

The use of bromide anionconcentrations supplements chloride measurements in explaining the salinity anomalies in ground waters (Morell *et al.*, 1986; Fisher and Mullican, 1997; Andreasen and Fleck, 1997; Hsissou *et al.*, 1999). In sea-water, the Br:Cl ratio is approximately 0.0034. This ratio is 0.0029 for well 2, 0.0036 for well 3, and 0.0024 for well 22 (Table 3). That would confirm the contamination by the sea-water. Wells 18 and 19 tap a karstic aquifer at a depth of between 766 m and 1,017 m under the vast Red River delta alluvial plain. The wells are artesian and the water temperatures are 38°C and 44°C. In wells 18 and 19, the Br:Cl ratios are 0.0104 and 0.0294 respectively. The enrichment in bromide could have been generated by sediments (Neogene and Pleistocene sus-jacents, Fig. 7)

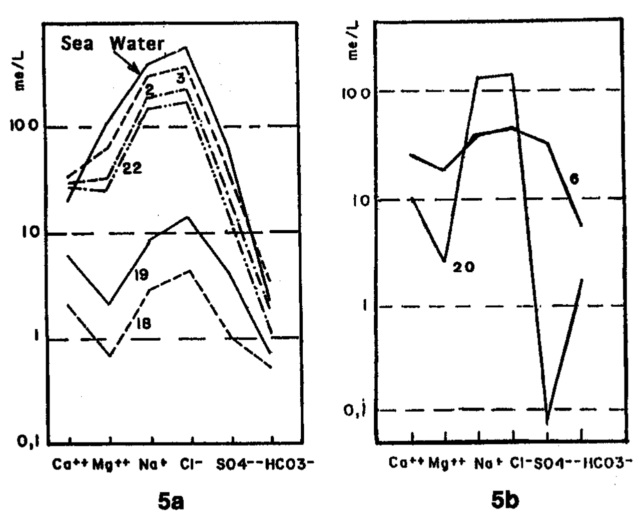


Fig. 5. *Sodium chloride type waters. (logarithmic diagram, after Schoeller, 1962). 5a: Intrusion of sea water in thermal wells. 5b: Thermo-mineral springs.*

(b) Spring water (6 and 20)

Although these two thermal springs also fall on the mixing line (Fig. 6), their geographical situation prevents contamination by sea-water.

The water from Kenh Gà spring (20) emerges at 52°C from a karstic massif lying south of the alluvial plain of the Red River. Its hydrochemical characteristics differ from the Na-Cl type waters analysed in the delta zone. The 8.54 g $l^{-1}$ Na-Cl concentration represents 96% of the TDS. The sulphate content (4 mg $l^{-1}$) and the $Mg^{2+}$ concentration (30 mg $l^{-1}$) are low in comparison with those of the waters contaminated by sea-water, in which the level is generally more than 300 mg $l^{-1}$.

This depletion of sulphate may be explained by traces of $H_2S$ observed during sampling. This is commonly accounted for by a bacterial reduction phenomenon; this occurs frequently in the strongly reducing environment of confined aquifers (Schoeller, 1962). The $SO_4$/Cl ratio is thus $6.10^{-4}$ here, whereas it is $10^{-1}$ in sea-water.

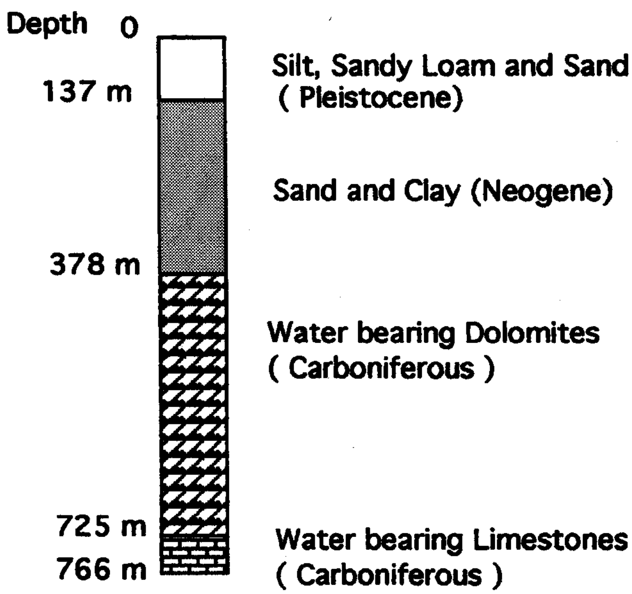


Fig. 7. *Lithologic log of well 18.*

The water from Muong Pià spring (6, temperature 55°C) clearly differs from the previous samples. Its Na-Ca-Mg-Cl-$SO_4$ ionic sequence is unique in the analyses and the $rSO_4/Cl$ ion ratio (0.7) is higher than that of sea-water. In fact, the geographical position of this spring is 150 km from the coast, ruling out a marine component. This hydrochemical feature led to the examination of other features. Thus, the concentrations of boron (1.5 mg $l^{-1}$) fluoride (1.6 mg $l^{-1}$) and silica (63 mg $l^{-1}$) may be characteristic of water that has flowed in contact with crystalline formations in the underlying basement.

### THE CA-$SO_4$ TYPE WATERS (1, 5, 8, 9, 10, 11, 12, 13, 17 AND 23) (FIG. 8)

There are ten analyses of this type, consisting of nine springs and a well (13) at Ba Vi near Hanoi. The chemical compositions of these sulphate waters can be grouped into three major ionic types: the Ca-$SO_4$ type where calcium represents more than 20% of the cationic sum (11, 13, 17, 23) (Fig. 8a), the Ca-Mg-$SO_4$ type (8, 9, 10, 12) and the Ca-Mg-$SO_4$-$HCO_3$ type (1, 5). The temperature of these sulphate waters ranges between 29°C and 68°C. The springs of Ban Hoc (11) and Thanh Tan (23) are, with Muong Pia spring (6–55°C), the warmest (53°C and 68°C) of all the springs in this study.

With TDS of 1 to 2.5 g $l^{-1}$ and $SO_4^{2-}$ contents of 0.5 to 1.5 g $l^{-1}$, the mineral contents of these waters are much lower than the sodium chloride type waters. Analyses 1, 8, 9, 10 and 12. which display high $Mg^{2+}$ content (up to 110 mg $l^{-1}$) belong to the Ca-Mg-$SO_4$ type (Fig. 8b).

Like the chloride contents (between 5.2 and 28.8 mg $l^{-1}$), the sodium contents were found generally to be low in these

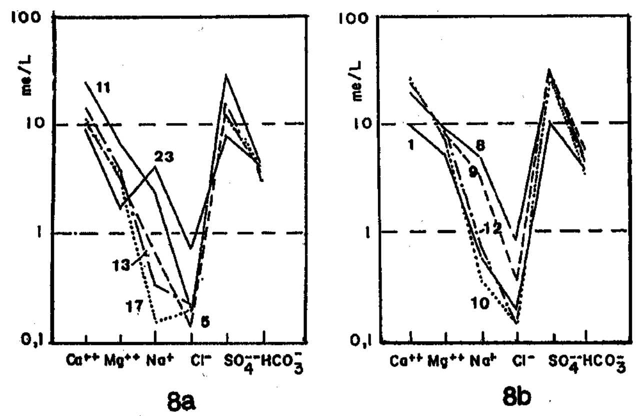


Fig. 8. *Calcium sulphate type waters. 8a: Ca-$SO_4$ type, 8b: Ca-Mg-$SO_4$ type.*

waters with $3.6 < Na < 52$ mg $l^{-1}$ in almost all cases. These levels probably indicate inflow of rain water as the source of Na and Cl ions.

For the purpose of the study, sulphate waters can be divided into two groups. The first has a temperature between 45°C and 68°C and includes analyses 8, 9, 11 and 23, which are characterised by relatively high $Na^+$ levels (72 to 111.7 mg $L^{-1}$). The second group is represented by the waters whose temperature is between 30°C and 45°C and whose $Na^+$ contents are lower than 35 mg $l^{-1}$ (1, 5, 10, 12, 13 and 17). These waters have generally a rNa/Cl ratio ranging between 1 and 5 close to the rNa/Cl ratio of rain waters.

### THE CA-$HCO_3$ AND MG-$HCO_3$ TYPE WATERS (4, 7, 14, 15, 16 AND 21) (FIG. 9A)

These consist of four springs and a well (4, 120 m deep) of the Ca-$SO_4^{2-}$ type and a spring of the Mg-$HCO_3$ type. Water temperatures are between 33°C and 39°C. TDS values are between 272 mg $l^{-1}$ and 440 mg $l^{-1}$, indicating the lowest mineralisation of all the waters studied. Spring 21 (Thuong Xung) is the only one of the Mg-$HCO_3$ type. It flows at the foot of calcareous-dolomitic plateaux (Ninh Binh region). With a content of 55 mg $l^{-1}$, magnesium forms 76% of total cations and the $HCO_3^-$ content (325 mg $l^{-1}$) is one of the highest after that of Muong Pia (6,338 mg $l^{-1}$). With regard to the other elements, this analysis is similar to that of the Son La karstic cold spring (25), with the same TDS of 430 mg $l^{-1}$ and comparable $HCO_3^-$ level. Only the $Mg^{2+}$ content is different, making the rCl/Mg ratio 0.2 rather than 0.7.

## Discussion and conclusion

In all parts of the world, karstic waters are subsurface waters

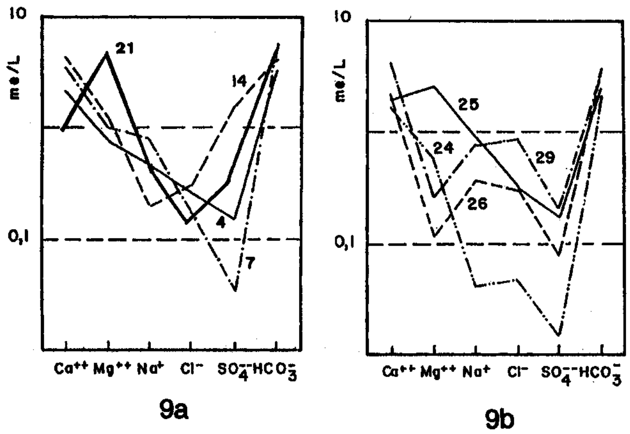


Fig. 9. *Calcium bicarbonate type waters. Examples of (9a) thermal waters and (9b) non-thermal karstic waters.*

*Table 3.* Bromide concentrations, chloride concentrations and bromide: chloride ratios of the thermo-mineral waters (Na-Cl type). The numbers are indicated on the map in Fig. 1.

| N° | Bromide (mg $L^{-1}$) | Chloride (mg $L^{-1}$) | $Br^-$:$Cl^-$ ratio |
|---|---|---|---|
| 2 | 25.6 | 8,842.1 | 0.0029 |
| 3 | 53.2 | 14,851.3 | 0.0036 |
| 18 | 2.4 | 231.0 | 0.0104 |
| 19 | 15.0 | 509.4 | 0.0294 |
| 22 | 17.6 | 7,301.3 | 0.0024 |
| Sea-water | 64.0 | 19,046.0 | 0.0034 |

different from deep-seated thermal waters and they generally display a chemical appearance of the calcium bicarbonate type (Back and Hanshaw, 1965; Hem, 1970). Examples of this water-type in northern Vietnam are found in analyses 24, 25, 26, 27, 28 and 29 (Table 2 and Fig. 9b). In these analyses, mineralisation is similar to that of bicarbonate type thermo-mineral waters (TDS between 172 mg $l^{-1}$ and 485 mg $l^{-1}$). As in most thermal waters, the $SO_4^{2-}$ contents are lower than the $Cl^-$ contents in all cases. The rNa/Cl ratio is close to 1 in the non-thermal waters, which would seem to show the effect of rain containing marine aerosols. In contrast, the values of this ratio differ from 1 in the thermal waters, possibly as a result of ion exchange with clay minerals.

This hydrochemical proximity of these thermal and non-thermal waters indicates that hot water flows only in carbonate rocks but that they are subjected to ionic exchange (Domenico and Schwartz, 1990) as indicated by the rNa/Cl ratio.

Calcium sulphate waters are the most frequently seen type. This water type has already been mentioned as being very common in northern Vietnam (Fontaine, 1969). In addition, Waring (1965) reported on several thermal springs in northern Vietnam and noted that the main chemical compound was the $SO_4^{2-}$ ion. This type of water may, therefore, be characteristic of the thermal waters in this region. The source of the sulphate cannot originate from dissolution of gypsum or anhydrite as these evaporitic deposits are not found in northern Vietnam. They are reported only in the Cretaceous deposits in central Vietnam (Geological Map of Vietnam, 1986). However, it is known that successive orogenic periods enhanced the magmatic activities that led to much mineralisation in northern Vietnam (Tran Cau, 1984) and especially sulphide mineralisation features (Fromaget, 1941) such as pyrite, molybdenite, arsenopyrite, sphalerite and lead sulphide in the Palaeozoic schists underlying the karst. Permian-Carboniferous limestones also contain pyrite (as in the cores withdrawn from well 13), arsenopyrite and sphalerite and also chalcosite. The $SO_4^{2-}$ ions may, therefore, originate from the weathering of pyrite or the leaching of other sulphides by hyporthermal waters of deep origin.

The sodium chloride waters are the result of contamination by sea-water (except for springs 6 and 20) and show the possibility of sea-water intrusion at great depth (to

*Table 2.* Results of the chemical analyses of non-thermal karstic waters in northern Vietnam. The numbers are indicated on the map in Fig. 1.

| N° | Location | T°C | TDS (mg$L^{-1}$) | $Ca^{++}$ (mg $L^{-1}$) | $Mg^{++}$ (mg$L^{-1}$) | $Na^+$ (mg$L^{-1}$) | $\Sigma r^+$ (meq/L) | $\Sigma r^-$ (meq/L) | $HCO_3^-$ (mg$L^{-1}$) | $Cl^-$ (mg$L^{-1}$) | $SO_4^{--}$ (mg$L^{-1}$) | Geol |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 24 | Pho Yen | 18 | 176.68 | 33.6 | 7.0 | 1.0 | 2.32 | 2.16 | 128.1 | 1.7 | 0.8 | T |
| 25 | Son La | 23 | 440.80 | 40.1 | 32.8 | 21.5 | 5.63 | 5.67 | 314.9 | 12.2 | 8.0 | T |
| 26 | Thi Xé (HG) | 24 | 297.73 | 43.5 | 15.5 | 8.6 | 3.82 | 3.81 | 206.9 | 11.5 | 4.1 | ? |
| 27 | Ha Long B. | 24 | 414.28 | 89.5 | 17.3 | 15.1 | 5.72 | 5.06 | 249.0 | 24.6 | 8.0 | C |
| 28 | Ha Long B. | 24 | 498.63 | 50.2 | 38.0 | 19.8 | 6.65 | 6.78 | 320.0 | 40.2 | 17.0 | C |
| 29 | Ha Long B. | 23 | 350.02 | 73.1 | 2.9 | 18.5 | 4.72 | 4.50 | 207.0 | 30.3 | 9.0 | C |

approximately 1000 m below sea level in well 19). The great depth of the karst resulting from the subsidence of the Red River delta makes the deep flows easier (Hanoi basin, wells 18 and 19) and also the coastal karsts of Halong bay that have been partially encroached by the sea (wells 2 and 3). The proportion of sea-water in the groundwater from these wells can be estimated from the $Cl^-$ concentration; this is 19,000 mg $l^{-1}$ in sea-water and an average of 20 mg $l^{-1}$ in uncontaminated karst water in the Halong region. The proportion of sea-water would thus be 42% in well 2 (8,842 mg $l^{-1}$ $Cl^-$) and 78% in well 3 (14,851 mg $l^{-1}$ $Cl^-$). However, these waters are at the same temperature (42°C) although the percentages of sea-water are very different. This indicates that there is a certain complexity in the deep flows which merits a closer study.

There is no clear relationship between the chemical facies of the waters and the temperature when the calcium sulphate waters are examined (between 29°C and 68°C) (Fig. 3). However, the average temperature of the calcium bicarbonate waters is close to 35.7°C whereas that of the sodium chloride waters is 46.7°C. This indicates that the calcium bicarbonate waters flow at a shallower level than the sodium chloride waters or result from the mixing with small proportions of thermal water. Different chemical geothermometers have been used successfully in many studies (Michard *et al.*, 1981; Kharaka and Mariner, 1989) and are often very helpful in interpreting such geochemical processes. However, concerning thermal waters emerging from sedimentary reservoirs, the processes affecting the deep mineralized fluids prevent the use of a chemical geothermometer (Pauwels *et al.*, 1997). In the case of the thermal waters of northern Vietnam emerging from carbonate aquifers, the maximum temperatures calculated are not significant or should be considered with caution. In light of the major element analyses, the thermal waters examined in the karstic aquifers of northern Vietnam have flowed mainly through carbonate rocks. Among the 23 samples analysed, only one has a composition that indicates deep flow in contact with a crystalline basement.

With this exception, the two main features of these thermal waters are the existence of a chemical facies rich in $SO_4^{2-}$ ions probably formed through sulphide minerals and high Na-Cl concentrations resulting from sea-water intrusion. The saline waters also result from the burying of the karstic aquifers during tectonic subsidence.

The data provided from the study of the major ions analysed in thermal karstic waters are not in themselves sufficient to detect a possible flow in deep crystalline basement, especially when the input is minor. Nevertheless, considerable chemical differences exist in thermo-mineral groundwaters from carbonate karstic formations in northern Vietnam. Also, the thermal springs studied occur neither in the same geographical context nor in the same geological units. Different hydrogeological conditions are the main factor affecting the chemical composition of these waters and the study of the major ions has provided some reliable conclusions.

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