



# Developments of auxiliary chemical geothermometers (Na-Li, Na-Cs) applied to the Los Humeros and Acoculco high-temperature geothermal fields (México)

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# Developments of auxiliary chemical geothermometers applied to the Los Humeros and Acoculco geothermal fields (Mexico)

Bernard Sanjuan, Frederick Gal (BRGM), Ruth Alfaro (Universidad Michoacana)

Potsdam, February 2020



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# Main objectives of this study

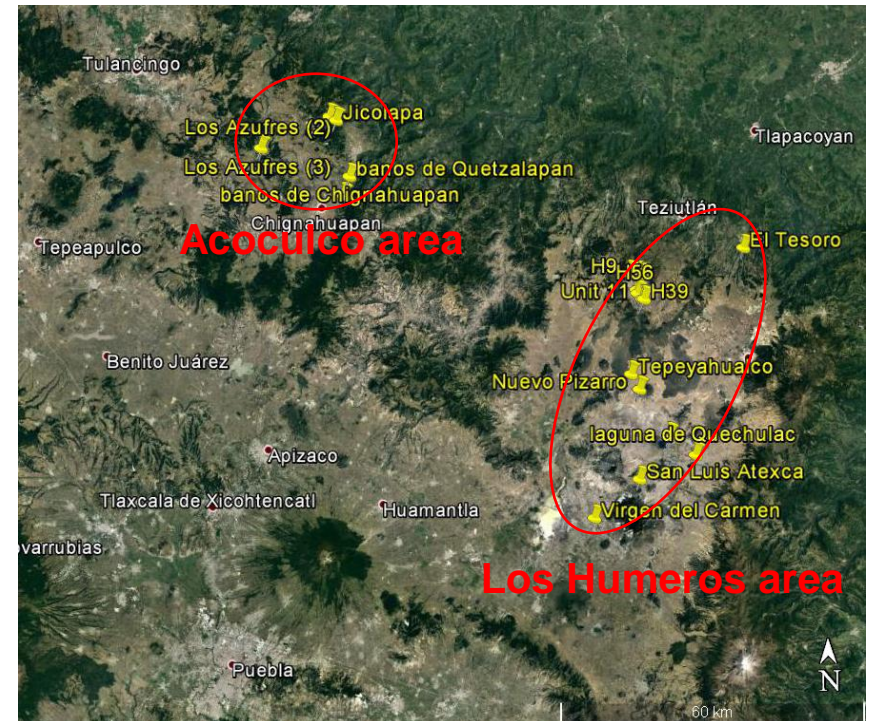
- > The knowledge of the **temperature** of the deep geothermal fluids, **rock permeability** and **water reservoir capacity** are three key parameters for developing deep geothermal energy
- > Improve the reservoir temperature estimation in high-temperature deep volcanic reservoirs such as Los Humeros and Acoculco by developing auxiliary chemical geothermometers like Na-Li, Na-Rb, Na-Cs, K-Sr, K-Mn, K-Fe, K-F, K-W, and compare the estimated temperatures with those using:
  - classical water geothermometers (Na-K, Na-K-Ca, K-Mg,  $\text{SiO}_2$ ,  $\delta^{18}\text{O}_{\text{H}_2\text{O}-\text{SO}_4\cdots}$ )
  - numerical multicomponent geochemical modelling
  - gas geothermometers ( $\text{CO}_2\text{-CH}_4\text{-H}_2\text{S-H}_2$ ,  $\text{CO}_2\text{-CH}_4\text{-H}_2$ ,  $\text{CO}_2\text{-CH}_4$ ,  $\text{H}_2\text{-Ar}$ ,  $\text{CO}_2\text{-Ar}\cdots$ )
- > Validate these geothermometers on the fluids from the Los Humeros geothermal wells where deep temperatures were measured
- > Test these geothermometers on fluids collected from thermal springs in the Los Humeros and Acoculco geothermal areas



- > Literature review relative to the Los Humeros and Acoculco geothermal areas
- > Collection of geological logs, temperature, pressure and geochemical data relative to waters discharged from 16 deep wells, located in the Humeros geothermal field (CFE documents)
- > Collection of geochemical data (including B isotopes for 5 waters) from several deep wells in the Humeros geothermal field (from Arellano *et al.*, 2003, JVGR, 124, 67-88; Bernard *et al.*, Applied Geochemistry, 2011; Pinti *et al.*, JVGR, 2017)
- > Collection of geochemical data of 39 waters collected from thermal springs in the Acoculco geothermal area (CFE report 34-86, Exploration Department, December 1986; Hernandez *et al.*, 2009; Peifer *et al.*, 2014)
- > Exploitation of these first data (**only the auxiliary Na/Li geothermometer could be tested because no data for the other trace elements was found**)



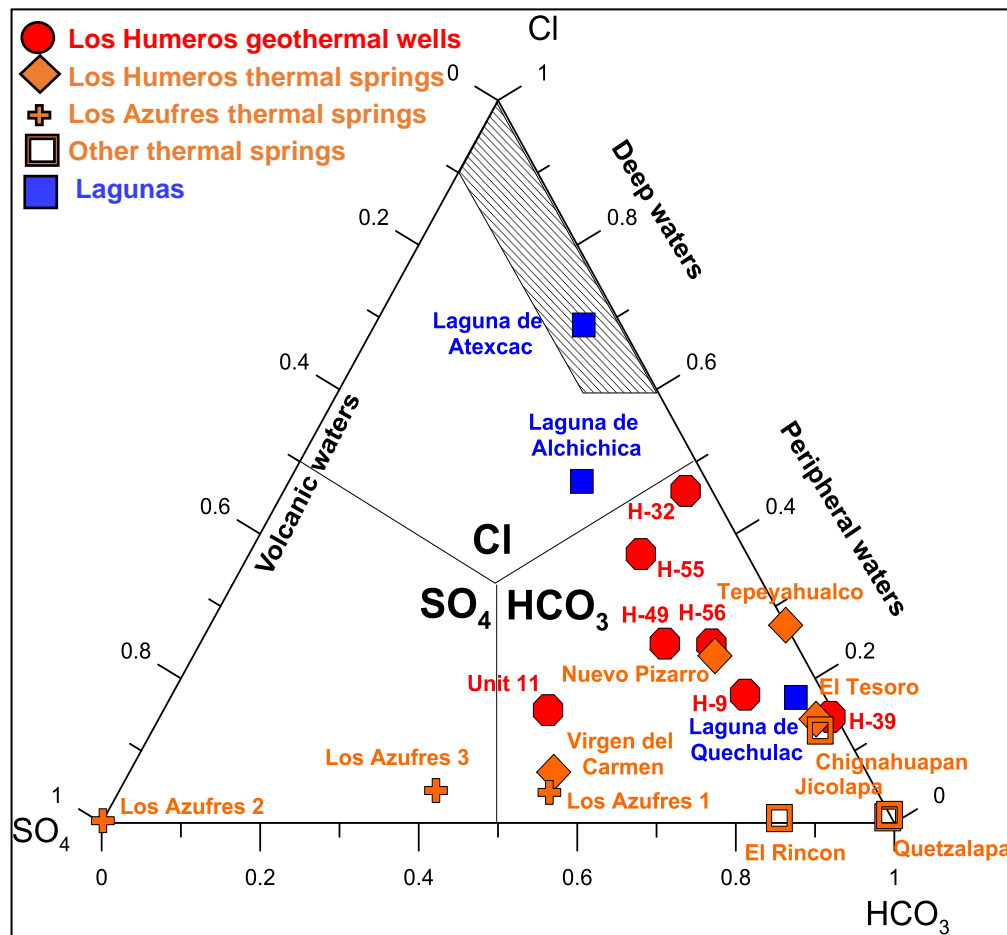
# Water sampling and analyses



- > Collection of waters from 7 geothermal wells, 4 thermal springs and 3 natural lagoons (crater lakes) in the Los Humeros area and from 7 thermal springs in the Acoculco area from March 22 to 28, 2018, in collaboration with the Italian CNR Lelli's team and Mexican teams (CFE, Ruth Alfaro)
- > Chemical and isotope analyses of these 21 water samples in the BRGM laboratories
- > Geochemical and geothermometric data treatment and interpretation



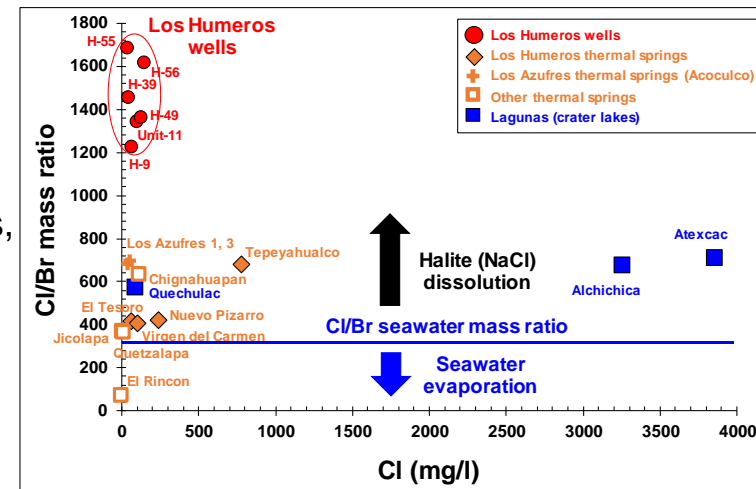
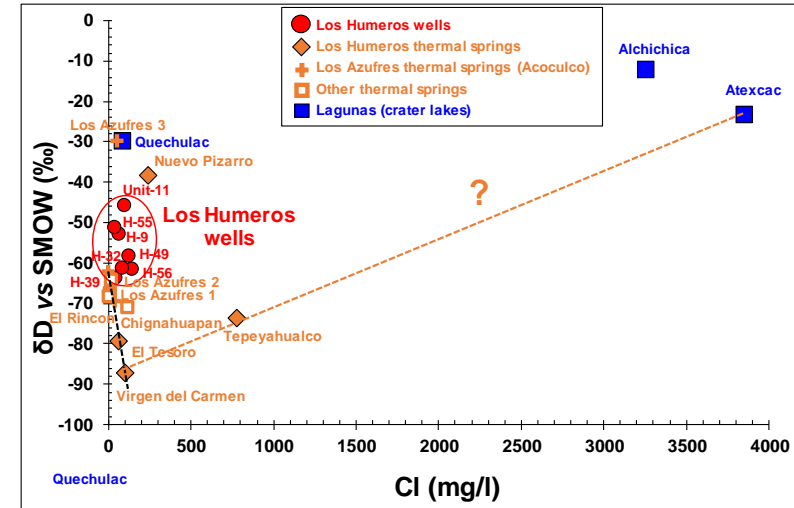
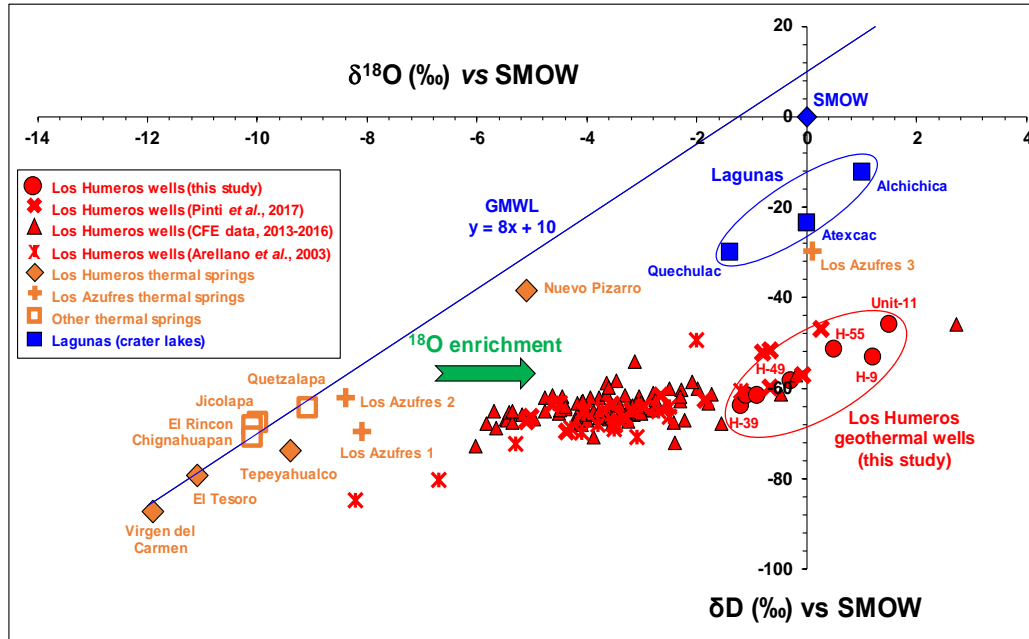
# Main chemical characteristics



- > TDS and pH values for thermal and geothermal waters range from 0.35 to 4 g/l and from 3.2 to 8.9, respectively
- > Different types of waters:
  - **HCO<sub>3</sub>-Cl-Na type:** Los Humeros geothermal waters, most of the thermal waters
  - **SO<sub>4</sub>-HCO<sub>3</sub>-Na type:** Los Azufres and Virgen del Carmen thermal springs
  - **Ca-Na-HCO<sub>3</sub> type:** Quetzalapa and El Rincon thermal springs
  - **Na-Cl type:** Lagunas de Atexcac and Alchichica



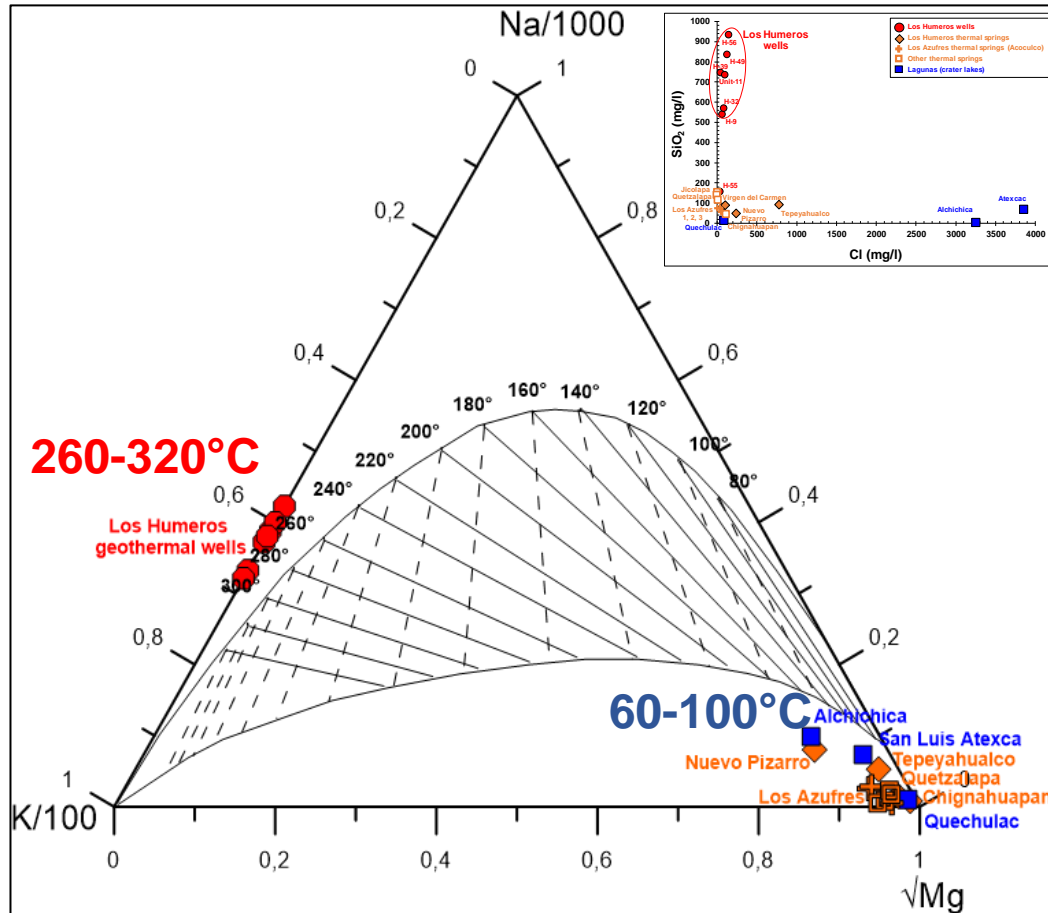
# Origin of the waters



- > All the thermal waters have a meteoric origin (GMWL)
- > Some of them and especially, the Los Humeros geothermal waters, indicate an  $^{18}\text{O}$  enrichment, which suggests water-rock processes at high temperature and/or low water-rock ratios
- > The Los Azufres, Chignahuapan, El Rincon, Jicolapa, Quetzalapa and Tepeyahualco thermal waters could have similar water recharge areas than those of the Los Humeros geothermal waters
- > The meteoric origin of the thermal and geothermal waters is confirmed (low Cl concentrations and Cl/Br values different from that of seawater). Different Cl/Br values between the Los Humeros geothermal waters (1200-1700) and the other thermal waters (70-700)



# Classical aqueous geothermometers

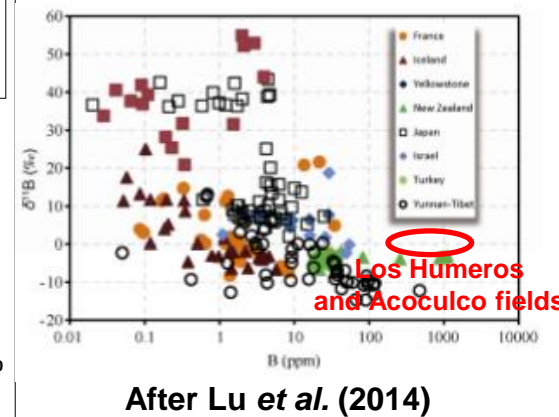
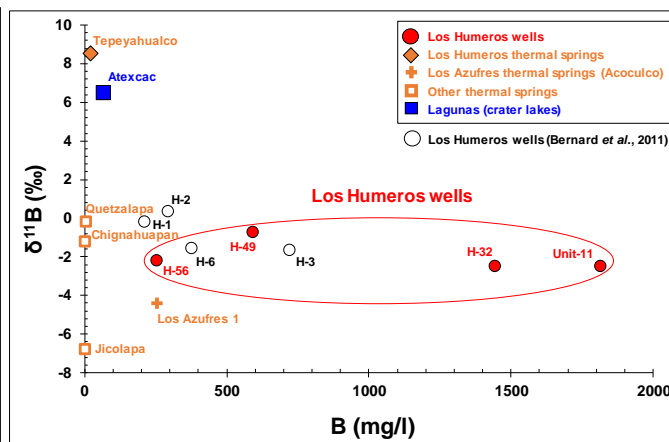
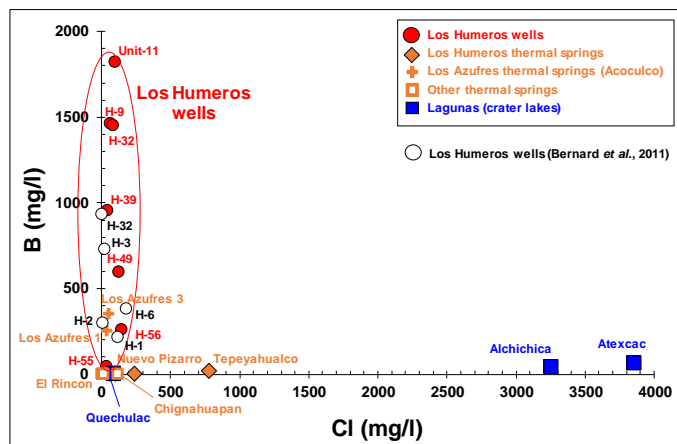


- > Classical geothermometers such as Silica-Qz, Na-K, Na-K-Ca, K-Ca,  $\delta^{18}\text{O}_{\text{H}_2\text{O}-\text{SO}_4}$ , etc., give an estimation of reservoir temperature of  $290 \pm 30^\circ\text{C}$  for the Los Humeros geothermal waters. This temperature is concordant with the presence of an upper liquid-dominated reservoir area, with neutral pH at  $290\text{--}330^\circ\text{C}$ , in augite and hornblende andesites, or in deeper basalts
- > Among the different Na-Li thermometric relationships existing in the literature, only the Na-Li auxiliary geothermometer defined for North-Icelandic HT basaltic geothermal dilute waters (Sanjuan *et al.*, 2014) give concordant temperature values ( $320 \pm 30^\circ\text{C}$ ). The Na-Cs auxiliary geothermometer defined by Sanjuan *et al.* (2016) also gives concordant reservoir temperature values ( $270\text{--}340^\circ\text{C}$ )

- > The classical Na-K-Mg ternary plot indicates that all the thermal waters are immature, having not reached full chemical equilibrium with the host rocks. Classical geothermometers such as Silica, K-Mg and K-Ca, based on fluid equilibration with chalcedony, muscovite, clinocllore, K-felspar and calcite, which can re-equilibrate relatively fast, as well as the  $\delta^{18}\text{O}_{\text{H}_2\text{O}-\text{SO}_4}$ , and the auxiliary K-Sr and K-F geothermometers defined by Sanjuan *et al.* (2016), indicate subsurface temperature estimations, which vary from 60 to  $100^\circ\text{C}$



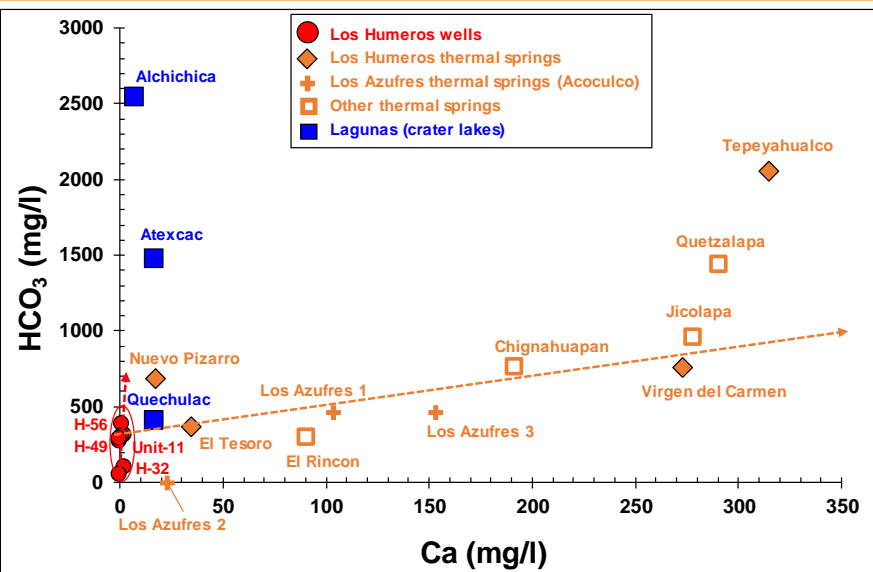
# Water-rock interaction processes



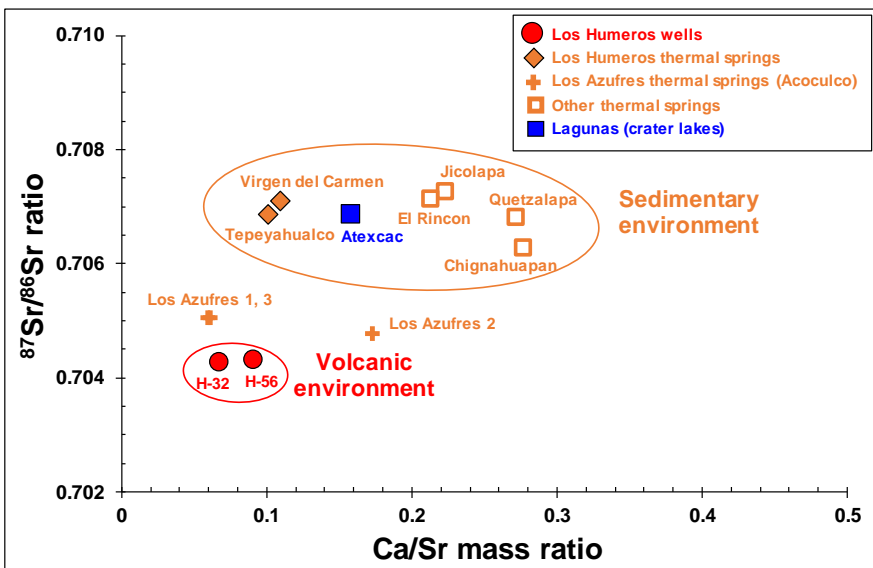
- > The waters collected from Los Humeros wells and Los Azufres thermal springs (Acoculco) are very enriched in B relative to the other thermal springs. In the world, only some geothermal waters from New Zealand seem to have similar high B concentrations and B isotope signatures close to those of the Los Humeros geothermal waters (cf. Lu *et al.*, 2014)
- > The B isotope signatures for the Los Humeros geothermal waters ranging from -2.52 to -0.74 ‰ are slightly lower than those obtained by Bernard *et al.* (2011) (from -1.7 to 0.3 ‰), and are in good agreement with B isotope fractionation between waters and illite minerals at about 300°C (Williams *et al.*, GCA, 2001)
- > For Los Azufres and Jicolapa thermal springs, the B isotope signatures are lower (-6.79 and -4.42 ‰, respectively). For the Chignahuapan, Quetzalapa and Tepeyahualco thermal waters, these signatures are higher (-0.17, -1.20 and 8.55 ‰, respectively)



# Water-rock interaction processes



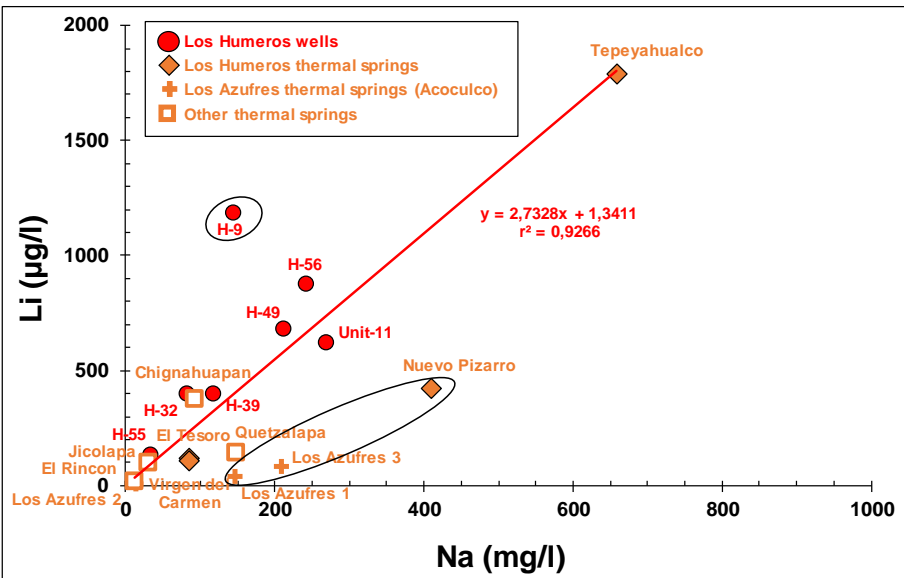
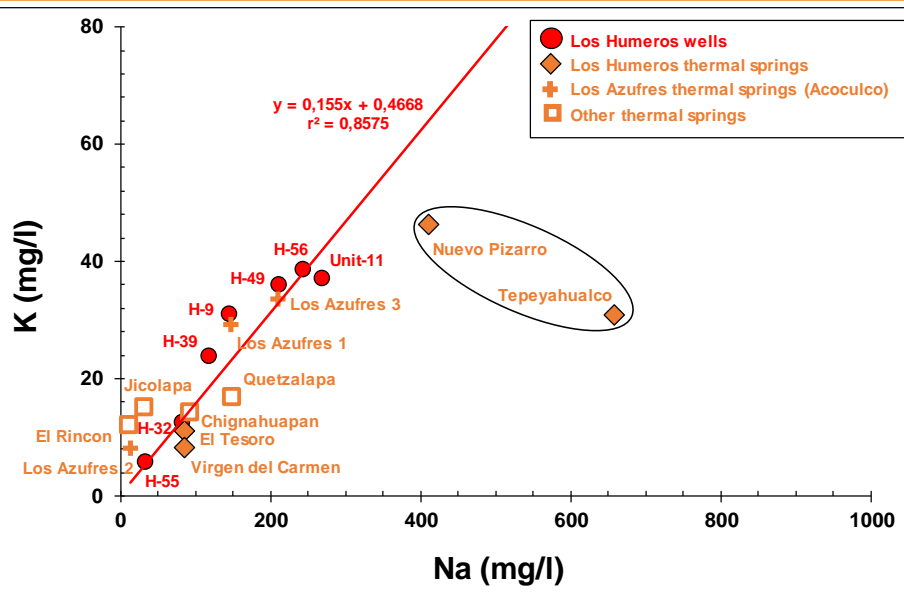
- > The Ca-HCO<sub>3</sub> diagram confirms high water-calcium carbonate interaction processes for most of the thermal waters
- > The Sr isotope signatures of these waters suggest interaction processes with marine carbonate minerals (close to the Mesozoic seawater values) and consequently, with predominance of more superficial waters than those of the Los Humeros geothermal waters
- > The Sr isotope signatures indicate interaction processes with volcanic rocks (andesite, basalt) for the Los Humeros geothermal waters and for Los Azufres thermal waters (but with mixture of more superficial waters)





# Water-rock interaction processes

- > It appears that the Na/K and Na/Li ratios, for numerous thermal waters, are close to those of the Los Humeros geothermal fluids
- > Associated with  $\delta^7\text{Li}$  values (4.7 to 6.5‰) and relatively high B contents, and some escapes of deep reservoir hot gases which reach the surface, these ratios suggest that small fluxes of deep waters, despite their low-permeability environment, could be able to preserve, more or less, their original Na/K and Na/Li ratios (and to a lesser extent, their Na/Rb and Na/Cs ratios), resulting from the temperature of their deep reservoir (about 300°C), even after significant mixing with cold waters and cooling, during their ascent up to the surface





- > The classical Na-K-Mg ternary diagram and main geothermometers such as Na-K, Na-K-Ca, K-Ca and  $\delta^{18}\text{O}_{\text{H}_2\text{O}-\text{SO}_4}$  indicate that **full chemical equilibrium conditions at about  $290 \pm 30^\circ\text{C}$  are only attained for the Los Humeros geothermal waters**. The Sr isotope signature of these waters ( $\approx 0.7043$ ) suggests an interaction **with reservoir volcanic rocks (basalt or andesite)**
- > This temperature and isotopic signature are concordant with the presence of an upper liquid-dominated reservoir area, with neutral pH at  $290\text{-}330^\circ\text{C}$ , located in augite and hornblende andesites, or in deeper basalts
- > Among the different Na-Li geothermometric relationships existing in the literature, **only the Na-Li auxiliary geothermometer defined for North-Icelandic HT basaltic geothermal dilute waters give concordant temperature values ( $320 \pm 30^\circ\text{C}$ )**. The Na-Cs auxiliary geothermometer defined in 2016 also gives concordant temperature values ( $270\text{-}340^\circ\text{C}$ )
- > The Los Humeros geothermal waters,  **$\text{HCO}_3\text{-Cl-Na}$  type, with a meteoric origin**, are characterized by low salinities ( $\text{TDS} \leq 3.5 \text{ g/l}$ ), high silica contents (up to  $930 \text{ mg/l}$ ) and very high B concentrations (up to  $1800 \text{ mg/l}$ )



- > For all the thermal waters (predominantly  $\text{HCO}_3\text{-Cl-Na}$  type):
  - **meteoric origin** like the Los Humeros geothermal waters, but with much lower Cl/Br mass ratios (70 to 700 instead of 1200 to 1700)
  - mainly constituted of **superficial waters interacting with marine calcium carbonate minerals probably formed during the Mesozoic period**
  - **immature waters (no full chemical equilibrium with the host rocks)**. Classical geothermometers like Silica, K-Mg and K-Ca, which can re-equilibrate relatively fast, as well as the  $\delta^{18}\text{O}_{\text{H}_2\text{O-SO}_4}$ , and the K-Sr and K-F geothermometers, indicate **subsurface temperature estimations, varying from 60 to 100°C**
- > However, the Na/K and Na/Li ratios (and to a lesser extent, the Na/Rb and Na/Cs ratios), for numerous thermal waters, are close to those of the Los Humeros geothermal fluids (corresponding at reservoir temperatures of about 300°C). Associated with  $\delta^7\text{Li}$  values and relatively high B contents, and some escapes of deep reservoir hot gases which reach the surface, these ratios suggest **the presence of small fluxes of deep waters**, despite the low-permeability environment, and perturbing processes during their ascent up to the surface
- > In such a context, these ratios may be useful tools for HT geothermal exploration in volcanic environments



# Acknowledgements



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