fitilbe.

# INTERPRETATION OF WATER COMPOSITIONS FROM THE MASAYA-CARAZO-GRANADA AREA IN SE-NICARAGUA

Marvin J. Martinez<sup>+</sup>, UNU Geothermal Training Programme, National Energy Authority, Grensásvegur 9, 108 Reykjavík, Iceland

<sup>+</sup>Permanent address: Instituto Nicaraguense de Energía (INE), Recursos Geotermicos, Managua, Nicaragua, Centro América Nr. 6

### ABSTRACT

The Masaya-Carazo-Granada area was selected for study because recent geothermal exploration in Nicaragua by Consorcio Ieco-Lahameyer indicated that this was a promising field and was given a high priority for further investigations.

Chemical data were studied and interpreted. Two geochemical anomalies were identified which reflect high temperature reservoirs. They are: Apoyo Lagoon (Masaya area) and Mombacho Volcano and surroundings (Granada area).

Evidence for depositions of silica and mixing was found in both areas. However, it is not possible to evaluate underground temperatures by assuming simple mixing.

The underground temperatures at Apoyo Lagoon are estimated to be of the order of 200°C. At Mombacho Volcano they are at least 170°C (quartz equilibrium temperature) but may be as high as 300°C (feldspar equilibrium temperature). From the water chemistry of Carazo it is deduced that these waters are surface waters and do therefore not provide any evidence on underground geothermal reservoirs.

LIST OF CONTENTS

ABSTI	RACT
1	INTRODUCTION
1.1	Scope of Work9
1.2	Thermal Activity in Nicaragua. The Quaternary
	Volcanic Chain11
1.3	Sampling Methods and Analytical Techniques
2	GEOCHEMICAL INTERPRETATION OF WATERS FROM THE
	MASAYA-CARAZO-GRANADA
2.1	Geology and Other Features
2.2	Chemical Characteristics
2.3	Evaluation of Underground Temperatures and Solution-
	Mineral-Equilibria
	2.3.1 Masaya Area
	2.3.2 Granada Area
	2.3.3 Carazo Area
3	RESULTS
4	RECOMMENDATIONS FOR FURTHER GEOCHEMICAL STUDIES
ACKNO	DWLWDGEMENTS
REFEI	RENCES

#### LIST OF TABLES ......

\_\_\_\_\_

	Page
1.	Analytical methods used by the Laboratory Amtech. Labs, San Diego,
	California
2.	Composite litho-stratigraphic chart of Western Nicaragua
3.	Geothermometers in °C25-26
4.	Chemical composition of representative samples of waters in
	Masaya-Carazo-Granada area

# LIST OF FIGURES

	Page
1.	Geothermal manifestations in Nicaragua10
2.	Index map-structural blocks12
з.	Schematic cross section of tectonic plates
4.	Structural geology of western Nicaragua15
5.	Principal geothermal anomaly in Masaya-Carazo-Granada area
6.	Silica saturation in the geothermal water with respect to amorphous silica and chalcedony solubility
7.	Comparison between feldspar (Na-K) and quartz equilibrium temperatures 30
8.	The state of fluorite saturation in water from the Masaya-Carazo- Granada area
9.	The state of calcite saturation in waters from Masaya-Carazo-Granada area
10.	The state of calcite saturation in waters from Masaya-Carazo-Granada area (quartz equilibrium temperature)
11.	The state of anhydrite saturation in waters from Masaya-Carazo- Granada area
12.	The state of anhydrite saturation in waters from Masaya-Carazo- Granada area (quartz equilibrium temperature)
13.	$Na^+/K^+$ ratios in thermal waters from Masaya-Carazo-Granada area in relation to equilibrium with $Na-K$ feldspars referring to measured
14.	temperature
15.	The temperature dependence of $\sqrt{Ca^{+2}}/H^{+}$ in waters from Masaya- Carazo-Granada area (guartz eguilibrium temperature)

- 7 -

# 1 INTRODUCTION

### 1.1 Scope of Work

During the last years exploration and development of geothermal resources in Nicaragua have received special attention. This is principally due to interest in using geothermal energy for power production instead of using imported oil, the prices of which increase constantly.

At present a geothermal staff covering all the major disciplines is being formed in Nicaragua. They are receiving specialized training in countries who have experience in geothermal resources exploration, development and exploitation. Some of the members of this geothermal staff are currently undergoing specialized training in programmes sponsored by the United Nations.

The author of this report was awarded a United Nations University Fellowship to attend the 1981 UNU Geothermal Training Programme held at the National Energy Authority in Iceland in the field of chemistry of thermal fluids. The Training Programme included an introductory lecture course (4 weeks) about the various aspects of geothermal science, a field excursion to areas in Iceland of geothermal and geological interest (2 weeks); and specialized training in the chemistry of thermal fluids: sampling techniques and methods of analysis (3 weeks), geothermometry and chemical thermodynamics (4 weeks), gas analyses (1 week). This report is the result of the research project accomplished mainly during the last 9 weeks of the training.

The chemical data used in this report were obtained from a report on Geothermal Resources Geochemistry Investigations, Volume 5.1, prepared by Geothermex Incorporated, Berkeley, California (Klein et al. 1980), which is a part of the report presented by Consorcio Ieco-Lahameyer to the Nicaragua Master Plan for electrical development for the years 1977-2000.

The conclusions in this report do not conflict with those of Klein et al. 1980 in any major way. However, the present interpretation of the data is that of the author under the supervision of Dr. Stefan Arnorsson and Dr. Einar Gunnlaugsson both from the University of Iceland.



The present study of the Masaya-Carazo-Granada geothermal area is undertaken for gaining more knowledge about the geothermal system. It was reported in the findings of Ieco-Lahameyer priority area, for further geological, geochemical and geophysical investigations. Preliminary assessment by the Ieco-Lahameyer suggests Masaya-Carazo-Granada has a geothermal power potential of approximately 1000 MWe for thirty years.

1.2 Thermal Activity in Nicaragua. The Quaternary Volcanic Chain The following account is mainly from Goldsmith et al. (1979). Figure 1 shows the distribution of geothermal manifestation in Nicaragua. The volcanic chain (Figure 2) in Nicaragua is a part of the "Pacific Ring of Fire", a zone of active volcanism that encircles the Pacific Ocean. In Central America, this volcanic chain extends from Panama northwestward through Costa Rica, western Nicaragua, southern Honduras, El Salvador, Guatemala, and into Mexico. The Central American chain started to form during the Tertiary time. The major buildup of the present volcanoes and volcanic complexes has continued into Holocene time with the last major eruption taking place at Volcan Cerro Negro in the El Hoyo Volcanic Complex (Figure 2) in 1972.

The relationship of the Central American volcanic chain to the Nicaragua Depression is shown in Figure 2. Northwest of Lake Managua, this chain forms the southwestern margin of the present Nicaragua Depression. In Lake Nicaragua to the southeast, the volcanic chain appears as isolated volcanic islands within the depression (Islas Zapatera and Ometepe). The Managua structural block represents a discontinuity in the volcanic chain of the structural blocks to the north and south and is the area of major displacement of the volcanic axis in Nicaragua.

The early phase of volcanic activity in Nicaragua resulted probably in the formation of volcanoes forming offshore islands which later coalesced to form a continuous sub-areal stretch west of the Nicaragua Depression. The oceanic Cocos Plate (Figure 3) is being subducted towards the northeast, sliding under the west-moving continental Caribean Plate. The Nicaragua coast roughly parallels the zone of subduction where the heat, pressure, and radioactivity combine to transform the rocks into magma, which may then rise through tension fractures to the surface, to form the volcanic features of the present Quaternary volcanic chain.

- 11 -



- 12



T

The project area covers a volcanically active area where heat sources (magma chambers) at moderate depth can be expected to exist. Sapper (1929) called the volcanic chain in Nicaragua the "most explosive" place on earth (Bullard, 1976). The volcanic chain (and the general coastal area) is broken into four separate transverse structural blocks (Figure 2). The limits of these blocks are based largely upon distinctive volcanic features, changes in the Pacific shoreline, and the shape of the Nicaragua Depression. The three central blocks range in length (northwest to southeast) from about 55 to 75 kilometers.

The volcanic chain of the Ometepe Block and the block itself, which is the southernmost block in Nicaragua, is offset about 40 kilometers to the southwest, so that the volcanic chain in Costa Rica is seen as a continuation of the volcanoes of the Ometepe Block (Figure 2). The forty-kilometer right-lateral offset mapped near the Nicaragua-Costa Rica border is the largest displacement of any of the structural blocks.

These blocks were possibly formed before Pliocene time as indicated by the absence of any displacement in the southwest shore of Lake Nicaragua near the 40 kilometers right-lateral displacement of the volcanic chain. No offsets or traces of the faulted block boundaries could be traced further to the northeast into the Central Highland, middle Tertiary, volcanic section. Seismic events evidently associated with the subduction zone of the underthrusting Cocos Plates show no concentration of earthquakes along the transverse faults at the boundaries between the structural blocks. The seismic events associated with this underthrusting of the Cocos Plate are indicated by their deep location along the entire coast and on the continental paltform. Shallow seismic events associated with volcanic activity occur along the Quaternary volcanic chain.

The structural blocks which comprise the Quaternary volcanic chain southwest from the Gulf of Fonseca are (Figure 2) :

- The Gulf of Fonseca Block (including Volcan Cosiguina)
- The Marrabios Range Block
- The Managua Structural Block
- The Ometepe Block

In Figure 4 the structural geology of western Nicaragua is presented.

- 14 -



- 16 -

# 1.3 Sampling Methods and Analytical Techniques

The author worked with Geothermex Incorporated during June to July 1978, in collecting gas and water samples for chemical analyses including measurements in the field. The pH and the conductivity were determined in the field during the collection time.

For analyses of Na, K,  $HCO_3$ ,  $SO_4$ , Cl,  $S_1O_2$ , B and F, water samples were filtered through a 0.45 micron membrane filter and collected in polyethylene bottles. They were not treated at the time of collection. Samples for analysis of Ca and Mg were acidified to pH 2 with HCl.

Samples for ammonia analysis were taken into ambar glass bottles, without any treatment and stored over ice in darkness until used for the determimnations. If a water was found to have a conductivity more than 1,000 µmhos/cm a filtered sample also was collected diluted with labtested deionized water to a conductivity about 500 µmho /cm to help insure against loss of solute by precipitation during sample storage prior to analysis.

Ammonia measurements were carried out using an Orion ammonia gas-sensitive electrode connected to a digital millivolt meter and strip chart recorder. All samples were analysed twice, at least, usually on the day of collection, then again on the following day.

The gas samples were collected in 300 ml glass flasks fitted with a single inlet valve of a design by Dr. A. Truesdell of the United States Geological Survey. The method used was adopted from Giggenbach (1976).

Each flask contained 100 ml of 4N NaOH under a vacuum prepared by gently boiling the caustic solution while vacuating the flask with a water aspirator pump. The caustic solution serves to absorb any  $CO_2$  and  $H_2S$  present in the sample gases, thereby concentrating the remaining constituents and enabling more precise chromatographic analyses. Samples were directed to the flasks via plastic and stainless steel funnels, and glass and tygon tubing fitted with control valves and pincess.

Samples were analyzed by gas chromatography, and wet chemical assay of the 4N NaOH solution for absorbed  $CO_2$  and  $H_2S$ . However, due to inadequate sealing of the flasks\_used, several samples resulted in near total contamination by air. All analyses were made in the United States, water samples at the Amtech Laboratories, San Diego, California, and gases at the Western Analytical Services, Orinda, California.

The methods used in these analysis are presented in Table 1.

### TABLE 1

Analytical methods used by the Laboratory Amtech Laboratories, San Diego, California.

Species	Method
Ca	Atomic Absorption
Mg	Atomic Absorption
Na	Flame Emission
K	Flame Emission
HCO3/CO3	Titration, electrometric
so <sub>4</sub>	Gravimetry
Cl	Colorimetric (Ferricyanide)
sio <sub>2</sub>	Atomic Absorption
В	Colorimetric (Carmine); 5 standards routinely
	run with each batch of unknowns
F	Specific ion electrode

# 2.1 Geology and Other Features

The Masaya-Carazo-Granada area is bounded by several volcanic features consisting in the northwest of the Masaya volcanic complex and the Masaya Lagoon, the Apoyo Lagoon (a large phreatic explosion crater) to the northeast and lastly the Mombacho Volcano located several km to the southeast.

This area is almost wholly covered with Quaternary rocks (Fig. 4). The Masaya and Santiago volcances are located on the eastern flank of the massive Quaternary volcanic chain.

A composite litho-stratigraphic chart of western Nicaragua is shown in Table 2.

Detailed geophysical and gravity surveys have been carried out in the area. The results are presented in a report by Ieco-Lahameyer who interpreted them as being very positive and gave the area accordingly a high priority for further exploration.

### 2.2 Chemical Characteristics

The waters from Masaya area can be divided into two groups, one includes slightly alkaline waters with high chloride and relatively high boron contents and with temperatures varying between 44°C and 75°C. The other water group has high bicarbonate content but low chloride and local groundwater temperatures at the surface and in shallow wells.

The waters from Carazo area are all high in bicarbonate and low in chloride and very low in dissolved solids. Surface temperatures are between 26°C and 28°C.

Most of the waters from the Granada area have high bicarbonate contents. Temperatures range from 26°C to 54°C. Waters from hot springs have the highest temperatures from 33°C to 54°C. These waters contain relatively high chloride and dissolved solids exceed 1000 ppm. The flow rate of individual hot springs sampled lies between 1-2 liters/sec (samples G-4, G-5, 3-4, 2-11, 2-13, for locations see Fig. 5).

# Composite Litho-Stratigraphic Chart of Western Nicaragua (From Goldsmith

et al. 1979).

AGE	FORMATION 6 SYMBOL	APPROXIMATE THICKNESS (m)	LITHOLOGY	DISTRIBUTION
Holocene	Alluvium and colluvium (Q <sub>1</sub> - Q <sub>5</sub> )	Thin surficial layer, sel- dom exceeding 30 m.	Very fine to very coarse-grained detrital sediments, mostly surfi- clal, nonconsolidated and poorly sorred.	
	U N C	ONFOR	H I T Y	
	Recent volcanics (Q <sub>a</sub> - Q <sub>c</sub> )	Mostly thin, reaching a few tens of meters local- ly, close to the eruptive centers.	Various lava flows and associated pyroclastic sediments.	Associated with the Quaternary eruptive centers.
	U N C	ONFOR	H I T Y	
Pleistocene	Las Sierras (QTs)	680	Poorly stratified pyroclastics, predominantly agglomeratic tuff.	Building the series of cuestas outlining from the southwest the lineament of the volcanic centers of Nicaragua.
	Older volcanics (QT <sub>a</sub> - QT <sub>c</sub> )	Same as Recent volcanics	Same as Recent volcanics	Northeastern fringes of the Nicaraguan Depression.
Pliocene	El Salto (Tps)	100	Tuffaceous sandstones and silt- stone with marls and coquina-li- mestone at the base.	In central part of the Pacific Coastal Zone, as partly eroded remnants, preserved in downfaulte blocks.
	Upper Coyol (T <sub>1</sub> , T <sub>2</sub> , T <sub>3</sub> )	Varying up to 800 m.	Basalt, rhyolitic ash flows, and agglomerates	Northeast of the Nicaraguan Depression and between Cosi- güina and San Cristobal Voica- noes.
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	U N C	ONFOR	н і т у	
Mocene	El Fraile (Tmf)	2700	Agglomerates, tuffaceous sand- stones and silstones with minor calcareous sandstones.	Crops out along the southwest slopes of the Pacific Ridges in the central part of Pacific Coastal Zone.
	Lower Coyol (T <sub>6</sub> -T <sub>7</sub> )	700	Andesitic lava flows, agglomerates and ash flows.	Northwestern part and northern fringes of the Nicaraguan De- pression. time-equivalent of Tamarindo.
	Tamarindo (T <sub>4</sub> - T <sub>5</sub> )	up to 600	Ash flows, agglomerate and andesi- tic lava.	Pacific Coastal Zone, time-equi- valent of Lower Coyol.
Oligocene	Masachapa	1500	Monotonous sequence of interbedded tuffaceous and calcareous shales, siltstone, and sandstone.	Crops out in the Pacific and Brito Ridges of the central part of Pacific Coastal Zone.
~~~~~~	U N C	U N F O R	H	
Eocene	Brito	3400	Graywacke,sandstone, tuffaceos silstone	Builds Brito Ridges along the southern Pacific Coastal Zone.
rateocene	Lunge	O N F O R	M L T Y	
Maestrichtian Campanian Santonian	Sapoa (TKs)	30	Biostromal reef	Limited location to Sapoa village in Rivas Province.
Turonian Cenomanian	Rivas (Kr)	3400	Tuffaceous shale, siltstones, gray- wackesandstone and conglomerate	Crops out in Rivas Province from beneath Brito formation of the Pacific Coastal Zone to the southwest and beneath the alluvial sediments of Lake Nicaragus to the northeast.
	million	ful mining	H I T Y	
Pre -Ceno- manian	(PTm)	1	Hildly metamorphosed graywacke, volcanic conglomerate, siliceous limestone, chert, basaltic lava, and agglomerates.	North and northwest Wicaragua is believed to comprise the ba- sement of the south Central- American Orogen.
	1	1		Colorada Col



T.

20

Waters with relatively high chloride have also been encountered in shallow wells (samples 2-52 and 3-5). These waters are slightly alkaline, high in dissolved solids and relatively high in boron, high in silica and with a temperature of 30°C and 38°C.

In the slope of Mombacho volcano, near the crater, there are fumaroles (sample 3-75 with surface temperature of 93°C) and some sulfate water (pH of 3).

On the whole the waters from the Masaya-Carazo-Granada area fall under the classification proposed by Ellis and Mahon (1964), and White (1957) for waters found in geothermal areas. Bicarbonate waters are found, low chloride hot waters containing high bicarbonate and variable sulfate concentrations and slightly alkaline sodium chloride waters. The reaction with rock produces neutral pH bicarbonate or bicarbonate suphate solution waters. A great deal of samples from Masaya-Carazo-Granada belong to these waters.

Acid sulfate waters, low in chloride, are considered to be steam heated surface waters and may be formed in volcanic geothermal area when steam condenses into surface waters. Hydrogen sulfide from the steam is subsequently oxidized to sulfate  $(H_2S + 2O_2 \rightarrow 2H^+ + SO_4^{-2})$ . These waters are invariably acid (pH 2-5). The water sample from Mobacho volcano in Granada area (sample 1-75) belongs to this group.

In the third group, the sodium chloride waters, the dissolved salts are mainly sodium and potassium chloride, although in the more concentrated waters calcium may occur in appreciable concentrations. The main dissolved gases are carbon dioxide and hydrogen sulfide. These waters often occur in areas with boiling springs and geyser activity and are common to many developed geothermal areas in both volcanic and sedimentary rocks. The most common type of water in deep geothermal systems is a sodium chloride solution at a pH within 1-2 units of the neutral pH at elevated temperature. Water samples of Masaya area (Masaya Lagoon) and one in Granada area (Mombacho volcano) fall within this group of water.

Surface waters or cold ground waters do not belong to any of the groups mentioned above. These waters show low chloride similar to rain water (0-10 ppm), relatively low pH, very low Na/K ratios and high magnesium

- 22 -

content. The silica is in the range of 10-40 ppm, occasionally as high as 100 ppm. This is possibly due to leaching of silica from the rock by the ground water and attainment of metastable equilibria with amorphous silica. The chemical composition of these waters indicates an overall non-equilibrium condition between water and rock. These characteristics distinguish this type of water from hot thermal waters which are considered to be indicative of deep groundwater circulation and thus of underground geothermal systems.

# 2.3 Evaluation of Underground Temperatures and Solution-Mineral-Equilibria

The basic assumption involved in the application of chemical geothermometers is that a chemical equilibrium between solution and the relevant minerals is attained at depth and that these equilibria are quenched in the upflow where cooling may take place. Experience in many geothermal fields of the world has indeed shown that underground temperature, predicted by chemical geothermometry are actually encountered at depth by drilling. This experience has largely been gained in fields of volcanic terrain, which, due to intense surface thermal manifestations and the results of exploratory work, were obvious as favourable for geothermal development.

An overall chemical equilibrium between solutes and alteration minerals is very often attained in geothermal systems for all the components which are incorporated in these minerals. Thus, geothermal waters are, as a rule, saturated with calcite and often saturated with anhydrite and fluorite. Mineral solute equilibria also fix the  $\sqrt{Ca^{+2}}/H^+$  activity ratios at a particular temperature. If degassing occurs in hot springs the waters may become significantly supersaturated with respect to calcite solubility.

Surface waters and shallow groundwaters are typically calcite undersaturated and have a very low  $\sqrt{Ca^{+2}/H^{+}}$  ratio. Relatively short underground residence time seems to be needed for cold groundwater to attain equilibrium with calcite. Waters of mixed origin have low  $\sqrt{Ca^{+2}/H^{+}}$  ratios for their temperature but are usually calcite-saturated (Gunnlaugsson et al., 1981).

The Na-K-Ca geothermometer proposed by Fournier and Truesdell (1973), which is empirically calibrated differs from the silica and Na-K geothermometers in the sense that it is not related to equilibrium with specific geothermal minerals. As demonstrated by Arnósson et al. (1981a), the ratios of all cations in geothermal waters are fixed at a particular temperature, if an overall chemical equilibrium is attained with the geothermal mineral assemblage. From this it is concluded that each of the cation ratios  $Na^+/K^+$  and  $\sqrt{Ca}^{+2}/Na^+$ , of which the Na-K-Ca geothermometer is composed, is determined by temperature alone. In other words, the application of this geothermometer involves the addition of two temperature dependent ratios.

The work of Arnórsson et al.(1981a) show much larger scatter of data points for the ratio  $\sqrt{Ca}/Na$  than for Na/K. They thought that the rather large scatter of the  $\sqrt{Ca}/Na$  ratio results from equilibrium with more than one mineral assemblage, whereas sodium and potassium activities seem to be governed by equilibrium with low albite and microcline over the whole temperature range. The large scatter of points for the  $\sqrt{Ca}/Na$  make the Na-K-Ca geothermometer inferior to the Na-K geothermometer over the whole temperature range whatever calibration curve and  $\beta$  value was used.

Estimates of temperature by the Na-K-Ca geothermometer are more conservative than estimates by the Na-K geothermometer because large monovalent cations take long to re-equilibrate, whereas divalent and trivalent ions and smaller ions re-equilibrate more rapidly. This implies that the ratios  $\sqrt{Ca}$ /Na would respond faster to cooling than the Na/K ratio.

In upflow zones where boiling takes place, calcium may precipitate as calcite in significant amounts. Such precipitation would yield high temperature estimated by Na-K-Ca geothermometer (Arnórsson et al. 1981b).

It is considered that evidence indicating chemical equilibirum conditions for components other than silica, sodium, potassium, and calcium gives improved confidence in the geothermometry results. For this reason, a computer program (Arnórsson et al., 1981) has been used to calculate the state of saturation for all the samples with respect to calcite, anhydrite, fluorite, Na- and K- feldspars as well as the  $\sqrt{Ca^{+2}/H^+}$  activity ratio. The calculations were performed at measured water temperature and at the quartz equilibrium temperature. These results along with the tempertures obtained from the conventional geothermometers at measured temperatures (Table 3) are used as a basis for the following discussion.

Most of the distinct thermal waters from the Masaya-Carazo-Granada area plot close to amorphous silica saturation (Fig. 6) whereas non-thermal waters (<30°C) vary from being slightly to strongly undersaturated.



# Table 3 Geothermometers in °C

Samble	Ec	Silie	ca Tempe	rature	Na /K	Na-K-Ca		
No.	µmho/cm Lab	- 1	2	3	4	5	Geothermometers	
1-8	3060	35	132	157	169	83		
1-9	6270	68	174	193	215	214	1: Amorphous silica (Fournier, 1977)	
1-52	307	10	101	129	(364)	58	731	
1-53	222	11	103	130	(368)	54	$t^{\circ}C = \frac{731}{4.52 - \log H_{4}SiO_{4}} - 273.15$	
1-54	373	1	90	119	(386)	77	$(SiO_{a} in ma/ka)$	
1-55	351	-	88	117	(451)	74	(SIO <sub>2</sub> III mg/kg)	
1-56	277	11	88	117	(433)	55	2: Chalcedony (Fournier, 1977)	
1-57	316	15	108	135	(462)	59	(0-250°C)	
1-58	317	17	111	138	(391)	68	1032	
1-59	262	15	108	135	(387)	57	$t^{\circ}C = \frac{1}{4.69 - \log H_4 SiO_4} - 273.15$	
1-60	312	-	88	117	(412)	74		
1-67	244	-	86	115	(533)	64	3: Quartz (Fournier, 1977)	
1-68	325	2	92	120	(446)	69	(0-250 C)	
1-69	272	15	108	135	(533)	84	1309	
1-70	283	15	108	135	(419)	52	$t c = \frac{1}{5.19 - \log H_4 SiO_4} - 273.15$	
1-73	294	12	104	131	(358)	66		
1-74	426	16	109	136	(394)	77	4: Na/K (White and Ellis, see Truesdell 1975, White, 1970) (100-275°C)	
1-75	769	20	115	141	176	30		
1-76	749	16	109	136	(333)	63	$t^{\circ}C =$	
2-8	257	20	115	141	(364)	61	$log(\frac{Na}{K}) + 0.8573$	1
2-9	339	25	120	146	(467)	65		25
2-10	839	26	122	148	266	26		1
2-11	1277	53	155	176,5	264	199		
2-12	6330	31	127.5	152	157	181		

 Sample	Ec	Silica	Tempe	erature				
 No.	µmho/cm Lab	1	2	3	Na/K 4	Na-K-Ca 5	Geothermometers	
2-13	546	39	137	161	(386)	66		
2-41	365	17	111	138	(302)	64		
2-42	304	17	111	138	(354)	57	5: Na-K-Ca (Fournier and Truesdell, 1973)	
2-43	315	17	111	138	(349)	50	(4-340°C)	
2-44	189	20	115	141	(>500)	71	1647	
2-45	444	15	108	135	(343)	40	$t^{\circ}C = \frac{1047}{\log(Na)} + \beta \log(\sqrt{Ca}) + 2.24$	
2-46	380	12	104	131	(513)	65	$\operatorname{Hog}(\mathbf{K}) + \operatorname{Hog}(\mathbf{V} = \mathbf{M}) + 2.24$	
2-47	257	13	105	133	(419)	55	$\beta = 4/3$ for $\sqrt{C_2}/N_2 > 1$ or $t \leq 100^{\circ}C$	
2-48	240	13	105	133	(404)	53		
2-49	311	18	112	139	(356)	48	$\beta = 1/3$ for $\sqrt{Ca/Na} < 1$ or t < 100°C	
2-50	842	16	109	136	(432)	61		
2-51	386	23	118	144	(436)	61	(Na, K, Ca in moles/liter)	
2-52	2270	23	118	144	233	212	-: Negative Amount	
2-84	416	-	76	105	(498)	93		
2-85	314	2	92	120	(402)	68		
2-89	495	14	107	134	268	67		
3-3	217	17	111	138	(368)	48		
3-4	1784	56	159	180	316	220		
3-5	1513	48	149	171	258	200		
3-6	1923	42	142	165	(295)	75		
3-75	1071	59	163	183	(325)	43		
G-4	2000	48	66	171	180	173		
G-5	2400	48	68	171	180	174		

- 26

In this study 10 samples from the Masaya area are considered. Of these, 3 are thermal (1-8, 1-9, 2-12) and 7 are non-thermal.

The thermal waters from Masaya area (1-8, 1-9, 2-12) show good correlation between the quartz equilibrium and the feldspar equilibrium temperature (Fig.7). The slight difference in these values is hardly significant. Samples 1-9 and 1-8 are near equilibrium with amorphous silica at measured surface temperature. If precipitation of amorphous silica was taking place in the upflow it must be insignificant as deduced from the similarity of Tatz and TNa/K These two samples are undersaturated with fluorite and anhydrite at the measured temperature (Figs. 8 and 11). However, they are slightly supersaturated at  $T_{qtz}$  (Fig. 12). Sample 1-9 is saturated with calcite at the measured temperature but sample 1-8 is slightly supersaturated (Fig. 9) and both samples are strongly supersaturated at Tgtz (Fig. 10). These waters have low Na/K ratio in relation to equilibrium with Na and K-feldspars at measured temperature (Fig. 13). They show low  $\sqrt{Ca^{+2}/H^{+}}$  activity ratios at measured temperature (Fig. 14), but relatively high ratios when reference is made to  $T_{qtz}$  (Fig. 15). Sample 2-12 is in equilibrium with anhydrite at  ${\tt T}_{\mbox{qtz}}$  and slightly undersaturated at measured temperature. It is supersaturated with calcite at measured temperature and  $T_{qtz}$  and undersaturated with fluorite at both measured temperature and Tgtz. This water has low Na/K ratio in relation to equilibirum with Na- and K- feldspars at measured temperature. It shows low  $\sqrt{Ca^{+2}/H^{+}}$  activity ratio at measured temperature but relatively high ratio when reference is made to Tatz.

These waters (1-8, 1-9, 2-12) were selected for running the computer program at  $T_{\rm Na/K}$  foreseeing precipitation of silica. The results obtained show that these samples compare well with the proposed equilibrium curves of Arnorsson et al. (1981a).

It is not possible to explain the composition of the cold water samples (1-70, 1-59, 1-69, 1-57, 2-45, 2-52, 2-85, 3-3) (Fig. 5) by simply using mixing where 1-9 sample would represent the hot water component and the Apoyo lagoon, or ground water, the cold water component. This is deduced from the relationship between chloride sodium and silica vs.temperature.

### Conclusions

The cold waters from Masaya do not provide any evidence of geothermal underground systems. Samples 1-8, 1-9, 2-12 reflect underground temperatures in the range of 200°C. This value may be low relative to existing underground temperatures due to interaction between water and rock in the upflow.

# 2.3.2 Granada Area

From Granada area 8 samples are considered in the present study. Of these 5 are thermal (2-11, 3-4, 3-5, G-5, G-4) and 2 are considered to be steam heated shallow waters (2-13, 3-6) and one represents fumarolic condensate (3-75).

Samples 1-4, G-5 show good correlation between the quartz equilibrium and the feldspar equilibrium temperatures and can be taken as true.

Sample 3-75 represents a fumarolic condensate and rainwater as deduced from its low pH of 3 and high sulphate content. It is necessary to collect gas from the fumarole and try to apply gas geothermometers  $(CO_2, H_2S)$  for estimating underground temperatures.

The water from which sample 2-13 was collected forms Rio Brujo, which goes underground at almost 800 meters a.s.l. in the slope of the Mombacho volcano. Sulphur deposits have been reported in this area 200 meters away from the discharge but gas emanations were not noticed.

There is a great discrepancy between  $T_{\rm qtz}$  and  $T_{\rm Na/K}$  in sample 2-13 and that may be due to mixing or amorphous silica precipitation. This sample is high in sulphate and bicarbonate and very low in chloride. It seems thus likely that this sample represents a steam heated shallow water. Sample 3-6 shows the same chemistry characteristics as sample 2-13.

Samples from the area in surrounding Mombacho volcano (2-11, 3-4, 3-5) (Fig. 5), show discrepancy between  $T_{\rm qtz}$  and  $T_{\rm Na/K}$  (Table 3), however, the chloride content is considered to be indicative of deep groundwater circulation. This difference may be due to mixing or silica precipitation in the upflow. They seem to be near equilibria for annydrite, Na<sup>+</sup>/H<sup>+</sup>

ratios, K<sup>+</sup>/H<sup>+</sup> ratios etc. It is thus concluded that a conservative estimate of underground temperatures is in the range of 170°C (Table 3). If temperatures are higher as indicated by the Na-K geothermometer (as much as 300°C) the fit of equilibria at  $T_{qtz}$  must have resulted from partial mineral/water re-equilibration in the upflow.

# Conclusions

A conservative estimate of underground temperatures in the Granada area is thus taken to be  $170^{\circ}$ C but they may be as high as  $300^{\circ}$ C (2-11, 3-4, 3-5, G-4, G-5).

The water samples 2-13, 3-6 are considered to be steam heated surface waters and have no major geochemical significance.

### 2.3.3 Carazo Area

All the samples from the Carazo area yield very high Na-K temperatures and have low or relatively low silica concentration with chloride content similar to rain water (Table 4).

# Conclusions

All the waters from the Carazo area are non-thermal (<30°C). They are considered to be surface waters or cold ground waters and do therefore not provide any evidence on underground geothermal reservoirs.



















Sample No.	Location	Measured C temperature	Type of sample W:depth(m) S:*flow1/s	Lab pH/25°C	sio <sub>2</sub>	в	Na <sup>+</sup>	к+	Ca <sup>++</sup>	Mg <sup>++</sup>	hco3-	so <sub>4</sub>	cl-	F-	Diss Solids TDS	NH 3	
1-8	MASAYA	44	W30	7.4	140	7.02	299	25	280	46.8	329.4	528	603.5	0.36	2306	0,014	
1-9		75	s	7.14	240	31.3	1012	128.7	96	80.4	109.8	268.8	1704	1.3	3,878	1.62	
1-60	"	27.5	Weo	7.85	68	0,060	23	9.36	26	9.72	189	<4.8	3.09	0.23	258	0,0048	
1-68	11	25	W275	7.47	73	0,030	20.1	9.36	34	8.76	189	<4.8	3.55	0.19	286	0,0034	
2-12	n	65	S	7.58	130	16.2	1104	82	130	30	671	480	1384.5	0.18	4,042	0.99	
2-84		26	W138	7.74	54	0.040	30	16.8	30	11.9	183	<4.8	29.1	0.27	302	0,0037	
	CARAZO		100														
1-52		26	W366	7.64	86	0,049	19.1	6.24	28	11.88	170.8	9.5	7.46	0.38	250	0,0046	
1-53		26.5	W214	7.45	88	0,039	14.03	4.68	20	8.4	128	4.8	4.97	0.32	188	0,0051	
1-54		27	W366	7.72	71	0,049	30	10.9	34	10.8	207	7.2	7.80	0.23	296	0,006	
1-55	"	27	W366	7.81	68	0.049	23	10.9	34	9.72	201	<4.8	5.68	0.23	272	0,0048	
1-56		26.5	W213	7.5	68	0,039	14	6.2	28	10.8	158.6	<4.8	4.97	0.65	226	0,0048	
1-57		26	W114	7.51	96	0,039	15	7.4	30	13.2	183	<4.8	5.68	0.36	290	0,0056	
1-67		28	W184	7.61	66	0,030	13.1	8.2	28	6.96	140	5.76	3.41	0.16	208	0,0053	
	GRANADA																
1-58		27	228 <sup>W</sup>	7.52	101	0.039	22.1	8.2	28	9.84	183	4.8	5.68	0.27	317	0,0039	
1-59		28	94 <sup>W</sup>	7.55	96	0.039	15	5.46	22	10.8	152.5	<4.8	2.7	0.25	262	0.24	
1-69		25	275 <sup>W</sup>	7.44	96	<0 030	13.1	8.42	22	10.8	152.5	<4.8	4.97	0.29	218	3.23	
1-70		26	98W	7.57	96	0.030	14	5.85	32	9.36	152.5	<4.8	3.55	0.11	264	0,0036	
1-73		Cool	W	7.57	90	0.049	22.1	7.02	26	9.24	164.7	<4.8	5.68	0.25	260	=	
1-74	**	Cool to	W	8.30	98	0.040	32.2	12.1	38	14.4	238	4.8	13.85	0.25	452	=	
1-75	**	si warm	14	0 17	107	0.040	41 4	2 7	00	20.4	200 4	4.0		0.00	566	=	

۰.

Table 4 Chemical Composition of Representative Sample of Water in MASAYA-CARAZO-GRANADA AREA

(Concentration in ppm)

- 39

- 40 -

. NH3	H.	0,0048	0,007	0,008	H	0,0054	0,0041	0,0048	0,0049	0,0049	0,011	0,0013	0,006	0,0071	600'0	0,061	1600'0	0,0048	0,061	11	0,0039	0 10
Diss Solids TDS	512	240(T)	301 (T)	(T)869	986 (T)	564	374	230	308	212	108	290	314	290	392	730	300	1304	294	350	207 (T)	1252/m/
۶.	0.21	0.16	0.59	0.65	0.40	0.68	0,141	0.15	0,181	0.12	0.23	0.21	0.16	0.23	0.19	0.97	0.27	0.59	0.25	1.65	0.19	1000
۲ <mark>۵</mark>	53.25	9.59	3.52	4.62	131,31	8.17	29.1	15.98	7.46	8.17	19.9	7.1	6.04	4.62	11	8.88	9.94	497	5.68	7.1	3.02	200000 000
so4	16.8	6.24	52.8	340,8	220,8	192	11.04	12	12	<4.8	57.6	7.68	<4.8	<4.8	<4.8	360	62.4	124.8	<4.8	11	<5.2	The New York
HCO <sub>3</sub>	360	128	128	128	341,6	85.4	152,5	152,5	170,8	91.5	183	213.5	128	122	79.3	91.5	128	189	183	158.6	122	COL REALER
Mg <sup>++</sup>	28.8	6.72	6.48	21.6	27.6	14.4	7.56	6.96	8.28	6.12	18	19.2	8.4	7.92	9.84	25.2	14.4	11.9	7.32	10.8	7.44	
Ca++	78	22	34	120	82	56	32	30	36	20	50	34	26	22	26	110	36	34	32	38	20	
ţ	10.9	5.85	6	4.3	25.7	10.9	7.02	6.24	5.46	10.1	4.7	9.4	5.85	5.1	4.7	14.1	8	50.7	8.6	7.8	4	Part of the second
Na <sup>+</sup>	39.1	17.9	17.9	23	140	30	30	20	17.9	8.28	16	16	14	13	15	32	17.9	345	22.1	41.4	12	No. of Concession, Name
æ	0,060	0,060	0• 040	0.030	2.6	0.19	0.28	0.13	0.080	0.030	0.050	0.040	0.050	0.040	<0.030	0.080	0,080	9	0,039	0,080	0,030	002
si02	98	107	116	120	190	150	101	101	101	107	96	06	92	92	103	98	113	113	73	94	101	Change of
Lab pH/25°C	80	6.90	6.66	6.59	7.15	6.74	7.58	7.47	7.44	6.88	7.08	7.36	7.29	7.24	7.19	7.03	7.13	7.74	7.69	7.73	7.11	11121 125205
Type of sample W:depth (m) S:*flow1/s	з	м	W100	*83 3	*S,	*S1.5	B5W	85W	M	WCCI	MOR	46W	MoM	M <sup>2</sup> S	MUC	MEC	M	MSW	M	M	M an I	2001
Measured 'C temperature	sl warm	30	32	33	54	45	31	30	29	29	30	32	26	23	28	27	28	30	28	27	23	1
Location	=				:		•	=				=	-	-				=				
Sample No.	1-76	2-8	2-9	2-10	2-11	2-13	2-41	2-42	2-43	2-44	2-45	2-46	2-47	2-48	2-49	2-50	2-51	2-52	2-85	2-89	3-3	

Table 4 Continued

Table 4 Con	t:	í1	nu	ed	
-------------	----	----	----	----	--

																		the second se
Sa	mple 1 No.	Location	Measured °C temperature	Type of sample W:depth (m) S:*flow1/s	Lab pH/25*C	sio <sub>2</sub>	в	Na <sup>+</sup>	К+	Ca <sup>++</sup>	Mg <sup>++</sup>	нсоз	so4	C1 <sup>-</sup>	F-	Diss Solids TSD	NH3	
3-	5		38	W	7.35	175	2.5	170	30	76	32.4	250	192	270	0.40	1070(T)	0,034	
3-	6	н	49	*S1	7.83	160	0.21	120	27	280	69.6	262.3	1008	9.94	0.76	1996	0,053	
3-	75	-	93	F	3.03	210	0.38	16.1	4.3	34	15.6	<5	288	0.39	0.55	798	=	
G-	4		45	*S1.5	7.7	175	0.35	277.5	25.9	82	42	458	220	291	0.2	1256	=	
G-	5		50	* <sup>S</sup> 1	7.0	175	1.1	307.5	29.1	100	68.4	817.4	100	330	N	1531	=	

P: Pond

F:Fumarole

S:Spring

W:well

(T) = by Summation

= Analysis not available

N: Negligible

- 41

# 3 RESULTS

Two geochemically anomalous sites have been identified in the Masaya Carazo-Granada area which reflect high temperature underground reservoirs. They are: Apoyo Lagoon and Mombacho Volcano and surroundings. Both sites have waters with relatively high content of chloride. Evidence for depositions of silica and mixing was found in both areas.

Underground temperatures in the Masaya Lagoon area are estimated to be of the order of 200°C. Actual underground temperatures may be higher and the low estimate would accordingly be due to silica precipitation and mixing in the upflow.

The Mombacho Volcano and surroundings which represent the other anomaly have estimated underground temperatures of at least 170°C (quartz equilibrium temperature), but they may be as high as 300°C (feldspar equilibrium temperature).

All the water samples from Carazo area are considered to be surface water or cold ground water and do therefore not provide any evidence on underground geothermal reservoirs, however, low resistivity was found in this area.

# 4 RECOMMENDATIONS FOR FURTHER GEOCHEMICAL STUDIES

On the basis of the present report the author wants to give some recommendations for further geochemical studies of thermal fluids in Nicaragua.

- a) Development and implementation of analytical techniques in our own laboratories.
- b) A complete revision of all the collection methods used in exploration and development of geothermal resources, especially in wells in the high temperature areas (Momotombo field).
- c) Collection of water and gas at the same pressure using a convenient and fitted miniseparator during the well testing period. These data would produce valuable information for further evaluation of reservoir characteristics by geochemical methods.
- d) Aluminum and iron should be analysed both in spring and well waters. Most of the minerals found in geothermal systems contain these elements and this could allow a more rigorous evaluation of water chemistry characteristics through study of mineral/solute equilibria.
- e) Collection of gas samples in springs, but especially in fumarole and steam wells with convenient equipment, should be carried out as soon as possible in all known steam fields in the country. The gas chemistry may be used to estimate underground temperatures and for identifying the major upflow zones.
- f) To collect samples of the deep water in the wells at Momotombo (Kuster Bottle), this information about the composition of the deep water well provides the best understanding of variations in fluid composition within the geothermal reservoir.

- 43 -

### ACKNOWLEDGEMENTS

The author wants to thank the organizers of the 1981 UNU Geothermal Training Programme in Iceland under the direction of Dr. Ingvar Birgir Fridleifsson. Special acknowledgement is due to Dr. Hjalti Franzson acting UNU resident co-ordinator during almost all of the training period for his interest and advice,

The author is much indebted to Dr. Stefan Arnorsson and Dr. Einar Gunnlaugsson, his supervisors, for their assistance, guidance, patience and recommendations in the preparation of this report as well as for all their useful teaching in the field of chemistry of thermal fluids. Their support is greatly appreciated. Many thanks to the Orkustofnun Drawing Office for the figures and to Erla Sigthorsdottir for typing the manuscript. Also many thanks to all the people in Orkustofnun who contributed to my progress in the present course.

- Arnórsson, S., Gunnlaugsson E., and Svavarsson, H. (1981a)
  The chemistry of geothermal waters in Iceland.
  II Mineral equilibria and independent variables controlling water
  composition. Geochimica et Cosmochimica. Acta, 45, in press.
- Arnórsson, S., Gunnlaugsson, E., and Svavarsson, H. (1981b)
  The chemistry of geothermal waters in Iceland.
  III Chemical geothermometry in geothermal investigations.
  Geochimica et Cosmochmica. Acta, 45, in press.
- Arnórsson, S., Sigurðsson S., and Svavarsson, H. (1981)
  The chemistry of geothermal waters in Iceland.
  I Calculation of aqueous speciation from 0° to 370°C. Geochimica
  et Cosmochimica. Acta, 45.
- Bullard, F.M., 1976. <u>Volcanoes of the Earth</u>. University of Texas Press, Austin, Texas.
- Ellis, A.J., and Mahon, W.A.J., 1964. Natural hydrothermal systems and experimental hot-water/rock interactions. <u>Geochimica et Cosmochimica</u>. Acta, 28, pp 1323-1357.
- Fournier, R.O. and Truesdell, A.H. (1973). An emperical Na-K-Ca geothermometer for natural waters. <u>Geochimica et Cosmochimica. Acta</u>, <u>37</u>, pp 1255-1277.
- Fournier, R.O. (1977). Chemical geothermometers and mixing models for geothermal systems. Geothermics. Vol. 5, pp 41-50.
- Giggenbach, W.E., 1976. A simple method for the collection and analysis of volcanic gas samples. <u>Bull. Volcanolgique. Vol. 39</u>, No. 1, pp 132-145.
- Goldsmith, L., Teilman, M., and Elliot D. (1979). <u>Geothermal Resources</u> <u>Inventory</u>. Consorcio Ieco-Lahameyer, Managua, Nicaragua. Vol. 5 of the Nicaraguan Master Plan for Electrical Development 1977-2000, pp. 165

- Gunnlaugsson, E., Arnórsson, S., and Matthiasson, M. (1981). MADAGASCAR. <u>Reconnaissance survey for geothermal resources</u>. Virkir, Consulting Group ltd. Reykjavík, Iceland. Vol. i of 2 pp. 4.2 -6.1.
- Klein, C.W., Koenig, J.B. and Wilde, W. (1980). <u>Geochemistry Investi-</u> <u>gations</u>. Consorcio Ieco-Lahameyer, Managua, Nicaragua. Vol. 5.1 of the Nicaraguan Master Plan for Electrical Development 1977-2000. Appendex A, pp 34-36, Appendex D, pp 1a - 16a.
- Sapper, Karl (1929). Volcanology, physics of earth. National Research Council Bulletin 77.
- Truesdell A.H. (1975). Geochemical techniques in exploration, summary of section III. Proceedings of the Second United Nations Symposium on the Development and Use of Geothermal Resources. Vol. 1, pp 53-79.
- White, D.E. (1957). Magmatic, connate and metamorphic waters. <u>Bull. Geol.</u> Soc. Am. Vol. 68, 1659-1682.
- White, D.E. (1970). Geochemistry Applied to the Discovery, Evaluation, and Exploitation of Geothermal Energy Resources. <u>Geothermics - special issue 2</u>. U.N. Symposium on the Development and Utilization of Geothermal Resources, Vol. 1, p. 58-80.