Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

Constraints of Las Derrumbadas Geothermal Conceptual Model by Gas Geochemistry, Puebla, Mexico

Typhaine Tual[1], Laurent Escaré[1], Snorri Gudbrandsson[2], Elodie Muller[3], Marie-Noëlle Guilbaud[4], Carole Cordier[5], Manuel Moreira[3], Lorraine Tual [6, 7]

[1] Storengy SAS, 12 rue Raoul Nordling, 92274 Bois-Colombes Cedex, France; [2] Reykjavik Geothermal Ltd, Höfðatorgi, Katrínartúni 2, 105 Reykjavík, Iceland; [3] Institut de Physique du Globe de Paris (IPGP) ,1 rue Jussieu, 75005 Paris, France; [4] Universidad Nacional Autónoma de México (UNAM) 04510 Mexico, Federal District, Mexico; [5] Univ. Grenoble Alpes, CNRS, IRD, IFSTTAR, ISTerre, 38000 Grenoble, France; [6] Swedish Museum of Natural History, Box 50007 SE-104 05 Stockholm, Sweden; [7] Department of Earth, Ocean, and Atmospheric Sciences, Univ. of British Columbia, Vancouver, Canada

Keywords: Volcanic gas geochemistry, noble gases, stable isotopes, geothermal exploration, geothermal reservoir

ABSTRACT

Las Derrumbadas volcano is a geothermal prospect located in the Mexican state of Puebla, in the eastern part of the Trans-Mexican Volcanic Belt. The target is a rhyolitic complex made of twin domes that break through the sedimentary cover of the Serdán-Oriental basin, mostly composed of Mesozoic limestones. Recent geochronological data suggest that Las Derrumbadas is merely 2000 years old. Fumaroles as well as intensive hydrothermal alteration at the summit indicate the presence of a high enthalpy geothermal system. These fumaroles were sampled in order to constrain the origin of the fluids and characterize the geothermal resources.

Las Derrumbadas fumarolic gases present high concentrations of CO_2 and CH_4, but no H_2S. Their isotopic composition shows a magmatic signature suggesting the presence of a deep, active heat source. Fumaroles are highly enriched in He (up to 38 ppm) with R/Ra ratios of respectively 4.37 and 4.56 measured on two samples, indicating the influence of a high mantellic contribution. The compositions in $\delta^{13}C_{CO2}$ (-9.26 ‰, and -9.56 ‰), $\delta^{13}C_{CH4}$ (-28.24‰ and -28.43‰) and δD_{CH4} (-144.27 ‰ and -143.06 ‰) also suggest a hydrothermal origin without any Mesozoic Limestones contribution. However, isotopic values of condensates, δD_{H2O} (from -126.53‰ to ¬-143,1‰) and $\delta^{18}O_{H2O}$ (from -18.87 ‰ to -19.97‰), show that water was freshly infiltered. The absence of sulfur in fumaroles associated with rhyolitic volcanoes is interpreted as resulting from neutralization by scrubbing in the geothermal aquifer. This is also in line with the CH_4 isotopic concentrations that confirms the geothermal origin, generally linked to the reduction of CO_2 in the geothermal aquifer. Gases geothermometers suggest temperatures higher than 300 °C.

The geothermal aquifer is expected to be located in the igneous basement, below the upper limestone formations and sealed by a strong alteration layer acting as a barrier for liquids. This alteration cap allows sulfur and carbon dioxide reduction but remains permeable to gases. The interaction of rainwater with hot gases at the surface causes their vaporization. Estimated temperatures are comparable to well measurements at the Los Humeros geothermal powerplant located 45 km to the North.

This study provides key constraints on the conceptual geological and geothermal models and demonstrate the strong potential of the Las Derrumbadas prospect.

1. INTRODUCTION

1.1 Geological Context

Las Derrumbadas is a volcanic complex of the Serdán-Oriental Basin, located in the eastern part of the Trans-Mexican Volcanic Belt (TMBV) in the Mexican state of Puebla. The TMVB volcanism is related to the subduction of the Cocos plate beneath the North American plate (Pardo & Suarez 1995; Ferrari et al., 2012; Ferrari et al., 2020).Rising at an average altitude of 2400 m, the Serdán-Oriental sedimentary basin is associated with a volcanic field that encompasses a remarkable range of edifices, including rhyolitic domes and maars, scoria cones, tuff rings and lava flows of basaltic to rhyolitic composition (Ferrari et al., 2012; Ferrari et al., 2020; Chédeville-Monzo et al.2019). This volcanic activity started during the Oligocene and formed various edifices during the Holocene (Bernal et al. 2014; Muñiz-Jáuregui et al., 2019; Chédeville-Monzo et al. 2019). Some stratovolcanoes bordering the basin are still active today, such as the Pico de Orizaba which last eruption occurred in 1846.

Regarding the hydrogeological aspect of the area, the Serdán-Oriental basin is an endorheic basin (Alcocer, 2005). Its surface is mostly covered with pyroclastic deposits (De La Cruz & Garcia, 2011), which favors a high infiltration rate. Therefore, the surface water system is almost inexistent and there are no perennial surface runoffs throughout the basin. Hydrogeologists subdivide the Libres-Oriental aquifer into three units (Alcocer,2005). The upper one is made up of granular sedimentary and fractured rocks of Quaternary formations, resulting from the erosion of volcanic deposits. Its thickness varies from a few meters on the mountain slopes to up to 200 m in the center of valleys. The lower units consist mainly of limestones. The middle unit is semiconfined, consisting of folded limestones, marls, and shales of the Mezcala formation (Upper Cretaceous). The deepest unit hosts a confined aquifer and is composed of Lower Cretaceous marine deposits of the Tecoma suchil and Atzompa formations (both made of reef limestone) underlaid by the Tecocoyunca Group (sandstone, gypsum and shales). CONAGUA (Comisión Nacional del Agua) considers that Libres-Oriental Aquifer is overexploited (Cigna, 2019).

The Serdán-Oriental Basin was mainly structured by the Laramide orogeny during the late Cretaceous to early Tertiary (Andreani et al., 2008) that created a regional fold-and-thrust system with a NW-SE orientation. The Las Derrumbadas and Cerro Pinto domes are also aligned along a N140 to N160 axis (Figure 1). Those deep crustal structures may then have provided the preferred pathways for the rising magma. Another set of structural features runs along NNE-SSW directions and are associated with major faults affecting the basement (Cofre de Perote - Orizaba trend).

The geomorphology of the region is also affected by Basin and Range type tectonics, characterized by normal faults with N40 to N70 orientations and that shaped the relief of the basin (Eatrop, 1982). The magneto-telluric data show a distribution of intrusive bodies following the NNW-SSE fault pattern. They seem to be correlated with thermal manifestations observed in the area.

Las Derrumbadas volcanic complex is characterized by two rhyolitic twin domes (Siebe & Verma, 1988) that are the most outstanding reliefs of the area, rising some 1000 m above the sedimentary basin (Samson, 2016). The southern dome reaches 3480 m asl and the northern one is slightly smaller with an altitude of 3420 m asl. Although they form one single volcanic unit, the two domes have their own local names: Las Derrumbadas Rojo (red in spanish) to the South and Las Derrumbadas Azul (blue in spanish) to the North. This denomination is explained by the higher degree of alteration of rhyolites of the south dome, in comparison to the north one, which corelates with the location of the active fumarolic field on top of the former. The flanks of Las Derrumbadas are cut by landslide scars that typically fed large debris avalanches and serve as pathways to lahars during the rainy season.

Until very recently, the volcanism of the Las Derrumbadas area was considered of Neogene age (Prol-Ledesma et al., 2018, 2019) based on early radiometric ages provided in the 1980's. At this time, the domes were dated to approximately 320 ka by the ^{40}K-^{40}Ar method (Yañez-García, 1980). Recently, Chédéville-Monzo et al. (2019) used radiocarbon and stratigraphic dating to reconstruct the volcanic history, assess the impact of past eruptions on the environment and pre-Hispanic populations, and estimate future volcanic hazards (Chédéville-Monzo et al. 2019). UNAM work identified 10 volcanoes less than 25,000 BC in the dome area, eight of which of the Holocene: Alchichica, Tecuitlapa, Atexcac, Cerro El Brujo, Tepexitl, Aljojuca, Las Derrumbadas, Piedras Negras. This work indicates that the central part of the Serdán-Oriental basin should be considered as potentially active. Indeed, the last eruption of Las Derrumbadas has occurred ~ 20 AD and this is the largest, effusive silicic eruption in Mexico for the Holocene period. The age of the eruption correlates with a migration of populations from the center of the basin towards the city of Cantona to the North. These results are in line with the results of Bernal et al. (2014) that, using the $^{230}Th/U$ method in zircon from Las Derrumbadas rhyolite, yielded a relatively contemporary age of 4.7 ka (+ 1.3 / -1.2 ka) and with the works of Muñiz-Jáuregui et al. (2019) who obtained an age of 6 ka (± 4 ka) applying the $^{40}Ar/^{39}Ar$ method on the rhyolite. These new data are more consistent (than early Neogene ages) with the significant height of the volcano, which dominates the sedimentary plateau despite the strong erosion it suffers. They are also more compatible with the presence of fumaroles on the summit of Las Derrumbadas Rojo.

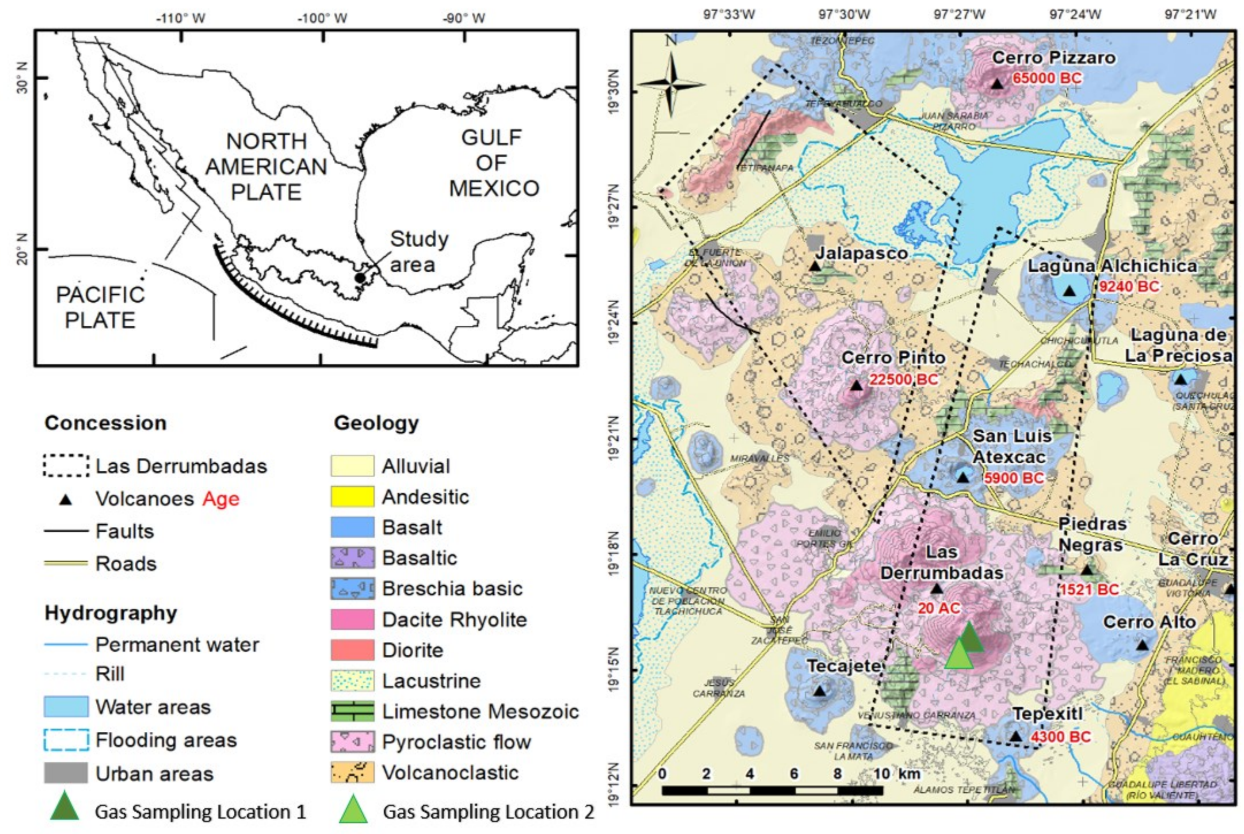

Figure 1 : Location of Las Derrumbadas domes in Mexico and geological context (volcano ages from Chédeville-Monzo et al., 2019). Sampling location at the summit of the Las Derrumbadas Rojo is referred to as sampling location 1 (red triangle) and the steam around the old bath house on the southern side is referred to as Sampling location 2 (purple triangle)

1.2 Geothermal Exploration History

Las Derrumbadas geothermal exploration began in the late 1970's and was carried out by the Mexican Federal national Electricity company CFE (Flores et al., 2015). The potential of Las Derrumbadas was highlighted by Yanez et al. (1979) and several prospecting studies followed until the 1990's (Siebe and Verma, 1986). They resulted in the drilling of two wells, without success. Two main reasons could explain these failures. First, the wells were not deep enough to reach the geothermal reservoir. Second, vertical drilling likely reduced the risk of crossing permeable and fractured areas. In addition, the efforts of the CFE then focused on the development of the Los Humeros geothermal power plant nearby, which is the third largest producer of geothermal electricity in Mexico (70 MW, Arzate et al., 2018). This inappropriate exploration strategy untruthfully concealed the potential of Las Derrumbadas and impeded its development.

In 2016, Storengy and Reykjavik Geothermal were granted approval to resume exploration at Las Derrumbadas. More modern exploration methods adapted to this perspective have been applied. Such as the magneto-telluric (MT) survey which provide MT picture shown a shallow conductive, deeper resistive body associated to a deep conductive structure. This feature is often associated to the presence of a geothermally altered clay cap overlying a deep hot reservoir with a possible deep magma chamber or intrusion acting as a heat source. Such as the InSAR (Interferometric synthetic-aperture radar) study shown the presence of a deep NNW-SSE structural axis along the Las Derrumbadas and Cerro Pinto volcanoes that may control the extension of the geothermal system toward the West and may be associated with a permeable damaged zone. As also, this work on the gas chemistry of the fumaroles of Las Derrumbadas, suggesting the presence of a deep reservoir with temperatures above 200 ° C, with a clear magmatic isotopic signature, indicates the presence of a geothermal reservoir. These studies corroborate and highlight the important prospect potential of Las Derrumbadas.

2. GAS SAMPLING AND CHARACTERISTATION METHODS

2.1 Fumaroles Area

Two permanent active geothermal manifestations have been found (Figure 1): the first at the summit of Las Derrumbadas Rojo (south dome) and the second on its southern flank, in the vicinity of an old bath house (Figure 2).

The most intense fumarolic activity is located at the summit of the dome, at 3500 m above sea level. The place can be described as a steaming, highly altered ground (given the red color of the rhyolite), which spreads over an area of up to 100 m^2. The steam rises to 93 °C, which indicates a shallow boiling point. Three additional steaming areas have been only observed during the rainy season. They are located 150 m to the SSW, from the sampled fumaroles. The hydrothermal active area seems to be aligned along in a NNW-SSE lineament. The level of vapor emissions is strongly enhanced during rainy seasons and possibly influenced by seismic activity.

The second area with fumarolic activity is located 2 km west of Las Derrumbadas Rojo peak, near a quarry into highly weathered rhyolite. The area is an old bath house located in an area where the riverbanks show temperatures of up to 40 ° C at less than 30 cm deep. This bathhouse is no longer in use. A PVC pipe where a moderate hot vapor of 36.6 ° C rises was the only possible place to take a gas sample.

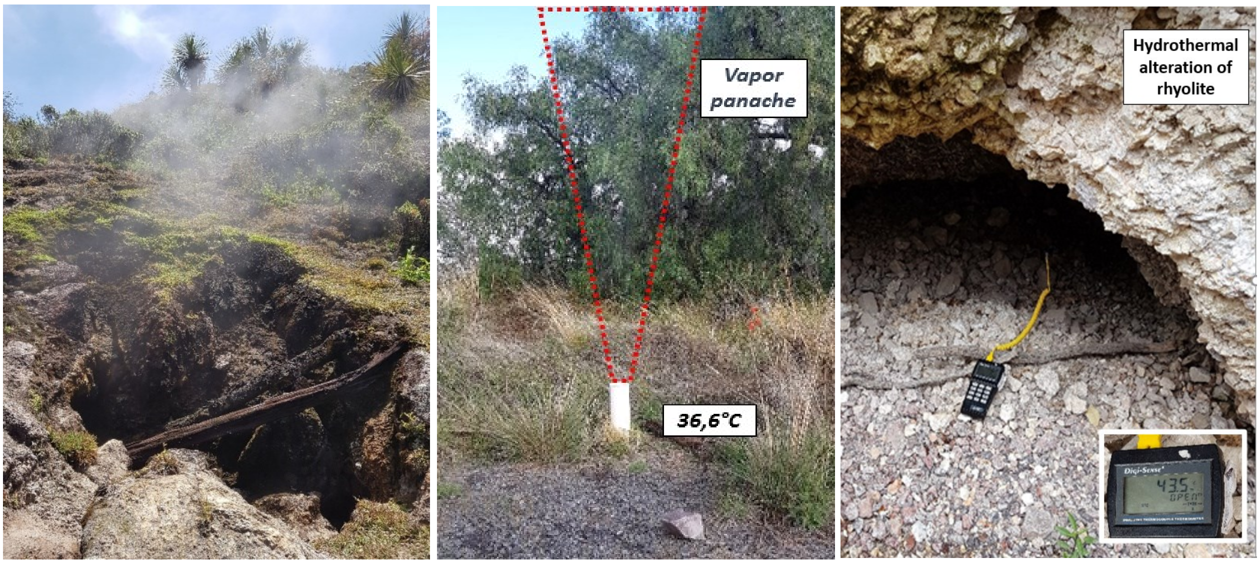

Figure 2 : Las Derrumbadas geothermal system surface manifestations. In the left picture: summit fumarole on the South dome. In the middle picture: southern PVC pipe fumarole close to the old bath house. In the right picture: vapor outlet next to the old bath house (unsampled).

The fumarolic activity of Las Derrumbadas has however already been known and exploited as revealed by the texts of Antonio Garcia Cubas published in "Escrito diversos from 1870 to 1874 - Mexico City, 1874 (pages 235 to 237)". The author relates observations on hills called "Las Derrumbadas", west of the hacienda de la Capilla, which reflect the geothermal power of activity in the 19th century. This text is in line with the presence of the steam baths, which were probably established there because the activity was more intense at this time.

2.2 Sampling campaign

Two gas sampling field surveys were carried out in the Las Derrumbadas area, in November 2017 and in May 2018. The 2017 mission was designed to confirm the presence of active hydrothermal surface manifestations at the summit of Las Derrumbadas Rojo and to try to get samples for the chemical analysis of major components, using Giggenbach bottles and gas-tubes. In 2018, the objectives of the mission focused on collecting samples specifically to trace sources and understand the origin of gases. Gas samples were taken to perform isotopic analysis such as gas composition, noble gas, and stable isotopes. The samples were also collected into gas-tubes, but steel tubes were used for noble gas.

Table 1 – Location of sampling points and sampling equipment:

Samples			Coordinate WGS84 / UTM 14N			Type
Date	Name	Location	Northing	Easting	Elevation	
05/05/2018	MXP-18-G01	LD-Summit Fumarole 1	663182	2131156	3436	Gas-tubes / flask
05/05/2018	MXP-18-G02	Old bath house Fumarole	661448	2129856	2660	Gas-tubes / flask
05/05/2018	TTU-LD-01	LD-Summit Fumarole 2	663181	2131159	3432	Gas-tubes / Steel tubes
05/05/2018	TTU-LD-02	LD-Summit Fumarole 1	663182	2131156	3436	Gas-tubes/Steel tubes

To sample gas, a silicon tube was inserted into the steaming orifice. Clay was used to isolate the vent from potential atmosphere contamination. The tube was connected to a “T” with two outlets. The first one fed a special steel tube designed to avoid leakage and external contamination. The second one was dedicated to the analysis of major components and fed a septum which allowed to simultaneously collect a 12 ml sample in a glass vial via a syringe. The gas circulated through the tube for a few minutes. The purity of the line was ensured by pumping to minimize the air contamination.

Samples MXP-18-G01 and MXP-18-G02 were collected also in Giggenbach flasks. After sampling the KOH solution with dissolved acid, geothermal gases were removed from the sampling bottles and analyzed for H_2S and CO_2. The bottles, with headspace gas inside, were transported to Iceland and analyzed by Iceland Geo Survey for O_2, N_2, CH_4, Ar and H_2. As for the 2017 campaign, the samples taken in a Giggenbach flask could not be analyzed in time (retained several months by US customs) and showed conservation problems. In this article, only the gas tube analyses that are more consistent are presented.

Two strategies have been defined to collect condensate to evaluate the isotopic composition of the water. For the first series MXP-18-G01 and MXP-18-G02, 100 ml was collected using a glass condenser for a long sampling period to avoid contamination. For sample TTU-LD-01, condensate was analyzed from 1 ml of water, which condensed in the gas tube.

Rock sampling in the area was carried out during a precedent field work expedition. Samples were collected from fresh outcrops with the aim of improving the geological map and to learn more about what serves as the main heat-source of the Las Derrumbadas geothermal system, and to obtain complementary information about the rocks which are potentially hosting of the geothermal reservoir. In addition to fresh rocks, altered rocks at the mouth of the fumaroles were analyzed.

Table 2 :Table : Location of rocks samples

Samples			Coordinate WGS84 / UTM 14N			Type
Date	Name	Location	Northing	Easting	Elevation	
24/11/2017	MXP-17-RYS26	Las Derrumbadas	663186	2131153	2876	Fresh lava
24/11/2017	MXP-17-RYS27	Las Derrumbadas	663188	2131157	2876	Altered Rhyolite
24/11/2017	MXP-17-RYS28	Las Derrumbadas	662804	2131100	3385	Altered Rhyolite
24/11/2017	MXP-17-RYS29	Las Derrumbadas	663167	2130932	3385	Fresh lava
24/11/2017	MXP-17-RYS30	Las Derrumbadas	663029	2131780	3385	Altered Rhyolite
24/11/2017	MXP-17-RYS31	Las Derrumbadas	663464	2132661	2839	Fresh lava
05/05/2018	LD_2018_02	Las Derrumbadas	663186	2131150	3152	Fresh lava
06/05/2018	DER1769B	Las Derrumbadas	660450	2132680	2540	Fresh lava
12/02/2016	MX-16-Y08	Las Derrumbadas	663464	2132661	2838	Altered Rhyolite
12/02/2016	MX-16-Y30	Las Derrumbadas	662822	2133092	2902	Altered Rhyolite

2.3 Analyses

The first series of samples (MXP-18-G01 and MXP-18-G02) was handled to ISOTECH for condensate analysis. The second one (TTU-LD-01 and TTU-LD-02), was analyzed by the Institut de Physique du Globe de Paris (IPGP) which also provided sampling equipment.

Geochemical analyses were performed on Las Derrumbadas and Cerro Pinto rhyolite samples. Major elements were analyzed at ISTerre Laboratory by Inductively-Coupled-Plasma Atomic Emission Spectrometry (ICP-AES) at ISTerre, University Grenoble Alpes, following the method of Chauvel et al. (2011).

Altered samples were also analyzed by X-ray Diffractometry Crystallography (X-ray Diffraction XRD). The analyzes were carried out by SGS and INGEN laboratories using their own internal method. We choice to performed this analyses in disoriented powder which allow a qualitative and semi-quantitative analysis of minerals and in oriented section, which is adapted to study of phyllosilicates. The clay fraction is collected by extraction by centrifugation, following physical treatments (grinding, disintegration, etc.) and appropriate chemicals (decarbonization, removal of organic matter, etc.). Glass slide allows the phyllosilicates to be oriented, for better identification. The relative proportions of the crystalline phases present were determined by semiquantitative analysis using different software, both for powders and for oriented slides.

3. RESULTS

3.1 Major Gas Composition

The results of gas analyses, including the major and trace gas composition, the isotopic composition of the major and trace elements as well as the isotopy of the condensate water are listed in Table 4.

Table 3 – Chemical composition of sampled gas:

Samples			***Composition (vol.%)***						***Isotopic composition*** (‰)					
Sample	Date	Laboratory	CO_2	CH_4	H_2S	N_2	H_2	O_2	$\delta^{13}C$-$_{CH4}$	δD-$_{CH4}$	$\delta^{13}C$-$_{CO2}$	$\delta^{18}O$-$_{CO2}$	$\delta^{15}N$-$_{N2}$	$\delta^{15}N$-$_{N2}$
TT-LD-01	**05/05/2018**	**IPGP**	39.16	11.2	ND	42.2	ND	9.08	-28.24	-144.27	-9.44	14.57	0.41	2.055
TT-LD-02	**05/05/2018**	**IPGP**	35.09	7.1	ND	48.5	ND	8.86	-28.43	-143.06	-9.55	18.05	0.23	0.724
MXP-18-G01	**05/05/2018**	**ISOTECH**	24.85	4.66	ND	57.49	ND	NA	-27.60	NA	-10.30	NA	NA	NA
MXP-18-G02	**05/05/2018**	**ISOTECH**	29.25	6.39	ND	53.54	ND	NA	-27.5	NA	-10.4	NA	NA	NA

Samples			***Rare gas concentration and isotopic composition***					***Isotopic composition of condensate***		
Sample	Date	Laboratory	He (ppm)	$^3He/^{22}Ne$	R/Ra ($^3He/^4He$)	$^{20}Ne/^{22}Ne$	$^{21}Ne/^{22}Ne$	$\delta^{18}O$-$_{H2O}$	δD	T°
TTU-LD-01	**05/05/2018**	**IPGP**	37.3	2.2	4.37	9.91	0.0297	23.1	-143.1	93°C
TTU-LD-02	**05/05/2018**	**IPGP**	19	1.3	4.56	9.84	0.0299	NA	NA	89°C
MXP-18-G01	**05/05/2018**	**ISOTECH**	NA	NA	NA	NA	NA	-18.87	-126.53	89°C
MXP-18-G02	**05/05/2018**	**ISOTECH**	NA	NA	NA	NA	NA	-19.97	-134.47	

(NA=Not Analyzed – ND=N not Detected)

The gas proportion of major components is clearly different from an atmospheric composition as highlighted by the high ratio of CO_2, and CH_4 in all samples. All samples have high CO_2 concentrations, a typical feature of geothermal areas, but the geological location of the Las Derrumbadas domes piercing through a thick carbonate basement makes further studies on the origin of CO_2 important.

As mention before, after sampling, the KOH solution titration was also performed on the Giggenbach bottles and analyzed for H_2S and CO_2. No H_2S was detected in any sample by titrations and is here reported at detection limits. The N_2 content is also high and associated with oxygen. Atmosphere contribution is not null, being difficult to avoid in such case of diffuse gas. It was evaluated using the oxygen concentration and the atmospheric N_2/O_2 ratio. The oxygen composition of the TTU-LD-02 water was not measured but deduced from the equilibrium with CO2 (Kim and O'neil, 1197) calculated from the following equation :

$$\delta^{18}O_{h2o} = \delta^{18}O_{co2-\varepsilon_{CO2-H2O}} \qquad \text{With } \varepsilon_{CO2-H2O} \text{ à 25°C = 41,2 ‰ and } \delta^{18}O_{co2} = 18{,}5 \text{ ‰}$$

The presence of nitrogen in the samples suggests some atmospheric contamination but not only. Indeed, the primary isotopic composition was recalculated to correct for the atmospheric component, which yielded values of 2.55 ‰ and 0.728 ‰ (δN_{AIR} = 0 ‰ vs $\delta^{15}N_{CRUST}$ = 7 ‰ in average). The sampled gas is enriched in helium compared to atmosphere. Helium values are 37.3 and 19 ppm.

3.2 Rocks analysis

The results of the major element analysis of rock samples from the domes are presented in Table 5.

Table 4 – Whole rocks Major analysis:

			Result in oxide wt. %											
Volcano	**Sample**	**Source**	SiO_2	TiO_2	Al_2O_3	Fe_2O_3 t	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Somme
Las Derrumbadas (south)	**DER1769B**	**This study ***	71,91	0,136	15,91	2,55	0,041	0,23	1,78	4,45	3,57	0,06	0,01	100,7
Las Derrumbadas (south)	**2017-RYS29**	**This study**	71,93	0,13	15,75	2,34	0,03	0,15	1,71	4,23	3,12	0,09	0,81	100,3
Las Derrumbadas (south)	**LD_2018_02**	**This study**	72,47	0,13	15,83	2,4	0,04	0,19	1,67	4,68	3,3	0,08	0,23	101
Las Derrumbadas (south)	**2017-RYS26**	**This study**	73,34	0,12	14,74	2,12	0,03	0,14	1,64	4,2	3,16	0,08	0,29	99,87
Las Derrumbadas (North)	**DER1748A**	**Guilbaud et al. (2019)**	73,68	0,05	14,41	1,51	0,05	0,1	0,92	4,3	3,96	0,05	0,77	99,8

**Sample furnished by MN. Guilbaud*

Las Derrumbadas lavas are rhyolitic in composition. They are rich in silica (>70%wt) and Al_2O_3 (>14%). They also present a high content in potassium (>3%wt). The samples present numerous garnets (such as DER1463B) that are observable to the naked eye.

Table 6 presents the results of the mineralogy obtained by XRD analysis on fresh rocks, an on altered rocks by hydrothermal fluids.

Table 5 : Mineralogy Analysis Results:

Samples			Description	
Name	**Type**	**Laboratory**	**Amount in %**	**Mineral phase**
MXP-17-RYS27	**High Altered Rhyolite**	**INGEN**	90 10	- Kaolinite - Boehmite - Quartz - Limonite / Goethite (trace)
MXP-17-RYS29	**Fresh lava**	**INGEN**	51.5 20.5 17.2 10.7	Andesine Paravauxite Labradorite Quartz
MXP-17-RYS31	**Altered Rhyolite**	**INGEN**	57.0 39.1 3.8	Albite Silica (amorphous) Biotite
MX-16-Y08	**Altered Rhyolite**	**SGS**	Major Moderate Traces Traces	Quartz Plagioclase/potassium-feldspar montmorillonite chlorite
MX-16-Y30	**Altered Rhyolite**	**SGS**	Major Minor Minor Minor Traces	Silica (amorphous) Plagioclase/potassium-feldspar Quartz, pyroxene Cupsidine/Fluorite Chlorite, Kaolinite

The sample MXP17-RYS27 is almost exclusively composed by Kaolinite and Boehmite (90 %). Those minerals are formed from weathering of feldspars and are usually associated with bauxite deposits. The sample MXP-RYS29 present 20.5% of Paravauxite, However, we note that the laboratory specified that this was not a perfect match but an overlap of the signal by 75% of the peaks. The MXP17-RYS31 sample shows biotite which, is a mineral that is often associated with high temperature hydrothermal metamorphism. Howeverit is a mineral that is frequently found in rhyolites, and it was observed in Las Derrumbadas samples. Therefore, it is probably not a product of alteration here. Samples MXP16-YS08 and MXP-YS30 were sampled and analyzed with the XRD during a previous mission. We note that the first sample contains Montmorillonite, Chlorite, and Kaolinite. Those minerals are typical from hydrothermal alteration. Sample MXP16-Y30 contains Cupsidine, that is a fluorine bearing calcium silicate mineral (sorosilicate) which occurs in contact metamorphosed limestone or in mellite bearing skarn.

4. DISCUSSION

4.1 Limited number of surface manifestations

The discreet surface manifestation of the Las Derrumbadas geothermal field is similar to other geothermal projects located along the TMVB. This is the case of the neighboring areas of Acoculco (Peiffer et al., 2014) and Los Humeros calderas. Despite this apparent weak potential, the capacity to produce geothermal power has already been proven in Los Humeros, where reservoir temperatures are as high as 350 °C (Norini et al., 2015; Reinsh et al., 2017). The geothermal sources in the TMVB are located relatively deep in the crust, which can account for the development of an important alteration zone which acts as a cap rock where permeability is dramatically decreased. Alvarez and Yutsis (2017) proposed a subsurface modeling method based on the analysis of the residual magnetic field and Bouguer anomaly in the Las Derrumbadas area, suggesting the presence of a high density and high magnetic deep dome shape susceptibility which would correspond to the signature of a magma chamber below the volcano.

A resistivity survey, MT/TEM was carried out in July 2018. This survey reveals a low resistivity anomaly, possibly a clay cap, in the southern part of the permit area, on the northeastern flank of the volcanic complex. This element can be interpreted as a hydrothermally altered clay cap overlying a deep hot geothermal reservoir (above 200°C). In addition, this feature is associated with a deeper conductive body, the possible signature of a deep magma chamber or intrusion. Both shallow and deep conductive features tend to overlay, displaying elongated shapes. This suggests a fault control on the geothermal fluid circulation.

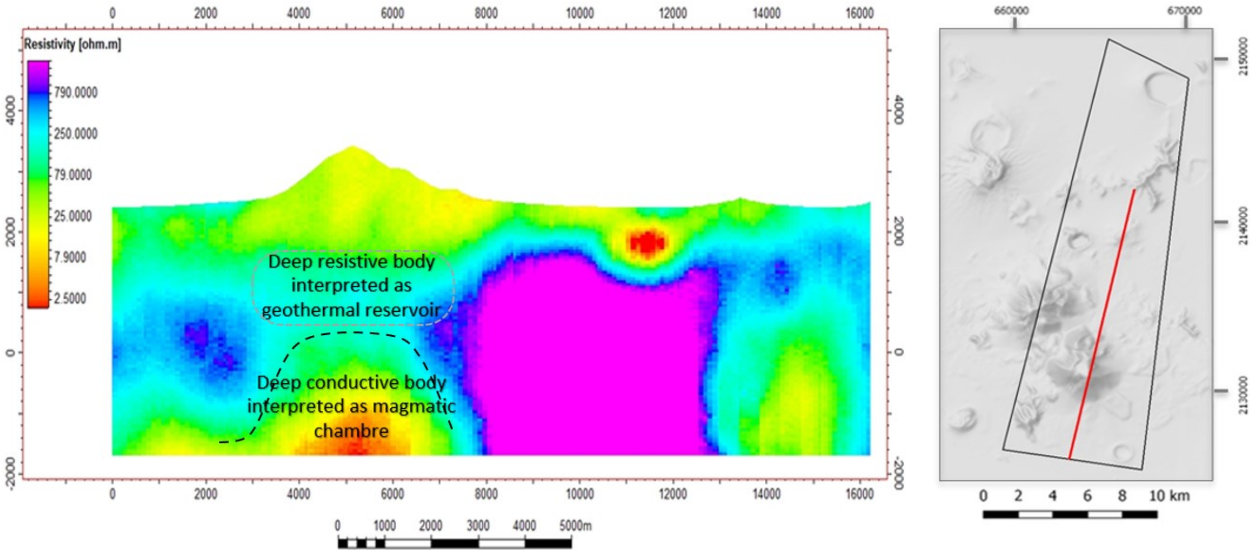

Figure 3 : North-South MT interpolated cross-section showing hot geothermal reservoir patterns (reddish color - conductive area: black-dashed area localizes the magmatic chamber / blueish color and the grey-dashed areas localize the resistive area which can be interpreted as the geothermal reservoir)

4.2 Origin of condensate water in sampled gas

The isotopic composition of the water from Las Derrumbadas sampled gases is displayed in Figure 4. The δD and $\delta^{18}O$ ratios were also measured from two wells close to the volcano base (MXP-18-W01 and MXP-18-W02). The stable isotopic ratios from condensates fall on the Sierra Madre meteoric water line (SMMWL) (Quezadas et al., 2015).

There is a difference between condensates which have been sampled from a long period (MXP-18-G01 and MXP-18-02) and the sample which have been collected during a few minutes in gas tubes (TT-LD-01). TT-LD-01 sample is displaced to the left of the water line, which means that samples have been subjected to an equilibrium with CO_2. The value of oxygen has not been measured but was deduced from the CO_2 content, considering that carbon dioxide and water were in equilibrium (Kim and O'Neil, 1997).

All samples have a meteorological origin without any trace of rock interaction, which means that the vapor is formed at a shallow depth, just below the volcano summit. The hot and dry gas reaches the surface at a high temperature. The unfiltered rainwater is then vaporized when it encounters the volcanic gas.

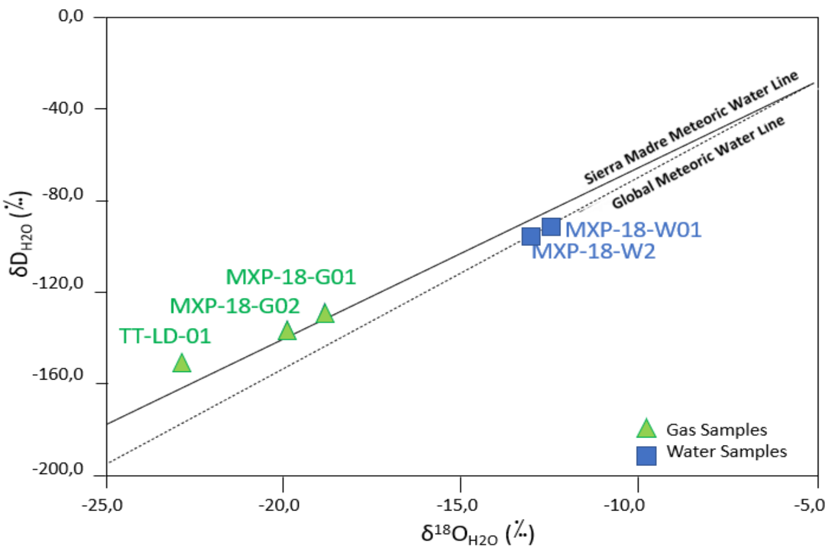

Figure 4 : Isotopes ratio of δD and $\delta^{18}O$ from Las Derrumbadas gas samples. The solid line corresponds to the Sierra Madre Meteoric Water Line (Quezadas et al., 2015) and the dotted line corresponds to the Global Meteoric Water Line (Levin et al., 2004).

4.3 Petrology and alteration mineral

Las Derrumbadas lavas are evolved calk-alkaline rocks that, considering the subduction context, may have been produced by partial melting of the mantle, and evolved through the process of differentiation, fractional crystallization, and contamination. The current volcanic activity in the basin is bimodal, that is, two main types of rocks are erupted: basic and acid, with a lack of intermediate compositions. Basic lavas have been sampled and analyzed but results are not presented here, because this study focuses on Las Derrumbadas volcano which formed only by rhyolite. However, rhyolites (acid lavas) dominate in terms of volume. Intermediate lava of andesitic composition is also found on the area, but correspond mostly to an older volcanism. Basic lavas correspond to the smallest volcanoes located around Las Derrumbadas domes.

Acidic lavas mainly consist (in volume) of the Las Derrumbadas domes, but rhyolitic rocks were also erupted at Cerro Pinto, Tepexitl and Jalapasco in the vicinity of the domes. These rocks are rich in silica and garnets were observed in some of them. The presence of evolved rocks like rhyolite suggests the presence of at least one large magma chamber under the volcanoes where magma can be stored and evolved. However, primitive rocks (such as basalt or andesite-basaltic) may suggest a faster magma ascent (without storage in a magma chamber) that is assisted by fracturing.

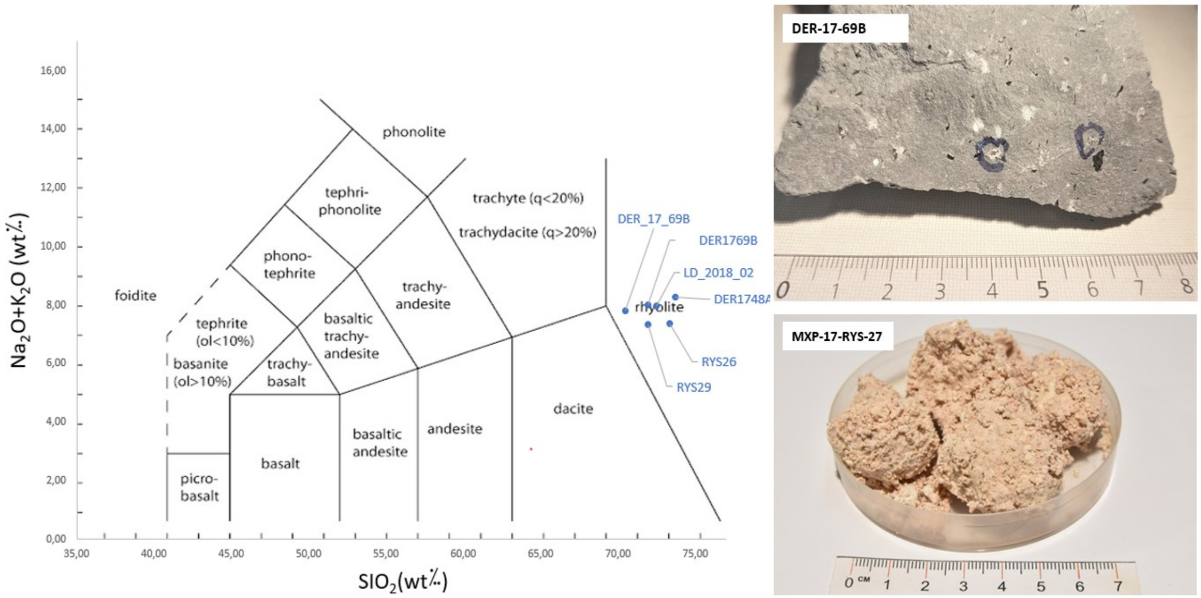

Figure 5 : TAS Diagram of Las Derrumbadas & Cerro Pinto field (Le Bas et al., 1986), and picture of Las Derrumbadas Rhyolite: DER17-69B which is unaltered with garnet visible with naked eyes and MXP-17-RYS-27 which is completely altered with hydrothermal gas.

Regarding the surface alteration, some samples present mineral assemblages, which suggest a strong hydrothermal contribution. The smectite (montmorillonite) / chlorite association is typical of temperatures above 150 ° C. One sample is almost exclusively composed of kaolinite and boehmite, which indicates rapid acid hydrolysis of the sample. Another also contains trace amounts of kaolinite that comes from weathered feldspar. Because these samples are taken at the outlet of the fumaroles, it is probable that this acid hydrolysis is a consequence of the circulation of hydrothermal fluids at shallow depth. A sample contains paravauxite, which is also a characteristic of hydrothermal deposits usually associated with granitic pegmatites, but that can also be formed by a connection between a phosphate source with a magmatic dike.

4.4 Carbon Origin of the System

4.4.1 Origin of carbon in methane (CH_4)

Methane (CH_4) is generally scarce in hot magmatic gases, but its origin can be key in unravelling interaction processes. In the context of the Las Derrumbadas' system, methane can be produced either 1) by reduction of magmatic CO_2 and constitute a component of reduced hydrothermal fluids (Giggenbach, 1987) or 2) by biodegradation resulting from interaction with the sedimentary environment. The plot of the deuterium isotopic composition in a $\delta^{13}C$ vs δD diagram proposed by Whiticar (1999) allows to make such discrimination Figure 6).

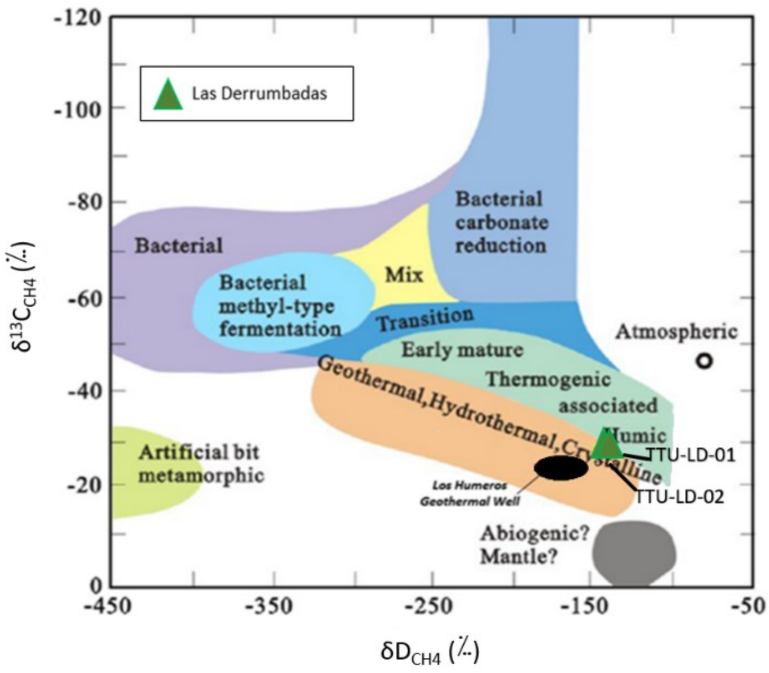

Figure 6 : Isotopic composition of Las Derrumbadas methane plotted on a discrimination diagram (Whiticar, 1999)

The isotopic value of methane from Las Derrumbadas gas lies far from the atmospheric or biogenic domains. Values in $\delta^{13}C_{CH4}$ (-28.24‰ and -28.43‰) and in δD_{CH4} (-144.27 ‰ and -143.06 ‰) suggest a hydrothermal origin without Mesozoic Limestone contribution. The methane isotopic composition shows instead a thermogenic origin. Samples are plotted into the geothermal, hydrothermal and crystalline domains. It is noteworthy that the signature of the Las Derrumbadas' methane is not mantelic, indicating that it is produced by the reduction of magmatic CO_2 in the hydrothermal system.

Portugal (1994), Truesdel (1987) and Tello (1992) also studied the isotopic composition of methane from Los Humeros geothermal wells. Methane isotopic compositions are in the same range as the Las Derrumbadas gas sample (the δD content ranges from -173 to -152 ‰ and δ13C from -27 to -22 ‰).

4.4.2 Origin of carbon in Carbon dioxide (CO_2)

The gases from Las Derrumbadas present a high CO_2 concentration, consistent with the volcanic and geothermal context, I.e. a rhyolitic magma degassing CO_2. In our context, high levels of CO_2 can also result from an interaction between the geothermal deposit and the Mesozoic sedimentary calcareous layer similar to examples described in Turkey (Arksoy 2015). The analysis of the origin of CO_2 is essential here, because it allows to discriminate the CO_2 source and decipher the geological layer which contains the geothermal reservoir: a limestone affinity would indicate a location within the Mesozoic layer of Libres Oriental aquifer; the reservoir would otherwise originate from the deeper silicic basement.

Isotopic data provide a better understanding of the origin of carbon. In fact, CO_2 could come from 4 main sources in the geothermal system (Jenden, 1993; Sano and Marty 1995): 1) from organic matter rich sediments (a $\delta^{13}C$ of CO_2 up to 20 ‰), 2) from mantle degassing or cooling of a magma body ($\delta^{13}C$ of CO_2 around 6 ± 2 ‰),3) from meteoric infiltrations or atmosphere related sample contamination (a $\delta^{13}C$ of CO_2 between -2 ‰ and + 2 ‰) or 4) from the carbonated layers (which have a $\delta^{13}C$ value of CO_2in the same range as the atmosphere).

Las Derrumbadas gas analyzes show relatively low negative values of the $\delta^{13}C$ of CO_2, between -9.26 ‰ and -10.4 ‰. Hence, CO_2 seems to be mainly mantellic with a possible contamination of organic matter-rich sediment, but does not show any trace of a carbonated layer contribution. The magmatic source is compatible with the supposed heating source of the geothermal system. Those values of $\delta^{13}C_{CO2}$ are slightly higher than the typical range of CO_2 degassed by magmas of MORB and OIB types, which can be explained by the subduction context.

Richard et al. (2019) published the R/Ra value of gases sampled from the producing wells of the 4 biggest geothermal projects of CFE (the Mexican federal electricity company) which are Cerro Prieto (CP-GF with a 570 MW production capacity), Los Azufres (LA-GF, 225MW), Los Humeros (LH-GF, 68.6 MW) and Las Tres Vírgenes (LTV-GF, 10 MW; Flores-Espino et al., 2017). On Figure 7, we compare our data to that from Richard et al. (2019) publication which focuses on the carbon sources of the four geothermal fields of the CFE.

CP-GF and LH-GF show $\delta^{13}C$ CO_2 ratio between −6 to −2 ‰, typical for MORB type gases. LTV-GF gas show lower values than mantle (-10.7 ± 0.5 ‰). For LTV-GF, such $\delta^{13}C$ values have been interpreted by the authors to be caused by the addition of organic matter-rich sediments from an old subduction plate. For Los Humeros gases, the low value of $\delta^{13}C$ of CO_2 are attributed to a contribution of the limestone. In fact, the Los Humeros geothermal reservoir base is mainly composed by limestones and shales (Aragón-Aguilar et al., 2017). Those values are compatible with the $\delta^{13}C$ composition of Los Humeros Limestone, which has been measured by González-Partida (1993) from 0.32 to −0.8‰. Therefore, while Las Derrumbadas share the same sedimentary basement as LH-GF, they both present a completely different $\delta^{13}C_{CO2}$. This may be due to the location of the geothermal system. In our case, it is located below the sedimentary layers, that is, the basement. In the case of Los Humeros, the caldera renders the geothermal system more superficial and is found in the sedimentary limestone formations that generate an important calcite contribution.

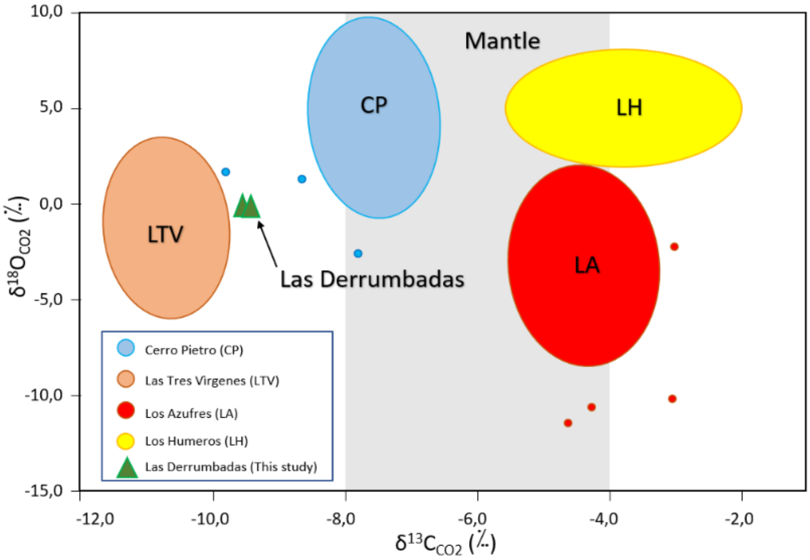

Figure 7 : Isotopic composition of the Las Derrumbadas fumaroles (this study) compared to the gas from the Mexican geothermal fields exploited by the CFE (figure modified from Richard et al., 2019)

4.4.3 Origin of the Noble Gases of the System

The isotopic composition of helium can help to further understand hydrothermal processes and better constrain the origin of gas (Burnard et al., 2013; Prinzhofer, 2013; Moreira et al., 2013). Helium 3 (^{3}He) is a primordial substance in the Earth i.e., produced only by the primordial nucleosynthesis at the first moments of the Universe formation. Then, during Earth formation, ^{3}He was entrapped inside the mantle, while Helium 4 (^{4}He) is also produced by the decay of radioactive elements. The R/Ra ratio is used to represent the ^{3}He/^{4}He content and is defined by the following equation:

$$\left(\frac{{}^3He}{{}^4He}\right)_{R/Ra} = \frac{\left({}^3He/{}^4He\right)_{Sample}}{\left({}^3He/{}^4He\right)_{atmosphère}}$$

Oceanic and terrestrial waters both have R/Ra = 1 as the atmosphere, while R/Ra of the continental crust is less than 1 due to the enrichment in ^{4}He by radioactive decay of crustal component such as uranium. Magmatic sources are enriched in ^{3}He compared to the atmosphere: the typical R/Ra ratio in the mantle is higher than 7 for Mid-Ocean Ridge Basalts (MORB) and 5 for hot spots (Prinzhofer 2013; Moreira et al., 2013). Due to those magmatic influences, thermal springs R/Ra values range between 3 to 11.

The gas in Las Derrumbadas is highly enriched in helium to up to 38 ppm, which is typical of magmatic sources. The R/Ra ratios are 4.37 for TTU-LD-01 and 4.56 for TTU-LD-02. The isotopic composition of sampled gas shows a mantellic origin as they are enriched in ^{3}He and indicates an active mantle contribution. In subduction zones, the helium source is a mixture of a mantle source and a radiogenic source as seen in volcanic arcs (R / Ra = 5.4 ± 1.9; Hilton et al., 2002).

Las Derrumbadas gases appear to be more similar to LTV-GF and CP-GF, given that their R/Ra ratios are in the same range, from 2,728 to 6,380 for LTV-GF and from 4.622 to 4.768 for CP-GF (Pinti et al., 2019; Birkle et al., 2016). In comparison, LH-GF and LA-GF present higher values, mostly between 6 and 8, typical of a subduction context (Pinti et al., 2017; Wen et al., 2018).
Hence, although the geological context of Las Derrumbadas compares to those of LA-GF and LH-GF, the R/Ra values obtained in Las Derrumbadas gases are quite low, which could be explained by a higher contribution of the crust, enriching the mixture in radiogenic helium. LH-GF shows a signature in ^{3}He/^{4}He closer to MORB type gas. Richard and al. (2019) attribute this difference to the particular geometry of the slab below central Mexico that is more vertical in this area causing a more enriched signature on the mantle component.

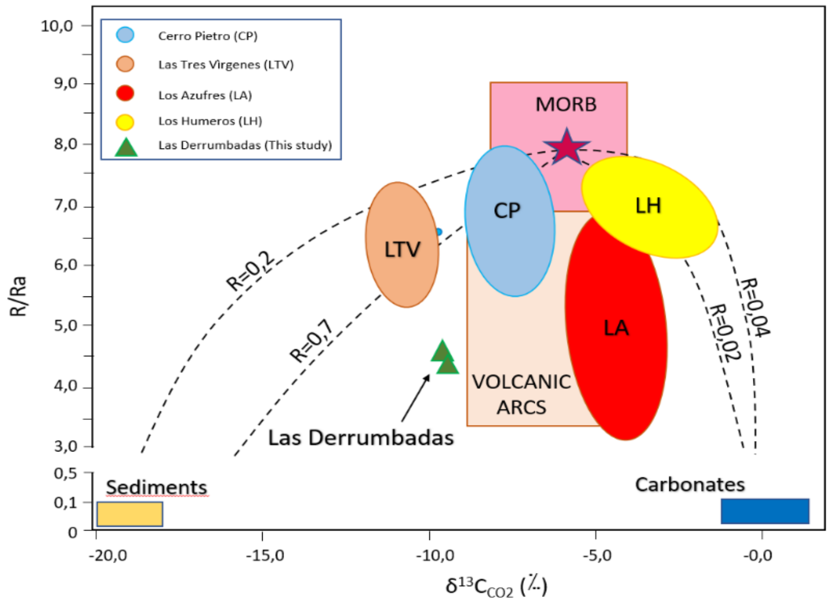

Figure 8: R/Ra and δ13C of CO2 discriminating diagram modified from Richard et al. (2019). Values from samples of Las Derrumbadas (this study) are plotted on the figure from Richard et al. (2019) with values field from Cerro Prieto, Los Azufres, Los Humeros, and Las Tres Vírgenes. Dashed lines represent mixing hyperbolas between the MORB mantle source and sediments and carbonates. Hyperbola curvature R-values are equal to the ratio (C/He) mantle/(C/He) organic/carbonate. Y-axis is split for clarity. Note that for this study, the Volcanic Arc field was modified using the values from Javoy (1986).

4.5 The absence of sulfur in the fumaroles

The absence of sulfur in the fumaroles constitutes an anomaly for this subduction context as volcanic gases usually show high levels of H_2S (Oppenheimer, 2011). The presence of H_2S is normally due to the transfer of the magmatic SO_2 to the geothermal fluids. The SO_2 is then converted to H_2S as it rises and cools.

The absence of sulfur can be explained by two hypotheses: 1) the source did not contain SO_2 or 2) sulfur has been neutralized during its ascent. The first hypothesis (that the volcanic gas did not contain any sulfur) is quite rare but described in the Cerro Pastos Grande volcano (Muller et al., 2017). Cerro Pastos Grandes is a volcano located on the Andean-Bolivian Altiplano. This configuration, namely an altiplano associated to an active subduction, is similar to the geological context of Las Derrumbadas. The presence of fractures and faults due to a caldera provides a strong hydrothermal field. Cerro Pastos Grande Gas did not contain any H_2S, and the isotopic composition $\delta^{13}C_{CO2}$ also indicated a magmatic source associated with a small crustal contribution, such as at Las Derrumbadas. The second hypothesis is more common and more probable: in this case, H_2S is neutralized and stored during the fluid ascent which is more typical in this type of environment. Either the sulfur is stored in liquid form or stored in mineral form in the form of native sulfur. The sulfur can also be associated with other chemical elements, especially metals. If this neutralization involves metal, such as iron, copper or manganese, a metallic porphyry can form, which is very common in Mexican volcanoes (Zimbelman et al., 2005) The region of Las Derrumbadas is well known for its production of metallic sulfur such as Alabandite (MnS; Mine Sangre de Cristo and Mine la Preciosa are two mines 10 km from the volcano).

As said earlier, the texts of Antonio Garcia Cubas (1874) relates testimonies on "Las Derrumbadas" that reflect a strong activity of the volcano in the 19^{th} century. One point that is particularly interesting in this testimony being that D. Cárlos Sartorius (1802) does not only describe thermal baths but of sulfurous baths, of a ground that releases sulfur also at the top of the mountain. However, we cannot be sure that it was actual sulfur baths, even if the smell of sulfur is characteristic.

Stix and Moor (2017) studied the composition of fumarolic gases to forecast phreatic eruptions driven by magmatic degassing. Their study is based on various recent studies of Central American volcanoes that shows how small changes in hydrothermal system result in significant and changes in sulfur fumarole composition. However, the absence of gas emission also has to be considered, as it may be due to the sealing of the hydrothermal system, resulting in an accumulation of gas and pressure in the system and ultimately leading to phreatic eruptions.

Sulfur dioxide is, usually, a major component of magmatic gas flux. However, sulfur dioxide is also a reactive gas, forming sulfuric acid via a process known as “scrubbing”. Scrubbing is characterized by two fundamental dissociation reactions:

$$4\,SO_{2\,(g)} + 4H_2O_{\ (l)} \rightarrow\ H_2S_{(g)} + 3H_2SO_{4(aq)}$$
$$3SO_{2(g,aq)} +\ 2H_2O_{(l)} =\ S^{\circ}{}_{(s,l)} + 2HSO^{\,-}_{\ 4(aq)} + 2H^{+}_{(aq)}$$

The first reaction produces H_2S, which can be expelled by fumaroles; the second one does not produce gas, but instead native sulfur and sulfuric acid which will be dissolved in the geothermal system fluids. Authors proposed that deeper hydrothermal systems associated with more explosive phreatic eruptions tend to be associated with H_2S, whereas shallower hydrothermal systems fed by air-saturated water generate eruptions which can be H_2S poor. Carbon dioxide behaves very differently to sulfur gases, Under the acidic conditions found in high enthalpy hydrothermal systems, CO_2 is in fact not removed from the gas phase by interactions with hydrothermal liquids.

Stix and Moor (2017) proposed a classification of gas compositions, Las Derrumbadas gas composition is, as expected, classified as a sulfur scrubbing system This means that the system has a very limited risk of phreatic eruption.

Again, according to the testimony of Antonio Garcia Cubas (1874), Las Derrumbadas thermal baths were qualified as sulfuric bath, but now gas do not contain any trace of sulfur, that imply that gas chemistry has changed over the last two centuries. At this stage, our results therefore point to a neutralization process to explain the absence of sulfur in the fumaroles.

4.6 Estimation of the reservoir temperature

The first temperature estimates of the Las Derrumbadas reservoir were made following the first exploration campaign by Galibert et al. (2017), based on geothermometers from Arnórsson et al. (1983). In average, H_2 and CO_2 geothermometers yielded reservoir temperatures between 190 and 270 °C. Temperature have been also calculate using CO_2 geothermometer from Giggenbach, provided extremely high temperatures of 360 and 400 ° C. However, leaks in the gas samples taken during this campaign were noticed and some chemical components at the limit of the detection threshold (such as H_2), suggests that these first estimates were not reliable.

For this study, CH_4-CO_2 gas geothermometers were used (Table 7). Using the first geothermometer proposed by Giggenbach (1991) yielded temperatures between 196 °C and 205 °C (196 °C for TTU-LD-01, 203 °C for TTU-LD-02, 205 °C for MXP-18-G01 and 201 °C for MXP-18-G02). Nonetheless, the temperature estimation provide by this geothermometer, gives imprecise results because they are very dependent on the geological context and the interaction processes (Giggenbach, 1991,). Horita (2001) proposed another geothermometer, also based on the carbon exchange between CO_2-CH_4 and the fractionation calculation lnα, yielded a range of 380 °C to 417 °C (382 °C for TTU-LD-01, 381 °C for TTU-LD-02, 412 °C for MXP-18-G01 and 417 °C for MXP-18-G02). This method is reliable when the CO_2 and CH_4 are equilibrated and is presumed to be more representative of the geothermal system.

Table 6 : Gas Geothermometers Estimation Results

Sample	CO2-CH4 - Giggenbach (91)	CO2-CH4 (eq) - Horita
TTU-LD-01	196	382
TTU-LD-02	206	381
MXP-18-G01a	205	412
MXP-18-G02b	202	417

The geological and geochemical characteristics of Las Derrumbadas indicate the presence of a high temperature geothermal system. Gases geothermometer most reliable suggests temperatures above 300 °C. These values are comparable to the temperatures measured at the nearby Los Humeros geothermal powerplant.

5. CONCEPTUAL MODEL

The compilation of the interpreted data allows to build a three-dimensional conceptual model using the software Leapfrog. The three-dimensional conceptual model is the result of the integration of all the geoscience data acquired during the exploration phase and we present here only parts relevant to this study. Cartography and numerical terrain models allow to represent and understand the structure of the geothermal system. The geophysical study, in particular its structural aspects study, such as the detection of faults and the study of seismicity, allowed to locate the porous structure where the best flow can be expected, while the new acquisition of magneto-telluric (MT) data allowed modeling of the heat sources and their extension. Figure 9B represents a filtered 3D visualization of Las Derrumbadas with some MT data to highlight the conductive body and cartography draped on DEM (Digital Elevation Model). For its part, The new geochemistry data made it possible to identify interactions identify interactions between the different elements of the system and temperatures. Likewise, the new hydrogeology data enable to connect the dynamics of recharge. A sketch summarizing the current view of the Las Derrumbadas geothermal system as it is understood at the present day is presented on Figure 9-A. Below we describe key aspects of the model as follows.

Rainwater infiltrates to the deep aquifer in the basement through the numerous faults affecting the Serdán-Oriental basin. This infiltrated water is heated at the contact of the deep cooling volcanic hot intrusion situated underneath Las Derrumbadas volcano, generating a local geothermal system. The deep aquifer is formed by fractured Paleozoic metamorphic rocks and granitoid intrusions and the infiltration occurs mainly along the raised reliefs of the Perote-Orizaba structural axis. Possible additional infiltration may occur along other faults in the Serdán-Oriental basin.

The gas sampled at the summit does not contain any trace of storage in the carbonated Mesozoic layers, indicating that the geothermal aquifer is likely located deeper. The geothermal upflow is nested within the hot intrusive rhyolitic rocks using the damaged fault basement of the Las Derrumbadas-Cerro Pinto structural axis as a vertical permeable drain; CO_2 and Helium isotopic signatures reflect a crustal contribution which can be attributed to the basement aquifer.

The cap rock of the geothermal system is likely to be formed by the impermeable shale and marl layers of Mesozoic formations and consolidated by the hydrothermal clays. The sealing capacity of the cap rock seems to be very effective as the observed fumaroles are mostly generated from meteoric waters heated by magmatic gases. In fact, at the top of the dome, the water vapor has no deep characteristic, only the hot gas has reached the surface. The water vapor sampled is freshly infiltrated and vaporized water at a shallow depth as shown by its isotopic composition. The gas, on the other hand, has a chemical and isotopic composition showing deep characteristics and implying the presence of an aquifer.

The absence of H_2S in the geothermal fluid constitute a great benefit to its exploitation. The magmatic gas may not contain it, but it is more probable that, instead, the H_2S is fixed at depth either in mineral form or in aqueous form in the geothermal reservoir. Indeed, many volcanoes in the region are associated with the formation of metal porphyry and sulfur mineralization.

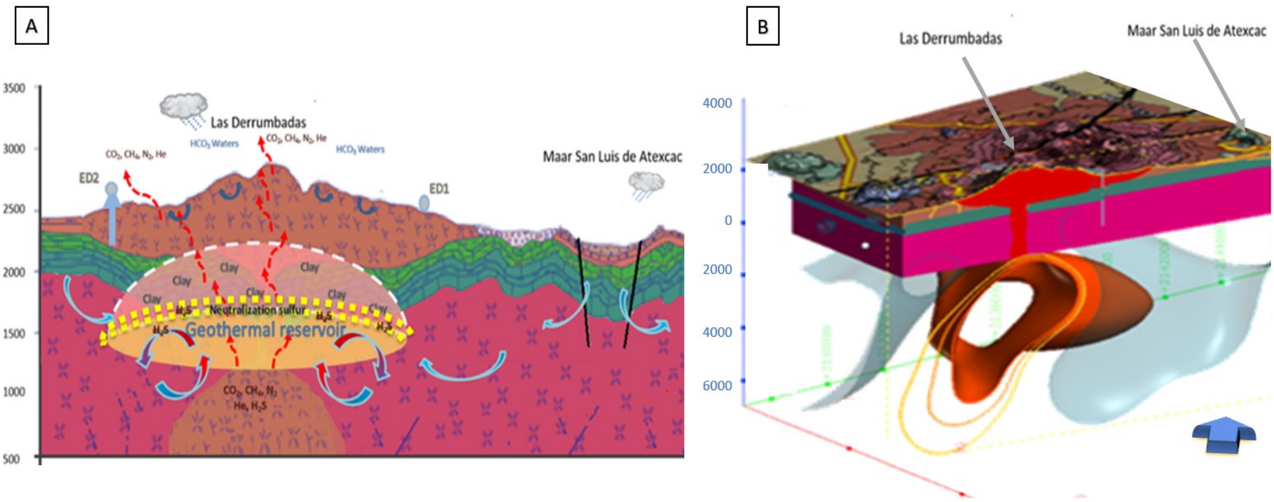

Figure 9 : Conceptual model of Las Derrumbadas reservoir / A: Sketch summarizing (figure 9A) our interpretation of Las Derrumbadas geothermal system / B: filtered 3D visualization of the Las Derrumbadas 3D Model with some MT Data to highlight the conductive body and cartography draped on MNT Figure 10 : Conceptual model of Las Derrumbadas reservoir / A: Sketch summarizing our interpretation of Las Derrumbadas geothermal system / B: filtered 3D visualization of the Las Derrumbadas 3D Model with some Magneto Telluric Pictures to highlight the conductive body and cartography draped on digital elevation model

6. CONCLUSIONS

The new geochemical data obtained from the few Las Derrumbadas fumaroles provided significant geological constraints on its geothermal system and greatly improves fundamental knowledge of volcanism along the Trans-Mexican Volcanic Belt.

Gas chemistry provides with crucial information for understanding the specificity of the Las Derrumbadas hydrothermal system, that cannot otherwise be deduced from analogues and studies of nearby sites, nor by interpretation of geophysical images alone.

In fact, Las Derrumbadas differs from the neighboring caldera-hosted geothermal systems (Los Azufres, Los Humeros) but also from the Mexican Geothermal field. This study allowed to locate the host rocks of the geothermal reservoir in the basement situated below the Mesozoic sedimentary layers. This location is crucial for the geothermal exploration for two main reasons: 1) the reservoir is deeper than previously thought and explains the failure of the exploration drilled in 1994; 2) The Las Derrumbadas geothermal system is supplied with the basement aquifer that is only reached by few wells in the basin. This Basement aquifer is distinct from the overexploited Libres-Oriental aquifer that supplies the Los Humeros System with water.

The gas composition is fundamental to attest the existence of a hot geothermal reservoir. Isotopic analysis of CH_4 also indicates a clear geothermal, hydrothermal, crystalline origin. Here the composition of the gas implies a significant reduction of magmatic gas by the hydrothermal system (reduction of CO_2, purification of sulfur). The chemistry of the gas also allowed us to estimate the temperatures of the reservoir. Until now, the geothermal prospect of Las Derrumbadas was considered as a medium enthalpy system. Since the resumption of exploration, it can be considers as high enthalpy one. Geothermometers indication showed very high temperatures, this information is necessary for calculating production capacity, and must be taken into account for the design of the future exploration drilling.

This study demonstrates the potential of the Las Derrumbadas geothermal system and opens an avenue for future exploration.

REFERENCES

Alcocer, J., Escolero, Ó., Marín, L., (2005) Problemática del agua de la Cuenca Oriental, estados de Puebla, Veracruz y Tlaxcala. In: B. Jiménez y L. Marín (eds.). *El agua en México vista desde la academia.* pp. 57-77.

Alvarez, R., Yutsis V. V., (2017) Potential fields modeling of the Serdán Oriental basin, Eastern Mexico*, Journal of South American Earth Sciences,* Volume 80, 2017, Pages 375-388, ISSN 0895-9811

Andreani, L., Rangin, C., Martínez-Reyes, J., Le Roy, C., Aranda-García, M., Le Pichon, X., Peterson-Rodriguez, R.., (2008) The Neogene Veracruz fault: evidence for left-lateral slip along the southern Mexico block. *Bulletin de la Société Géologique de France;* 179 (2): 195–208

Aragón-Aguilar, A., Izquierdo-Montalvo, G., López-Blanco, S., Arellano-Gómez, V., (2017) Analysis of heterogeneous characteristics in a geothermal area with low permeability and high temperature, *Geoscience Frontiers*, Volume 8, Issue 5, 2017, Pages 1039-1050

Aksoy, N., Gök, Ö., Mutlu, H., Kılınç, G., (2015). CO2 Emission from Geothermal Power Plants in Turkey, *Proceedings World Geothermal Congress* 2015 Melbourne, Australia, 19-25 April 2015

Arnórsson S., Gunnlaugsson E., Svavarsson H. (1983) The chemistry of geothermal waters in Iceland. III. Chemical geothermometry in geothermal investigations. *Geochimica et Cosmochimica Acta*, V 47, pp 567-577

Arnórsson, S., Bjarnason, J.Ö., Giroud, N., Gunnarsson, I., Stefánsson, A. (2006) Sampling and analysis of geothermal fluids, *Geofluids*, V 6, pp 203-216

Arzate, J., Corbo-Camargo, F., Carrasco-Nuñez, G., Hernandez, J., Yutsis V. (2018) The Los Humeros (Mexico) geothermal field model deduced from new geophysical and geological data – *Geothermics,* V 71, pp 200-211

Bernal.P., L.A. Solari, A. Gómez-Tuena, C. Ortega-Obregón, L. Mori, M. Vega-González, D.G. Espinosa-Arbeláez, (2014) In-situ 230Th/U dating of Quaternary zircons using LA-MCICPMS, *Quaternary Geochronology*, Volume 23, Pages 46-55, ISSN 1871-1014

Birkle, P., Portugal, E., Pinti, D. Castroc, M. C., (2016) Origin and evolution of geothermal fluids from Las Tres Vírgenes and Cerro Prieto fields, Mexico – Co-genetic volcanic activity and paleoclimatic constraints, *Applied Geochemistry*, V 65, pp 36-53

Campos-Enriquez, J.O. & Garduño-Monroy, V.H. (1987) The shallow structure of Los Humeros and Las Derrumbadas geothermal fields, Mexico – *Geothermics*, V16, No 5/6, pp.539-554.

Cigna, F., Tapete, D., Garduño-Monroy, V.H., Muñiz-Jauregui, J.A., García-Hernández, O.H., Jiménez-Haro, A., (2019) Wide-Area InSAR Survey of Surface Deformation in Urban Areas and Geothermal Fields in the Eastern Trans-Mexican Volcanic Belt, Mexico. *Remote Sensing* 11, 2341.

Chauvel, C., Bureau, S., Poggi, C., (2011) Comprehensive chemical and isotopic analyses of basalt and sediment reference materials, *Geostandart Geoanalyses. Ressources* V 35, pp 125-143

Chédeville, C., Guilbaud, M.N., Siebe, C., (2019) Stratigraphy and radiocarbon ages of late-Holocene Las Derrumbadas rhyolitic domes and surrounding vents in the Serdán-Oriental basin (Mexico): Implications for archeology, biology, and hazard assessment. *The Holocene*, vol 30.

Oppenheimer, C., Scaillet, B., Martin, R.S., (2011) Sulfur Degassing From Volcanoes: Source Conditions, Surveillance, Plume Chemistry and Earth System Impacts. *Reviews in Mineralogy and Geochemistry, Mineralogical Society*, 2011, 73, pp.363-421.

De La Cruz, S., A., & Cayetano García A., I., (2011) Carta Geológico-Minera Guadalupe Victoria E14-B35, Tlaxcala, Pueble Y Veracruz, Cartografía y edición por el *Servicio Geológico Mexicano*

ENRG (2016) Las Derrumbadas geothermal prospect reconnaissance report – *License application file*, pp 99

Eatrop, G.P., (1982) The Basin and Range Province: Origin and Tectonic Significance, Annual *Review of Earth and Planetary Sciences*, V 10, pp 409

Ferrari, L., Orozco-Esquivel, T., Manea, V., Manea, M., (2012) The dynamic history of the Trans Mexican Volcanic Belt and the Mexico subduction zone. *Tectonophysics,* 522-523 September 2011 122-149.

Ferrari, L., Conticelli, S., Vaggeli, G., Petrone, C. M., Et Manetti, P., (2000) Late Miocene volcanism and intra-arc tectonics during the early development of the Trans Mexican Volcanic Belt. *Tectonophysics,* 318, December 1999 161-185

Flores, M.F., Ramirez Montes, M. & Diez Leon, H.D. (2015) Mexican geothermal activities and the new electricity market – CFE presentation – *Geothermal Resources Council* 2016 Annual Meeting, 25p.

Flores-Espino, F., Booth, S., Graves, A., (2017) Mexico's Geothermal Market Assessment Report, *Technical report* NREL/TP6a20-63722

Galibert, S., Gíslason, G., Guðbrandsson, S. & Samson, Y. (2017) 2017 Trilogy field trip: Las Derrumbadas / Cerro Pinto memo – *Internal, Storengy* / RG, ref. EISE-DGSM-SGA-2017-00392.

García Cubas, A., (1874) Escrito diversos from 1870 to 1874 - México, México, *Imprenta Ignacio Escalante* (pp. 235-237)

Guilbaud, M.N, Pedroza Aldana, K.G, Chedeville Monzo, C. Siebe, C. (2019) Origin of Bimodal Magmatism in Continental Arcs: The Case of Las Derrumbadas Area, Trans-Mexican Volcanic Belt; *Goldschmidt abstract* 2019

Horita, J. (2001) Carbon isotope exchange in the system CO2-CH_4 at elevated temperatures. *Geochimica Cosmochimica Acta,* V 65, pp 1907-1919

Hilton, D.R, Fischer, T.P., Marty, B., (2002) Noble gases and volatile recycling at subduction zones *Reviews in Mineralogy and Geochemistry*, 47, pp. 319-370

Javoy, M., Pineau, F., Delorme, H. (1986) Carbon and nitrogen isotopes in the mantle, *Chemical Geology*, V 57, pp. 41-62

Jenden, P.D., Hilton, D.R., Kaplan, I.R., Craig, H. (1993) Abiogenic hydrocarbons in and mantle helium in oil and gas fields, in: Howell, D.G. (Ed.), The future of energy gases, U.S. G*eological Survey Professional Paper* 1570. U.S. Geological Survey, pp. 31-56.

Kim S.-T. and O'Neil J. R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochimica Cosmochimica* Acta 61, 3461–3475

Lebas, M.J., Lemaitre, R.W., Streckeisen, A. and Zanettin, B. (1986) A Chemical Classification of Volcanic-Rocks Based on the Total Alkali Silica Diagram. *Journal of Petrology* 27(3) pp 745-750.

Moreira, M., Kurz, M.D. (2013) Noble Gases as Tracers of Mantle Processes and Magmatic Degassing – *in Burnard P*, The Noble Gases as Geochemical Tracers, pp 371-391

Muñiz-Jáuregui, J. A., Guzmán-Cervantes, C. S., Garduño-Monroy, V. H., Jiménez-Haro, A., Layer, P., (2019) Geomorphology of Las Derrumbadas dome complex, Puebla Mexico, *Journal of Maps*, 15:2, 601-610, 2014, Pages 46-55, ISSN 1871-1014,

Norini, G., Carrasco-Núñez, G., Corbo-Camargo, F. Lermo, J., Hernández Roja, J., Castro, C., Bonini, M., Montanari, D., Corti, G., Moratti, G., (2019) The structural architecture of the Los Humeros volcanic complex and geothermal field. *Journal of Volcanology and Geothermal Research*, 381, 312–329.

Pardo, M., Suarez, G., (1995) Shape of the subducted Rivera and Cocos plates in southern Mexico: seismic and tectonic implications. *Geofisica International*, *Geophyical. Research*. 100, 12357-12373

Planczner, W.D. (1987) Minerals of Mexico, Springer; 1987 edition

Pinti, D.L., Castro, M.C., Lopez-Hernandez, A., Han, G., Shouakar-Stash, O., Hall, C.M.., Ramírez-Montes, M., (2017) Fluid circulation and reservoir conditions of the Los Humeros Geothermal Field (LHGF), Mexico, as revealed by a noble gas survey – *Journal of Volcanology and Geothermal Research*, V 333–334, pp 104-115

Pinti, D. L., Castro, M.C., Lopez-Hernandez, A., Hernández, M.A., Hernández, Shouakar-Stash, O., Richard L., Nuñez-Hernández, S., Hall, C.M., Ramírez-Montes, M., (2019) Signature of ongoing brine reinjection on noble gas isotopes and fluid chemistry at Las Tres Vírgenes geothermal field, Mexico, *Journal of Volcanology and Geothermal Research*, V 377, 1 June 2019, pp 33-42

Peiffer, L., Bernard-Romero, R., Mazot, A., Taran, Y.A., Guevara, M., Santoyo, E., (2014) Fluid geochemistry and soil gas fluxes (CO_2–CH_4–H_2S) at a promissory Hot Dry Rock Geothermal System: The Acoculco caldera, Mexico, *Journal of Volcanology and Geothermal Research*, 284, June 2014, pp 122-137

Portugal, E., Verma, M. P., Barragán, R., M. And Mañón, A., (1994) Geoquímica isotópica de ^{13}C, D, y ^{18}O de fluidos del sistema geotérmico Los Humeros Puebla (México). *Geofisica International*, V 33 (4), pp 607-618

Prinzhofer, A., (2013) Noble Gases in Oil and Gas Accumulations – *in Burnard* P, The Noble Gases as Geochemical Tracers – pp 225-247

Quezadas, P., Cortés Silva, A., Inguaggiato, A., Salas Ortega, M., Cervantes Pérez, J., Heilweil, V.M. (2015) Meteoric isotopic gradient on the windward side of the Sierra Madre Oriental area, Veracruz - *Mexico Geofísica International*,. 2015, V 54, n.3, pp 267-276

Reinsch, T., Dobson, P., Asanuma, H., Huenges, E., Poletto, F., & Sanjuan, B., (2017) Utilizing supercritical geothermal systems: a review of past ventures and ongoing research activities. *Geotherm Energy* 5, 16

Richard, L., Pinti, D., Hélie, J.F., López Hernández, A., Shibata, T., Castro, M.C., Sanoe, Y., Shouakar-Stash, O., Sandoval-Medinag, F., (2019) Variability of deep carbon sources in Mexican geothermal fluids *Journal of Volcanology and Geothermal Research,* V 370, 15 January 2019, pp 1-12

Sano, Y., Marty, B. (1995) Origin of carbon in fumarolic gas from island arcs, *Chemical Geology,* V 119, pp 265-274

Sano, Y., Takahata, N., Nishio, Y., Fischer, T. P., Williams, N.S (2001) Volcanic flux of nitrogen from the Earth, *Chemical Geology*, V 171, pp 263–271

Samson, Y. (2016) Las Derrumbadas and Las Vigas de Ramirez – Journal of the field trip, 9-15/02/2016 – *Internal, Storengy*, ref. CE/DESS-YSA-2016-00064

Siebe, C. & Verma, S.P. (1988) Major element geochemistry and tectonic setting of Las Derrumbadas rhyolitic domes, Puebla, Mexico – *Chemie Erde* 48, pp.177-189, VEB Gustav Fischer Verlag Jena.

Stix, J., de Moor, J.M. (2018) Understanding and forecasting phreatic eruptions driven by magmatic degassing. *Earth Planets Space* 70, 83

Yáñez-García, C., (1980) Informe Geológico del proyecto Geotérmico Los Humeros-Derrumbadas, Estado de Puebla, y Veracruz México, DF., *informe interno,* Comisión Federal de Electricidad, Área de Geología y Minería

Whiticar M. J. (1999) Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, *Chemical Geology* 161 _1999. 291–314

Wen, T., Pinti D.L., Castro, M.C., López-Hernández, A., Hall, C.M., Shouakar-Stash, O., Sandoval-Medina, F., (2018) A noble gas and 87Sr/86Sr study in fluids of the Los Azufres geothermal field, Mexico – Assessing impact of exploitation and constraining heat sources, *Chemical Geology*, V 0483, pp 426-441

Zimbelman, D.R., Rye, R.O., Breit, G.N., (2005) Origin of secondary sulfate minerals on active andesitic stratovolcanoes*, Chemical Geology,* Volume 215, Issues 1–4, Pages 37-60