# Silicification Process in the Reservoir Rocks of the Los Humeros Geothermal Field, Mexico

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### ABSTRACT

The Los Humeros is a high-temperature geothermal field. Wells produce high steam fraction, with a vast resource potential. With 43 deep wells, many of which encountered > 300°C steam, producing 63 MWe. The low intrinsic permeability of deep reservoir rocks is affected by the production of an acid condensed fluid. Evidence of acid fluids occurrence is noted at depths between 1700 and 2000 m depth, particularly in wells located in the central and northern part of the exploited area. From the mineralogical point of view, alteration minerals in the reservoir rocks are typical of the interaction with neutral to alkaline pH waters. The evidence of interaction with acid fluids observed is bleaching, dissolution of minerals, and intense silicification of deep rocks. At depth, the altered rocks consist almost entirely of microcrystalline quartz, with relic pseudomorphs of plagioclase phenocrysts and traces of chlorite, pyrite and mica. The silicification process is interpreted to result from lateral flow where corrosive fluids form. The origin of these acid fluids is still a subject of debate. They may represent emanations from a magma chamber or be due to post-exploitation processes, e.g. reaction of water and salts forming hydrogen chloride by hydrolysis at high temperatures (Truesdell, 1991) and the very high boron content of the fluids produced by the Los Humeros wells suggests that the ultimate source of the acid gases is most likely magmatic. These acid gases have not reacted widely with the rocks. The silicified zones are formed locally where descending waters encounter superheated steam containing acid gas and form low pH liquids that react and leach the rocks that become neutral after reacting with the rock walls. In this work comparison of results for a pair of wells are presented, well H-11 and well-58 both drilled in the same platform with a difference of 30 years. The silicification process, "quartzification" at the deep reaction zone has been studied by microscopic observation, petrography and X-ray diffraction in pairs of wells, drilled in the same platform with a difference of 30 years between each other.

# 1. INTRODUCTION

The Los Humeros geothermal field (LHGF) is situated within a large caldera in the western part of the state of Puebla, Mexico, about 280 km east of Mexico City (Figure 1). The Los Humeros caldera lies in the north-eastern part of the calc-alkaline Trans-Mexican Volcanic Belt. It is associated with the subduction of the Cocos Plate along the Middle American Trench (Verma, 1983).

The Los Humeros caldera has had a complex history (Ferriz and Mahood, 1984). Its dimensions are 21 by 15 km, but its margins tend to be obscured by younger volcanic rocks, except in the northeast quadrant where the topographic rim is visible. The oldest rocks of the caldera are > 1.6 Ma porphyritic andesites and ferrobasalts of the Teziutlán Formation. These rocks have a volume of 60 km<sup>3</sup>. At 0.46 Ma, the main collapse of the Los Humeros caldera was initiated by the eruption of the mostly non-welded Xáltipan Ignimbrite, aphyric high-silica rhyolite; which has an estimated volume of 115 km<sup>3</sup>. The ignimbrite is overlain by air-fall lapilli tuffs ranging from rhyodacite to andesite in composition. The amount of collapse, determined by the offset of the lower contact of this ignimbrite is about 450 m. The next pyroclastic eruption was the Faby Tuff with a volume of approximately 10 km<sup>3</sup>, a thickness of 16 m, and age of 0.2 to 0.3 Ma. This eruption was followed by a period of quiescence, erosion and the formation of lake deposits.

The next pyroclastic eruption formed the 0.1 Ma Zaragoza Tuff, which has a volume of 12 km<sup>3</sup>. It consists of non-welded ignimbrite and an overlying lithic-rich air fall tuff. The Zaragoza Tuff was associated with the collapse of the 10 km diameter of the Los Potreros caldera in the southern part of the Los Humeros caldera. This rhyodacite tuff contains pumice with phenocrysts of pyroxenes, plagioclase, and Fe-Ti oxides. Based on an apparent displacement of 375 m of the base of the Xáltipan Tuff between boreholes H-2 outside the collapsed structure and H-3 and H-4 within it, the estimated volume of the magma erupted during this collapse was 17 km<sup>3</sup>. There was then a change to magmas of more variable composition. The next major eruptions produced 6 km<sup>3</sup> of andesite at 0.04-0.02 Ma and 10 km<sup>3</sup> of rhyodacite at 0.03-0.02 Ma. The most recent eruptions produced 0.25 km<sup>3</sup> of olivine basalt, aged at around <0.02 Ma (Ferriz and Mahood, 1984).

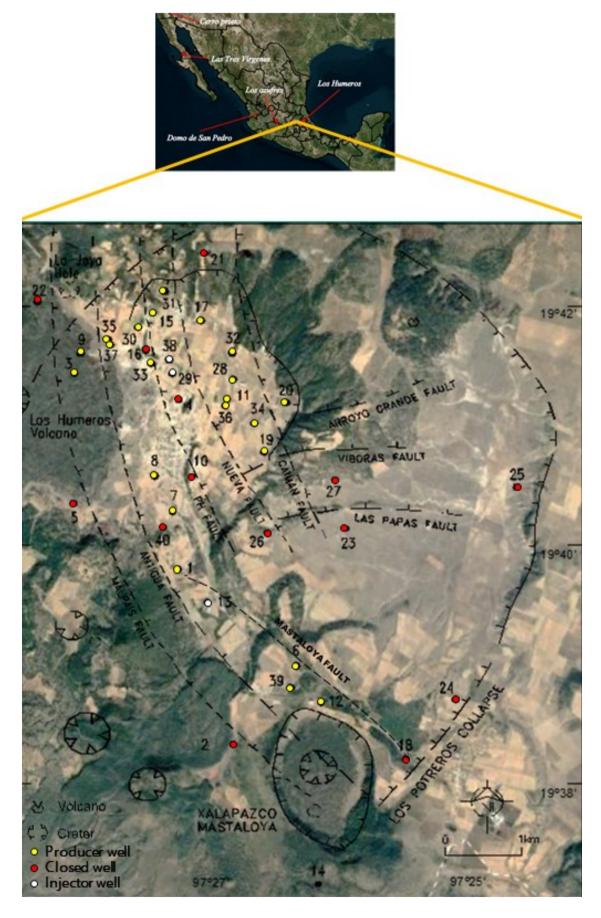


Figure 1: Map of the Los Humeros geothermal field within the" Los Potreros Collapse" caldera in the southern part of the larger Los Humeros caldera, showing the smaller volcanic crater "Xalapazco Mastaloya" together with known and inferred faults. The numbered well locations are shown without the preceding letter "H."

#### 1.1 Los Humeros Geothermal Field

The Los Humeros geothermal field (LHGF) lies entirely within the Los Potreros Collapse caldera (Figure 1). 45 exploration, production and injection wells have been drilled to depths between 1500 and 3100 m. These wells have encountered temperatures as high as 378°C at less than 3,000 m depth. The subsurface geology of the field has been described by (Viggiano and Robles (1988) Cedillo (1997) and Gutiérrez-Negrín and Izquierdo-Montalvo (2010). These authors identified four basic units with variable thicknesses. However, not all of the units are observed in every well.

Unit 1. Post-Caldera Volcanism; Quaternary, 0.1 Ma. This unit is composed of andesite basalt, dacite, rhyolite flows and tuffs, pumice, and ejecta from phreatic eruptions. Its thickness is between 90 and 1010 m but averages 340 m. It contains shallow cold aquifers.

Unit 2. Volcanic Caldera; Quaternary 0.51–0.1 Ma. This unit consists of lithic and glassy ignimbrites, from two eruptive centers; Los Humeros and Los Potreros. It includes tuffs, andesitic lavas, and rhyolite domes. Its thickness is between 185 and 880 m but averages 600 m. This unit forms a low permeability aquitard or caprock.

Unit 3. Pre-caldera Volcanism: Miocene – Pliocene, 10–1.9 Ma. This unit is composed of andesite flows, with interbedded tuffs, basalts, dacite, and rhyolite. In the upper andesite flows the characteristic mafic mineral is augite and in the deeper andesites, hornblende. The unit is between 90 and 2600 m thick but averages 1200 m. Unit 3 is the host rock for the geothermal fluids, its permeability varies from low to medium.

Unit 4. Basement; Jurassic-Oligocene, 140–31 Ma. The basement complex is composed of limestone with subordinate shale and chert. Intruded by stocks of granite, granodiorite, tonalite younger (Miocene) dikes of diabasic composition. Contact metamorphism has altered the sedimentary rocks to marble, skarn, and hornfels. The total thickness of the unit is unknown. High temperature and low permeability characterize this basement complex.

## 1.2 Chemical characteristics of the Los Humeros geothermal fluids

Most of the wells in the LHGF produce high steam fraction with a small liquid fraction and enthalpies greater than 2600 J/g. The chemical composition of separated water indicates steam condensates. Except for boron and silica; the concentration of the major cations is low. Geothermal fluids from the wells are generally of sodium chloride type with lesser amounts of sodium sulfate. Representative fluids from the hottest producing wells are characterized by high boron concentrations (> 2,000 ppm), relatively high but variable concentrations of SiO<sub>2</sub> (80 - 800 ppm) and low concentrations of cations such as Na, K, Ca and Mg. Despite the acid nature of the condensed steam, in the majority of the total produced flows is reported to have pH near neutral with low Cl concentrations (Tello, 1992). The steam fraction of the wells has increased, favoring the transport of volatile species. The origin of the high concentrations of boron is unknown, but it is likely a mobile magmatic species; as there are no boron-rich minerals found in the reservoir. We suggest the relatively high and variable concentration of SiO<sub>2</sub> is due to interaction of the acid condensates with the rocks. Our studies of the hydrothermal alteration indicate that locally acid condensates cause reactions with the reservoir rocks preferentially dissolving Na, K, Ca, and Mg from primary and secondary minerals leaving behind microcrystalline quartz and fluid with higher pH.

# 1.3 Hydrothermal Alteration in the Los Humeros Geothermal field

The results of fluid/rock interactions are ubiquitous in moderate to high-temperature geothermal systems. The nature and abundance of hydrothermal minerals are functions of temperature, fluid composition, pH, and water/rock ratio (Browne, 1978). Assemblages of hydrothermal minerals thus record the processes and conditions that have occurred in a geothermal reservoir (Elders, 1977). Two broadly different hydrothermal assemblages are commonly recognized (Browne, 1978; Henley and Ellis, 1983, Reyes, 1990; 1992). The most common is produced by interactions with neutral pH to basic sodium chloride fluids. At the surface and shallow levels, less commonly, acid argillic alteration is formed by the reaction of the rocks with fluids of low pH, usually hydrochloric or sulfuric acids (argillic). Unit 3 shows intense hydrothermal alteration between 600 and 1800 m deep. Studies indicate that the main alteration minerals are chlorite, epidote, quartz, calcite, and minor leucoxene and pyrite. Other alteration minerals identified include smectite, kaolinite, illite, anhydrite, amphiboles, muscovite and garnet. Figure 2 shows some sulphides and garnet deposited in the reservoir rocks at Los Humeros. The intensity of alteration of these rocks is variable, depending on rock permeability. Mineralogy changes as a function of temperature, rock and fluid composition.

Evidence of acid fluids occurrence is noted at depths between 1700 and 2000 m depth, particularly in wells located in the central and northern part of the exploited area. From the mineralogical point of view, alteration minerals in the reservoir rocks are typical of the interaction with neutral to alkaline pH waters. However, evidence of interaction with acid fluids observed is bleaching, dissolution of minerals, mineral deposition, silicification and "quartzification" of deep rocks. Locally the results of acid alteration can be seen in the reservoir rocks in the form of bleached silicified zones that indicate that lateral flow of corrosive fluids formed zones of bleaching, leaching and silicification. Because the locations and volumes of acid altered rocks in the reservoir are quite restricted, despite the acid nature of the fluids produced by the wells, these acid fluids could not have been widespread in the reservoir or could not have had a long residence time in the geothermal system. Figure 3a and 3b graphically resume the effects of the interaction of the reservoir rocks with a low pH fluid.



Figure 2: Hydrothermal minerals found in the reservoir rocks of Los Humeros geothermal field.

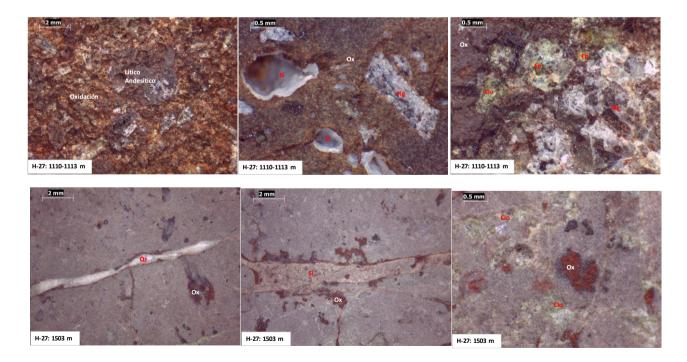


Figure 3a: Evidence of silicification in the reservoir rocks of the Los Humeros geothermal field is shown: bleaching, leaching, dissolution and deposition and replacement by SiO2 in its polymorphs.

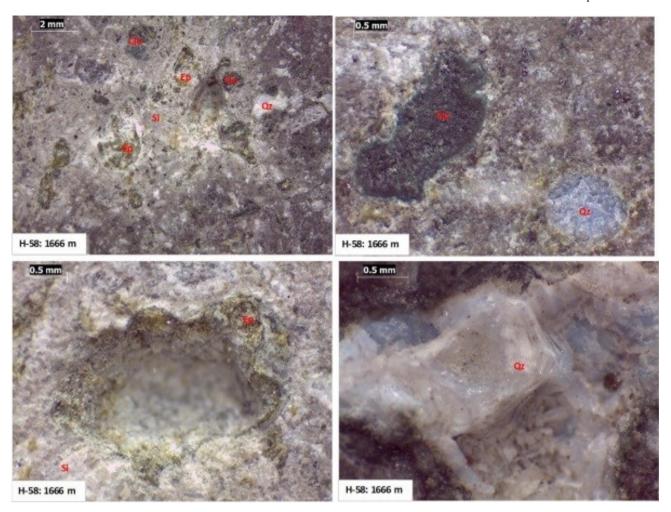


Figure 3: Evidence of silicification in the reservoir rocks of the Los Humeros geothermal field is shown: bleaching, leaching, dissolution and deposition and replacement by SiO<sub>2</sub> in its polymorphs.

## 2. RESULTS

Wells H-11 and H-58 were studied considering H-11 was a good producer; well H-58 was drilled in the same platform expecting to get similar or the same production. Evaluation of the well is the responsibility of the Comision Federal de Electricidad (CFE, Electricity Utility on Mexico). By analyzing the reservoir rocks and the chemistry of fluids of well H-58 offers the opportunity to record changes during 31 years of production of the LHGF. The well H-11 is located in the Central sector of the LHGF, Figure 1; with UTM coordinates: X = 662574, Y = 2177476, Z = 2815 m.a.s.l. The well was drilled vertically at a depth of 2389 m. The drilling began in July 1985 and ended n November 1985. Well H-58 is also located in the Central sector of the LHGF. The drilling of this well is located within the platform of the H-11 well, with the UTM coordinates: X = 662555, Y = 2177456, Z = 2804 m.a.s.l. The drilling of the well began December 2016 and ended March 2016. The well is drilled vertically at a depth of 2200 m (CFE report for H-11 and H-58).

# 2.1 Fluid Chemistry

During May 2018 most wells at LHGF were sampled and analyzed for separate water and steam phase. Main components are Si and B low concentrations of cations such as Na, K, Ca, Mg, Fe and Mn. As most sampled fluids contain a variable fraction of condensed steam, the chemical composition is not representative of typical geothermal brine at Los Humeros. In this work, the chemical concentration of major elements in the steam phase is used just as a guide to identifying possible processes in the reservoir.

Some chemical components are represented graphically in Figure 4. The most significant are Si, Mn, Fe and B. The highest Si content is observed in well H-20, this well is characterized by high liquid fraction and leaching of Si from deep rocks released into the liquid and steam phase. Fe and Mn occur commonly in very low concentration in geothermal fluids; At Los Humeros, it is considered that they may be indicative of corrosion of pipes by acid attack. Highest Fe content was quantified for H-20 and H-58 (close to H-11). Well H-58 also shows the highest concentration of Mn in the steam fraction. H-11 and H-58 show intense interaction between dep rocks and low pH fluids. The high content of B in the steam phase is reported in well H-11, located in the central part of the exploited area; possibly indicating proximity to a magma chamber as is the case of H-58.

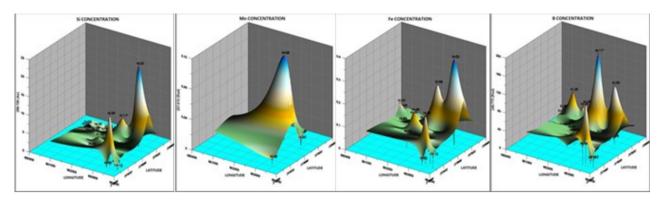


Figure 4: Graphical representation of chemical components in condensed steam produced by productive wells at LHGF.

### 2.2 Petrography and X-ray diffraction

Cores and drill cuttings from wells H-11 and well H-58 were observed in a Leica binocular microscope. Thin sections were studied in an Olympus petrographic microscope. A selection of samples was analyzed in an X-Ray powder diffractometer (Stoe, StadiPi, with Co filtered radiation). Based on observation, description and optical microscopy, the lithological column for each well was drawn founding small differences among the two wells. Also, careful observations were carried out in order to observe possible differences in the intensity of the alteration of the pair of wells H-11 and H-58.

In order to observe possible differences in the intensity of the hydrothermal alteration of the pair of wells H-11 and H-58; both drilled in the same platform with a difference of 30 years, the range of depth between 1500 m and 2250 m was considered for well H-11 and the range between 1500 m and 2110 m for well H-58. In the mentioned ranges for the two wells, hydrothermal alteration of the propylic type is observed. However, in the H-58 well, the intensity of the alteration is considered greater than in well H-11. This is an indication that water-rock interaction has continued for over 31 years between the drilling of one and another well. Preliminary results comparing other pairs of wells seem to indicate similar information.

The interest to compare the range between 1500 m and 2250 m is because a silicified unit has been observed in other wells (Izquierdo et al., 2011, Elders et al., 2014). This unit is composed of microcrystalline quartz with the highest permeability measured in the reservoir rocks (H-26, Elders et al., 2014). For several wells, this unit has been reported as silicified andesite; as well as a silicified tuff. With the information generated to date, there is still uncertainty about the nature of this unit; which can either be tuff or andesite.

To distinguish from a silicification process, in which any form of SiO<sub>2</sub> may exist in a range of temperature and a process in which the main phase is microcrystalline SiO<sub>2</sub>, we will refer it to "quartzification." The quartzified zone is distinguished optically by the abundant presence of microcrystalline quartz and by X-ray diffraction where the dominant phase is quartz. It is assumed that the "quartzification" process occurs when volatile species could react with a condensed fluid forming an acid solution that leached the components of the rock leaving a permeable mass of microcrystalline quartz. The "quartzified" zone is located in the two wells between 1900 and 2000 m. At this depth the liquid fraction is low (Aragón 2019, personal communication); so the transformation of the rock is not due to a process of water interaction: rock itself. We believe is the result of acid leaching of the rock and because of the pressure and temperature conditions well developed micro crystals of quartz are formed. Due to the intergrowth of the quartz crystals the unit is permeable. At this depth, where the intense leaching and "quartzification" occur the unit with the highest measured permeability corresponds to the loss of circulation at depth has been reported by CFE.

Early interpretation of the deep geological unit in the area of Los Humeros, was referred as vitreous tuff; it was considered as an impermeable interface separating the two andesitic units, the deeper identified as hornblende andesite and the upper known as augite andesite. Now, from experimental data, it is known that it is the permeable unit at depth. The leaching and "quartzification" processes favored the movement of deep fluids. Considering that at the depth near to 2000 m, the main phase is steam; which is the mobile phase which transports deep magmatic species that will react with condensed fluids forming low pH fluids that react either with andesite, tuff, or with both leading to the permeability unit. This low pH fluid will react with the wall rocks reaching the surface as a neutral fluid; however volatile species will be moving to the surface.

To distinguish from a silicification process, in which any form of  $SiO_2$  may exist in a range of temperature, and a process in which the main phase is microcrystalline  $SiO_2$ ; we will refer to "quartzification." The quartzified zone is distinguished optically by the abundant presence of microcrystalline quartz and by X-ray diffraction where the dominant phase is quartz. Table 1 shows the results of the analysis by X-ray diffraction of a selection of samples, particularly from the interest zone (1900-2000 m). By X-ray diffraction, only two phases are identified: quartz and plagioclase (Albite). Table 1 shows a summary of results, the amount of minerals is automatic semi quantification by the software, it is considered only indicative. However, it is possible to distinguish where the amount of quartz is higher respect to each other.

H-11			H-58		
Depth	%	%	Depth	%	%
m	Albite	Qtz	m	Albite	Qtz
			1790	57.4	42.6
1854	67.1	32.9			
			1860	54.2	45.8
1900	67.0	33.0	1900	58.7	41.3
			1930	28.7	71.3
1952	59.7	40.3			
			1960	21.8	78.2
			1980	27.2	72.8
1996	22.3	77.7			
			2000	22.1	77.9
			2030	79.6	20.4
			2110	68.9	31.1
			2130	62.9	37.1
2150	68.1	31.9			
2200	76.9	23.1			

Table 1. Summary of XRD data for well H-11 and well H-58. Albite and quartz are represented as semi quantitative data.

It was not possible to obtain cutting samples for the two wells at the same depth; table 1 data shows the closest depth for both wells. In well H-11, from 1854 m the amount of quartz is increasing, at 1996 m the highest amount of quartz is recorded, deeper samples show less percentage of quartz. For well H-58, from 1790 m the amount of quartz increases, between 1960 m and 2000 m the highest percentage of quartz is recorded. Deeper samples show less percentage of quartz. Preliminary results for other pairs of wells, located in the central part of the field, indicate an increase of quartz in the deep unit referred to as andesite or vitreous tuff. Pairs of wells in the south part of the field do not show significate "quartzification" of cuttings in the considered range.

The lithological column and petrography of selected samples for well H-11 and well H-58 from 1600 to 1854 m is presented in Figure 5a. The lithological column and petrography for well H-11 and well H-58 in the range from 1900 to 1996 m is presented in Figure 5b. Both figures include the hydrothermal mineralogy; which corresponds to propylitic alteration of medium intensity, as a result of the interaction with basic to neutral pH fluids in the range of temperature between 200 and 250 °C.

In the area where the main leaching process occurs, the proportion of microcrystalline quartz in well H-58 is greater compared to well H-11. Possibly the result of continuous activity over 31 years. For both wells an increase in crystalline quartz is observed between 1900 and 2000 m. According to the drilling reports of CFE this depth corresponds to the deep loss of circulation. In Figure 5a, microphotographs of thin sections for well H-11 and H-58 from 1600 m to almost 1854 m are presented between the two lithological columns. The main alteration minerals are referred as: Ep for epidote, Cl for chlorite, Qz for quartz, Cal for calcite, Py for pyrite; followed by its abundance in %. At shallow levels, Epidote may be contaminant from deeper drill cuttings. Some features can be distinguished such as the type of alteration: mainly substitution and deposition.

The main difference in lithology from one well to the other is in the description of tuff (pink color) may be described as tuff, vitreous tuff or crystalline tuff. There are small differences in thin layers of different composition. In both columns there is coincidence of the occurrence of andesites, the upper andesite where is the highest rate of water-rock interaction. At the bottom of well H-11 evidence of an intrusive was found; at the same depth in well H-58 it is not observed.

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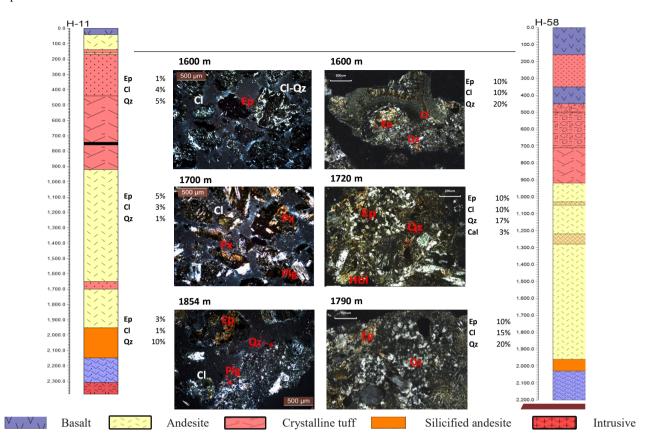


Figure 5a: Comparison between well H-11 and well H-58 at almost the same range of depth were the production zone is referred from other wells in the field (1600 m to 1850 m).

In Figure 5b microphotographs of thin sections for well H-11 and H-58 from 1900 m to almost 2000 m are presented between the two lithological columns. In the range of depth considered the dominant mineral phase is quartz. In both wells, between 1952 m to almost 2000 m, the samples are 100% micro crystalline quartz. The only difference is the size of the crystals. In H-58 seem to be larger than in H-11.

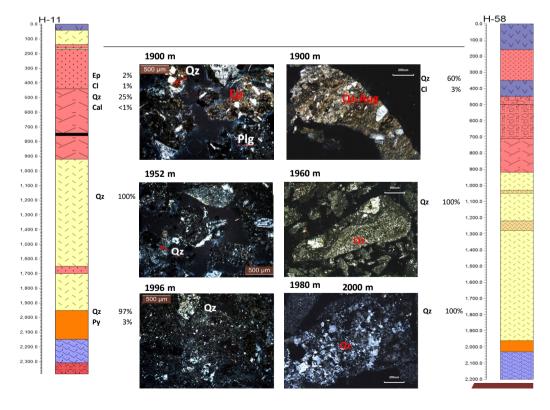


Figure 5b: comparison between well H-11 and well H-58 at almost the same range of depth were the main "quartzification" process occurs (1900 m to 2000 m).

#### 3. CONCLUSIONS

The evidence of the occurrence of low pH fluids, at depth, is given by the processes previously recognized (Elders et al., 2014). Due to the neutralization of the fluids with the wall rocks the fluids at the wellhead are neutral. However, the chemistry of fluids gives evidence of the reaction of low pH fluids with pipes. Comparing hydrothermal mineralogy between wells H-11 and H-58, with 31 years of difference in their drilling; we conclude that water-rock interaction has been a continuous process; as well as the deep "quartzification" process due to leaching of the rocks. Preliminary results indicate that for pairs of wells located in the central and northern part of the field show the same results; pairs of wells in the south part of the field do not show significate "quartzification" of cuttings in the considered range. Additional experimental work on the mineralogy, petrography, and geochemistry is carried out in order to support our assumptions of the processes that are occurring in the reservoir rocks that might affect the production.

The silicification process is interpreted to result from lateral flow where pH fluids form. The origin of these acid fluids is still a subject of debate. They may represent emanations of volatile species from a magma chamber. The silicification process may affect the physical properties of reservoir rocks by deposition of silica in all its forms. If amorphous silica is deposited in pores and connected cavities may reduce permeability. The "quartzification" of rocks may provide conduits where the fluids move. However, as the main "quartzification" process occurs in the deep hot zones of the reservoir where the liquid fraction is low or nonexistent and transport of deep magmatic volatiles occur. Additional work is being done in order to support assumptions presented in this work.

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