

Low-medium enthalpy geothermal systems on the eastern flank of the Sierra Madre Oriental, México

Sistemas geotérmicos de baja a media entalpía en el flanco oriental de la Sierra Madre Oriental, México

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ABSTRACT

This study presents the discovery of four hot springs, located across an area of 65 181 km², on the eastern flank of the Sierra Madre Oriental in Mexico. These springs emerge from sedimentary formations dating back to the Cretaceous period, displaying surface temperatures that range from 26.3° to 38 °C with electrical conductivity measurements varying between 1049 and 2421 µS/cm. The altitudinal range of these springs is documented from 55 to 1229 meters above sea level. The results from this research indicate that these springs are likely fed by rainwater infiltrating into the mountainous regions, where carbonate-evaporite rocks exist at probable depths of 3.5 km. The equilibrium temperatures at depth calculated using a multicomponent geothermometric model and isotopic geothermometers based on the chemical-isotopic composition of the four springs, fall within the range from 34° to 120 °C. These temperature values indicate the presence of geothermal groundwater flow systems. This geothermal resource has significant potential for utilization in electricity generation using binary plants and for various direct applications. This potential is especially relevant in regions where fossil fuels constitute the predominant source of energy.

Keywords: saturation index, ionic imbalance, geothermometric model.

RESUMEN

Esta investigación presenta el descubrimiento de cuatro manantiales termales en un área de 65 181 km², en el flanco oriental de la Sierra Madre Oriental en México. Estos manantiales emergen en formaciones sedimentarias del período Cretácico, con temperaturas superficiales que oscilan entre 26.3° y 38 °C, conductividad eléctrica entre 1049 y 2421 µS/cm, y altitudes que varían entre 55 y 1229 metros sobre el nivel del mar. Los resultados de este estudio sugieren que los manantiales pueden estar alimentados por agua de lluvia que se infiltra en las zonas montañosas, donde hay rocas evaporíticas-carbonatadas a profundidades probables de hasta 3.5 km. Las temperaturas en profundidad calculadas con un modelo geotermométrico de multicomponentes y geotermómetros isotópicos a partir de la composición químico-isotópica de los cuatro manantiales se sitúan en el intervalo de 34° a 120 °C. Estas temperaturas sugieren la presencia de flujos de agua subterránea geotérmicos, un recurso que puede utilizarse para la producción de electricidad con centrales binarias y para usos directos, lo que reviste especial importancia en una zona en la que los combustibles fósiles dominan el suministro energético.

Palabras clave: índice de saturación, desbalance iónico, modelo geotermométrico.

1. Introduction

Geothermal springs are present in areas where the geothermal gradient is higher than average or where meteoric water circulation reaches deep layers with high temperature due to the average thermal gradient (Qiu et al., 2018). Faults and fractures constitute preferential pathways that typically control the geothermal fluid convection (Yang et al., 2019). Carbonate aquifers play a crucial role in several hydrothermal systems, including the Larderello geothermal field (Arias et al., 2010) and the Buda Thermal Karst System (Stober and Jodocy, 2009) which operate at both high and low temperatures, respectively. Those geothermal systems are utilized for space heating, electricity generation, and recreational purposes, making them valuable resources (Goldscheider et al., 2010).

The urgency of climate change has increased global interest in geothermal energy as a clean energy source. Mexico is a country that has significant potential for geothermal energy due to its tectonic evolution. (Espinoza-Ojeda et al., 2023). Currently, only five high-enthalpy geothermal fields in Mexico—Cerro Prieto, Los Azufres, Los Humeros, Tres Vírgenes and Domo San Pedro—are utilized for electricity production. However, Mexico is home to more than 2000 low and medium-enthalpy thermal manifestations that can be harnessed (Iglesias et al., 2015; Espinoza-Ojeda et al., 2023). Recent research has been conducted in tectonic regions with lower activity and limited information of the northwest (Almirudis et al., 2018), northeast (Wolaver et al., 2013; Batista-Rodríguez et al., 2024), the high plateau (Billarent-Cedillo et al., 2021), and the central part of the Trans-Mexican Volcanic Belt (Martínez-Florentino et al., 2019) to better understand the origin and characteristics of the geothermal groundwater flow systems in these areas.

In northeast Mexico, a region characterized by low seismicity and minimal recent volcanic activity (Ramos-Zúñiga et al., 2012), several hydrothermal manifestations remain untapped

for energy production or direct use (Prol-Ledesma and Morán-Zenteno, 2019). Unfortunately, the over-exploitation of surface and groundwater for agriculture and human consumption has resulted in significant depletion of water resources in these drought-prone areas. Thus, it is critically important to study these resources before the visible surficial geothermal manifestations subside due to the depletion of groundwater flow systems (Roy et al., 2021).

This study identified, mapped, sampled, and characterized four hydrothermal manifestations and one cold spring: Potrero del Prieto hot spring, Mainero Azufroso cold spring, Ojo Caliente hot spring, Taninul hot spring, and Balneario El Bañito hot spring (Figure 1; Table 1). Although the Mainero Azufroso spring does not exhibit significant thermal activity, it was included in the study due to its H₂S emissions and the presence of microbiologic communities that precipitate mineral salts, predominantly calcite and anhydrite, similar to those observed in other hot springs (Chacón-Baca et al., 2015; Porras-Toribio et al., 2022). The characterization of these springs provides essential data for the development of a conceptual model for the associated hydrothermal systems and will support future advanced exploration initiatives.

2. Study area

The region covers 65 181 square kilometers on the eastern flank of the Sierra Madre Oriental (EFSMO), in northeastern Mexico. It encompasses the Sierra Madre Oriental province (CD2-SMO), which is recognized as one of the unexplored geothermal provinces in Mexico (Prol-Ledesma and Morán-Zenteno, 2019). The region is characterized by a NW-SE trending mountain belt, featuring elongated and narrow ridges that act as the recharge zone for regional groundwater flow systems.

The primary aquifers in this region have developed in a tropical karst environment

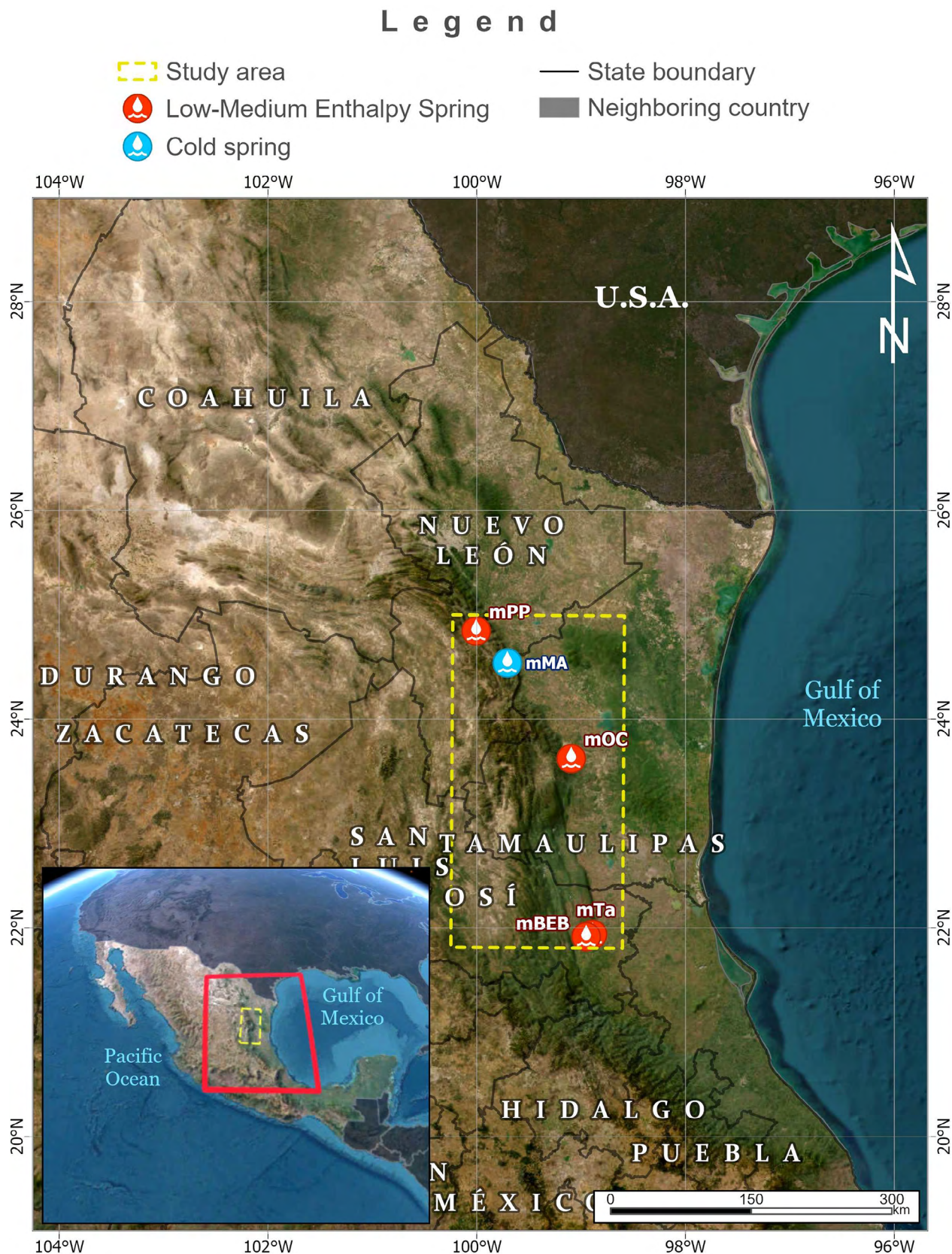


Figure 1 Low-medium enthalpy geothermal systems on the eastern flank of the Sierra Madre Oriental, México. Springs ID in Table 1.

Table 1. Name, location and general features of the studied springs in northeastern Mexico.

Spring Name	Spring ID	(UTM) Coordinates		Altitude (m a.s.l.)	Use	State
		E	N			
Potrero del Prieto	mPP	399671	2748264	1229	None	Nuevo León
Mainero Azufroso	mMA	428458	2713795	715	None	Tamaulipas
Ojo Caliente	mOC	490339	2612313	364	Cattle	Tamaulipas
Taninul	mTA	511344	2425851	64	Spa	San Luis Potosí
Balneario El Bañito	mBEB	505000	2423405	55	Spa	San Luis Potosí

consisting of folded and faulted mountains in the south and an inactive karst in the north (Espinasa-Pereña and Nieto-Torres, 2015). The Sierra Peña Nevada, which reaches 3450 m a.s.l., marks the highest elevation on the border between Nuevo León and Tamaulipas, while the lowest point is below 100 m a.s.l., in the southern part of the State of San Luis Potosí.

Runoff in the mountainous region occurs only during precipitation events, due to the karst environment, which allows rapid infiltration. However, several important rivers emerge at the base of the eastern slope, located in the center and in the southern areas of the region. The aquifers tapped in this region are mostly semi-confined and confined (Velázquez-Aguirre and Ordaz-Ayala, 1993). They are primarily found within strongly folded carbonate rocks from the Jurassic to Neogene periods, which exhibit high primary and secondary porosity (Velázquez-Aguirre and Ordaz-Ayala, 1993). The rugged topography of EFSMO creates a diverse range of climates and ecosystems, well-documented in the northeastern region of Mexico (Rzedowski, 1978; Luna et al., 2004; Castro-Navarro et al., 2017).

During the Precambrian and Paleozoic eras, the rocks that currently outcrop in Mexico were located in the equatorial western region of the supercontinent Pangea. As the supercontinent began to break apart during the Late Triassic period, the tectonic plates reorganized, resulting in continental drift and the formation of the Atlantic Ocean. The Yucatan block rotated counterclockwise and shifted southward,

contributing to the formation of the Gulf of Mexico (Martini and Ortega-Gutiérrez, 2018).

This geological activity led to the creation of intracratonic basins which became filled with thick layers of continental red sediments due to extensional tectonic processes (Busby and Centeno-García, 2022) and compressive tectonic events (Wengler et al., 2019). During the Bajocian period, warmer climatic conditions and shallow marine environments allowed seawater to flow into the basins, which resulted in extensive sedimentation of evaporite rocks, primarily located to the east of the Gulf of Mexico (Figure 2). These rocks exhibit important thickness (Pindell, 1985; Molina-Garza et al., 2020) and might influence the chemistry of nearby hot springs.

The geological formations in the highlands of the Coahuila block, the Tamaulipas archipelago and the Miquihuana island, date back to the Kimmeridgian-Oxfordian period. During this time, large deltaic fans were formed, transporting sediments from the exposed basement and from volcanism caused by subduction along the Pacific Ocean margin (Ocampo-Díaz et al., 2022). Continuous eustatic changes led to the deposition of calcareous rocks, a process that was influenced by tectonic evolution promoting sedimentation.

The Mexican orogeny (Fitz-Díaz et al., 2018; Nemkin et al., 2019), which occurred in the northeastern Mexican basins altered sedimentation conditions by combining the siliciclastic contributions from the west with the carbonate environments from the east. During the Oligocene period, compressive tectonics

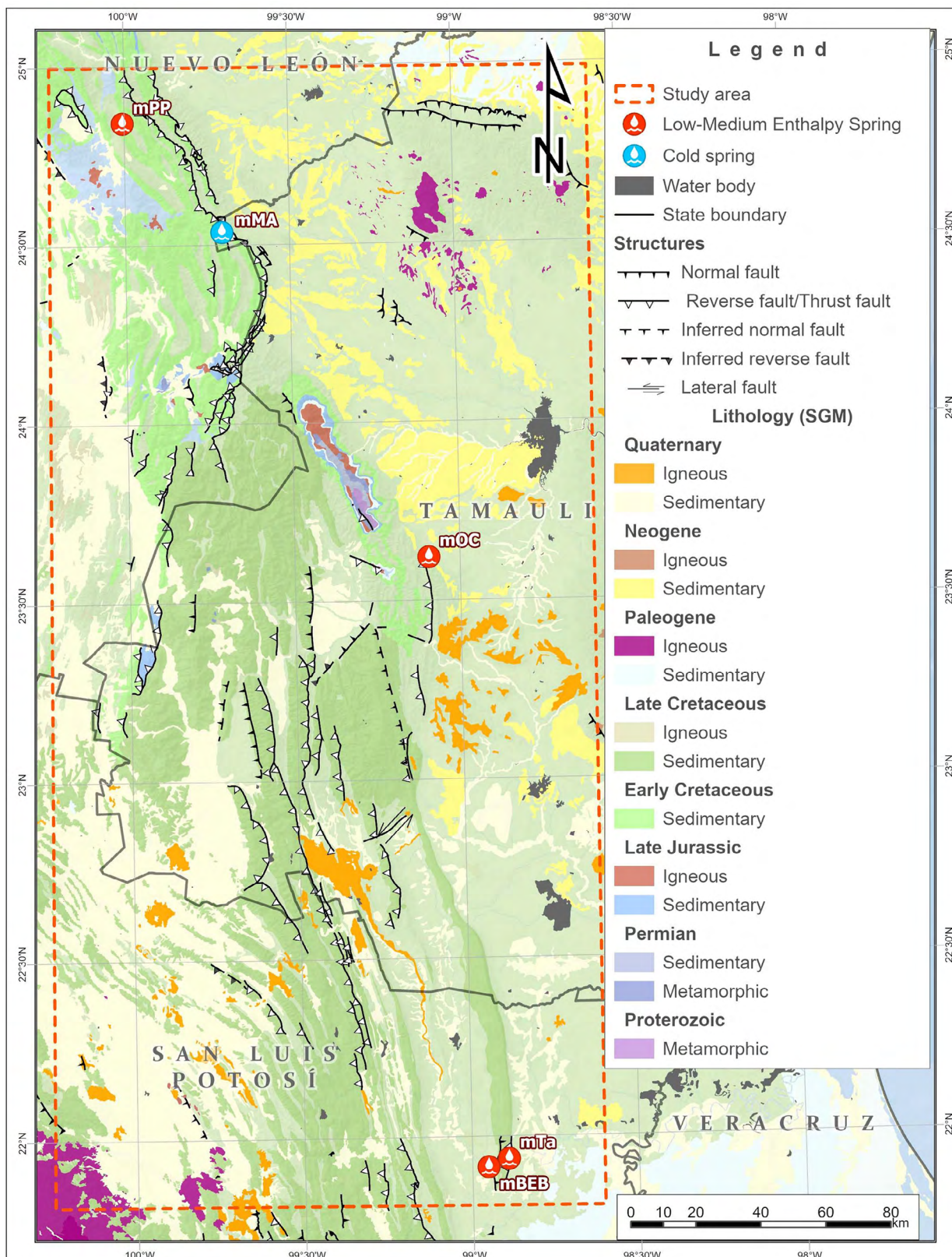


Figure 2 Geological map of the springs on the eastern flank of the Sierra Madre Oriental in México (modified from Servicio Geológico Mexicano (1996), Springs ID in Table 1.

ceased, giving way to extensional tectonics that resulted in the exhumation of eastern Mexico (Gray et al., 2021), and generated alkaline volcanism in the thinnest portions of the Earth's crust (Elizondo-Pacheco et al., 2022). Despite these changes, continental sediments continued to flow into the Gulf of Mexico through the Quaternary hydrological network.

2.1 DESCRIPTION OF THE SPRINGS

The diversity of plant communities and microbiome at each spring is described by Pantoja-Irys et al. (2025a, 2025b). The location and general features of the springs are presented in Table 1 and illustrated in Figure 1.

The Potrero del Prieto hot spring is located near the Prieta Linda waterfall and the town of El Potrero del Prieto de Arriba, between the Iturbide anticline and the El Mezquital syncline in the Sierra El Baño, on the bed of the Cabezones River (Figures 2 and 3). This hot spring, at an elevation of 1229 m a.s.l. is the highest hot spring in EFSMO. The nearest meteorological station, 19073 Galeana (Servicio Meteorológico Nacional, 2021) records an annual average precipitation of 361.8 mm. The climate in this area is classified as dry semi-warm (INEGI, 2023). This hot spring originates from the Lower Tamaulipas Formation of the Lower Cretaceous period and currently has no known specific uses beyond supporting the ecosystem.



Figure 3 Discharge area around EFSMO springs. Springs ID in Table 1.

The Mainero Azufroso cold spring (Figures 2 and 3) emerges at an altitude of 715 m a.s.l., along the bed of an intermittent stream, in the Sierra La Guitarra, at the base of the San Manuel Mountain range. The closest meteorological station, 3735 Villa Mainero (Servicio Meteorológico Nacional, 2021) reports an average annual precipitation of 993.8 mm, and the area is characterized by a temperate subhumid climate (INEGI, 2023). The spring emerges from the Taraises Formation of the Lower Cretaceous and has no specific use.

The Ojo Caliente hot spring (Figures 2 and 3), emerges at an altitude of 364 m a.s.l., in the Sierra El Filo at the base of the El Platanillo mountain range. According to the nearest meteorological station, 28218 La Boca (Servicio Meteorológico Nacional, 2021) the average annual precipitation in the area is 743 mm. The region has a temperate subhumid climate (INEGI, 2023). This hot spring, which is located on private property in the San Felipe Formation of the Upper Cretaceous, is used as a water source for livestock.

The Taninul hot spring (Figures 2 and 3) is locally renowned for its medicinal and recreational uses, possibly dating back to pre-Hispanic times. It has now become part of a hotel. This spring is located in the Sierra El Abra-Tanchipa at the foothills of El Abra mountain range, emerging from the Cretaceous El Abra Formation at an altitude of 64 m a.s.l. The closest meteorological station, 3145 El Choy (Servicio Meteorológico Nacional, 2021) reports an annual precipitation of 1165.4 mm and identifies the area as having a warm subhumid climate (INEGI, 2023).

Balneario El Bañito hot spring (Figures 2 and 3) is currently used for recreational activities. It is located in the Ciudad Valles municipality, characterized by gently sloping hills, at an elevation of 55 m a.s.l. The closest meteorological station, 24012 Ciudad Valles (Servicio Meteorológico Nacional, 2021) records an annual precipitation of 1241.2 mm. Similar to the aforementioned springs, this source originates from the San Felipe Formation and is also found within a warm subhumid climate zone (INEGI 2023).

3. Methods

3.1. SPRING MAPPING AND SOFTWARE

Digital thematic maps featuring geological sections were created using ArcGIS Pro 2.6.0. and based on a digital elevation model (DEM) from INEGI (2022). Field measurements of lithological sections were taken with staff-mounted Garmin model GPSMAP 64sx GPS devices equipped with Garmin GLONASS antennas. A DJI Mavic 3 Enterprise Thermal drone was used to map geological outcrops and capture thermal images of each spring and its surrounding influence area. Petrographic descriptions were made using an Olympus BX53M model polarized microscope. The saturation index, speciation and multicomponent geothermometric model for the groundwater in the springs were calculated using the PHREEQC geochemical package, version 3, wateq4f database (Parkhurst and Appelo, 2013). Geochemical geothermometers were calculated using the Sol Geo software (Verma et al., 2008), and plots were created using Veusz, version 3.2.1.

3.2. GROUNDWATER SAMPLING

Sampling was carried out by inserting the sampling equipment into the main discharge of the spring. Several parameters were determined in situ, including temperature, pH, electrical conductivity (EC), ORP (Pt electrode), and dissolved oxygen (DO) by immersing a multiparameter probe in the spring water. The field equipment was calibrated daily: pH was adjusted using buffer solutions of 4.0 and 7.0, EC was calibrated with a solution of 1413 mS/cm, and the accurate functioning of the Pt electrode was verified using a calibration solution at 240 mV for ORP. Additionally, the DO measurements obtained from a polarographic sensor were verified using a sodium sulfite buffer (0 mg/l) under atmospheric conditions. Total alkalinity was also measured on-site through acidimetric titration of syringe-filtered samples (0.45 µm) using a digital titrator with H₂SO₄. The alkalinity calculator (U.S. Geological

Survey, 2012) from the US website (<https://or.water.usgs.gov/alk/index.html>) was used to determine the titration curve and to calculate total alkalinity.

3.3. SPRING DISCHARGE MEASUREMENT

The area-velocity method was used to determine the discharge of spring flow, assuming laminar conditions. The flow velocity was determined using an acoustic current meter. Several flow velocity measurements were taken along the different sections of each selected site. In instances where the spring discharge was visually assessed under turbulent conditions, flow estimates were made using the dilution method (Rantz, 1982). A selected mass of tracer (sodium chloride) was dissolved in 20 liters of water, and then it was injected into the flow using a Dirac injection. Automatic electrical conductivity (EC) measurements were recorded every 2 seconds downstream of the injection point, which allowed the identification of the EC peak. Chloride concentration was calculated based on the relationship between salt concentration and EC. The flow rate was determined by dividing the injected mass of the tracer by the integral area under the curve in the time-EC diagram (Moore, 2005).

3.4. ANALYTICAL METHODS

Samples were collected and analyzed in the laboratory to determine various major, minor, and trace elements, as well as environmental isotopes. Multiple aliquots were filtered through 0.45 μm filters and collected in separate acid-washed low-density polyethylene bottles. One aliquot was acidified by adding 1% ultrapure HNO_3 to reach a pH of approximately 2 for analysis of major cations (Na, K, Ca, Mg), total S, and Si using ICP-OES (Thermo Scientific ICAP 7400). Additional trace elements (see Table 2) were determined using an inductively coupled plasma mass spectrometer (ICP-MS, PerkinElmer, ELAN 9000) according to the standard protocols described in APHA (2005).

A second aliquot was acidified ($\text{pH} \leq 2$) with 1% of ultrapure H_2SO_4 for nitrate determinations using automated colorimetry. The third aliquot remained unacidified and was used for the determination of Cl (titration with AgNO_3) and F (ion-selective electrode).

The accuracy of the elemental data was confirmed through a comprehensive quality control process. Diluted certified high-purity standards and internal natural water control standards were used for the calibration of ICP-OES and ICP-MS analyses. Accuracy was further verified through the analysis of both laboratory duplicates and internal quality control standards. Additionally, the data were validated with internationally recognized reference materials: NIST-1643f for trace elements and ERM CA616 (groundwater) for major elements. The coefficient of variation was within 4%, with recoveries ranging from 95% to 98% for ICP-OES and 95% to 102% for ICP-MS, thereby ensuring the integrity of our results. The overall values showed ionic charge imbalances ranging from 0.3% to 4.1%, as calculated using PHREEQC with the wateq4f database.

For the analysis of environmental stable isotopes, two additional aliquots were collected and measured in 2 ml glass vials. This was done using a Picarro L2130-i isotopic liquid water analyzer for $\delta^{18}\text{O}$, $\delta^2\text{H}$) and a Thermo Finnigan Delta Plus XL mass spectrometer in continuous flow mode, which was connected to a Gas Bench equipped with a CombiPAL autosampler for $\delta^{13}\text{C}$. The results were reported relative to the Vienna Standard Mean Ocean Water (VSMOW) for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, and Vienna Pee Dee Belemnite (VPDB) for $\delta^{13}\text{C}$. The precision of the measurement was $\pm 0.03\text{‰}$ for $\delta^{18}\text{O}$, $\pm 0.48\text{‰}$ for $\delta^2\text{H}$ and $\pm 0.08\text{‰}$ for $\delta^{13}\text{C}$.

The springs were identified to have the characteristic of dissolved sulfide, which could be easily detected by its characteristic odor (the odor threshold for sulfides is approximately 0.2 mg/L; (NHWC, 1978). To prevent sulfide oxidation, exposure to atmospheric oxygen and

Table 2. *In situ* measured parameters for the EFSMO springs.

Sample ID	Potrero del Prieto	Mainero Azufroso	Ojo Caliente	Taninul	Balneario El Baño
Mean annual temperature (°C)	19	25.24	25.35	19.47	19.47
Field parameters					
Q (L/s)	15.94	3	-	12.88	2.58
T (°C)	26.3	19.9	31.3	38	32.6
pH	6.94	7.4	6.82	6.52	7.27
Eh (mV)	-48	55.8	264.9	180.8	38.9
EC (μS/cm)	2421	362	1049	1671	1102
DO (mg/L)	0.81	3.56	1.29	0.05	1.22
CO ₃ ⁽²⁻⁾ (mg/L)	0.1	0.15	0.1	0.4	0.2
HCO ₃ ⁽⁻⁾ (mg/L)	195.2	180.5	149.8	291.5	203.2

manipulation of the aliquots were minimized during sampling for sulfide determination. For the spectrophotometric determination of inorganic total sulfide using the reagents of the Cline method (Cline, 1969), special preservation techniques were employed. This involved using a 10% solution of Zn acetate and a 6% solution of NaOH (5:1) previously mixed to facilitate sulfide precipitation (Gilboa-Garber, 1971), in order to eliminate potential chemical interferences that could affect color development.

The values of $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ were determined by precipitation of BaSO_4 under acidic conditions (pH approximately 2-4). This was accomplished using an elemental analyzer (Flash EA2000, Thermo Fisher) connected to a Delta V Advantage mass spectrometer (Thermo Fisher) within a continuous He flow system. The results are expressed in terms of δ (‰) relative to the international standards Canyon Diablo Troilite (V-CDT) for sulfur and VSMOW for oxygen. The precision for $\delta^{34}\text{S}_{\text{SO}_4}$ was $\pm 0.2\text{‰}$ and for $\delta^{18}\text{O}_{\text{SO}_4}$ was $\pm 0.3\text{‰}$.

The Sr isotope composition was determined from a small fraction of Sr extracted from the water sample using the standard cation exchange technique. The analysis of strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) was conducted using a Finnigan-

MAT 261 thermal ionization inductively coupled plasma mass spectrometer (MC-ICP-MS) in static collection mode calibrated to the NBS987 standard value of 0.71024 ± 0.00002 (2σ error).

4. Results

4.1. HYDROGEOCHEMICAL CHARACTERIZATION

Water sampling was performed at each of the five springs during the dry season (March 2-6, 2023), to minimize the influence of runoff and local groundwater flows on the spring discharge. The in-situ measurement records are displayed in Table 2, while the analytical results are presented in Table 3.

The recorded water temperatures indicate that most springs in the study area can be classified as geothermal springs, as their temperatures exceed the local mean annual temperature by at least five degrees (Tamburello et al., 2022). An exception is the Mainero Azufroso spring, which has a temperature below the local mean annual temperature. However, its chemical results were included in the discussion for comparative purposes, although it was excluded from the estimation of the equilibrium temperature at depth using geothermometric methods.

Table 3. Laboratory results (chemical and isotopic composition) of the EFSMO springs.

Sample ID	Potrero del Prieto	Mainero Azufroso	Ojo Caliente	Taninul	Balneario El Bañito
Major Cations (mg/L)					
Na ⁺	252.3	6.16	19.24	85.38	7.67
K ⁺	9.77	0.32	1.09	6.3	0.43
Ca ²⁺	213.51	67.9	179.34	116.07	158.07
Mg ²⁺	43.01	5.76	23.49	17.41	37.01
Si ⁴⁺	11.07	6.27	12.82	9.99	12.63
Major Anions (mg/L)					
F ⁻	3.06	3.07	2.53	3.1	3.8
Cl ⁻	296.6	11.7	13.7	197.1	17.6
N-NO ₃ ⁻	0.1	0.5	0.9	0.3	0.3
SO ₄ ⁻	692.5	41.6	446	27.5	390
Isotopes (‰)					
δ ² H _{H2O} (VSMOW)	-64.72	-46.08	-38.17	-34.55	-34.31
δ ¹⁸ O _{H2O} (VSMOW)	-9.59	-7.46	-6.39	-5.71	-5.46
δ ¹⁸ O _{SO4} (VSMOW)	11.96	9.89	14.06	11.05	13.47
δ ³⁴ S _{SO4} (VCDT)	15.26	12.86	16.16	18.33	15.99
δ ¹³ C _{DIC} (VPDB)	-7.52	-11.54	-11.54	-8.87	-7.56
⁸⁷ Sr/ ⁸⁶ Sr _{H2O}	0.70737	0.707285	0.707392	0.707671	0.707449
Trace Elements (µg/L)					
Br	64	<0.01	4	1568	<0.01
Li	40.68	4.66	12.09	138.7	14.25
I	13.29	<0.01	22.9	11.52	74.31
Cr	<0.01	0.34	0.63	3.59	2.05
Mn	13.2	<0.01	2.01	20.79	2.77
Fe	5.69	<0.01	< 0.01	< 0.01	0.9
Ni	0.73	<0.01	< 0.01	< 0.01	< 0.01
Ga	<0.01	0.1	0.24	7.29	0.84
As	<0.01	0.02	< 0.01	0.83	< 0.01
Rb	3.75	0.01	1.88	12.35	0.12
Sr	4567	329	1416	1389	4746
Cs	0.72	<0.01	< 0.01	2.51	< 0.01
Ba	21.16	57.26	57.18	265.8	70.53
Pd	2.79	0.19	0.81	0.72	2.55
U	0.5	0.261	0.29	0.17	0.58
Others					
Alkalinity (mg/L CaCO ₃)	160	148	122.8	238.9	166.6
Σ[HS ⁻] (µmol/L)	41.6	45.5	0.19	35.2	13.4
Ionic Imbalance (%)	-1.40	-2.50	-2.81	0.21	-4.11

Water chemistry reveals several key characteristics. The pH values are approximately neutral, while dissolved oxygen (DO) levels are low ranging from 0.05 to 3.6 mg/L. Electrical conductivity (EC) varies between 363 and 2421 $\mu\text{S}/\text{cm}$. The presence of dissolved sulfide measured at 0.05 to 45.5 $\mu\text{mol}/\text{L}$, suggests that reducing conditions are prevalent in the subsurface. Electrode potential (Eh) measurements indicate positive values (except for Potrero del Prieto spring), implying disequilibrium conditions for redox-sensitive reactions and/or mixing with shallow groundwater during the ascent. Alkalinity is moderate to high, with bicarbonate being the predominant anion over carbonate.

The Taninul spring stands out due to having the highest temperature and the highest

concentrations of carbonate and bicarbonate. Its pH is slightly lower than that of the other springs. Most trace elements are below the detection limits, except those listed in Table 3.

The evolution of groundwater hydrochemistry is influenced by complex processes that occur along its flow path. As deeper groundwater flows through the subsurface, it interacts with the host rock and surrounding subsoil, acquiring a variety of chemical components. This process results in the formation of distinct water types, each characterized by a unique chemical signature. The classification and visualization of these signatures, as well as the identification of key processes like water-rock interaction, can be effectively accomplished using Piper and Stiff diagrams (Figure 4).

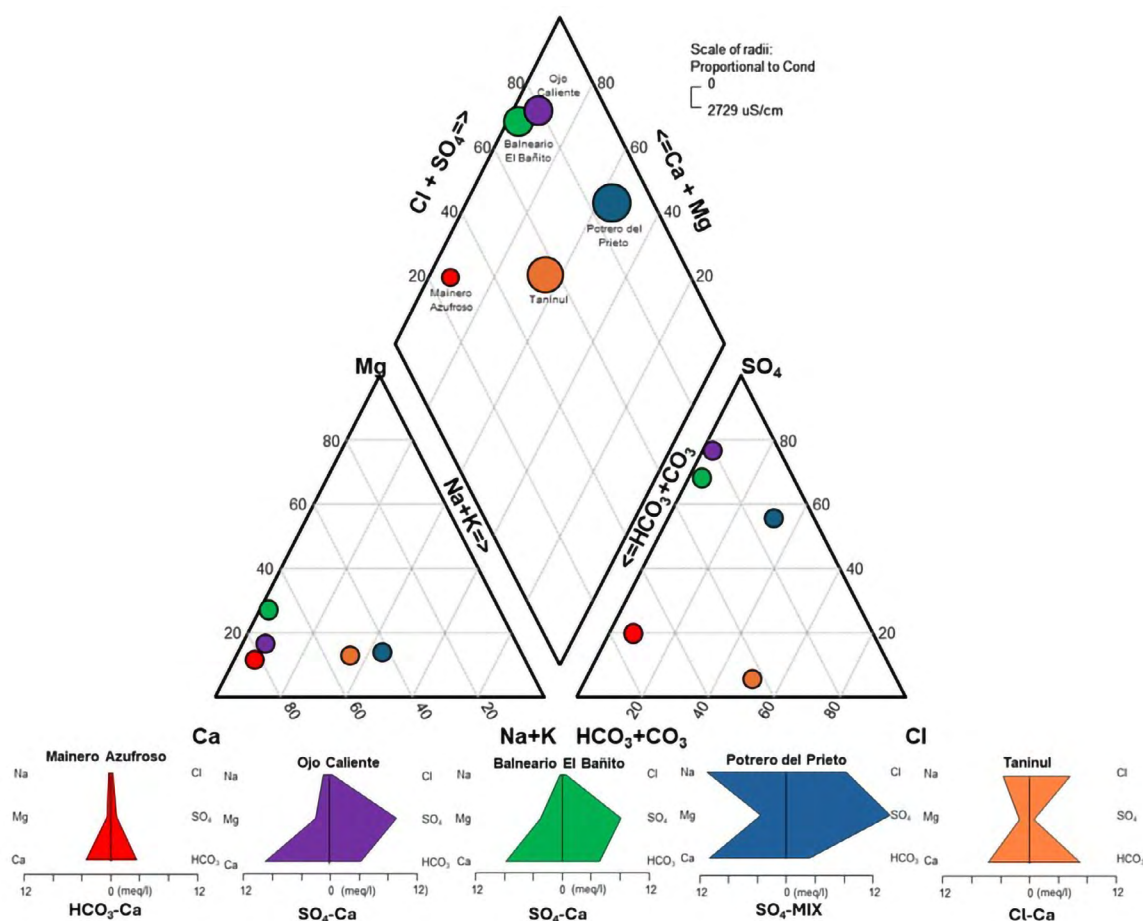


Figure 4 Piper and Stiff diagrams that illustrate the chemical compositions of the EFSMO springs.

The Mainero Azufroso spring which has a HCO_3 -Ca composition (Stiff diagram, Figure 4), exhibits the lowest discharge temperature at 19.9 °C and EC of 362 $\mu\text{S}/\text{cm}$. These values indicate shallow circulation in contact with carbonate rocks. Additional interaction with gypsum and deeper circulation raises both water temperature (approximately 32 °C) and EC ($\approx 1200 \mu\text{S}/\text{cm}$) resulting in a SO_4 -Ca composition for Ojo Caliente and Balenario El Bañito springs. The Taninul spring, on the other hand, has the highest discharge temperature at 38 °C, and is characterized by a Cl-Ca water type; however, its CE is lower than that of Potrero Prieto spring, which is categorized as a SO_4 -MIX water type.

Selected trace elements that indicate water-rock interactions, such as Li and Rb (Liu et al., 2025), suggest the following general evolution of geochemical water types: i) HCO_3 -Ca, ii) SO_4 -Ca, iii) SO_4 -Mix, and iv) Cl-Ca.

4.2 ENVIRONMENTAL ISOTOPE CHARACTERIZATION

Stable isotopes of $\delta^2\text{H}_{\text{H}_2\text{O}}$ (VSMOW) and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (VSMOW) have values ranging from -64.72 to -34.71‰ and from -9.59 to -5.46‰ respectively. These isotopes align with both local and global meteoric lines (see Figure 5; Table 3). The lowest values were observed in the Potrero del Prieto spring, which emerges at higher altitudes, while the highest values were found in the Balneario El Bañito spring, which emerges at lower altitudes.

The results obtained for oxygen and hydrogen in sulfate, carbon, sulfur and strontium are summarized in Table 3. Key observations include the following: the Mainero Azufroso spring exhibited the lowest value of $\delta^{13}\text{C}_{\text{DIC}}$ isotope, whereas the Potrero del Prieto spring had the highest value, ranging from -11.54 to -7.52‰. The Taninul spring was notable for having the highest ratio of $^{87}\text{Sr}/^{86}\text{Sr}_{\text{H}_2\text{O}}$ with 0.707671, whereas the Potrero del Prieto spring had the highest value, ranging from -11.54 to -7.52‰. The Taninul spring recorded the highest ratio of $\delta^{34}\text{S}_{\text{SO}_4}$ VCDT

with 18.33‰, while the Mainero Azufroso spring had the lowest value with 12.86‰. As for the $\delta^{18}\text{O}_{\text{SO}_4}$ VSMOW, the Ojo Caliente spring displayed the highest value of 14.06‰, while the Mainero Azufroso spring had the lowest value at 9.892‰.

5. Discussion

Recent studies on low-medium enthalpy geothermal systems in sedimentary basins indicate that the water infiltrating from recharge areas is primarily of meteoric origin (Pantoja-Irys et al., 2022). This water descends into deep strata, where it is heated due to a normal elevated geothermal gradient. As it rises, the water becomes heated and enriched in various solutes, depending on the composition of the surrounding strata. The water is chemically and isotopically modified by its interaction with the host rock (Blasco et al., 2019; Yang et al., 2019; Bao et al., 2022).

There have been no previous geochemical and isotopic studies reported on the low and medium enthalpy springs that emerge in the EFSMO. Therefore, the data generated in this study represent the first contribution to the development of a conceptual model aimed at determining the depth, type of enclosing rock, and temperature that characterize the potential geothermal reservoirs that generate these springs.

The five springs studied are of meteoric origin, and their isotopic compositions plot close to the calculated meteoric water line of the Ciudad Victoria station (Sánchez-Murillo et al., 2023) as well as the global meteoric water line (Craig, 1961), as clearly illustrated in Figure 5. The absence of a noticeable shift in oxygen isotopes, commonly observed in geothermal waters, is consistent with the low temperatures of these springs and indicates a weak low-temperature water-rock interaction in the groundwater flow systems.

The negative range values from -7.56‰ to -11.56‰ of $\delta^{13}\text{C}_{\text{DIC}}$ (VPDB) in the EFSMO springs are similar to other sedimentary basins where

thermal aquifers are hosted in carbonate-evaporite rocks (Blasco et al., 2019; Yang et al., 2019). As the thermal groundwater flow systems are enriched with solutes and the temperature rises, the water ascends to the surface and is discharged by the springs. The low temperatures and the mixing processes that occur during the ascent of the thermal water produce immature waters in the Na-K-Mg ternary diagram (Giggenbach, 1988) and in the peripheral and steam-heated water in the Cl-SO₄-HCO₃ ternary diagram (Romano and Liotta, 2020). Consequently, the typical geothermometric estimation of deep temperatures is not applicable in this context.

The Mainero Azufroso cold groundwater sample and the Taninul, Balneario El Bañito, Potrero del Prieto and Ojo Caliente hot groundwater samples were all plotted in the $\delta^{34}\text{S}_{\text{SO}_4}$ (VCDT), $^{87}\text{Sr}/^{86}\text{Sr}_{\text{H}_2\text{O}}$ isotopic ratio, groundwater temperature and Li versus pH (Figure 6).

The linear relationship observed among these samples suggests a binary mixing of two end-member components (Faure, 1977). Specifically, groundwater from these springs is a mixture of deep geothermal water from Taninul and cold groundwater from Mainero Azufroso. Although each geothermal groundwater system might be independent of each other.

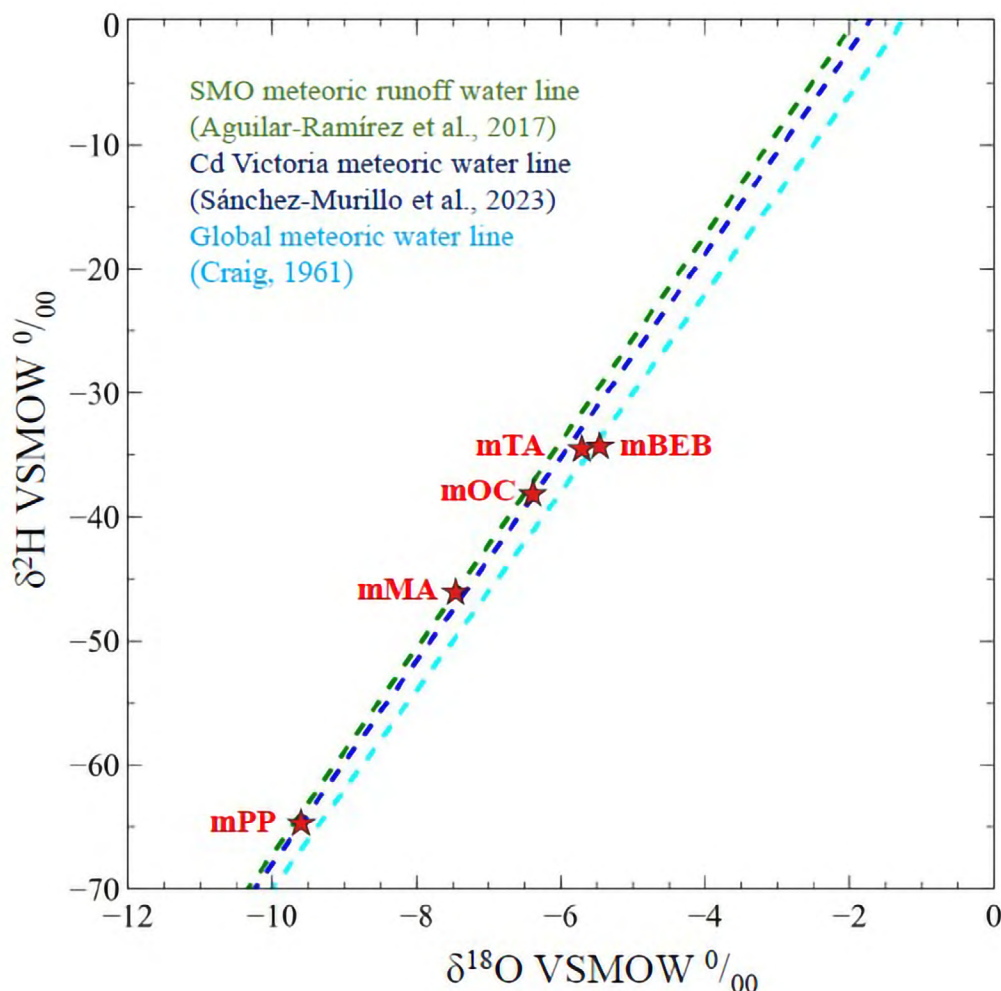


Figure 5 Isotopic behavior of the sampled springs in relation to the SMO meteoric runoff water line, the meteoric water line of Ciudad Victoria and the global meteoric water line. Springs ID in Table 1.

As shown in Figure 6A, the proportion of this mixing can be inferred by designating “regional” end-members with rainwater having a pH of 7.8 (Pantoja-Irys et al., 2022) and brines with a pH of 6.1 (Porras-Toribio et al., 2022). Additionally, the mixing ratio can be estimated using Equation 1 (modified from Han et al., 2010) with the values of (highest R^2) $\delta^{34}\text{S}_{\text{SO}_4}$ (VCDT), considering the groundwater from Mainero Azufroso (end-member A, 100%) and Taninul (end-member B, 0%).

$$Ma = \frac{|\delta^{34}\text{S}_T| - |\delta^{34}\text{S}_{mix}|}{|\delta^{34}\text{S}_T| - |\delta^{34}\text{S}_C|} \times 100(\%) \quad (1)$$

The mixing ratio (Ma), expressed as the percentage of non-thermal groundwater (%), is determined using isotopic concentrations from the Mainero Azufroso and Taninul springs as end-members. In this context, $\delta^{34}\text{S}_{mix}$ refers to the isotopic concentration in the mixed groundwater of the spring; $\delta^{34}\text{S}_T$ refers to the isotopic concentration of the Taninul geothermal groundwater and $\delta^{34}\text{S}_C$ refers to the isotopic concentration of the Mainero Azufroso groundwater.

The proportion of mixing with the upper aquifer groundwater during its ascent is calculated as follows: for Ojo Caliente spring would be 22%, for Potrero del Prieto spring it would be 30%, and for the Balneario El Bañito spring it would be 48%.

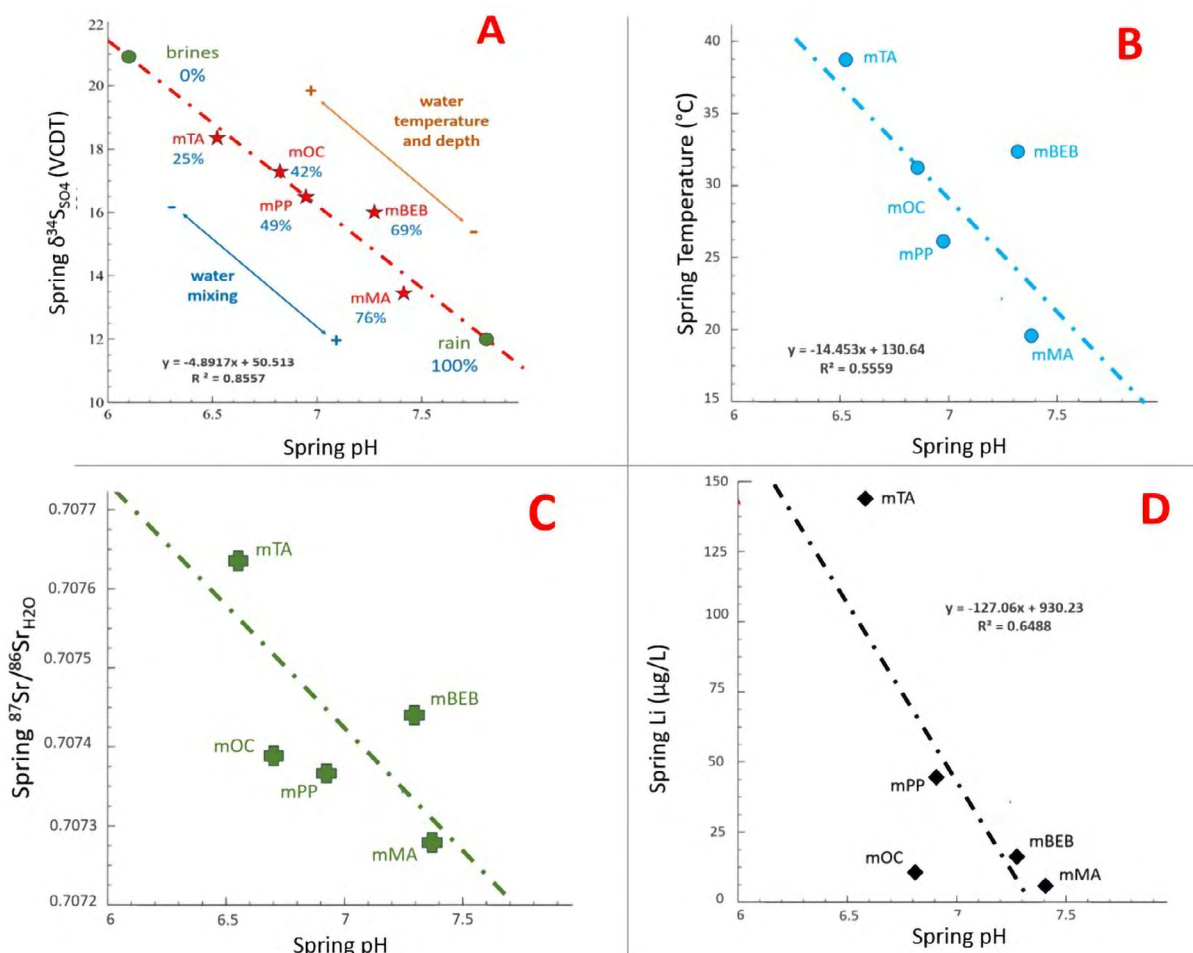


Figure 6 Plot of the relationship between the $\delta^{34}\text{S}_{\text{SO}_4}$ (VCDT) and $^{87}\text{Sr}/^{86}\text{Sr}_{\text{H}_2\text{O}}$ isotopic ratios, groundwater temperature and Li concentration and pH levels of the springs. ID of the springs in Table 1.

When recalculating the percentages, using the pH levels and brines as end-members, of rainwater (Equation 2): the adjusted mixing ratios are as follows: for Taninul the ratio is 25%; for Ojo Caliente it is 42%, for Potrero del Prieto it is 49%, for Balneario El Bañito it is 69%, and for Mainero Azufroso it is 76%.

$$Mb = \frac{|pH_T| - |pH_{mix}|}{|pH_T| - |pH_c|} \times 100(\%) \quad (2)$$

Where Mb = mixing ratio, expressed as the percentage of non-thermal groundwater (%), using brine and rain pH as end-members pH_{mix} = pH value in the mixed groundwater of the spring; pH_T = pH value of the brine; pH_c = pH value of rain water.

The mineral phases found in the spring discharge area indicate a sedimentary host rock, as they predominantly consist of calcite, gypsum, anhydrite, dolomite and halite, among others (see Table 4). These minerals, which are enriched in elements such as Li, U, Tl, Ta, Ba, Mg, Rb, As, Ge, Sr, Zn, V, and B, are commonly found in the carbonate and evaporite sedimentary rocks of northeastern Mexico (Kroeger and Stinnesbeck, 2003; Gonzalez-Sánchez et al., 2007; Pindell et al., 2019).

Based on the saturation indices, the water from these springs is either undersaturated or near equilibrium with minerals such as anhydrite, aragonite, calcite, celestite, chalcedony, quartz, gypsum and dolomite. The Potrero del Prieto spring exhibits the largest variety of mineral phases, while the Taninul spring has the fewest. The high mixing ratio in all the springs also accounts for the saturation indices of the mineral phases identified in groundwater being mostly close to zero or negative.

The prevalence of evaporite and carbonate rocks is further supported by the relationship between the $\delta^{18}O_{SO_4}$ VSMOW and $\delta^{34}S_{SO_4}$ VCDT isotope ratios. As illustrated in Figure 7, all the springs fall within the zone indicative

of sedimentary evaporite rock dissolution. In addition, the $^{87}Sr/^{86}Sr_{H_2O}$ isotope ratios range from 0.707285 (sample 2) to 0.707671 (sample 4). These ratios have also been reported for hot spring water circulating through sedimentary rocks from the Cretaceous period of the Cuatro Ciénegas basin (Wolaver et al., 2013) and for cold spring water flowing through sedimentary rocks of the same period in the Cerro La Silla Mountain range (Pantoja-Irys et al., 2022).

5.1. ESTIMATION OF SUBSURFACE TEMPERATURE

In recent decades, the use of isotopic and geochemical data to estimate subsurface temperatures in geothermal reservoirs has advanced significantly (Verma et al., 2008; Cooper et al., 2013; Chatterjee et al., 2017; Gorietal., 2023). However, low to medium enthalpy geothermal systems, such as those in EFSMO still pose challenges in establishing a reliable method for estimating equilibrium temperature (Bao et al., 2022; Blasco et al., 2017a, 2017b, 2018; Chiodini et al., 1995; Gori et al., 2023). By utilizing isotopic geothermometers designed for geological and geochemical conditions similar to those of the studied hot springs (Boschetti et al., 2013; Fowler et al., 2013), we have determined that the geothermal reservoirs of the four low enthalpy systems have temperatures ranging from 75 °C to 120 °C (see Table 5).

The geochemical geothermometers yield inconsistent results across different systems, which raises concerns about their reliability. This variability may stem from the distinct processes occurring in each system. To gain a better understanding of reservoir temperatures, geothermometric modeling was performed (Blasco et al., 2017a, 2017b, 2019), calculating mineral phases up to a temperature of 120 °C, the maximum expected temperature. Figure 8 presents the multicomponent geothermometric models for water samples collected from the four hot springs. The temperature ranges shown for each spring are broader and more diffuse than

Table 4. Saturation indices for mineral phases present in the springs discharge area.

Sample ID	Potrero del Prieto	Mainero Azufroso	Ojo Caliente	Taninul	Balneario El Bañito
Anhydrite	-0.8606	-2.173	-0.9676	-2.2085	-1.0686
Aragonite	-0.2929	-0.1884	-0.4388	-0.4435	0.1134
Barite	0.059	-0.0914	0.3784	-0.0393	0.4106
Calcite	-0.15	-0.0409	-0.2994	-0.3087	0.2518
Celestite	-0.5988	-2.5473	-1.1514	-2.2395	-0.6766
Chalcedony	0.4661	0.2906	0.4712	0.29	0.4492
Dolomite	-0.6475	-0.8736	-1.0909	-0.9743	0.2761
Fluorite	0.116	0.0504	-0.0601	-0.0376	0.2211
Gypsum	-0.6463	-1.9356	-0.7761	-2.0551	-0.884
Halite	-5.776	-8.6966	-8.207	-6.4039	-8.4984
Manganite	-12.3923	-12.1978	-8.2923	-9.5989	-10.5855
Pyrochroite	-8.3823	-10.4178	-9.3623	-8.9089	-8.3555
Pyrolusite	-22.0951	-20.7084	-12.1348	-14.1949	-17.5293
Quartz	0.8912	0.7358	0.881	0.6802	0.8551
Strontianite	-1.3725	-1.8777	-1.9782	-1.8389	-0.8528
Witherite	-4.7418	-3.5479	-4.3994	-3.492	-3.6972

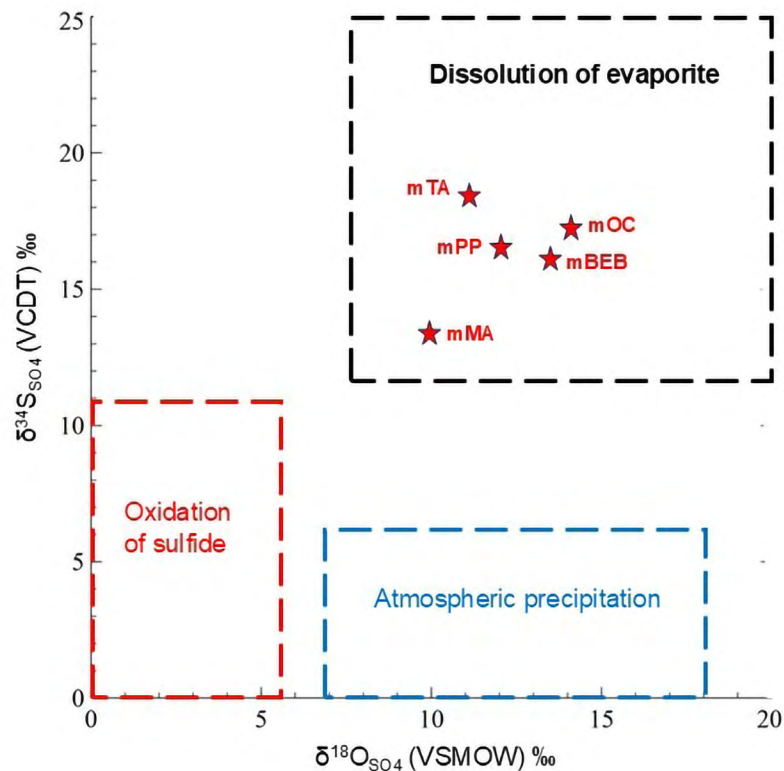


Figure 7 Relationship between sulfur and oxygen isotopes in sulfates dissolved in spring water (modified from Jiang *et al.*, 2022). Springs ID in Table 1.

Table 5. Isotopic geothermometers of the EFSMO hot springs.

Reservoir Temperature (°C)	Potrero del Prieto	Ojo Caliente	Taninul	Balneario El Bañito
$\delta^{18}\text{O}_{\text{SO}_4\text{-H}_2\text{O}}$ (Fowler et al., 2013)	75	83	111	94
$\delta^{18}\text{O}_{\text{CaSO}_4\text{-H}_2\text{O}}$ (Boschetti et al., 2011)	82	90	120	102

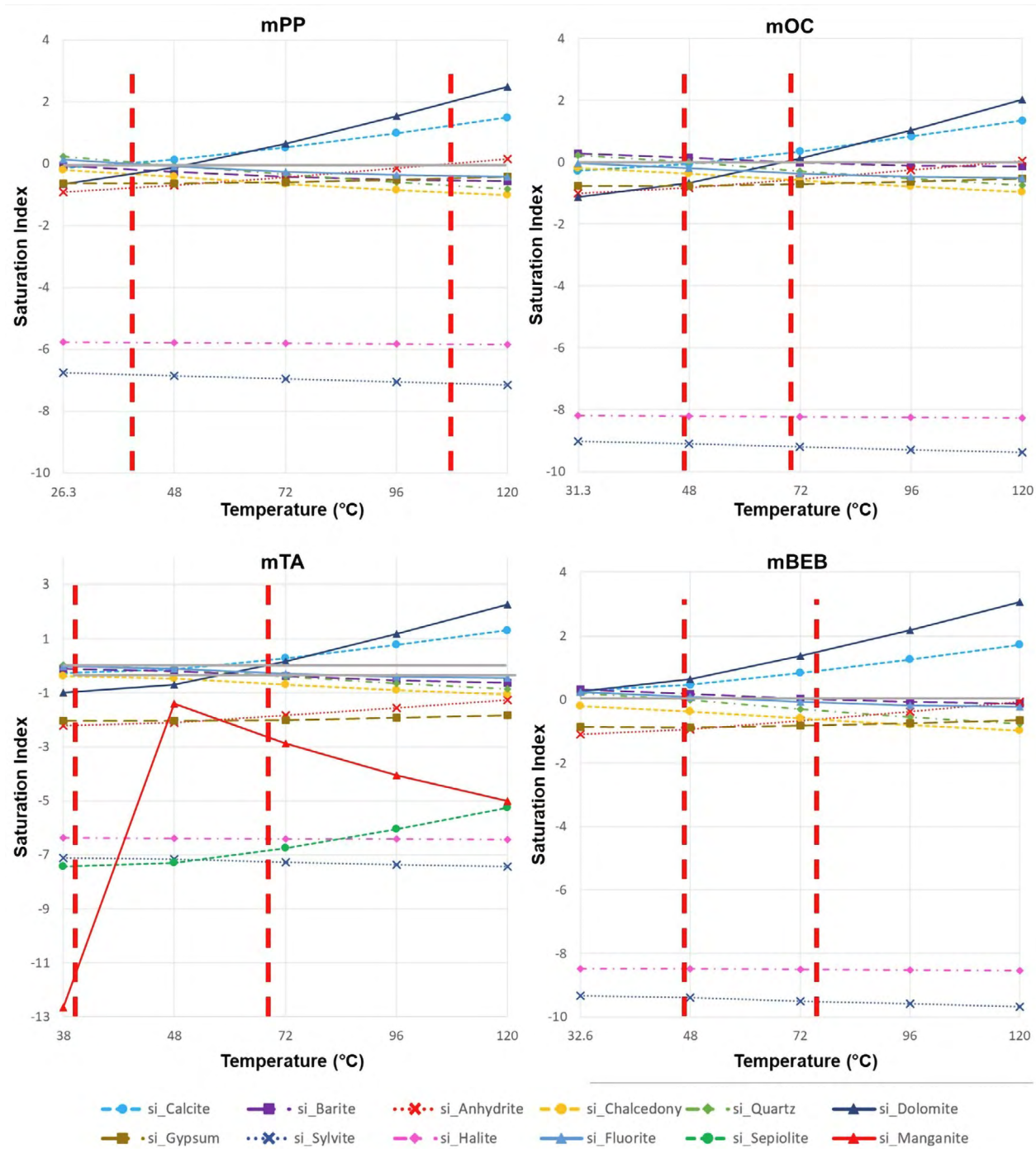


Figure 8 Multicomponent Geothermometric Model of thermal water from the EFSMO Springs. Springs ID in Table 1.

those obtained from isotopic geothermometers, likely due to factors like mixing and dilution.

Based on the analysis of probable deep temperature from Taninul, and Balneario El Bañito springs these can be classified as medium enthalpy systems. In contrast, the Ojo Caliente and Potrero del Prieto springs are classified as low enthalpy systems (Muffler and Cataldi, 1978; Lee, 1996).

The inversion of the thermal gradient in evaporite rocks, as proposed by Daniilidis and Herber (2017), produces a similar effect to that of an energy source in the upper layers of these geological formations, due to the high thermal conductivity of evaporite rocks. The genesis of the 4 low and medium enthalpy springs in the EFSMO region aligns with the conceptual model of geothermal activity observed in the low-enthalpy El Bañito spring located in the Cerro de la Silla mountain range, as proposed by Pantoja-Irys et al. 2022.

To accurately assess the depth of the geothermal aquifers, the best stratigraphic and structural control can be established for the Potrero del Prieto spring. At a depth of approximately 1100 m from the upwelling, which is perpendicular to the sedimentary strata (Figure 9), evaporite rocks from the Middle Jurassic of the Minas Viejas Formation are exposed in the center of the anticline, according to Kroeger and Stinnesbeck (2003). When extrapolating to depth, it is estimated that the geothermal aquifer associated with the Potrero del Prieto spring surface manifestations is located at a depth of approximately 1100 meters from the spring's emergence.

The stratigraphic and structural control for the other springs is less clear. However, information on carbonate-evaporite rocks from the Middle and Upper Jurassic has been identified in oil wells drilled by PEMEX in northeast Mexico (Eguiluz de Antuñano, 2001). The tops of these evaporite-carbonate successions have been found at depths ranging from 1000 meters to 3500 meters (Retama-1, Guayalejo-1, Pinole 1, Tamuin 101, and Aquisquemón 1 oil wells, among others).

The geostatic pressure at both minimum and maximum depths can be calculated using Equation 3, which describes the pressure regime in a stratigraphic unit that exhibits higher lithostratigraphic pressure than the hydrostatic pressure in its pore structure (Khan and Islam, 2007).

$$P_g(z) = P_0 + g \int_0^z \rho(z) dz \quad (3)$$

Where $P_g(z)$ is the geostatic pressure at depth z in Pa; ρ is the density of the overlying rocks at depth z in kg/m^3 ; g is the acceleration due to gravity in m/s^2 , z is the depth in m; and P_0 is the surface pressure in Pa, resulting in $P_g(1000)=25$ MPa; $P_g(3500)=88$ MPa; for a $\rho=2600$ kg/m^3 (average value of limestone and shale rocks); $g=9.778$ m/s^2 ; $z=1000$ and 3500 m and $P_0=92990$ Pa, which was obtained from the average of historical data from the Cumbres de Monterrey El Diente automatic weather station (Servicio Meteorológico Nacional, 2021).

The secondary porosity created by the concatenation of folds, thrusts, transcurrent faults, normal faults, and fractures in the deep paleo-basins of northeast Mexico facilitates both downward and upward flow. This process connects the geothermal groundwater flow systems of the low and medium-enthalpy springs of the EFSMO.

6. Conclusions

In a wide region spanning 65 181 square kilometers in EFSMO, five springs were identified and sampled. Among them, four hot springs appear to be linked to hydrothermal systems: two low-enthalpy systems named Potrero del Prieto and Ojo Caliente, and two medium-enthalpy systems named Taninul and Balneario El Bañito. These geothermal groundwater flow systems are located in carbonate-evaporite rocks from the Middle and

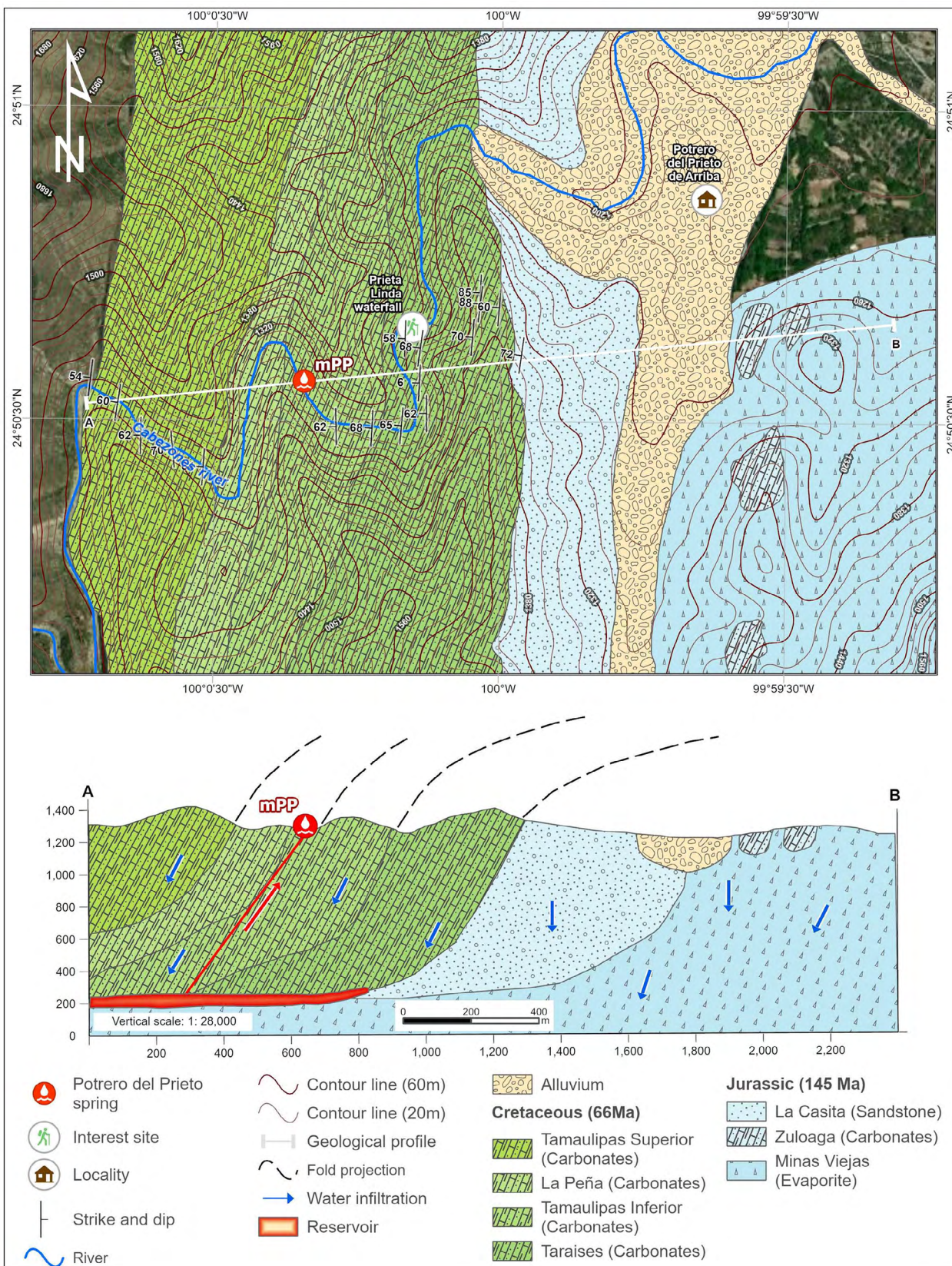


Figure 9 Geological map and cross section of the Potrero del Prieto hot spring area.

Upper Jurassic periods, with estimated depths ranging from 1000 to 3500 meters. The geostatic pressure within the reservoirs varies from 25 and 88 MPa.

The geothermal groundwater flow systems found in deep sedimentary basins are the result of tectonic phenomena and the presence of carbonate-evaporite rocks from the Middle and Upper Jurassic at these depths. This combination facilitates the deep infiltration of rainwater, which reaches higher temperatures as it descends, eventually rising to the surface at these relatively understudied springs. These geothermal resources could play a significant role in the essential transition to clean energy sources in northeastern Mexico.

Contributions of authors

(1) Conceptualization and writing: JRPI, ACB, RMPL; (2) Field sampling and analytical QA/QC review: CTDL, HMS, CSG; (3) Review and editing: JRPI, ACB, RMPL, CTDL, HMS, CSG; (4) Funding: JRPI, HMS.

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Conflict of interest

The authors declare no conflict of interest.

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