

Geochemical Modeling of a Shallow Submarine Hydrothermal System at Bahía Concepción, Baja California Sur, México

Ruth E. Villanueva-Estrada¹, Rosa Ma. Prol-Ledesma¹, Ignacio S. Torres-Alvarado², Carles Canet¹

¹Instituto de Geofísica, UNAM, Cd. Universitaria. Coyoacán, 04510, MEXICO, D.F.

²Centro de Investigación en Energía, UNAM, A.P.34, Temixco, 62580 MEXICO

estherv@icmyl.unam.mx

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ABSTRACT

Shallow submarine hydrothermal activity has been reported in Bahía Concepción at the Gulf coast of the Baja California Peninsula. It is located along faults, which are probably related to the Tertiary extensional tectonics of the Gulf of California region. Diffuse and focused hydrothermal venting of water and gas occurs in the intertidal and shallow submarine areas at 15 mbsl along a NW-SE trending fault. Temperatures in the submarine vents vary from 50°C at the sea bottom up to 87°C at a depth of 10 cm in the sediments. Chemical analyses revealed that thermal water is enriched in Ca, As, Hg, Mn, Ba, HCO₃, Li, Sr, B, I, Cs, Fe and Si with respect to seawater. The observed chemical and isotopic composition of vent water agrees with a simple mixing model between local seawater and a thermal end-member, where the thermal end-member component is about 40% of this mixture. The temperature calculated using chemical geothermometers points to a deep reservoir temperature of approximately 200°C, and a shallow equilibrium temperature of about 120°C.

Chemical modeling of the hydrothermal solutions and deposited minerals suggests that the interaction of deep circulating thermal water with underlying sediments and mixing with seawater constrain the composition of the vent fluids.

1. INTRODUCTION

Many studies have been devoted to the physicochemical processes of the hydrothermal fluids: water-rock interaction, cooling, boiling, and mixing with other fluids (Bethke, 1996). With the advance of modeling software in the 1970's a variety of geochemical modeling programs for economic geology and geothermal research were developed. As a result, the first applications of geochemical modeling have addressed the reaction of hydrothermal fluids. Helgeson (1970) simulated ore deposition and alteration processes in hydrothermal vein deposits. Reed (1977) used computer modeling to study the origin of precious metals in an ore deposit. Garven and Feeze (1984), Sverjensky (1984, 1987) and Anderson and Garven (1987) modeled the behavior of sedimentary brines in the formation of Mississippi Valley's ore deposits. Wolery (1978), Janecky and Seyfried (1984), Bowers et al. (1985) and Janecky and Shanks (1988) simulated hydrothermal processes along the mid-ocean ridges; and Drummond and Ohmoto (1985) and Spycher and Reed (1988) modeled the effect of mixing and boiling of hydrothermal fluids in ore deposition.

Shallow submarine hydrothermal vents are a common feature in the western coasts of Mexico. On the northern

Pacific coast of Baja California Peninsula, gasohydrothermal vents have been documented near Punta Banda (Fig. 1) at a depth of 40 mbsl with temperatures of 102°C (Vidal et al., 1978). Thermal water is enriched in Si, HCO₃, Ca, K, Li, B, Ba, Rb, Fe, Mn, As and Zn in comparison with seawater. The geological setting and chemistry of the vent fluids do not provide any evidence of magmatic sources, and isotopic data suggest a 1:1 mixture of local meteoric water and "old" seawater (Vidal et al., 1981). The most abundant hydrothermal precipitates are pyrite and gypsum. The hydrothermal deposits are highly enriched in As, Hg, Sb, and Tl.

Submarine hydrothermal vents also occur off the southern coast of Punta Mita, in the Bay of Banderas, Mexico (Fig. 1) (Prol-Ledesma et al., 2002; Canet et al., 2003). The area of hydrothermal activity in Punta Mita attains approximately 300 m² at a depth of about 10m. Water and gas venting occurs at 85°C along a sand-covered fissure hosted in basaltic rocks, and consists of both, focused and diffuse discharge of thermal water (Prol-Ledesma et al., 2002). The thermal water is enriched in SiO₂, Ca, Li, B, Ba, Rb, Fe, Mn, and As with respect to seawater. The gas discharged contains mostly nitrogen and methane with minor amounts of CO₂, Ar, He and H₂.

In both above-mentioned hydrothermal systems, the thermal water is more dilute than seawater and stable isotopic composition of water and gas shows that they are formed by deep circulation of meteoric water, and that they are not related to the active volcanism.

In this paper, we present the results of geochemical modeling of the vent fluids of the shallow submarine hydrothermal system of Bahía Concepción in the eastern shore of Baja California Peninsula (Fig. 1). The chemical model allowed us to estimate the fluid mixing processes that may occur assuming that diverse proportions of three end-members, which are the main components of the hydrothermal system. These end-members are (1) seawater, (2) deep thermal water from the Las Tres Vírgenes geothermal field, and (3) local meteoric water.

2. GEOTECTONIC SETTING AND VENT DESCRIPTION

Bahía Concepción is a large fault-bounded bay within the Gulf of California at the east coast of the Baja California peninsula (Fig. 1). The occurrence of shallow hydrothermal vents in western Mexico is related to the recent extensional tectonic regime. The hydrothermal activity is restricted to the presence of regional faults that serve as channels for the deep penetration of meteoric water in high heat flow areas (Prol-Ledesma et al., 2003).

The distribution of the vents (NW arrangement) coincides with the main regional faults. Fluid venting takes place at depths ranging from 5 to 15 m in intertidal hot springs. Temperature varies from about 50°C at the sea bottom to 87°C at a depth of 10 cm within the sediments (Prol-Ledesma et al., 2004). In addition, intertidal discharge of thermal fluid is observed on Santispac at the western coast of Bahía Concepción (Fig. 1). Seawater covers the spring only during high tide; otherwise, the spring discharges subaerial towards the sea with a temperature of 62°C (Prol-Ledesma et al., 2004).

Las Tres Vírgenes geothermal field is located 100 km north of the submarine vents. Its water composition indicates significant secondary water-rock interaction processes of fossil meteoric water with the host rock (Portugal et al., 2000). No influence of marine water intrusions can be observed in the field (Portugal et al., 1998 a, b).

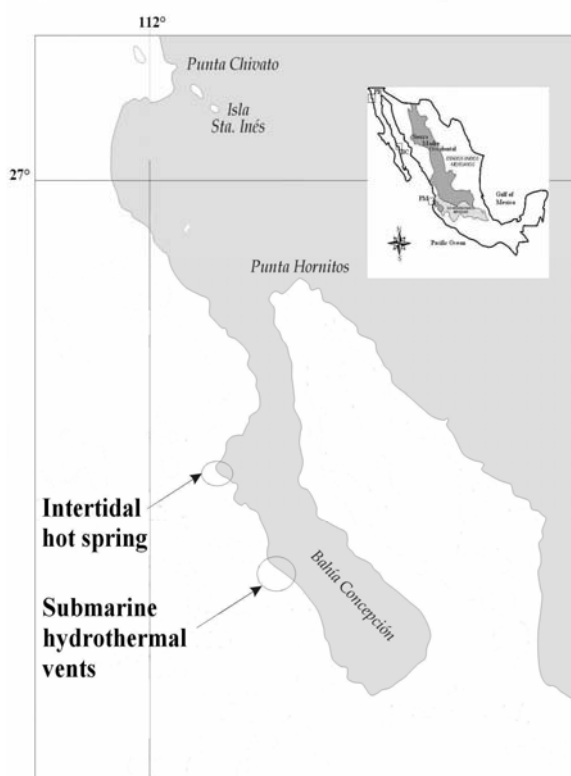


Figure 1: Location of submarine and intertidal vents in Bahía Concepción.

3. VENT WATER CHEMISTRY

The chemical and isotopic composition of the thermal water was reported by Prol-Ledesma et al. (2004), and the gas analyses are given by Forrest and Melwani (2003). Chemical analyses of the thermal water show that all samples correspond to sodium-chloride water type. The correlation of chemical components in the thermal water samples with Mg concentration was used to determine the chemical composition of a hypothetical thermal end-member (EMPL) by extrapolation of Mg= 0 (Table 1).

Vent water from Bahía Concepción is depleted in Cl, Na, Mg, SO₄, Br with respect to seawater (positively correlated with Mg). The water discharged by all the sampled springs in Bahía Concepción is of the Na-Cl type and is enriched in Ca, Mn, Si, Ba, B, As, Hg, I, Fe, Cs, Li, Rb, Sr, and HCO₃ with respect to seawater (Prol-Ledesma et al., 2004). Na,

Cl, SO₄ and Br in the vent samples are added to mixing of thermal fluid and seawater.

Prol-Ledesma et al. (2004) concluded that the thermal water discharged in Bahía Concepción might be the result of mixing between deep reservoir water from Las Tres Vírgenes geothermal field and seawater according to isotopic data.

4. GEOCHEMICAL MODELING

The mixing model of the hydrothermal solutions was developed using the computational program "The Geochemist's Workbench" release 3.0. The main assumption of this program is the existence of chemical equilibrium between dissolved chemical species and the minerals present in the system. This equilibrium is governed by the equilibrium constants calculated using a thermodynamic dataset for different temperatures (Bethke, 1996). The activities of the dissolved species were calculated using the Debye-Hückel model for activity coefficients considering that the ionic strength of the thermal fluids is about 0.53 molal. The modeling calculations were performed as follows:

Step 1- First mixing process between a geothermal well (LV-1) and meteoric recharge in Las Tres Vírgenes geothermal field was assumed. Mezquital spring water was chosen as meteoric recharge fluid in agreement with $\delta^{18}\text{O}$ and δD isotopic data (Portugal et al., 2000). This mixing process should yield the end-member composition (EMPL) that was calculated by Prol-Ledesma et al. (2004) from a linear mixing model with the local seawater.

Step 2- A second mixing process was assumed between the fluid resulting from the first mixing process and seawater sample (BC9 from Prol-Ledesma et al., 2004).

The results obtained are presented in three plots: Cl vs. Mg, Si vs. Mg and Ca vs. Mg (Fig. 2) and compared to the end member of the hydrothermal submarine vents (EMPL) obtained by Prol-Ledesma et al. (2004). Table 1 shows the data used for geochemical modeling calculations.

5. RESULTS AND DISCUSSION

Results of geochemical modeling (Fig. 2) show that the intertidal hot spring (BC10) contains an important component of the thermal end-member (the composition that results from Step 1, mixing of Las Tres Vírgenes deep reservoir thermal fluid and meteoric water). BC10 has approximately 90% of the end-member. On the other hand, submarine vent water has a greater influence of seawater of about 60% (Fig. 2). Thus, the intertidal spring (BC10) water is similar to the thermal fluid composition (Las Tres Vírgenes water) before mixing with seawater.

The presence of Las Tres Vírgenes geothermal field near the study area offers reference values for regional circulation of deep geothermal fluids. The thermal water of Bahía Concepción vents (intertidal and submarine) present an isotopic composition very close to the meteoric line, but mixing with seawater probably takes place before the thermal water is discharged into the seafloor (Prol-Ledesma et al., 2004).

BC1 and BC4 samples have a similar proportion of thermal end-member and seawater. BC1 is composed by approximately 65% of thermal end-member and 35% of seawater. In the case of BC4, the result consists of 60% thermal end-member with 40% seawater. BC6 has only 40% thermal end-member and 60% seawater.

Silica concentration in geothermal fluids is controlled mainly by temperature; therefore, it shows a homogeneous variation in the results of the chemical model. The thermal end member calculated from the geochemical modeling (Step 1, mixture of geothermal deep reservoir water from Las Tres Vírgenes and local meteoric water) has 8.35 mmolal of Si and a temperature of 203°C. This result is in agreement with EMPL. However, this thermal end-member (EMPL) is enriched in chloride and calcium with respect to Step 1 end-member.

The plots for Cl and Ca indicate that the thermal end-member (EMPL) calculated by Prol-Ledesma et al. (2004) for Bahía Concepción could have a contribution from another fluid with higher salinity than the deep reservoir fluid mixed with local meteoric water obtained from Step 1. These data suggest that another intermediary component may be added to the geothermal fluid before it mixes with seawater and discharges to the seafloor. However, presently, no chemical and isotopic composition of a possible fossil marine component data are available. Further work is needed to determine the characteristics of this component.

6. CONCLUSIONS

Mixing calculations were performed in order to determine the processes that could have resulted in the chemical composition observed in the vent fluid. The program Geochemist's Workbench was used to calculate the result of mixing three end-members: (1) seawater, (2) thermal water similar to that discharged by the deep wells in the Las Tres Vírgenes geothermal field, and (3) the local meteoric water.

The results show that calculated Si concentrations agree with the vent fluid chemistry. However, the Cl and Ca concentrations suggest the incorporation of high saline water to the mixture between the Las Tres Vírgenes thermal fluid and meteoric water. This high concentrated water still remains to be characterized.

The intertidal vent water has a better proportion of geothermal fluid and meteoric water (90%) than the seawater (10%). The submarine vent fluids are composed of 60-65% of geothermal fluid plus meteoric water and 40-35% of seawater. The obtained results agree with the mixing model proposed by Prol-Ledesma et al. (2004).

REFERENCES

- Anderson, G.M., and Garven, G.: Sulfate-sulfide-carbonate associations in Mississippi Valley-type lead-zinc deposits, *Economic Geology*, **82** (1987), 482-488.
- Bethke, C.M: *Geochemical Reaction Modeling. Concepts and applications*. Oxford University Press, New York (1996), 397 p.
- Bowers, T.S., Von Damm, K.L., and Edmond, J.H.: Chemical evolution of mid-ocean ridge hot springs, *Geochimica et Cosmochimica Acta*, **49**, (1985), 2239-2252.
- Canet, C., Prol-Ledesma, R.M., Melgarejo, J.C. and Reyes, A.: Methane-related carbonates formed at submarine hydrothermal springs: a new setting for microbially-derived carbonates?, *Marine Geology*, **199**, (2003) 245-261.
- Canet, C., Prol-Ledesma, R.M., Rubio-Ramos, M.A., Forrest, M., and Torres-Vera, M.A.: Characteristics of Mn-Ba-Hg mineralization at shallow hydrothermal vents in Bahía Concepción, Baja California Sur, México, *Chemical Geology* (2004), (submitted).
- Drummond, S.E., and Ohmoto, H.: Chemical evolution and mineral deposition in boiling hydrothermal systems, *Economic Geology*, **80**, (1985), 126-147.
- Forrest, M.J., and Melwani, A.: Ecological consequences of shallow-water hydrothermal venting along the El Requesón Fault Zone, Bahía Concepción, B.C.S., México. GSA General Meeting Abstracts with Programs, Seattle, Washington, USA (2003), 236-10.
- Garven, G., and Feeze, R.A.: Theoretical analysis of the role of groundwater flow in the genesis of stratabound ore deposits, 2, quantitative results, *American Journal of Science*, **260**, (1984), 57-66.
- Helgeson, H.C.: A chemical and thermodynamic model of ore deposition in hydrothermal systems, *Mineralogical Society of America Special Paper*, **3**, (1970), 155-186.
- Janecky, D.R., and Seyfried, Jr., W.E.: Formation of massive sulfide deposits on oceanic ridge crests, incremental reaction models for mixing between hydrothermal solutions and seawater, *Geochimica et Cosmochimica Acta*, **48**, (1984), 2723-2738.
- Janecky, D.R., and Shanks, III, W.C.: Computational modeling of chemical and sulfur isotopic reaction processes in seafloor hydrothermal systems, chimneys, massive sulfides, and subjacent alteration zones, *Canadian Mineralogists*, **26**, (1988), 805-825.
- Portugal, E., Barragán, R.M., and Bautista, J.: Estudio isotópico de fluido de pozos productores, de reinyección y manantiales del campo geotérmico de Las Tres Vírgenes, B.C.S. Instituto de Investigaciones Eléctricas, Cuernavaca, Report IIE/11/10933/101/F, (1998a), 35 pp.
- Portugal, Barragán, R.M., Arellano, V.M., Tello, E., and García, C.: Estudio químico-isotópico de fluidos de pozos productores y manantiales del sistema Las Tres Vírgenes, B.C.S., México, *Geotermia, Revista Mexicana de Geoenergía*, **14**(3), (1998b), 125-139.
- Portugal, E., Birkle, P., Barragán, R.M., Arellano, V.M., Tello, E., and Tello, M.: Hydrochemical-isotopic and hydrogeological conceptual model of the Las Tres Vírgenes geothermal field, Baja California Sur, México, *Journal of Vulcanology and Geothermal Research*, **101**, (2000), 223-244.
- Prol-Ledesma, R.M., Canet, C., Melgarejo, J.C., Tolson, G., Rubio-Ramos, M.A., Cruz-Ocampo, J.C., Ortega-Osorio, A., Torres-Vera, M.A., and Reyes, A.: Cinnabar deposition in submarine coastal hidrothermal vents, Pacific Margin of Central México, *Economic Geology*, **97**, (2002), 1331-1340.
- Prol-Ledesma, R.M., Canet, C., Torres-Vera, M.A., Forrest, M.J., and Armienta, M.A.: Vent fluid chemistry in Bahía Concepción coastal submarine hydrothermal system, Baja California, México, *Proceedings, Cordilleran Section Geological Society of America 99th Annual Meeting – Puerto Vallarta Jalisco, México* (2003).
- Prol-Ledesma, R.M., Canet, C., Torres-Vera, M.A., Forrest, M.J., and Armienta, M.A.: Vent fluid chemistry in Bahía Concepción coastal submarine hydrothermal

- system, Baja California Sur, México, J. Volc. Geoth. Res., (2004), (in press).
- Reed, M.H.: Calculations of hydrothermal mesomatism and ore deposition in submarine volcanic rocks with special reference to the West Shasta district, California. Ph.D. dissertation, University of California, Berkeley, (1977).
- Spycher, N.F., and Reed, M.H.: Fugacity coefficients of H_2 , CO_2 , CH_4 , H_2O and of H_2O - CO_2 - CH_4 mixtures, a virial equations treatment for moderate pressures and temperatures applicable to calculations of hydrothermal boiling, *Geochimica et Cosmochimica Acta*, **52**, (1988), 739-749.
- Sverjensky, D.A.: Oil field brines as ore-forming solutions, *Economic Geology*, **79**, (1984), 23-37.
- Sverjensky, D.A.: The role of migrating oil field brines in the formation of sediment-hosted Cu-rich deposits, *Economic Geology*, **82**, (1987), 1130-1141.
- Vidal, V.M.V., Vidal, F.V., and Isaacs, J.D.: Coastal submarine hydrothermal activity off northern Baja California, *Journal of Geophysical Research*, **83-B**, (1978), 1757-1774.
- Vidal, V.M.V., Vidal, F.V., and Isaacs, J.D.: Coastal submarine hydrothermal activity off northern Baja California 2. Evolutionary history and isotope chemistry, *Journal of Geophysical Research*, **86-B**, (1981), 9451-9468.
- Wolery, T.J.: Some chemical aspects of hydrothermal processes at mid-ocean ridges, a theoretical study, I., Basalt-seawater reaction and chemical cycling between the oceanic crust and the oceans, II. Calculation of chemical equilibrium between aqueous solutions and minerals. Ph.D. dissertation, Northwestern University, Evanston, IL, (1978).

Table 1: Chemical composition of water samples from Bahía Concepción vents, used for geochemical modeling calculations (after Prol-Ledesma et al., 2004), and composition of the calculated end-member (EMPL). Also included are the Las Tres Vírgenes deep reservoir fluid and local meteoric recharge (Portugal et al., 2000).

Sample number	pH	$T_{\text{reservoir}} (^{\circ}\text{C})$	Ca mmol/Kg	Mg mmol/Kg	K mmol/Kg	Na mmol/Kg	Cl mmol/Kg	SO_4 mmol/Kg	HCO_3 mmol/Kg	Si mmol/Kg	Li $\mu\text{mol/Kg}$	B $\mu\text{mol/Kg}$
BC1	5.95	62 ¹	23.3	35.8	12.7	394.5	458.4	17.0	4.9	3.1	344.0	829.0
BC4	6.02	54 ¹	19.4	41.9	12.5	414.7	500.7	21.2	4.3	2.1	254.0	646.0
BC6	5.97	56 ¹	20.6	40.2	12.5	408.9	493.6	20.6	4.5	2.4	275.0	631.0
BC9 (seawater)	7.75	-----	9.8	58.3	12.5	485.9	527.5	26.6	1.6	0.0	68.0	356.0
BC10 (Intertidal hot spring)	6.68	68 ¹	28.9	25.0	12.2	334.0	409.0	12.4	1.9	4.5	370.0	685.0
END-MEMBER (EMPL)	N.D.	200 ²	44.5	0.0*	13.0	230.7	380.3	4.2	10.3	7.8	761.9	1459.8
Tres Vírgenes geothermal field	7.7	-----	7.0	0.0	19.8	177.8	220.2	0.2	0.7	19.2	2738.1	14337.2
Local meteoric water	8.53	-----	0.9	0.6	0.1	2.8	1.3	0.0	4.7	2.1	1.4	25.0

¹ Temperature of reservoir was calculated using the Mg-Li geothermometer

² Temperature of reservoir was calculated using Na-K-Ca, Na/Li and Si geothermometers

* Assumed to be zero for calculation of end-member composition.

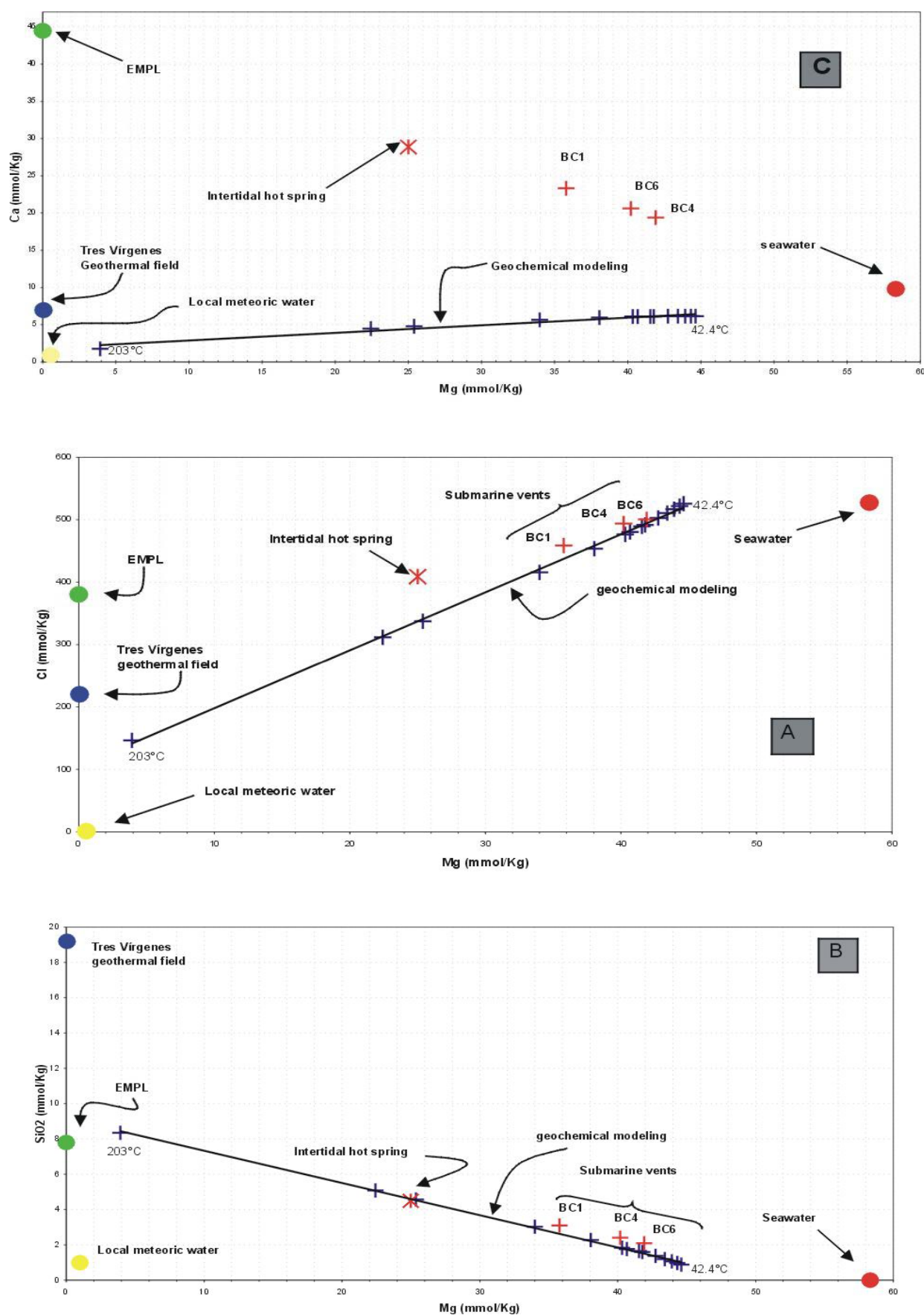


Figure 2: Results of geochemical modeling considering a mix between geothermal deep fluid from Las Tres Virgenes (Portugal et al., 2000), meteoric recharge (Portugal et al., 2000) and seawater (Prol-Ledesma et al., 2004). Data from submarine (BC1, BC4 and BC6) and intertidal (BC10) hydrothermal vents and thermal end-member from Bahía Concepción (Prol-Ledesma et al., 2004). Geothermal deep fluid (LV-1) and meteoric recharge (Mezquital) from Las Tres Virgenes (Portugal et al., 2000).