A HYDRO-THERMO-HALINE NUMERICAL APPROACH OF THE GROUNDWATER FLOW TO EXPLAIN THE EXTREME LI-ENRICHMENT IN THE SALAR DE ATACAMA (NE CHILE)

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May 5th, 2020

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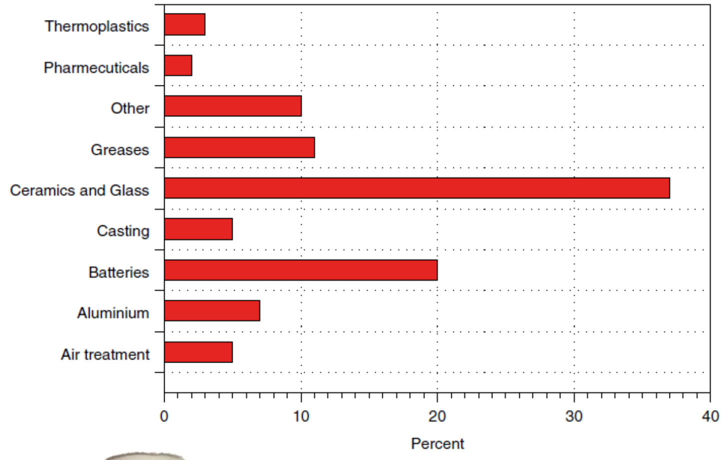
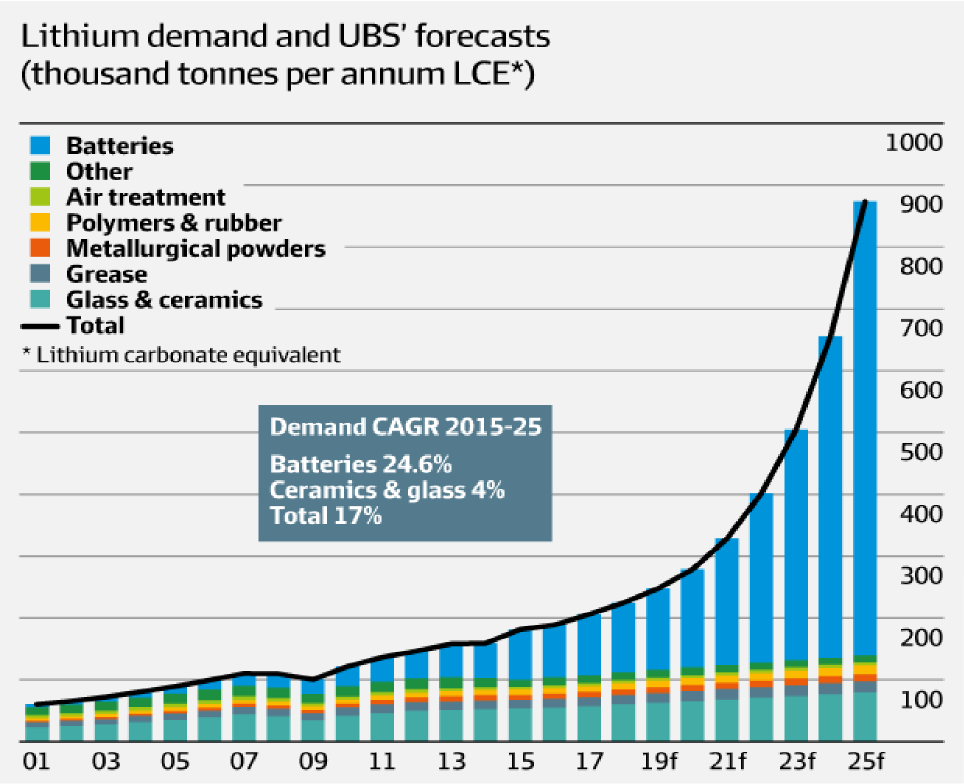
Motivation

Technological and pharmaceutical development → The demand of **Li, B, I, K, Mg, NaCl** and other **raw materials** will increase in the coming years

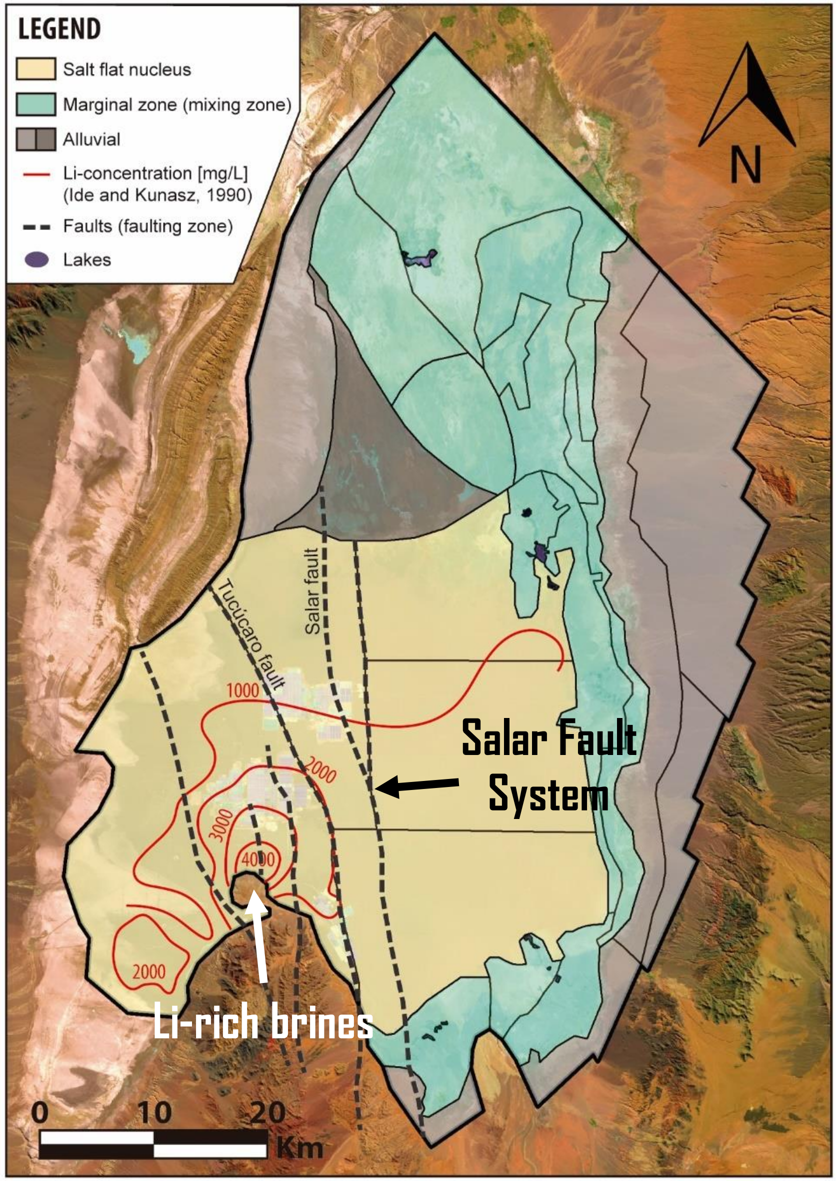
Lithium (Li) uses





These raw materials are extracted from the brines of **salt flats (*salars*)**

Motivation



Marazuela et al. (2020b)

The **Salar de Atacama is the world's largest Li reserve**...

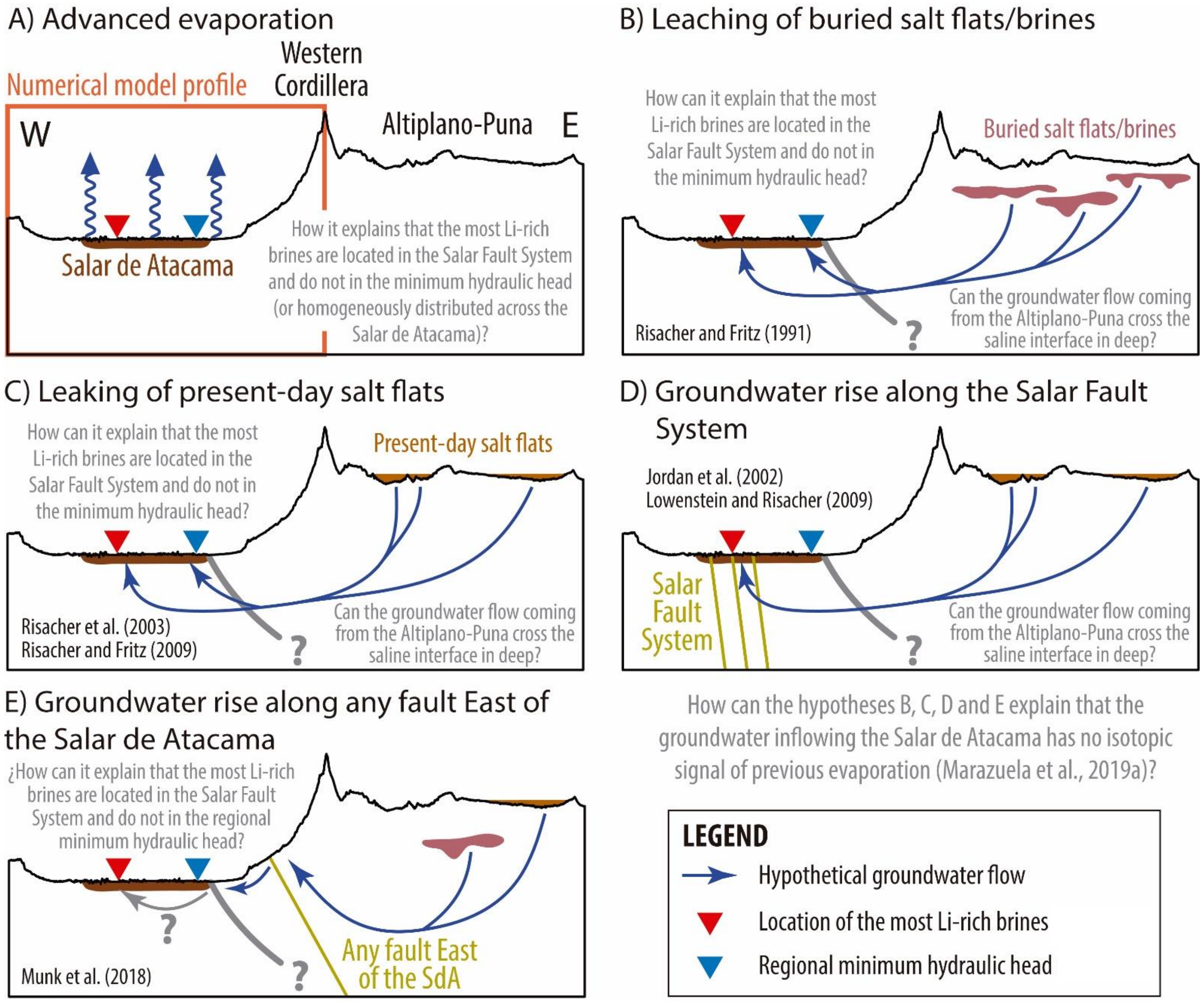
...but the **genesis of its extreme Li enrichment is still unknown**

Li concentration:

- Salar de Atacama **>7000 mg/l**
- Geothermal springs around the Salar de Atacama scarcely reach 50 mg/l

Motivation

Previous hypotheses of Li enrichment



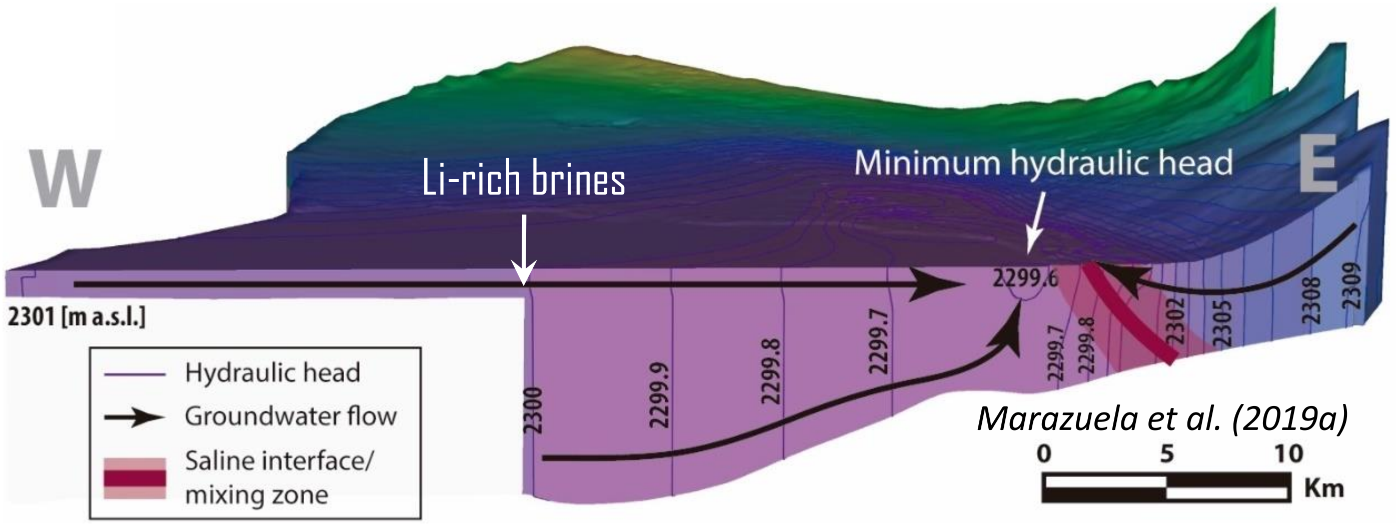
The barrier effect of the saline interface for the hypothetical flow paths coming from the Altiplano-Puna has not been taken into account by most of the previous hypotheses.

In addition, the flow paths coming from W to E of the Salar de Atacama and the location of the minimum hydraulic head of the regional water table have also been frequently ignored.

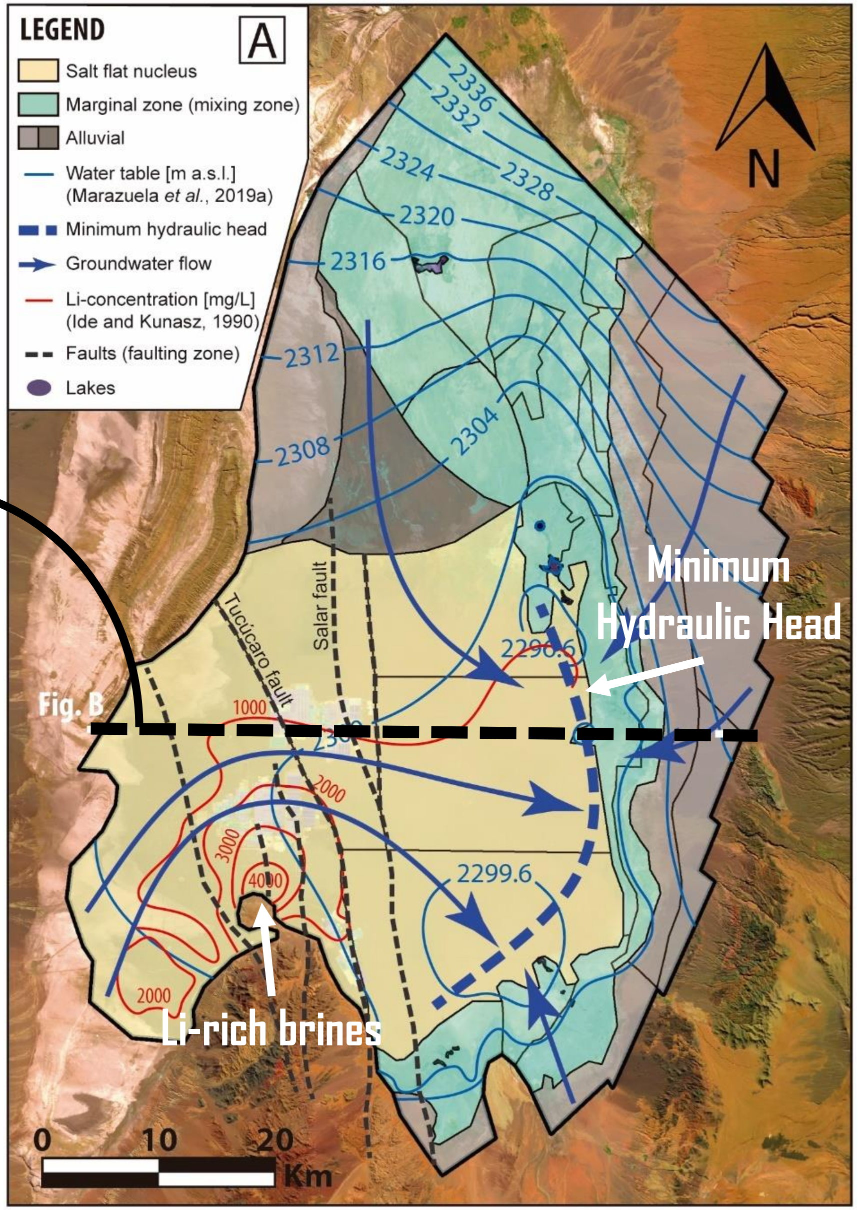
Motivation

New data question the previous hypotheses

- The **barrier effect** of the saline interface and the minimum hydraulic head has been recently explained for the shallowest aquifers of the Salar de Atacama (Marazuela et 2018, 2019a, 2019b, 2020a):



Marazuela et al. (2019a)



Marazuela et al. (2020b)

- The **spatial mismatch between the minimum hydraulic head and the Li-rich brines** seems incompatible with the previous hypotheses.

Objective

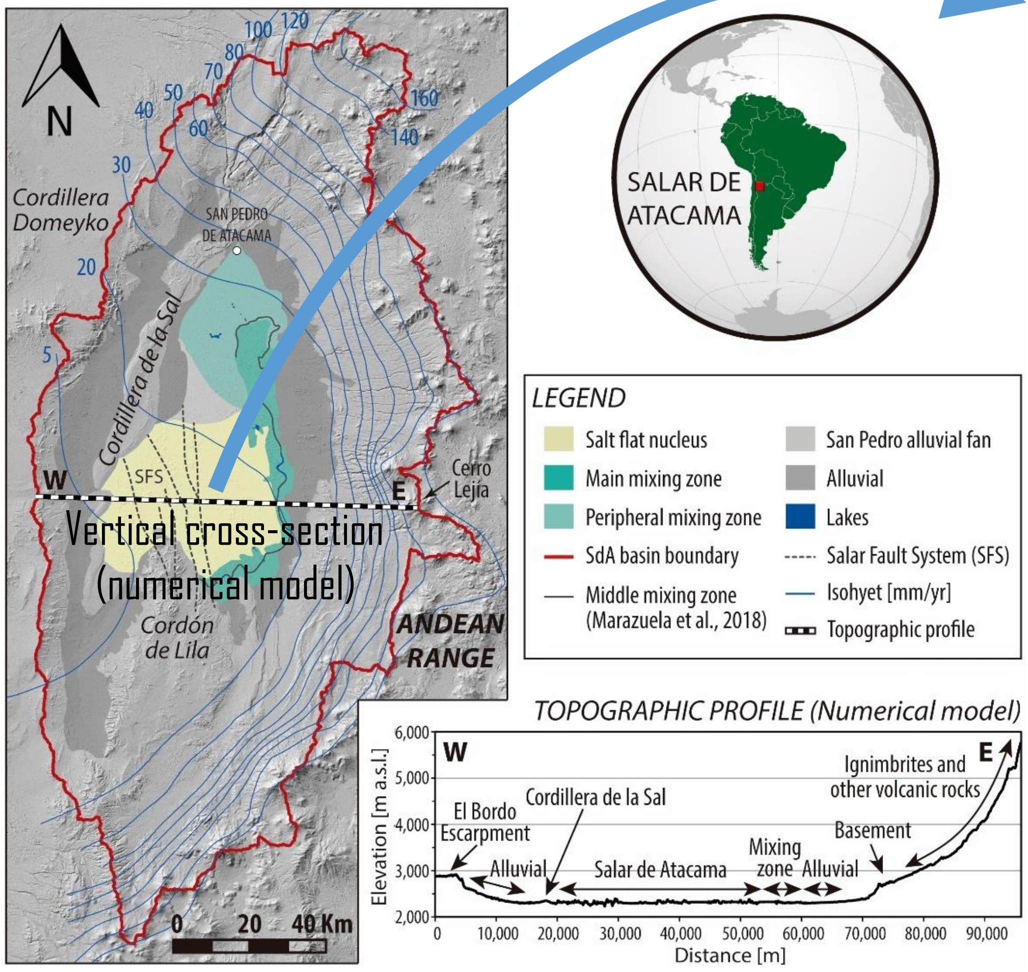
To explain the **thermohaline groundwater flow** of the Salar de Atacama to account for the **genesis of the world's largest lithium reserve** and discuss the feasibility of the previous hypotheses

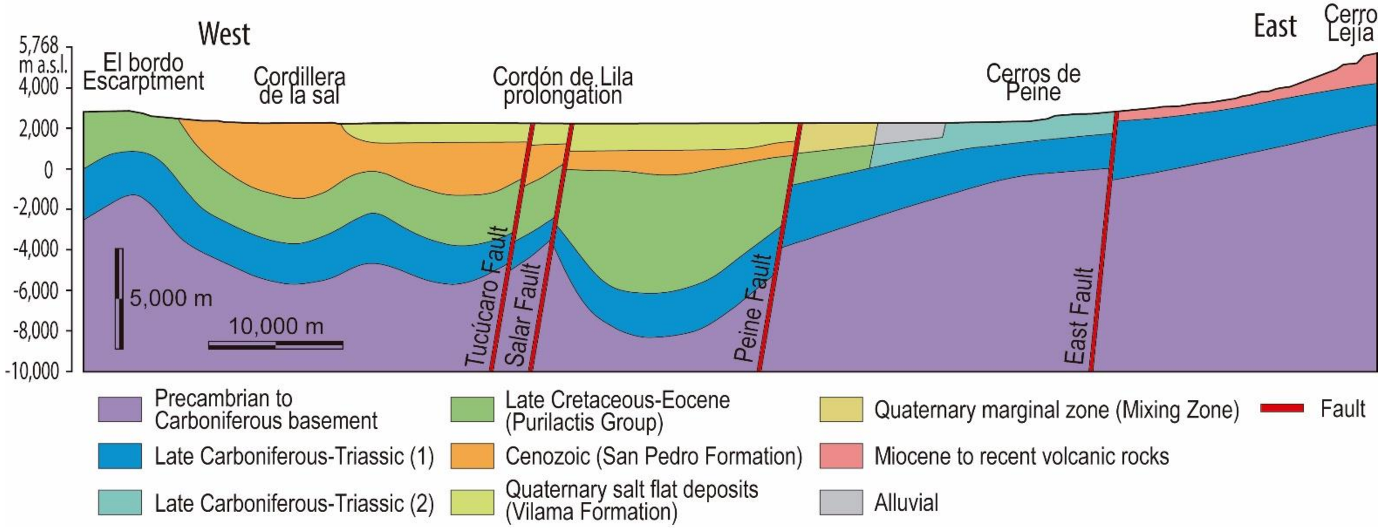
Three numerical simulations of the groundwater flow have been carried out to understand the **location of the most evaporated brines in saline systems** and characterize the **thermohaline circulation of the present-day Salar de Atacama**:

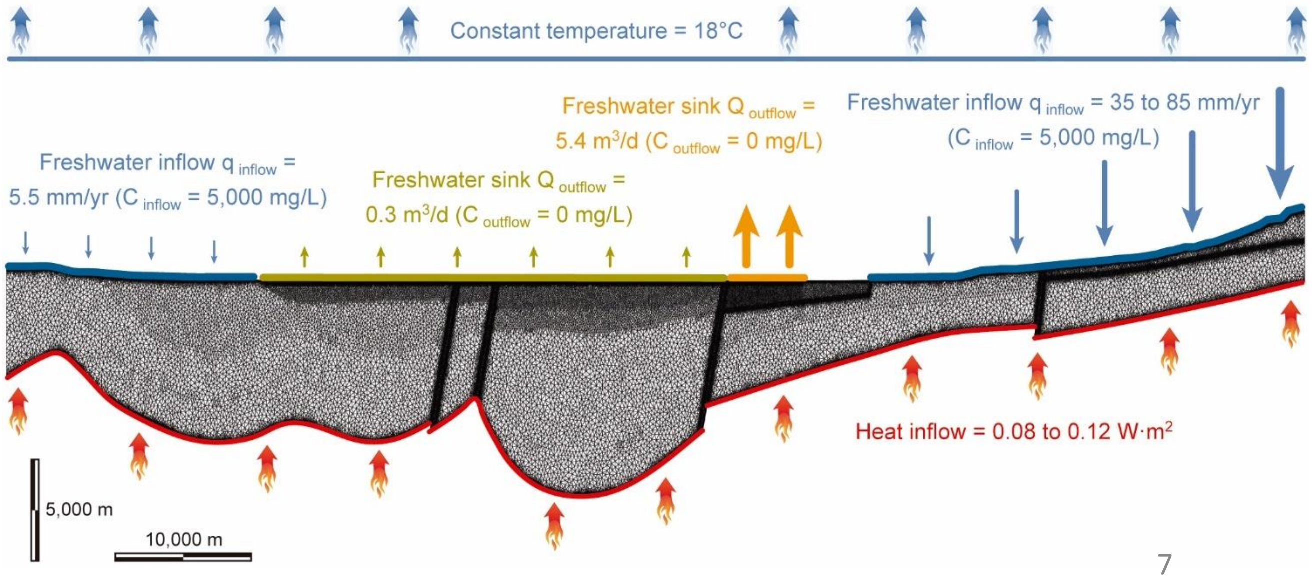
Simulation	Time	Objective	Specific considerations
Symmetric evaporation	100,000 yr (enough to see the final location of the minimum hydraulic head in each case)	Location of the most evaporated brines in a hypothetical ancient salt lake or salt flat with symmetric evaporation	$E_{nucleus} = E_{mz}$
Asymmetric evaporation		Location of the most evaporated brines in a salt flat considering the present-day asymmetric evaporation from its origin	$E_{nucleus} <<< E_{mz}$
Mature stage	Quasi-steady-state	The groundwater flow of the present-day Salar de Atacama basin	(1) $E_{nucleus} <<< E_{mz}$ (2) Pore water of San Pedro Fm. is saturated in halite

Numerical model

The Salar de Atacama basin







Marazuela et al. (2020b)

Numerical model

FEFLOW®

Groundwater flow

$$S_s \frac{\partial h}{\partial t} + \nabla \cdot \mathbf{q} = 0 \qquad \mathbf{q} = -\mathbf{K}\left[\nabla h + \frac{\rho^f - \rho_o^f}{\rho_0^f}\mathbf{u}\right] \qquad \mathbf{K} = \frac{\mathbf{k}\rho_0^f g}{\mu^f(C,T)}$$

Mass-transport

$$\phi \frac{\partial C}{\partial t} + \mathbf{q}\nabla C - \nabla \cdot (\mathbf{D}\nabla C) = 0$$

Heat-transport

$$\frac{\partial}{\partial t}\left(\left(\phi\rho^f c^f + (1-\phi)\rho^s c^s\right)T\right) + \nabla \cdot \left(-\boldsymbol{\lambda}\nabla \mathrm{T} + \rho^f c^f T\mathbf{q}\right) = 0$$

$$\rho^f = \rho_0^f\left(1 - \bar{\beta}(T,p)(T-T_0) + \bar{\gamma}(T,p)(p-p_0) + \frac{\bar{\alpha}(T,p)}{C_s - C_0}(C - C_0)\right)$$

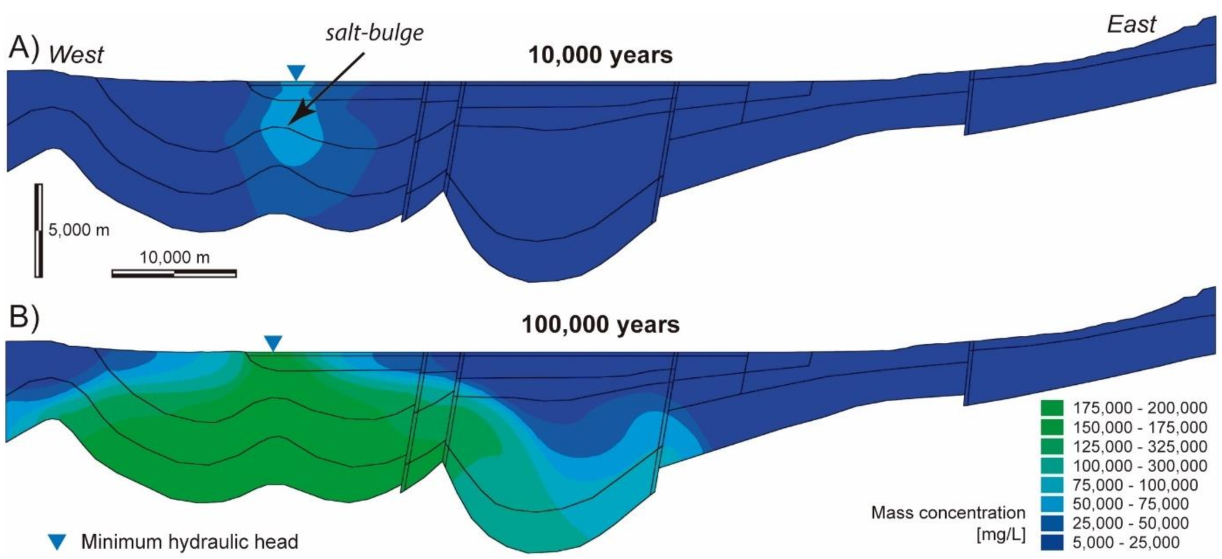
Magri (2009)

$$\mu^f(C,T) = \mu_0 \, x \, \frac{1 + 1.85\omega - 4.1\omega^2 + 44.5\omega^3}{1 + 1.85\omega_{(C=C_0)} - 4.1\omega^2_{(C=C_0)} + 44.5\omega^3_{(C=C_0)}} \, x \, \frac{1 + 0.7063\varsigma_{(T=T_0)} - 0.04832\varsigma^3_{(T=T_0)}}{1 + 0.7063\varsigma - 0.04832\varsigma^3}$$

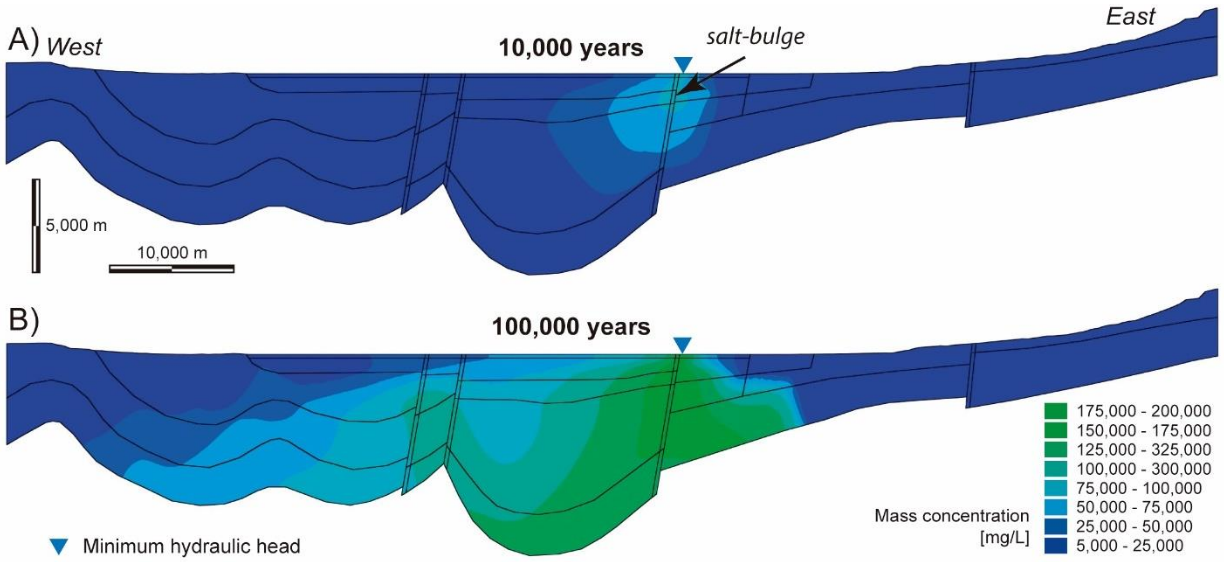
The location of the minimum hydraulic head

Considering the present-day recharge in the basin, the **evaporation** distribution **determines the location of the minimum hydraulic head (MHH)**

If Ev nucleus = Ev marginal_zone (salt lake or ancient salt flat)



If Ev nucleus <<< Ev marginal_zone (like present-day salt flat)



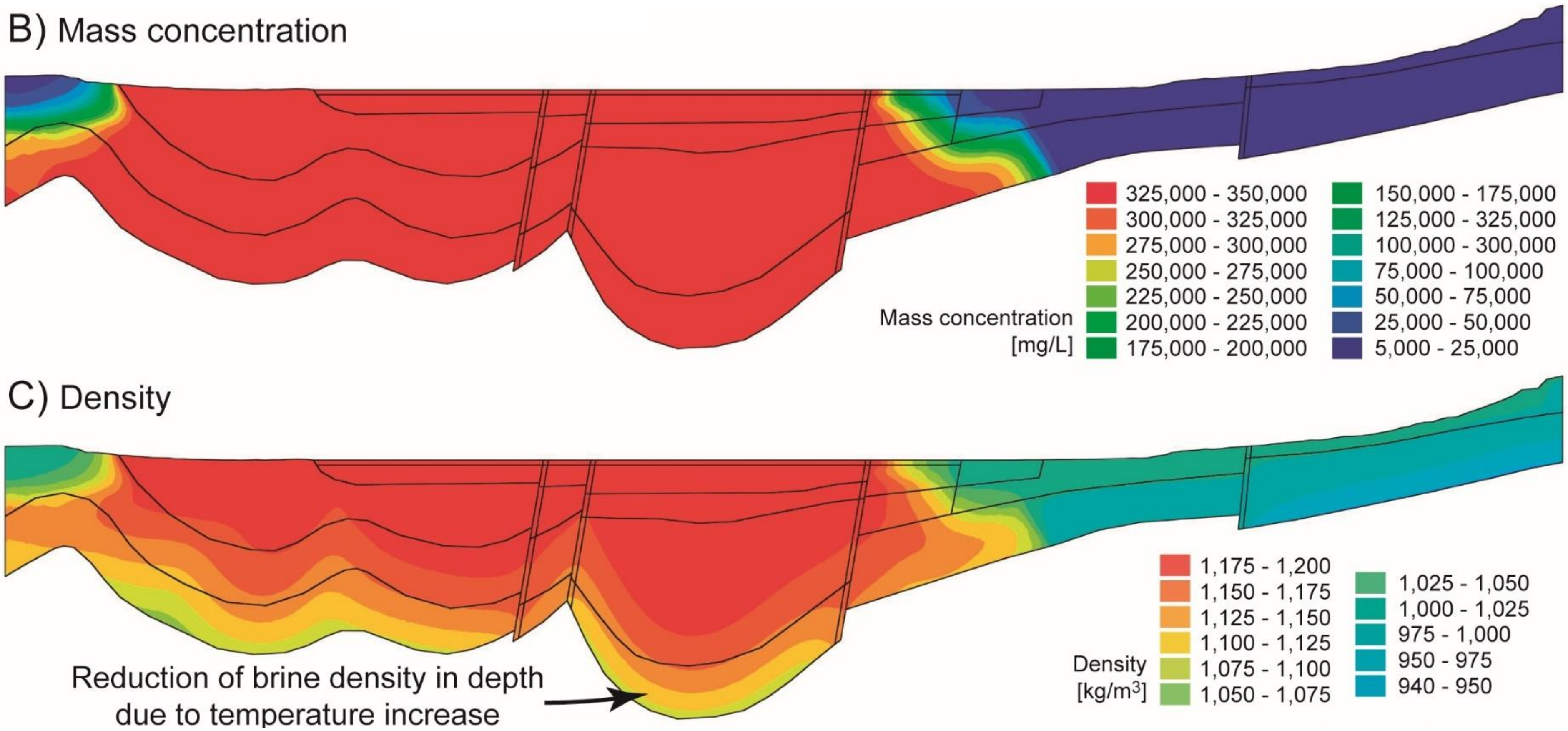
The most evaporated brines are expected toward the MHH

Results

The present-day Salar de Atacama basin (mature stage)

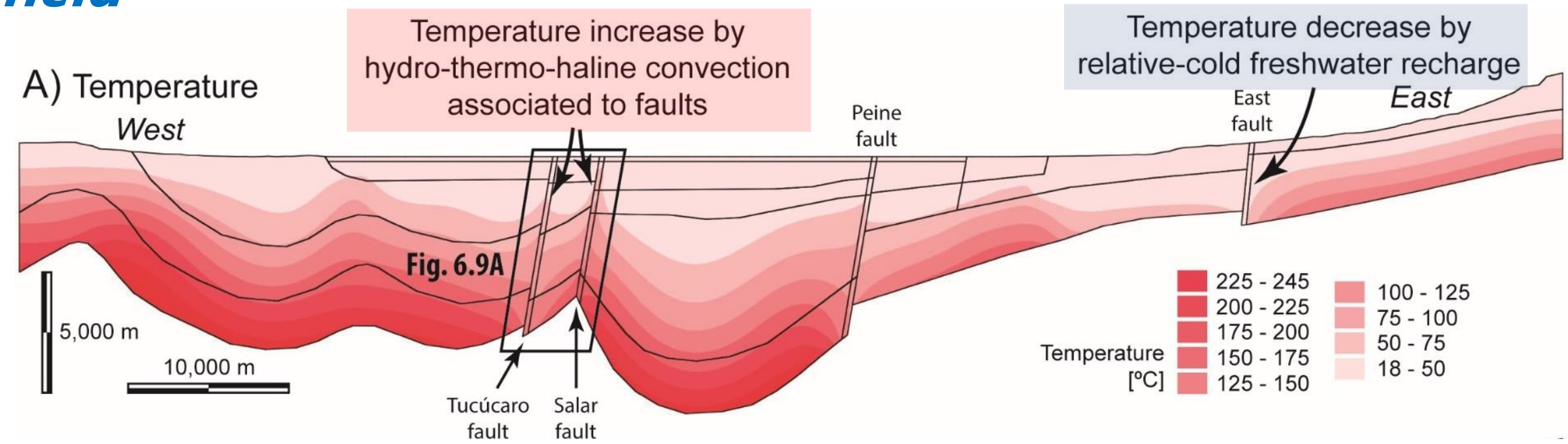
Saline interface

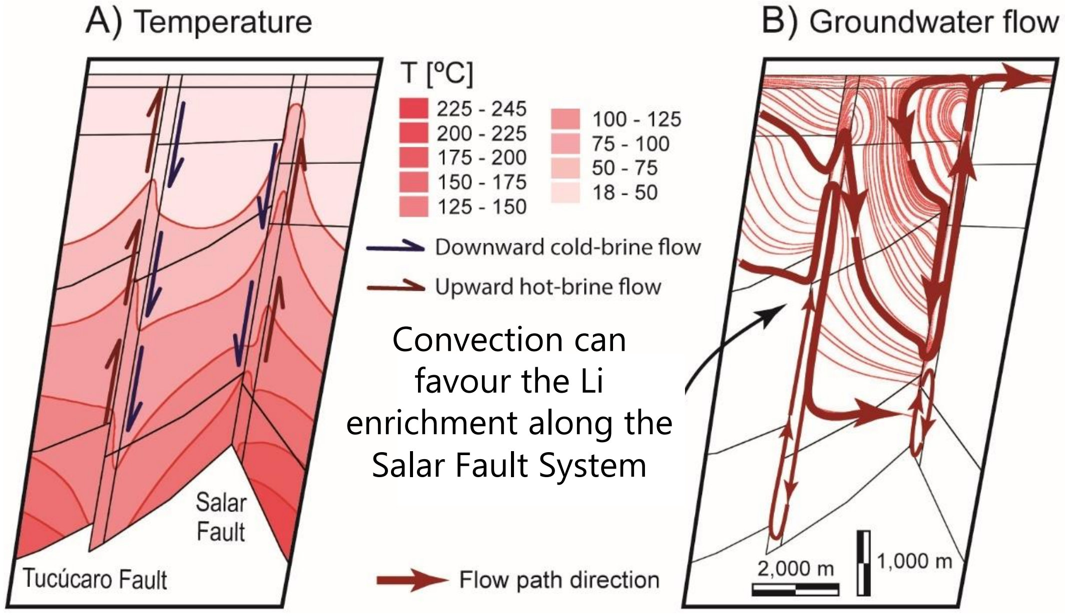
- ❑ The **mixing zone persists in deep** in spite of the temperature increase
- ❑ **Density decreases in deep** favoring the leaking from salt flats



The present-day Salar de Atacama basin (mature stage)

Temperature field

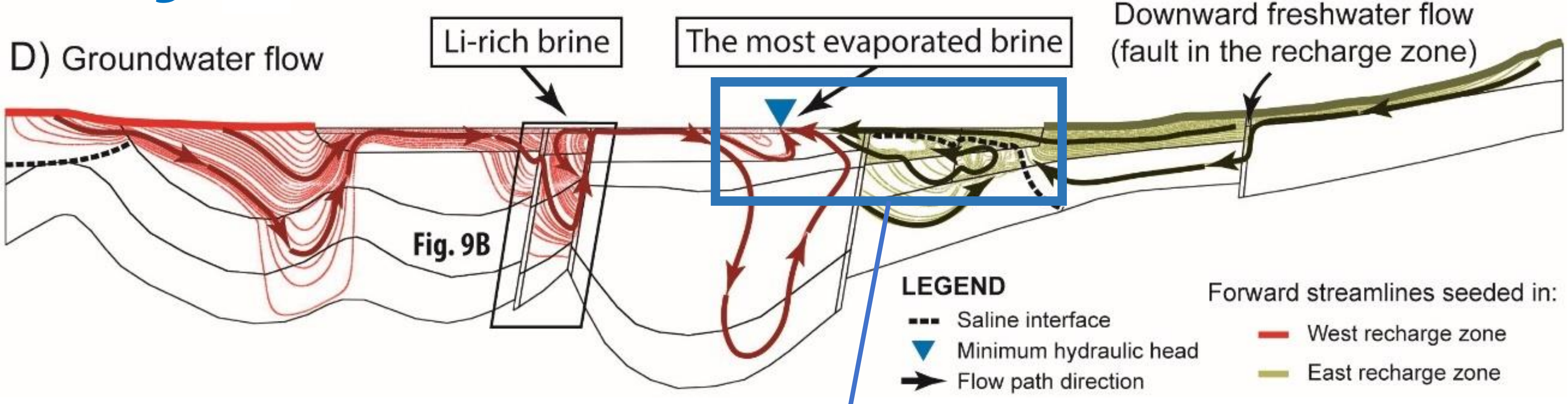


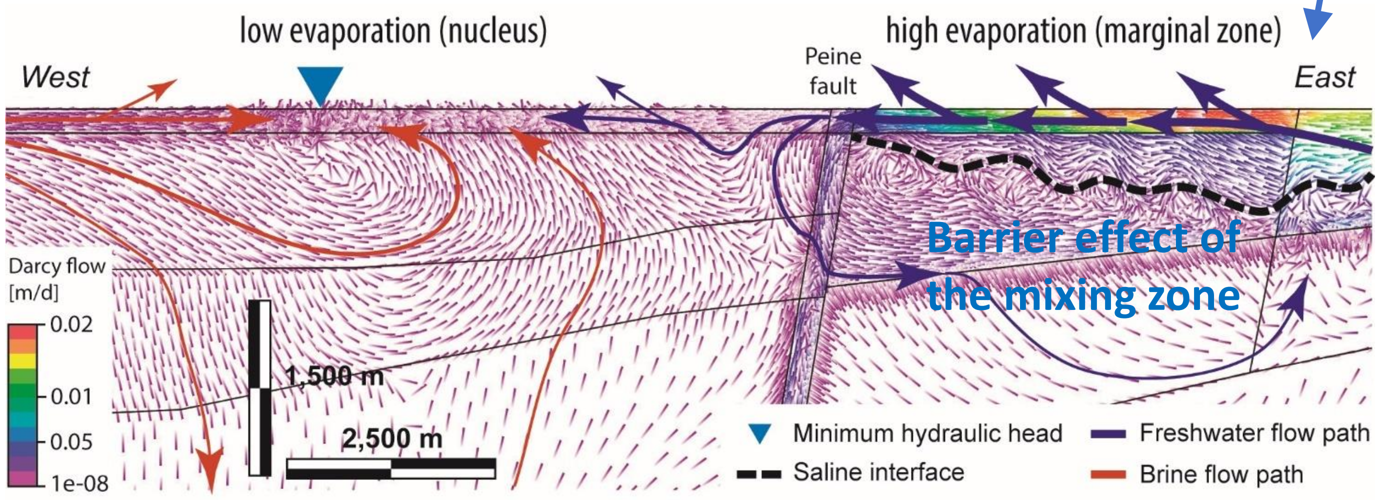


- **Relative cooler crust below the nucleus** (25°C/km) than below the Altiplano-Puna (35°C/km)
- **This does not prevent thermohaline convection** in the Salar Fault System, located below the most Li-rich brines
- The temperature field is distorted by convection cells in the faults

The present-day Salar de Atacama basin (mature stage)

Thermohaline groundwater flow





- The **MHH divides the basin** into **two isolated and antisymmetric systems**
- **All flow paths converge** toward the **MHH**
- The groundwater coming from the W can be **Li-enriched through the Salar Fault System**
- None flow path coming from the Altiplano-Puna can reaches the Salar Fault System as a consequence of the barrier effect of the mixing zone.

Conclusions

The thermohaline modelling of the Salar de Atacama basin has demonstrated:

- ✓ The critical effect of the **minimum hydraulic head (MHH)** in the groundwater flow of salt flats.
- ✓ The **MHH** divides the basin into **two isolated and antisymmetric systems.**
- ✓ All **flow paths converge toward the MHH** where the **most evaporated brines are expected.**
- ✓ The location of the MHH prevents to consider advanced evaporation as present-day Li enrichment mechanism.
- ✓ The **persistence of a saline interface in depth** also precludes lateral inflowing from the Altiplano-Puna as Li enrichment mechanism.
- ✓ **NEW HYPOTHESIS**: Remobilization of ancient layers of Li-enriched salts and/or clays by diluted recharge waters coming from the W-SW. This process is favored by convection cells in the Salar Fault System.

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