GEOPHYSICAL LITHIUM EXPLORATION IN ARGENTINA: STATE OF THE ART, MULTIPHYSICS INTEGRATION AND FUTURE DIRECTIONS

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ABSTRACT

La reacción del mercado energético debido a la demanda de tecnología, la conciencia climática, la pandemia y la caída de oportunidades del sector del petróleo y gas, ha fomentado y acelerado la transición energética de la industria de hidrocarburos a otros mercados energéticos como la exploración y producción de minerales críticos, entre ellos las tierras raras y el litio, brindando así una gran oportunidad a la Argentina que conforma junto a Bolivia y Chile el conocido triangulo del litio que posee el 60% de las reservas mundiales del mismo.
Desde el punto de vista de la prospección geofísica, el problema de exploración de Litio depositado en salares, posiblemente sea hoy uno de los problemas más desafiantes, ya que prospectivamente presenta condiciones extremas por su baja resistividad eléctrica, baja impedancia acústica, variabilidad en densidad; por otro lado, la logística para realizar el relevamiento en la Puna Argentina así como la poca disponibilidad de información del subsuelo y la hostilidad de las áreas inhóspitas que dificultan la adquisición, son factores que enriquecen el valor del dato de campo y posterior reconstrucción de la imagen del subsuelo.
El objetivo del presente trabajo es inducir al entendimiento de las bondades y debilidades de los diferentes métodos geofísicos en el problema de exploración de Litio, comparando así, la respuesta de los mismos a través de casos de estudio en la Puna Argentina; se recorrerá un flujo de trabajo desde la planificación de la adquisición hasta la construcción del modelo dinámico y se discutirá sobre el estado del arte y el futuro de las tecnologías geofísicas.
Se revisan los puntos débiles de las tecnologías descartadas, y se presenta un metodología multifisíca (magnetotelurica de tensor completo, tomografía de resistividad eléctrica y gravedad) efectiva en prospección de salares, validándose la misma en el salar de Pozuelos. La interpretación geofísica está en concordancia con los pozos de exploración someros y profundos; además, se integraron la magnetotelúrica y la gravedad a través de la construcción de pseudo-pozos.
Finalmente, la integración de datos geofísicos y de pozo permitió la construcción de un modelo estático que encuentra el área de basamento más profunda a aproximadamente 900 metros de profundidad y discrimina ocho litofacies. Este modelo estático será la base del modelo dinámico que impactara en ajustes económicos.

INTRODUCTION

The Energy transition drives the energy sector to renewable energy and electrification, which, in consequence, increases the world mineral consumption. Critical minerals are mineral sources that are essential to the world economy and whose supply can be disruptive. They comprise rare earth elements and 35 other elements including lithium, which is used in rechargeable lithium-ion batteries, electric cars and high tech devices. The lithium criticality, among other reasons, is due to the fact that the 60% of its world reserves are in the so-called lithium triangle located in Argentina-Bolivia-Chile that host salt flats with brines that contains this mineral (Curcio 2022).

The low electrical resistivities, variations in salt concentrations, low acoustic impedances and dynamics of the hydrogeological system, makes brine monitoring a complex geophysical exploratory problem. Logistically, the situation is not better: the salt flats are located in inhospitable areas, at altitudes of 3600 m-4200 m, and, in many cases, the mechanical instability of the ground surface makes accessibility and surveying very difficult.

The scope of this work is to find a suitable combination of geophysical techniques that fit the lithium exploration objectives, which are the characterization of the salt flat in depth; basement delineation, definition of the main structures and main faults and detection of semi-fresh water aquifers in the edge of the salt flat that contribute to its recharge and that are key to the water balance of the endorheic basin, which has the resource in solution. For this purpose, the evaluation of several prospecting methods in different salt flats was executed, concluding that full tensor magnetotellurics, electrical resistivity tomography and gravity comprises a toolkit that fit the objectives set (Curcio *et al.*, 2022).

Concept models

There are different types of deposits associated with lithium (Li) such as pegmatites (lithium-rich granites), oilfield brines (and deep sedimentary brines), lithium clays and lithium zeolites (lacustrine sediments), geothermal brines and closed basin brines (Piethe 2021).

Munk (2016) presents the global distribution of the locations of the best lithium brines from North America, South America (Argentina, Bolivia, and Chile), and Asia (China), independent of whether the brines are in production or not, highlighting that the majority of important lithium-rich brines are located in the Altiplano-Puna region of the Central Andes of South America (Figure 1).

Many authors studied and proposed different geological concept models. Bradley *et al*. (2013) conceptualized a deposit model for lithium brines and mention at least seven

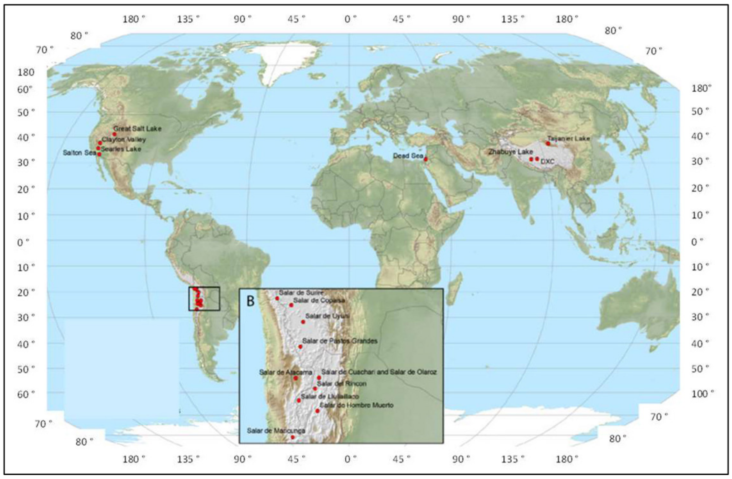

Figure 1. World map of lithium brine deposits with inset showing detail in South America (Munk 2016).

first order characteristics in all producing lithium brine deposits:(1) arid climate; (2) closed basin containing a playa or salar; (3) tectonically driven subsidence; (4) associated igneous or geothermal activity; (5) suitable lithium source-rocks; (6) one or more adequate aquifers; and (7) sufficient time to concentrate a brine In addition, they present a schematic deposit model for lithium brines showing part of a closed-basin system consisting of interconnected subbasins. They also note that some ancient oilfield brines are enriched in lithium (Collins 1976). The model seeks to account for the sources, sinks, and processes that mobilize, sequester, and concentrate lithium (Figure 2 (a)).

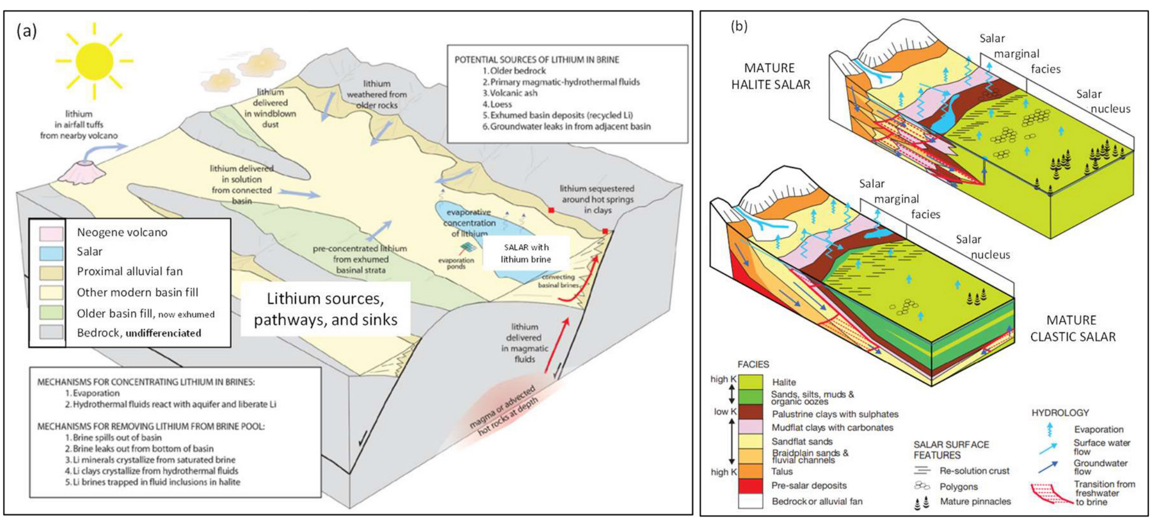

Figure 2. (a) Schematic deposit model for lithium brines, mechanisms and potential sources in a global basis (Munk, adapted from Bradley *et al*., 2013); (b) Block models of mature and immature salars, focused on the Altiplano Puna region of the Central Andes salars, showing the distribution of facies and main hydrological components (Houston *et al*., 2011).

Houston *et al.*, (2011) reviewed the requirements for brine resource and reserve evaluation, taking most of the examples in the Central Andes. Note that their concepts are specific to the range of salars observed in the Altiplano-Puna region of the Central Andes and are not necessarily transferable, in a global sense, to other Li-rich brines, but clearly applies to the Argentinian salt flats models. They classified the salars in the Altiplano-Puna region of the Central Andes in terms of the relative amount of clastic versus evaporite sediment; the climatic and tectonic influences, as related to altitude and latitude; and the basin hydrology, which controls the influx of fresh water (Figure 2 (b)). Their analysis include different block models of mature and immature salars showing the distribution of facies and main hydrological components, concluding that the brines are hosted in closed basin aquifers of two types: mature, halite dominant, and immature, clastic dominant. Finally, they provide an overview of the mean annual precipitation, salar type and brine type of different salar in Chile, Bolivia and Argentina.

In Argentina, a detailed and complete description of most of the salt flats is given by Alonso (1999). Several scientists are currently working on this topic, but it is still need a depth imaging of this endorheic basins. We can find as an example, the De la Hoz model (2021) which is an updated version of the Bradley *et al.* (2013) model.

Similarities between hydrocarbon and lithium exploration.

There are some similarities between hydrocarbons and lithium exploration that shall be interesting to remark. In general terms, Vergani (2021), mentioned that the hydrocarbon basins, marine or continental, are ‘old’ (millions of years), extended in important areas (hundreds to thousands of km^2) and filled with sedimentary rocks with several superimposed and independent geological cycles, separated by unconformities whereas the salt flats are geomorphic basins of continental origin, geologically modern (hundreds of thousands to a few million years), where terrigenous (clastic) and evaporitic sedimentary environments predominate.

Piethe (2021) explained why the critical minerals are so important in the energy transition context, being essential to actual life standards, required for world transition to a low carbon of economy and that they will become a sustainable source of critical minerals for global demand. He noted that lithium produced from brines resources have great similarity with hydrocarbon exploration workflow and production, providing, in this way, opportunities to geoscientists from the hydrocarbon industry.

In the typical oil and gas field, the basin configuration is in a shared basin: the hydrocarbon accumulation is dispersing in a basis complex configuration. On the other hand, in salt flats, the typical lithium basin is the whole basin and the Li resource is distributed heterogeneously in the entire basin, so, it is disperse all around the basin. But, how is lithium been concentrated? The elevate heat flow from young volcanoes or hot springs, promotes the circulation in the basin; the source rocks, that are abundant and rich in Li, move brines sufficiently to circulate, evaporate and concentrate the resource; basement rocks with process like lixiviation moves the Li from the basement rocks to the salt flat basin and the geothermal fluids by hydrothermal sources (Figure 3). The exploration frontier is currently analyzing the clay deposits with lithium anomalous concentrations and their production times much shorter than from brines resources (Piethe 2021).

In a lithium project the exploration challenges comprises the following items

- Understand Li source and migration process to the endorheic basins.
- Water availability in an extremely arid environment and understanding of the hydric balance.
- Resource exploration and definition. Spatial and temporal variability of concentrations during production.
- Brine recovery factor. How much resource will be produced economically? Reservoir understanding.
- Reinjection of brine to maintain piezometric levels and pressure since there are many landholders over the same resource.

The importance of shallow to deep geophysics and well log data (spectral gamma ray, resistivity, acoustic, caliper, nuclear magnetic resonance and core testing information) provides a cross-industry opportunity. De- risking workflows, that increase the asset values, integrates geophysics, well data and hydrogeological data, also find similarity between lithium and hydrocarbons industry (Figure 4).

This workflow allows constructing the dynamic groundwater numerical model for brine projects, supporting minerals reserve estimates. Note that the brine movement is a 3D process and the numerical model combines geology, geophysics, fresh water and brine flows, density driven flow and optimal setting for production wells. Also, fresh water intrusion and dilution effect must be considered (aquifers, river, and precipitation events). In consequence, the model predicts extracted brine over time and brine chemistry over time.

Finally, the geoscientists that might jump to lithium industry, should pursue in five focus areas:

- Basin geometry definition. Structural timing and tectono-magmatic evolution
- Stratigraphic understanding in narrowly relation with climate auto cyclic controls
- Better defining on wells proposals
- Improve reservoir efficiency and pursue sweet spots and diversify sweet spots.
- Develop endorheic basin environmental sustainability and life cycle of new developed minerals.

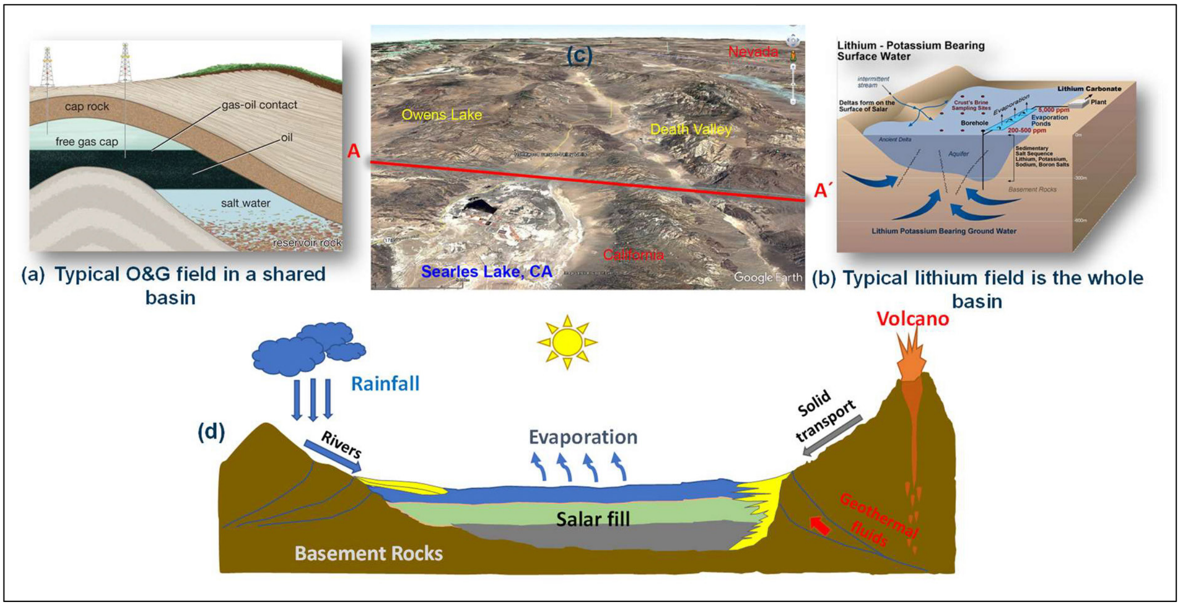

Figure 3. (a) Typical O&G field in a shared basin (b) Typical lithium field is in the whole basin (c) Image showing the transect trace along Searles Lake, California (d) Concept model (taken from Piethe 2021).

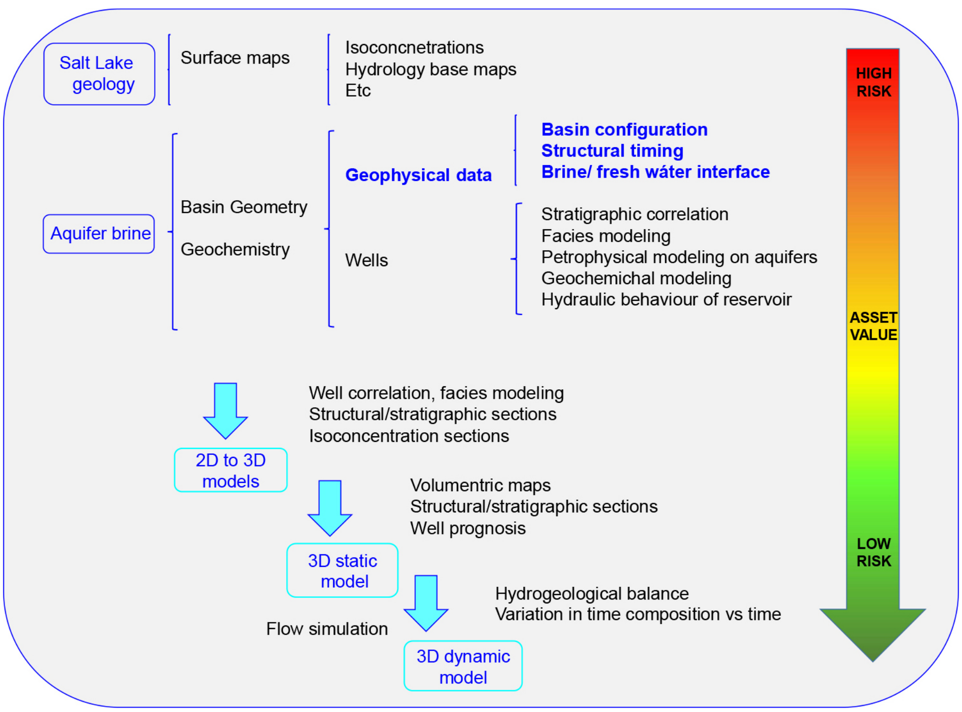

Figure 4. Workflow used in lithium exploration and production, similar to hydrocarbon industry (Piethe 2021).

State of the art in geophysics

The exploration and quantification of in situ resources of lithium accumulations has been approached from mining as if it were a stationary resource located in the shallow portion of the subsurface. On the other hand, the economical evaluation, price commodities, logistics among others reasons, resulted in the fact that geophysical methods applied in most of the cases in the past have not been used to understand the configuration of the basin and for fluid detection purposes, but rather to inspect resistivity contrasts in the subsurface.

Coolbaugh *et al.*, (2010) provided the analysis of lithium and other elements in tufa deposits that could serve as exploration guides for hot spring lithium deposits; Coolbaugh and Hickson (2017), reported the use of reflection seismic (for structural characterization), gravity (to estimate the thickness and distribution of basin- fill sediments) and magnetics (to understand the distribution of magnetized rocks, especially in the central portion of the basin) in Nevada, US.

Wang *et al.*, (2020) summarizes the Chinese prospecting progress in lithium in China that presents lithium reserves in pegmatite rocks, granite rocks and sedimentary rocks. They report the use of gravity, magnetics, audiomagnetotellurics and electric methods for pegmatite-host lithium exploration recognizing the difficulties to find a measurable anomaly which depends mainly on the size of the orebody or pegmatite vein. Lechuga (2021) analyzed reports, evaluations and exploration surveys on 23 Chilean salt flats completed during the last decade, providing an updated view on the current situation of lithium production, reserves, resources and exploration in Chile. He highlights that still the studies must be carried out to define the exact location and thickness of brine deposits within the basins and he mentions that Time Domain electromagnetics is currently used for brines exploration in Chile.

Several technical reports or brochures from Canada, Chile and Argentina, claims the use of Time Domain Electromagnetics (TDEM), Controlled Source Audio Magnetotellurics (CSAMT), Audio Magnetotellurics (AMT), Vertical Electric Sounding (VES). However, those methods are not effective in terms of depth of penetration, sensitivity to lateral variations and, moreover, some of them provides a one-dimensional earth model, a strong hypothesis in lithium brines exploration.

Since 2018, Lítica Resources has been carrying out various feasibility studies, field tests, analysis of previous acquisitions and also performed geophysical acquisitions in many salt flats, concluding that full tensor magnetotellurics, gravity and electrical resistivity tomography are currently the best combination to reach the exploration objectives, which are: characterization of the salt flat in depth; basement delineation; definition of the main structures and main faults and detection of semi-fresh water aquifers in the edge of the salt flat that contribute to its recharge and that are key to the water balance of the endorheic basin, which has the resource in solution.

We provide the modeled, reprocessed data and field tests that justify the reasons for discarding some geophysical techniques. Also, the geophysical (magnetotellurics, gravity and electrical resistivity tomography) results in the Pozuelos salt flat in the Argentine Puna are presented, which were acquired, processed and interpreted during the year 2021. Finally, all these data were integrated into the static reservoir model that includes 18 wells (Curcio *et al.*, 2022).

GEOPHYSICAL RESPONSE IN SALT FLATS MONITORING

Once the objectives have been set and given the complexity of the lithium geophysical prospecting problem as a result of the low electrical resistivity, variations in salt concentrations, low acoustic impedances and dynamics of the hydrogeological system, let us review the benefits and limitations of each geophysical method in brines exploration.

In brine exploration, as in other industries, it is of our interest to operate with one or more methods that are sensitive to the following parameters: structure, fluid detection, depth of investigation, lateral variability, and dimensionality. Figure 5 shows a table of the four 'big groups' in geophysical prospecting: seismic methods, magnetics, gravity and electric/electromagnetic methods, which are divided according to the physical principles in which they operate being in this way sensitive to different physical properties of the earth.

In group 1, general equation motion for compressional (1a) and shear (1b) waves are shown, d is density, λ and μ are the Lamé constants; in group 2, μ is the magnetic permeability in H/m; σ is the electrical conductivity tensor (S/m); $E = (E_x, E_y, E_z)$ is the electric field in (Volt/m); $H = (H_x, H_y, H_z)$ is the magnetic field intensity (ampere/m) related with the magnetic field flux $B = (B_x, B_y, B_z)$ through the constitutive relation $B = \mu H$; and $J = (J_x J_y J_z)$ is the electrical current (ampere/m), V is the electric potential and Q is the charge; in group 3, g is the gravity acceleration, G is the gravity constant, m is the mass of the body that exerts the gravity attraction and r is the distance from a given location to the mass center of the body; and, finally in group 4M $= (M_x, M_y, M_z)$ is the magnetization vector in ampere/m in and κ, adimensional, is the magnetic susceptibility tensor.

The electric and electromagnetic methods are promising in lithium exploration, but, due the low electrical resistivity (0,1 ohm-meter) that the brine-saturated multilayers present, these methods, for certain equipment characteristics used in near surface, conventional mining prospecting (Zhang, 2011) and groundwater prospecting (Everett and Meju, 2005), might not be efficient in terms of depth of investigation and basin characterization for brines prospecting. In consequence, and given the inhospitable location of salt flats, that weigh a selection of certain technologies due to the benefits in logistics, the main questions that we might answer are: should be used Direct Current (DC) methods, Electromagnetic methods (EM) or both of them? In the case of electromagnetic methods, should be used natural source (MT) with a risk of having too low signal or should be used an artificial source with the risk of a 'waveguide-type' effect? On the other hand, what characteristics of the equipment are needed to obtain a characterization of a multilayer ultra-conductive system?

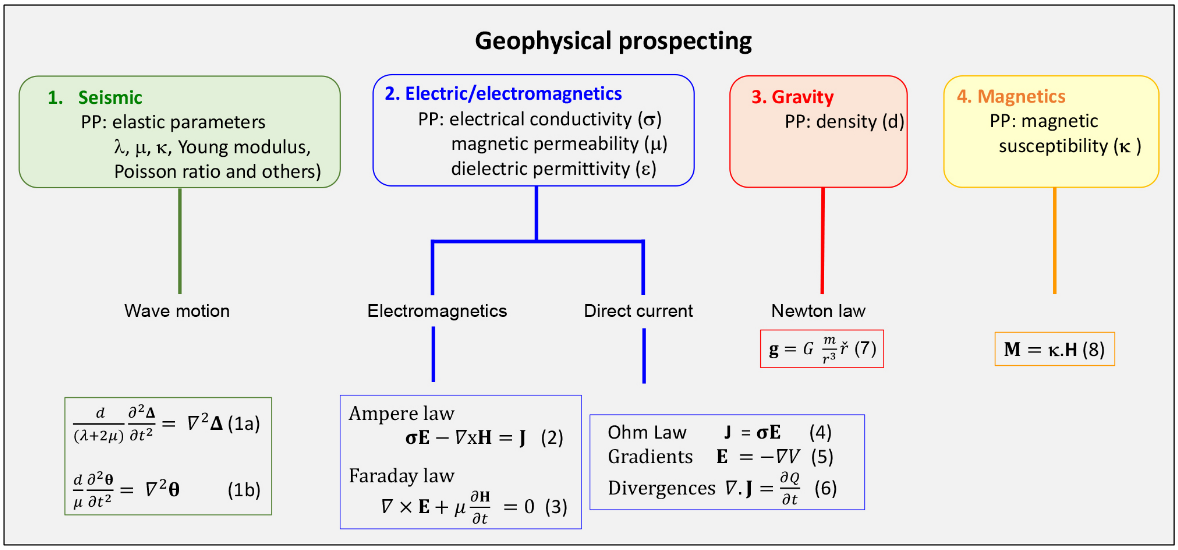

Figure 5. General description of the different methods in geophysical prospecting, physical principles and physical properties (PP) that each method is sensitive to. Bold letter means vector or tensor.

In the EM methods, the primary source induces electrical currents in the subsurface (with a given electrical resistivity distribution), which, in turn, induces a secondary EM field that is measured in surface. The physical principles of the EM methods rely in the Ampere law (equation 2) and Faraday law (equation 3).

The equations allow us to introduce the skin depth concept, in meters, which is the depth of penetration of the electromagnetic energy in a conducting medium when displacement currents can be neglected and the depth at which the amplitude of a plane wave has been attenuated to 1/e (or 37%),

$$\delta = \sqrt{\frac{2}{\mu\omega\sigma}} \tag{9}$$

where ω is the angular frequency (rad/s). The skin depth physics indicates that the more conductive is the layer the lesser depth of investigation is reached; and, the higher operation frequencies, the lesser depth of investigation is reached. Both skin depth and, in an analogue way, the diffusive distance controls the depth of investigation of an electromagnetic method, in frequency domain or time domain respectively. The physics of the EM prospecting works in the following way: after injecting the time-varying primary current, secondary currents are induced in the subsurface, which undergo to a diffusive process known as 'smoke ring current', whose details can be reviewed in Nabighian (1979) and Oristaglio and Hohmann (1984).

In Direct Current, the highest density of currents flow through the most conductive layer, which has less resistance to flow, therefore, in-depth investigation, is more difficult when the electrical resistivity values are extremely low, such as in salt pans (Curcio *et al*, 2022).

TDEM (Time Domain Electromagnetics)

Time domain electromagnetics is a geophysical method in which the waveform of the transmitted signal is a train of pulses, step-functions, ramps, or other waveforms, and measurements are made in the off-times between pulses, usually after the primary field has turned off (Strack, 1992). It was evaluated a TDEM acquisition with an artificial source transmitter of 30 A, lowest operating frequencies of 0,25 hertz and above and a loop of 200 meters times 200 meters in the Arizaro salt flat. Figure 6 shows the preliminary models and a reprocessing of field results, showing that this 1D method does not penetrate a conductive column more than 100-150 meters. In consequence, TDEM with these characteristics might be only useful to delineate the first conductive layer of the subsurface multilayer group, but definitely it is not useful for geological characterization within it. In addition, the method provides a 1D solution, which is a strong hypothesis in brines exploration; hence, 2D profiles obtained by the interpolation of 1D model could result in a high degree of uncertainty.

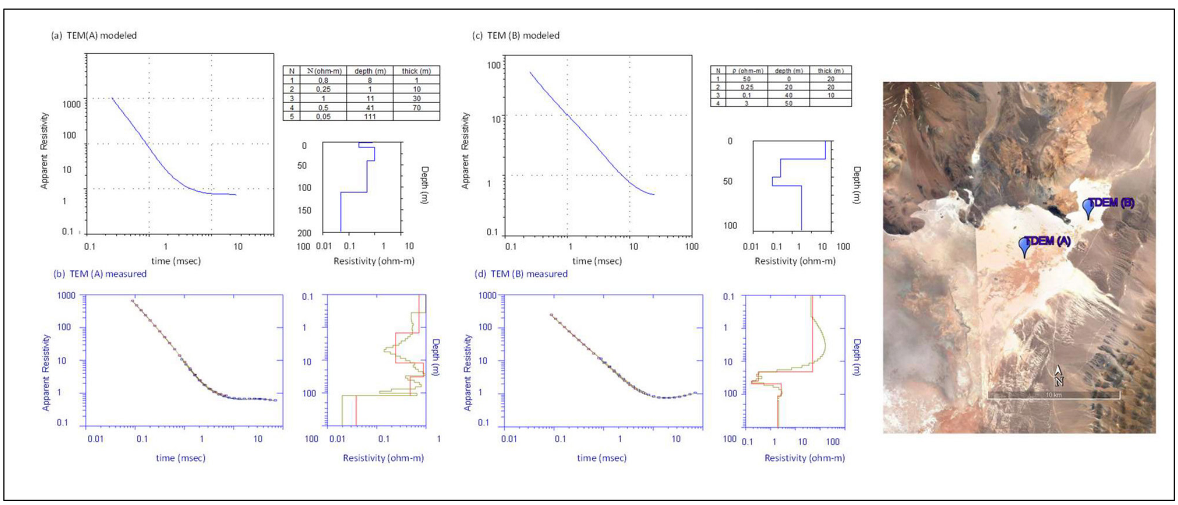

Figure 6. TDEM. Numerical modeling, (a) and (c), and field example, ((b) and (d), of TDEM (A) and TDEM (B) respectively. Both models and field results show that, the depth of penetration is below 100 meters. In the right, the location of the TDEM (A) and TDEM (B) reprocessed stations in Arizaro salt flat.

Controlled Source Audio Magnetotellurics (CSAMT)

This hybrid method, which is not full tensor, has an artificial source of 1 kilohertz frequency and above, combined with an audiomagnetotellurics (AMT) natural source. The artificial source provides the strength of CSAMT because it increases the signal to noise ratio in its frequency band. However, for lithium prospecting purposes, the CSAMT with these characteristics is limited due to the skin depth physics in a ultra-low resistivity layer (equation 9), showing a depth of penetration less than 20 meters in the transmitter-frequency range. Figure 7 (a) modeled data for the AMT band; Figure 7 (b) presents a reprocessed data in Rio Grande salt flat, showing the apparent resistivity, phase and coherency. The minimal frequency is 10 hertz and the coherencies are lower than 0.5 (with an exception around 5000 hertz where the transmitter enhances the signal) while the resistivity range moves from 0.5 to 50 ohm meters; Figure 7 (c) shows a maximum depth of penetration of 150 meters; Figure 7 (d) shows the location of the station analyzed.

Although the AMT frequencies in CSAMT are lower than the artificial source frequencies, they are not enough to pass a 100-150 m thickness, ultra-conductive layer. In addition, the AMT signal is too low and perform a good statistic is needed, which is not achievable with a low storage capacity equipment.

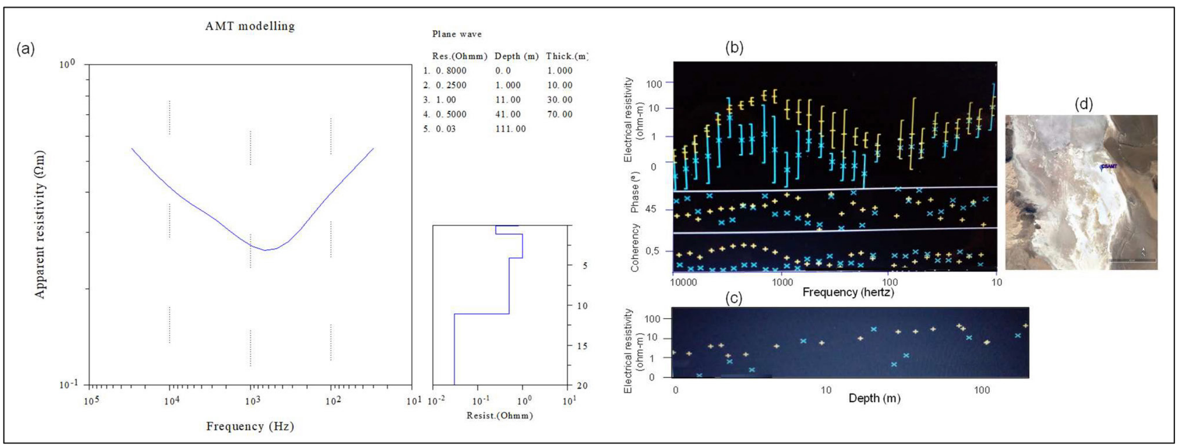

Figure 7. (a) The strength of CSAMT method is in the enhanced signal generated with a 1 khz (and above frequencies) transmitter. The AMT numerical modeling shows that for a group of ultra-conductive layers the depth of penetration is below 150 meters; in (b) reprocessed data is shown: apparent resistivity, phase and coherency; (c) is the depth of penetration (Curcio *et al.*, 2022) (d) CSAMT location in Rio Grande salt flat.

Scalar Controlled Source Audio Magnetotellurics (SCSAMT)

This methodology was discarded mainly to the fact that it works with two or three EM field components (E_x, H_y; or E_x, H_x, H_y). So, it only solves the 1D Cagniard resistivity, a strong hypothesis for lithium exploration.

Vertical Electric Sounding (VES)

The VES is a DC method that could be useful to delineate the freshwater-brine contact at the edge of the salt flat. However, due to its 1D and homogeneous assumption, it can carry a high degree of error. Figure 8 shows VES field results located (a) in the edge (VESa) and (b) in the center (VESb) of the Pozuelos salt flat showing that the penetration depth is less than 50 - 100 meters.

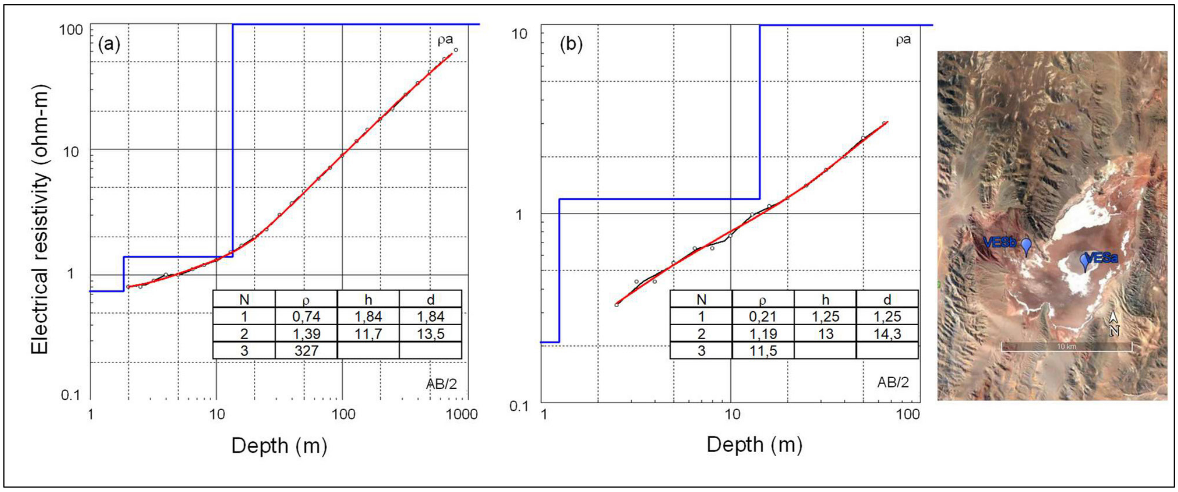

Figure 8. VES field results located (a) in the edge (VESa) and (b) in the center (VESb) of the Pozuelos salt flat. N is the number of layers, ρ is the electrical resistivity calculated, h is the thickness of the layer and d is the depth to the surface (referred to zero meters); (c) shows the location of the VES stations. (Curcio *et al.*, 2022).

Refraction tomography

Seismic Refraction Tomography uses P- or S-wave travel times to map vertical and lateral changes in the subsurface. A hammer blow or explosive charge (the shot) generates a seismic wave that travels through the ground. It was reprocessed and evaluated field data from Pozuelos salt flat. In this case, device has 48 channels with 9 hz uni-axial geophones separated 20 meters each other resulting in a length of 960 meters. The seismic source is a 100 kg weight. The results show a velocity range of 3500 m/s to 4000 m/s and penetration less than 60 meters depth, so, is not possible to reach the ordovicic basement which is expected to have a seismic velocity above 6000 m/s (Figure 9).

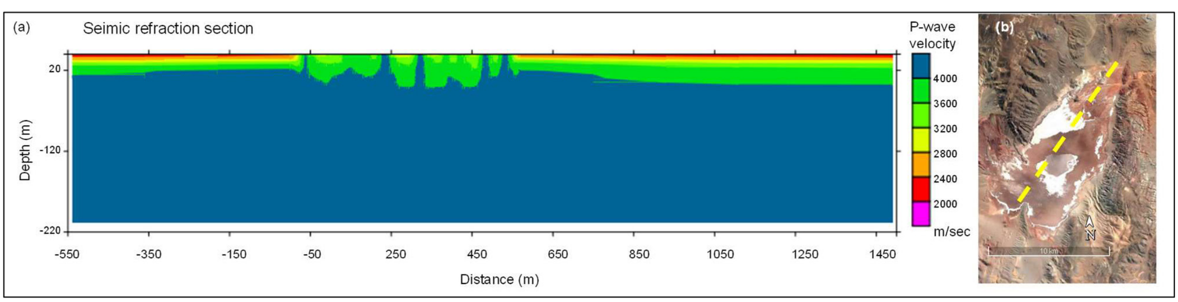

Figure 9. Reprocessing of a refraction seismic tomography section, located in the center of Pozuelos (Curcio *et al.*, 2022).

Reflection seismic

This method might work for basement delineation purposes and not within the multilayers system, since they present low acoustic impedances. However, it is not recommended due to its complex logistics that other methods such as gravimetry do not have. Note that, the basement in salt flat might be a hydrogeological basement (typically clays) and, in this case, the method is fully discarded (Figure 10).

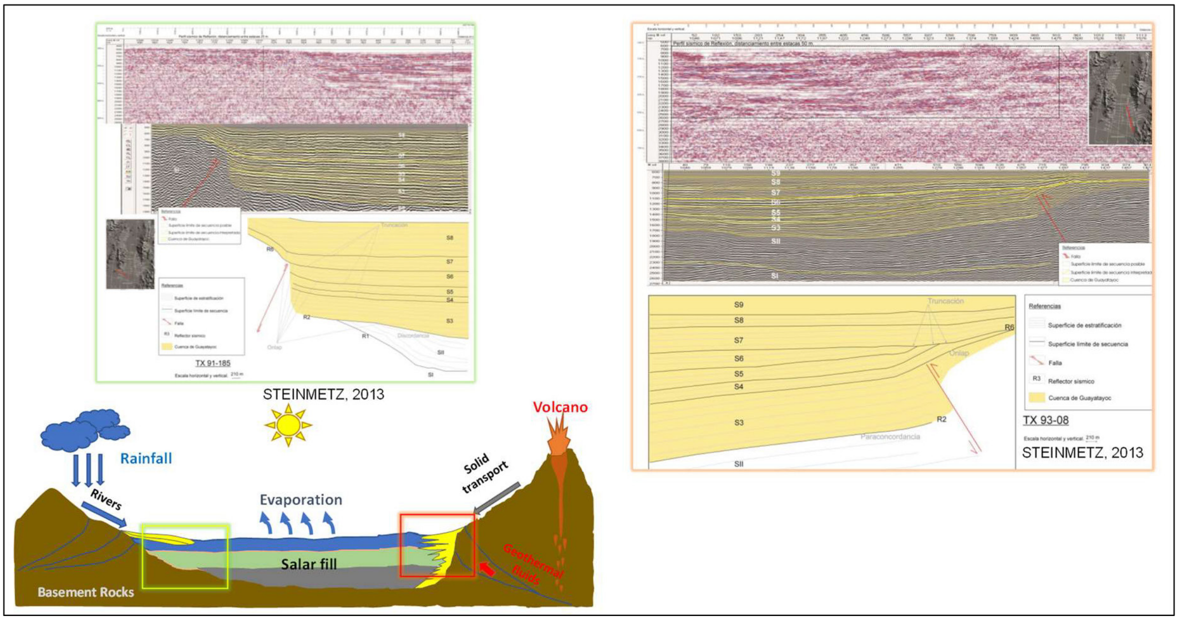

Figure 10. Example of a reflection seismic line in Guayatayoc basin (taken from Piethe 2021).

Magnetics

From the point of view of this method, the problem of the salt flats is similar to the exploration of sedimentary basins: detect a magnetic basement covered by non-magnetic sediments. There are various semiautomatic methods for depth to magnetic basement calculations but the magnetic data cannot be easily integrated with the MT data because susceptibility data are very scarce.

The effective multiphysics toolkit

The multiphysics toolkit comprises full tensor magnetotellurics gravity and electrical resistivity tomography.

Electrical Resistivity Tomography (ERT)

The ERT is an evolution of the 1D geoelectric techniques; hence, ERT is a DC method. However, it has many advantages over VES, since it is a high-resolution 2D/3D method and has high data density (Locke 1994). The field technique consists of a multichannel cable extended in the ground surface and configure the electrode device axially (Schlumberger, Wenner, etc.), so, a series of electrodes will be connected to the ground, to which a current in pairs will circulate, measuring the electric potential generated by that current in another electrode pair; after sending it out with a pair (emission pair), the current is transferred to another pair (reception pair). On the other hand, the same set of emission electrodes is used as reception electrodes at another moment of the survey, being able to calculate the apparent resistivity in the entire ERT profile.

The objective of the ERT survey for brines prospecting purposes is to determine the freshwater-brine contact at the edge of the salt flat. This information is very important since it allows studying the hydrogeological equilibrium in the charge-recharge system of the endorheic basin.

Full tensor magnetotellurics (Full tensor AMT/MT)

The magnetotelluric method study the diffusion of a natural electromagnetic wave over a wide range of frequencies to find a model (1D, 2D, 3D) of the electrical resistivity of the subsurface at depth. The natural sources of electromagnetic fields are originated in the ionosphere for the highest frequencies, corresponding to audio-magnetotelluric (AMT) frequency band, typically between 1 hertz to 104 hertz; and, in the magnetosphere for the lowest frequencies, corresponding to the magnetotelluric frequency band, typically between 1 hertz to 10-4 hertz. Cagniard (1953) and Vozoff (1972), provide the physical principles and development of magnetotellurics; Berdichevsky (1976), Smucker (1971), Chave *et al.* (1978), Egbert and Booker (1986), Jones *et al.* (1989), Ledo *et al.* (2002), Booker (2013), among others, provide and/or reviewed important contributions to MT development, processing, modeling and interpretation.

The main MT assumptions comprises the far field hypothesis and quasi-static hypothesis, hence, it is correct to consider the EM field as diffusive plane-polarized waves at the surface. Also, the variations in magnetic permeability of the rock are assumed negligible compared with variations in bulk rock conductivity. Note that due to the absence of artificial source, and assuming isotropy, the equation (2) becomes

$$\sigma\mathbf{E} - \nabla x\mathbf{H} = \mathbf{0}.. \tag{10}$$

The electric field and magnetic field, are related through the frequency dependent impedance tensor Z, which contains the information of the electrical resistivity distribution in the subsurface,

$$\begin{bmatrix} E_x \\ E_y \end{bmatrix} = \begin{bmatrix} Z_{xx} & Z_{xy} \\ Z_{yx} & Z_{yy} \end{bmatrix} \begin{bmatrix} H_x \\ H_y \end{bmatrix}, \tag{11}$$

and, the magnetic field components are related through the frequency dependent transfer function T or tipper vector

$$H_Z = \begin{bmatrix} T_X & T_Y \end{bmatrix} \begin{bmatrix} H_X \\ H_Y \end{bmatrix}. \tag{12}$$

The tipper is sensitive to lateral conductivity gradients. So, the Parkinson (1959) or Wise (1962) induction arrows, provides information of the localization, extension and polarity of the electrical current concentrations. The field measurement of E_x, E_y, H_x, H_y, H_z is called full tensor magnetotellurics and provides the geological information contained in both the impedance tensor Z and in the transfer function T. At this point it is important to highlight the following:

- CSAMT is not full tensor since it does not measure Hz so it does not solve equation 11.
- SCSAMT do not solve equation 11 and 12. Moreover, it does not provide a complete Z tensor in equation 11, since, as mentioned earlier, it measures 2 or 3 field components.

Recalling that some EM technologies are suitable in water prospecting and conventional mining prospecting, methods like TDEM, CSAMT, SCSAMT, AMT, among others, are not efficient in terms of deep of investigation. So, the question is why MT is an effective tool for lithium exploration purposes and basin characterization? The explanation relies in the low frequencies at MT method operates, that compensates the effect of the low electrical resistivity values in the skin depth relation (equation 9). Sensitive to conductance, MT prospects the entire conductive column and characterize the basement. Although the signal could be low, the equipment used has an outstanding storage capacity which provides enough dataset that resulted in enhanced signal to noise ratio during the advanced data processing (Smirnov 2003). On the other hand, a full tensor magnetotellurics provides extra interpretation attributes that cannot be achieved with other EM methods.

Gravity

The third leg of this tripod is a much older method but not for that less efficient: gravity. The measurements based in the, too well known, Newton's equation applied to geophysics, equation 7 in Figure 5, do not require further explanation. However, it is clear the inherent ambiguity of the method. With one value (g= gravity acceleration), two unknowns have to be cleared, the mass; m, (or density) of the geological structure creating the attraction and the distance from the point of measurement to the same (r). But it is also well known that having the value of one of the unknowns (usually, vertical distance: depth) the other is solved easily. In this study depths come from wells and from the results of MT soundings conveniently transformed. The overlapping of gravity effects of structures near one to the other is resolved in the stage of what is called qualitative interpretation. That consists in the application of filters that separate or enhace the effects of each one of the structures, laterally or in depth. And helps to locate faults, contacts, anticlines, lenses, etc. In few words it allows to know the architecture of the region of study. For example, the tilt derivative map (TDR) flat (Verduzco *et al.*, 2004).

$$TDR = tan^{-1}\left[\frac{VDR}{THDR}\right], \tag{13}$$

where VDR is the first gravity vertical derivative and THDR is the total gravity horizontal derivative.

$$THDR = \sqrt{\left(\frac{\partial g}{\partial x}\right)^2 + \left(\frac{\partial g}{\partial y}\right)^2} \quad . \tag{14}$$

The good results of the application of this filter are also discussed below. In all the salt flats the important density contrast between the basement and the overlaying sediments allows detecting faults and main structures by means of the application of filters and finally delineating, in depth, the base of the salt flat. The method reinforces its benefits because it integrates with the MT depths results, in a relatively direct way, to get the basement depth map, acting as an intelligent interpolator. Another benefit of gravity is that the depth data from new wells can be easily included in the calculation of a new, and better controlled, inversion.

Figure 11 shows a summary of the weakness and strength of each geophysical method in lithium exploration, based in the physical principles and information analyzed.

GEOPHYSICAL RESPONSE IN LITHIUM EXPLORATION - SALT FLATS							
Methods		Sensitivity to structure	Sensitivity to fluid	Depth of Investigation*	Field operation	Dimensionality	Main application
Seismic Methods	Refraction seismic	++	-	Shallow	+	2D, 3D	Lithology - Risk with high velocities halites
	Reflection Seimic	++	-	Deep	-	2D, 3D	Basement and structure
Electric (DC) / Electromagnetic (EM) methods	DC - SEV	~	+	Shallow	+	1D	Detect contact fresh water - brine, detect first conductive layer mapping
	DC -TE	++	++	Shallow	+	2D, 3D	Detect freshwater-brine contacts in environments that present lateral variation (fans and stratification)
	EM (TEM)	-	++	Shallow	++	1D	Detect contact freshwater/brine - First conductive layer mapping
	EM (CSAMT)	~	+	Shallow	+	2D	Ultrashallow mapping - first conductive layer mapping
	EM (full tensor AMT+ MT)	++	++	shallow to deep	+	2D,3D	Structure and fluid; **lateral variation**; attributes
Potential Methods	Gravity	++	-	shallow to deep	++	2D,3D	Structure and Basement
	Magnetics	++	-	shallow to deep	++	2D,3D	\` Magnetic\` Basement (metamorphic, igneous)

Figure 11. Geophysical response in brines exploration in salt flats. For all parameters (structure, fluid, depth of investigation, field operation and dimensionality), it is evaluated the performance of each technology: excellent (++), good (+), low (~) and not recommended (~).

METHODOLOGY VALIDATION IN POZUELOS SALT FLAT

Geologic Setting

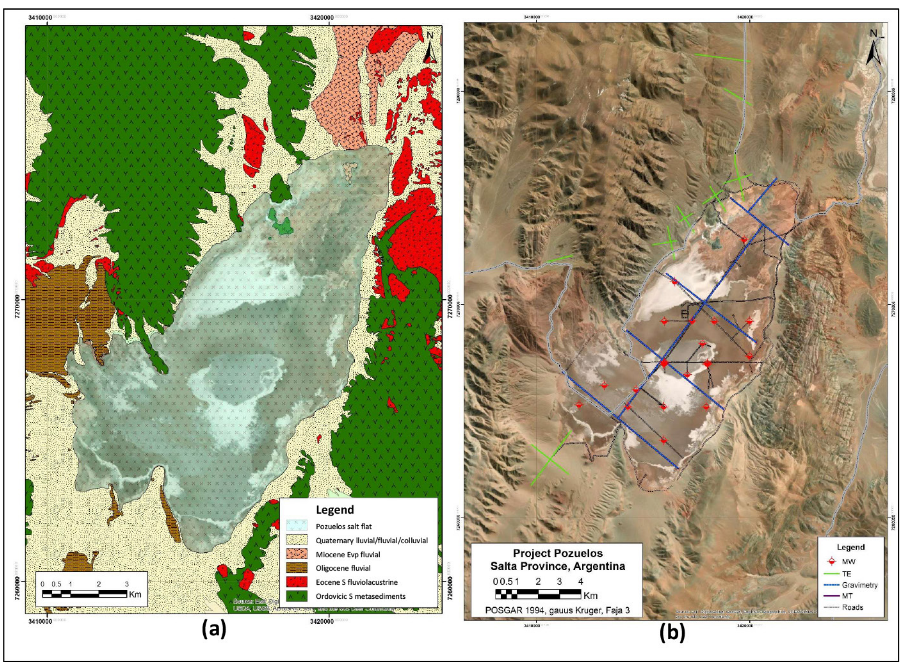

Figure 12. (a) Geological setting of Pozuelos salt flat (b) AMT/MT and Gravity survey (blue) and ERT survey (green). The red dots are the monitoring wells.

Regionally, the Pozuelos salt flat (Figure 12) was defined as an intra-arc/intra-plateau basin (Jordán and Alonso, 1987), which evolved in a seismically active volcanic framework, in an arid climate, with endorheic drainage and intense thermalism (Alonso, 1991). Several authors have proposed a more detailed genesis of these late Neogene intermontane basins as a result of transtensive and transpressive efforts (Kraemer *et al.*, 1999; Reijs and McClay, 2015).

The geology of the Pozuelos salt is made up of Ordovician and Cenozoic rocks. It is limited by two mountainous blocks of Ordovician age: Pozuelos edge (West) and Copalayo edge (East). The latter is strongly hydrothermalized and instructed by a Miocene porphyry body called Cerro Juncal (Argañaraz and Innes, 2003). On the northern edge, there are Cenozoic deposits such as the Geste Formation (Upper Eocene), which lie in angular unconformity on the Copalayo Formation (Ordovician). In the southwest there are red clastic sediments from the Vizcacheras Formation (Oligocene) and the rest of the formations correspond to deposits of the undifferentiated Pastos Grandes Group (Neogene) (Figure 12a).

Survey Design and Interpretation

It was collected ~30 km of ERT, which were distributed in the edges of the salt flat. The area covered by the salt flat is surveyed with magnetotellurics and gravimetry methods, both distributed the stations in ~40 km, with a depth investigation of 2 km for MT and of 5 km for gravity (Figure 12b). Examples of the field acquisition in Pozuelos and Pocitos salt flats are shown in Figure 13.

The ERT and MT interpretation is divided in three geophysical units: the highest electrical resistivity in red are interpreted as basement, which is also detected with gravity; the electrical resistivity in blue - violet (with the lowest resistivity of 0,1 ohm-meter to 1 ohm-meter) are interpreted as rock saturated with brine or wet clay; and green (mid resistivity) interpreted as rock saturated with fresh water with lower content of salinity than the violet unit.

Figure 14 shows 6 out of 13 ERT sections integrated in a 3D Volume. With each device of 120 channels, 10 meters of electrode separation and 23 levels, this survey achieved a depth of investigation higher than 150 m. The conductive blue unit has above a mid-resistivity green unit showing in this way the water recharge into the salt flat, whereas the red corresponds to the hard rock coincident to the topography 'out of the salt flat'.

The full tensor magnetotelluric results are shown in Figure 15, Figure 16, and Figure 17 (a) and (b). The first one, Figure 15, is a 1D section that presents 3 ultralow resistivity layer of electrical conductivity less than 0,1 ohm meter with its apparent resistivity and phase.

The second one, Figure 16, shows a 2D section in 1out of 7 lines collected, in this case, a SW – NE line, indicated in the map in yellow across the Pozuelos salt flat.

We report that the polar diagrams and skew indicate that the AMT/MT data dimensionality is 2D/3D. Recalling that the magnetotelluric method is sensitive to conductance (Keller, 1972; Strack, 1992), it is found two main conductive units. The shallower one, from surface, can reach 400 m thickness with exception in the NE of the area, where a fault indicates the end of the unit. According to the production wells, this unit couple a clastic or evaporites multilayer system where most of them are saturated with brine.

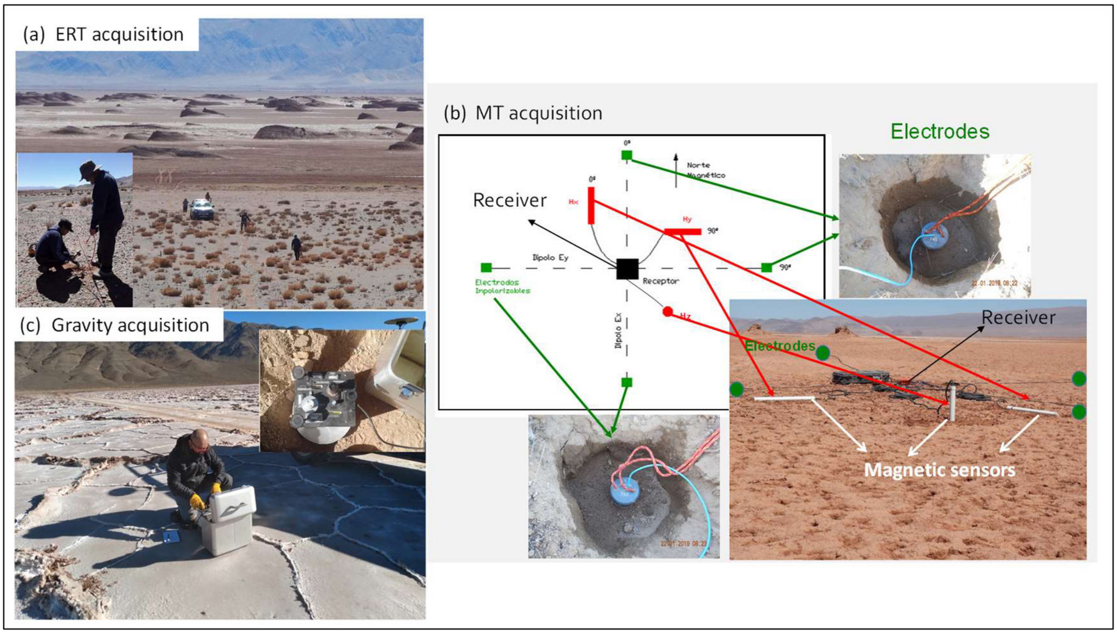

Figure 13. Field acquisition of (a) ERT (b) full tensor magnetotellurics and (c) Gravity. Pictures taken in Pozuelos and Pocitos salt flats (Courtesy of Proingeo SA, www.proingeo.com.ar).

The shallower portion of mid zone of the model has mid resistivity values that indicates a zone of recharging with low-salinity water. Note that would be impossible to monitor this unit with the TDEM or CSAMT with the characteristics described. Figure 17 (a) and 17 (b) presents a map view at 300 meters depth and 1000 meters depth that, respectively, showing the the ultra-low conductivity distribution at these depths. In the NE portion of the maps two high resistivity structures are detected and also correlate with the gravity results in Figure 18. The West part of the maps presents a resistive unit for all model depths. In green, is seen mid resistivity units which might be sediments with low salinity water content.

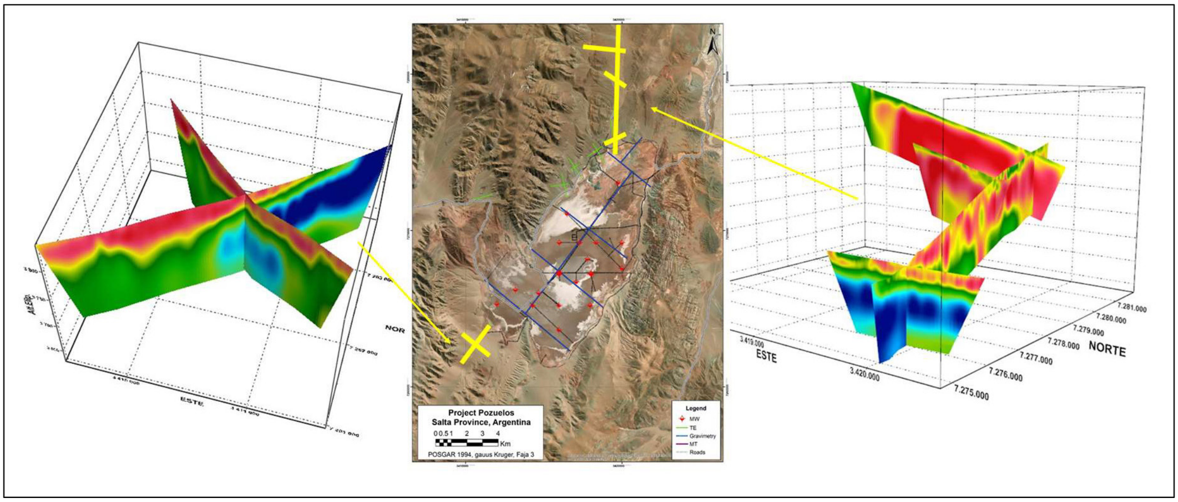

Figure 14. ERT results in Pozuelos salt flat (Curcio *et al*.,2022).

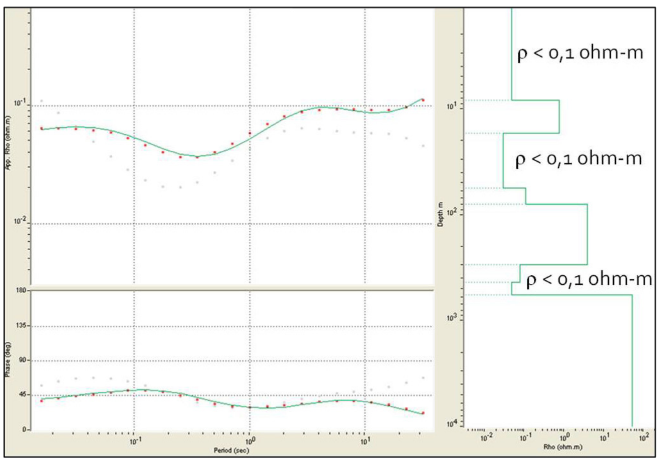

Figure 15. 1D model of magnetotelluric data. Note that the system is a multilayer system in concordance with well information.

The deeper conductive unit can reach a thickness of 500 meters in the mid - NE part of the model. This unit is also detected in the cross-lines but we cannot affirm if its low conductivity is due to a deeper multilayer system saturated with brine, or if it is due to wet clay, because the wells are shallower than 500 meters. We find an important inverse fault that divides the deeper part of the model. Figure 16 also shows 3 monitoring wells (MW): SP-2017-12 (close to MT16), SP-2017-06 (close to MT11) and PZ-18-02 (close to MT06) that will be used to validate the model.

The results of the gravity survey are shown in the complete Bouguer anomaly map calculated for a density of 2.40 g/cm^3 in Figure 18a. Relative maximums and minimums are shown, respectively, with red and blue lines with arrows. The thick dotted white lines indicate the interpreted faults/contacts. The black dots are the wells drilled in the salt flat. In the western and southern part of the map the yellow zone matches the limit of the salt flat with the mountain range that surrounds it.

The toolkit discussed here includes the qualitative interpretation of the gravity data. A complete set of enhancement/separations filters are applied, in the space and in the frequency domain. As an example, Figure 18b shows the tilt derivative map. The map, with the same interpretative scheme explained previously, shows the central minimum divided by a relative maximum, confirmed by the DDH-400 drilled well (which has a density log used in the next step).

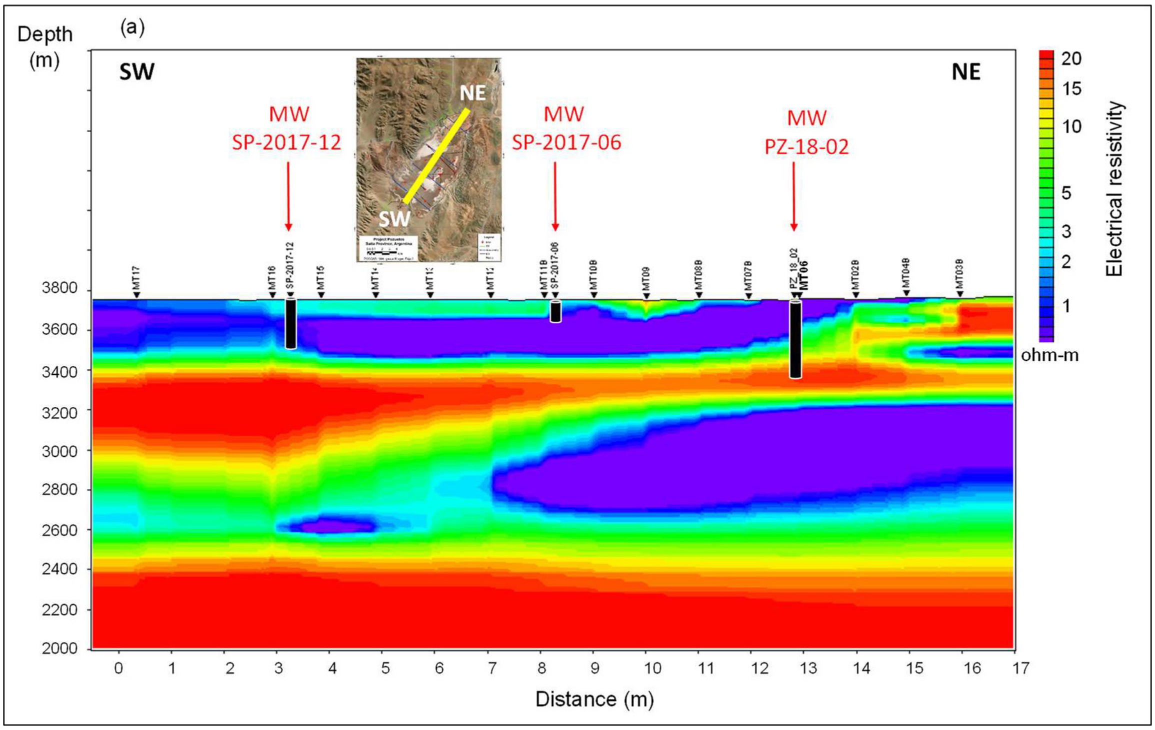

Figure 16. 2D SW-NE section of MT data, Pozuelos salt flat. The multilayer system is grouped in one conductive unit (Curcio *et al*., 2022).

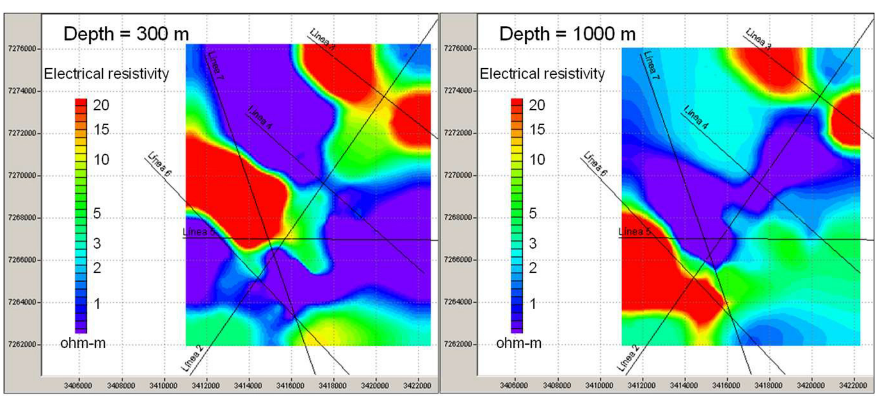

Figure 17. Map view of the MT survey at (a) 300 m depth and (b) 1000 m depth (Curcio *et al*, 2022).

Finally, the gravity and the magnetotelluric data are integrated in a 3D depth calculation. The magnetotelluric data is transformed in pairs density – depth, in the position of each MT sounding, in the following way: first, it was applied the Hacikoylu resistivity to compressional velocity (V_p, in km/sec) relation (Hacikoylu *et al.*, 2006),

$$V_p = 2.888 \left(\frac{\rho_t}{\rho_w} z\right)^{\frac{1}{6}}, \tag{15}$$

where ρ_t and ρ_w are the formation and water electrical resistivity, respectively (being their ratio adimensional) and z the depth of the formation in km. Note that this is an alternative expression to the conventional Faust's equation (Faust, 1953). Then, was used the Gardner's equation (Sheriff, 1991), which provides a density (d, g/cm^3) to V_p velocity relation

$$d = 0.31 \ (V_p)^{0.25} \ . \tag{16}$$

These pseudo - wells, and the wells drilled in the salt flat with density logs are the input to the 3D density inversion that provides the depth to the basement shown in Figure 18 (c). Finally, Figure 18 (d) shows the density sections along the gravity acquisition lines, where the positive structures are clearly delineated.

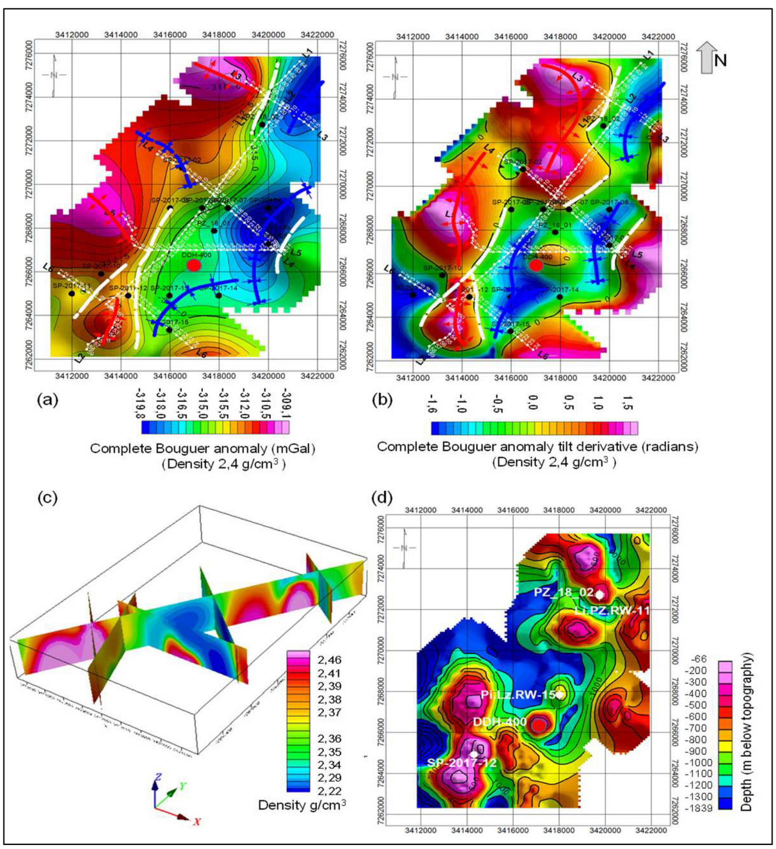

Figure 18. (a) Complete Bouguer anomaly; (b) Tilt derivative map; (c) density sections from the 3D inversion; and (d) Basement map.

The Pozuelos reservoir static model

The static reservoir model of the Pozuelos salt flat was constructed from geophysics and information from 18 wells drilled with the diamond system from which also were obtained cores (Figure 19).

As mentioned before, the filled salt flat is brine saturated. It has a density of 1.2 gr/cm3 and is highly conductive, whereas the basement conductivity presents 2 orders of magnitude higher than the brine-host rock, which indicates the base of the basin.

The deepest well reaches 470 meters, so, the sedimentary fill was earlier established at this depth. From the geophysical data and information of the density of the rocks, which were previously calibrated with a neutron-density profile in the northern area of the salt flat, the limit density between the in-filling and the basement was established as 2.40 gr/cm^3. The static model incorporates the basement, presenting its deepest area at 900 meters in the center of the salt flat.

Finally, it was differentiated eight lithofacies: 1. HBF (Fractured-banded halite, turquoise): made of halite crystals intercalated with clastic material in bands-shape, it represents an upper aquifer that reaches 30 meters depth indicating which in turn indicates a calm environment with depositional detrital material. 2. HBC (Massive halite ,blue): made up of massive halite crystals that extend up to 100 m thick; 3.Gr (Lower matrix- supported gravel, orange): consisting of an angular breccia with abundant sandy matrix, this facies is

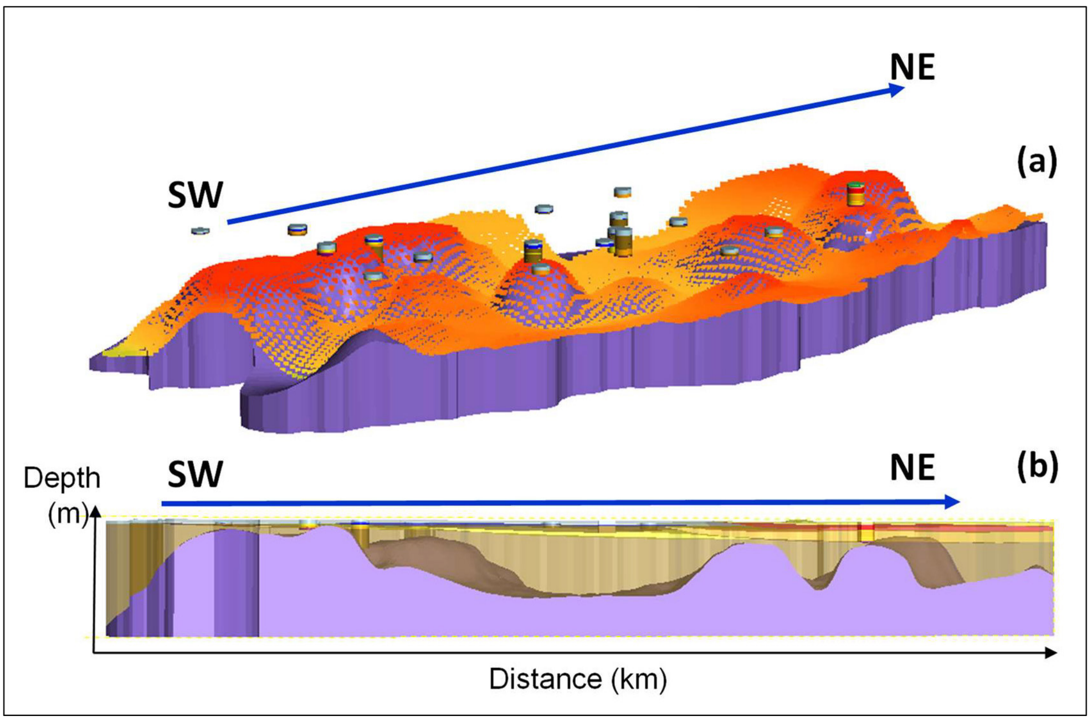

Figure 19. Pozuelos 3D static model that differenciates 8 facies.

interpreted as a high-energy flow on the margins of the salt; 4. Gra (Upper clast-supported gravel, red): constituted by a clast-supported gravel with clasts of size between 1.5 and 7 cm, it represents a high energy environment; 5. Sn (Lower sand, yellow): facies of fine to medium reddish sand with abundant clay; 6. Snd (Upper sand, yellow): facies of fine to very fine greenish sand with the presence of diatomite and abundant organic matter; 7. Si (Silt, brown): red silt and clay facies finely laminated in some sectors; 8. Bas (violet, Basament): strongly folded and fractured greenish pelite facies (Curcio *et al.*, 2022).

Model Validation

Figure 20 (a) shows the lithological description of 4 out of 18 monitoring wells (MW), which are included in the profile and maps shown in this paper (Figure 16, MT and Figure 18 (a), (b), (d), Gravity).

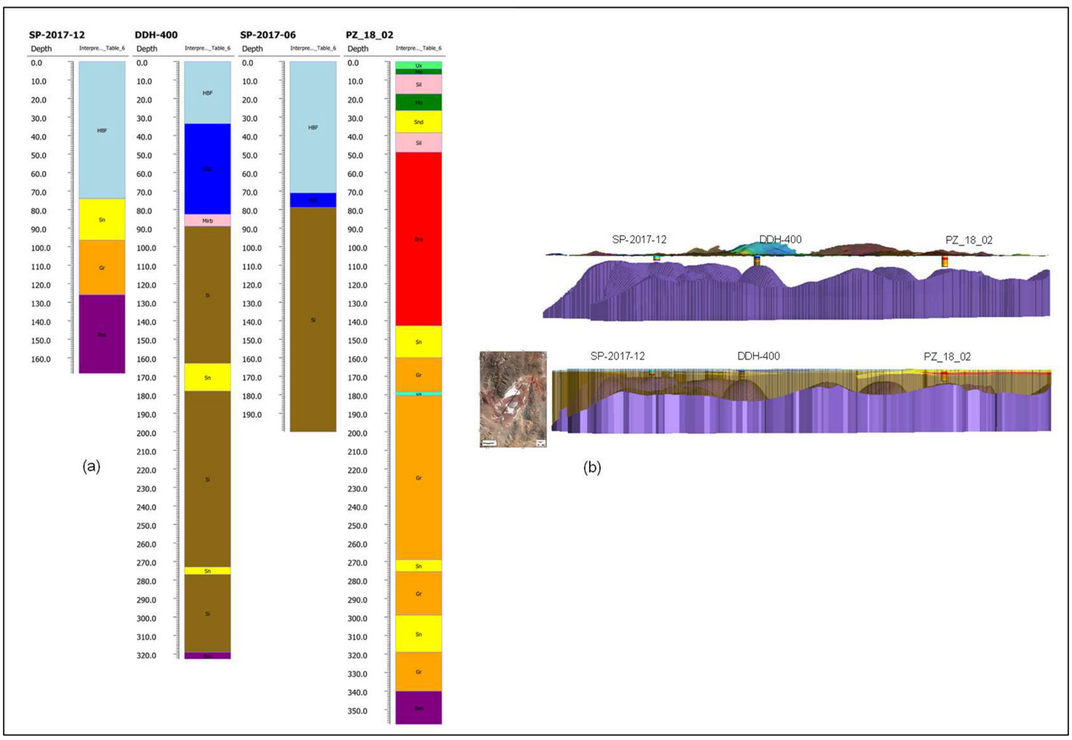

Figure 20. (a) Wells used for validation (b) Basement model with wells.

The SP-2017-12 MW and SP-2017-06 MW are shallow brine-saturated wells with TD in ~170 m and ~200 m respectively, both contains lithium in all its lithological column (with exception of the basement); the SP- 2017-12 finds the basement in ~130 m whereas the SP-2017-06 do not find the basement. The Pz-18-02 MW, with TD at ~360 m also is brine-saturated in all the column and finds the basement in ~340 m. The DDH-400, with TD at ~325 m, finds the basement at ~320 m. The petrophysical characteristics are good, with porosity average values of 10 % for evaporites and 8-15% for clastic rocks.

Figure 16 includes the SP-2017-12 (close to MT16), SP-2017-06 (close to MT11) and PZ-18-02 (close to MT06). The model presents a shallower part that is very conductive, in concordance with 2017-12 and SP- 2017-06 that are brine-saturated in all the column (with exception of the basement). The PZ-18-02 finds the basement at 340 m whereas MT finds the basement at 300 meters depth. Regarding SP-2017-06, as mentioned, it does not find the basement and MT11 predicts a basement at 350 meters depth. As MT is sensitive to conductance, we can affirm that the differences are within the 5 to10% of MT uncertainty.

Regarding Gravity, recall that Figure 18 (a), (b) and (d), shows the central minimum divided by a relative maximum, confirmed by the DDH-400 drilled well. In addition, Figure 20 (b) shows a selected basement profile obtained from gravity showing a good well tie with SP-2017-12, DDH-400, and Pz-18-02. The average of the absolute value of the errors/misties of the 4 wells used in gravity is around 70 m.

In consequence, the well validation confirms full tensor magnetotellurics and gravity as an effective tool for lithium prospecting and basin characterization. In addition, see the consistency between gravity and MT results that reinforces the feasibility of this geophysical techniques. Finally, with the ERT results we can affirm that the ERT-MT-Gravity toolkit satisfies the current exploration objectives.

CONCLUSIONS

We introduced to the Lithium industry and its and exploration frontiers and presented conceptual models and similarities with hydrocarbon industry. We found a suitable combination of geophysical techniques that fit the brines exploration objectives, which are the characterization of the salt flat in depth, fluid detection, basement delineation, definition of the main structures and main faults and detection of semi-freshwater aquifers in the edge of salt flats that contribute to its recharge and that are key to the water balance of the endorheic basin, which has the resource (lithium) in solution.

An analysis of the effectiveness of different geophysical techniques in terms of lithium prospecting is provided, concluding that full tensor magnetotellurics, electrical resistivity tomography and gravity comprises a multiphysics toolkit that fit the objectives set. This analysis comprises the state of the art in brines monitoring and might push the development of novel acquisition, processing and interpretation techniques.

The toolkit was validated in many salt flats, and we present the Pozuelos salt flat results, which is located in Northwest Argentina, Puna region; in addition, we provide the first deep imaging of the salt flat. Located in the edges of the salt pane, the fresh water-brines contact was well defined with ERT, which effectively contribute to the understanding of the freshwater recharge into the salt flat. The full tensor magnetotellurics results show 2 conductive units: the shallower one, reach 400 m thickness and is interpreted as a multilayer system saturated with brines, whereas the deeper one has a 500 thickness and could be either rock hosted with brine or wet clay. Both magnetotellurics and gravity characterizes the basement whereas gravity successfully delineated the main structures.

The results are in concordance with shallow and deep exploration wells. A methodology for the integration of AMT/MT and gravity through the construction of pseudowells was presented. Then, the construction of a static model though the integration of geophysical and well data provides a 3D model that finds the deepest basement area at approximately 900 meters depth. This work is ongoing and further processing and interpretation techniques are evaluated. Finally, this static model is the basis for the dynamic model to be used to understand the hydrodynamic behavior of the brine reservoirs and perform economical predictions.

FUTURE DIRECTIONS

As a result of the energy transition, the lithium industry is changing its exploratory conception, extending the exploratory frontiers and searching for the resource at higher depths; therefore, geophysics will be focused in the near future on regional integration, to achieve greater resolution, depth and dimensionality.

It was justified why today some geophysical methods do not give the desired response in lithium exploration; in many cases, the explanation lies in the low physical response of the earth to a given physical property, and, in other cases, it is due to the fact that 'good technologies' in near-surface, conventional mining prospecting and water prospecting find a technology limitation in brines exploration, opening in this way, potential technology development and implementation.

A methodology that integrates several geophysical methods has been presented and validated in several salt flats, including the Pozuelos salt flat. The effectiveness of the methods in 2D sections has been demonstrated, therefore, the next step is to densify and perform the 3D acquisition of magnetotelluric/EM, electrical resistivity tomography and gravity, in order to contribute to the development of reservoir and refine the interpretation, that includes the addition of the new deep wells drilled as control points, specially in 3D gravity inversion. Note that 3D magnetotellurics/EM and 3D gravity are processes that are very well developed and known in the hydrocarbon industry, as well 3D ERT in groundwater prospecting.

The fluid flow dynamics of lithium reservoirs, and brines in general, drives the exploration and production problem into a time lapse or 4D, hence, the inclusion of time lapse electromagnetics and gravity will be another frontier to inspect. Again, 4D in both electromagnetics and gravity are proven technologies in the hydrocarbons industry, in particular in waterflooding. In consequence, feasibility studies of using time lapse surface gravity, or a borehole gravimeter, and electromagnetics for reservoir monitoring are the next steps.

Also we can mention the feasibility study of making a drone-borne magnetic survey to be integrated with the gravity depths to the basement derived from wells, and MT data.

Finally, we know from data that this type of reservoir presents anisotropy. So, distortions coming from electrical anisotropy must be corrected in the future to reduce risks (Curcio 2020).

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