Lithium in Brines

Ihor A. Kunasz
Foote Mineral Company, Route 100, Exton Pennsylvania, USA

ABSTRACT

Beginning with the early production of lithium from brines at Searles Lake several lithium-bearing brine bodies have been identified in North and South America: Clayton Valley, Nevada; Salar de Uyuni, Bolivia; and Salar de Atacama, Chile.

Although all these occurrences are closely associated to past or more recent volcanic activity, which probably supplied similar lithium input into these basins, each basin exhibits a particular geochemical character reflecting specific structural, climatic and hydrological conditions. Salar de Uyuni appears to have undergone a relatively recent single evaporation cycle. The lithium in Clayton Valley can be traced to Upper Tertiary volcanism and a multi-cycle evaporation mechanism in the Quaternary period. In the Salar de Atacama, the high lithium concentrations have developed under intense evaporation-concentration conditions which resulted in a sodium chloride section exceeding 1,200 feet in thickness.

INTRODUCTION

In the lithium chapter of the 1975 edition of "INDUSTRIAL MINERALS & ROCKS," the 1960s were called the brine decade. Since then, this contention has held up and has been well supported by the identification of a number of lithium-bearing brine deposits in South America. Considering the territorial magnitude of this arid sector of the South American continent, and the number of saline desert basin occurrences, brines may conceivably become the predominant sources of lithium in the future. In passing, lithium-rich brines have also been discovered in association with numerous oil fields, but these occurrences are not treated in this paper.

Although salars are similar in many respects, they nevertheless exhibit individual characteristics. Various papers have been written on South American salars. The best comprehensive study is that of George Ericksen in Professional Paper No. 811. Much needs to be done, however, on the chemistry of these brines. Three salars have been selected for this presentation: Salar de Uyuni, Bolivia, Salar de Atacama, Chile, and Clayton Valley, Nevada USA.

GENERAL CHARACTERISTICS OF LITHIUM-BEARING SALINE BASINS

Lithium-bearing salares or desert basins have the following similar characteristics: 1) They occur within Tertiary or Recent volcanic belts, 2) They are closed structural depressions, and 3) They occur within the desert belts of the earth. These are also fundamental requirements for the occurrence of economic lithium concentrations. The first requirement simply establishes the source of lithium. The volcanic environment supplies the lithium either directly through hot springs or geothermal solutions or indirectly through the leaching of lithium-bearing volcanic or clastic sediments or by the recycling of trapped lithium-bearing solutions. This condition is met by all three salars. A corollary of these conditions is that ancient shields are not candidates for the occurrence of lithium in brine form.

The second requirement provides the necessary mechanism for retaining the dilute solutions introduced into the basin. Strong structural control is evident in Clayton Valley, Nevada and in Atacama, Chile. Direct structural involvement is not obvious at the Salar de Uyuni.

Finally, all "commercial" lithium concentrations are the result of concentration by solar evaporation. With the exception of the Imperial Valley Geothermal field where lithium concentrations as high as 280 ppm have been recorded, high lithium concentrations are not primary, but secondary phenomena, caused by concentration under proper climatological factors.

Although the fundamental character of the salars is similar, cursory examination reveals great variability in size, surface character, stratigraphy, structure, and chemistry.

The general character of the three salars has been portrayed in the following idealized diagram (Fig. 1) Clayton Valley is the smallest of the three. Its total surface area covers approximately 100 km². Salar de Uyuni on the other hand occupies a very large surface area of approximately 10,000 km², and thus represents the largest such desert basin in the world. The Salar de Atacama basin has an approximate surface area of 3,000 km² while the salt nucleus proper covers approximately an area of 1,400 km². The idealized stratigraphic column of each of the three basins indicates significant differences between them as well, and reveals their individual historical evolution. Salar de Uyuni appears to have undergone a single evaporitic cycle with little associated subsidence; Salar de Atacama formed under an intense evaporative cycle with associated major subsidence. Clayton Valley underwent alternative dry-wet climatic cycles under conditions of structural instability.

Salar de Uyuni. Salar de Uyuni is located in southwestern Bolivia at an elevation of 3653 meters. The Salar represents an immense body of salt, with a maximum surface dimension reaching 120 kms. The surface of the Salar is smooth permitting travel at high velocity; sample collection was thus relatively easy. Because of the dimension of the Salar, however, constant sighting on distant peaks was necessary in order to navigate. The meager subsurface information available suggests that the salt crust may be only about 15–20 meters thick. Extensive development of algal reefs some 75 meters above the present surface of the salar attests the existence of a much larger and less saline ancestral body of water—Lake Minchin. The presence of several algal terraces suggest lowering of the lake level in several stages. The ultimate stage represents saturation with respect to sodium chloride and resulted in the precipitation of the present crust. A sample collected from a depth of 15 cm. beneath the surface of the salt crust by W.D. Carter of the U.S.G.S. gave a radiocarbon date of 3,520 +/− 600 years suggesting that salt precipitation may have begun some 350,000 years ago. A comprehensive report of the details of work accomplished at the request of the Bolivian government is presented in an open file report (IR) BOL-7 written by George E. Ericksen and James D. Vine of the U.S.G.S. and Raúl and Ballón A. of the Servicio Geológico de Bolivia.

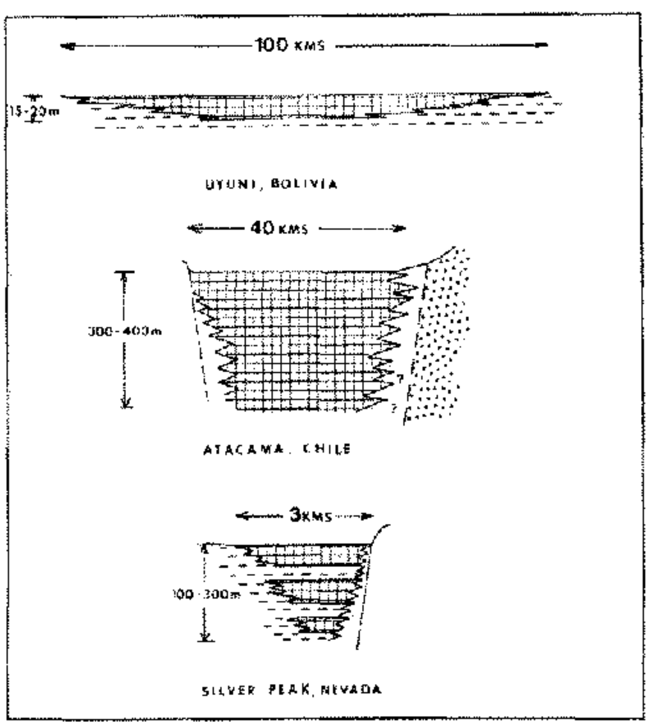

Figure 1. Idealized cross sections of three basins.

Salar de Atacama. The Salar de Atacama is located in northern Chile where it straddles the Tropic of Capricorn. The basin proper has a surface area of approximately 3,000 km² and the salt nucleus proper covers approximately 1,400 km². The salar is bounded on the eastern side by the Andean Cordillera and on the western side by the Cordillera Domeyko. The salt nucleus consists almost exclusively of halite facies with a development of very narrow marginal facies of sulfate and carbonate. From the north, large volumes of water discharge into the salar through the Rio San Pedro. The surface of the salar is one of the most rugged terrain known to this author. It is similar in many respects to the Devils Golf Course of Death Valley in California. Access to the salar is primarily through a 37 km. road or by helicopter.

The Salar de Atacama basin has been interpreted as a graben. The area is tectonically still quite active as witnessed by the presence of numerous fault scarps. Drilling performed over various parts of the basin indicates a minimum amount of 360 meters of halite diminishing to about 50 meters towards the margin of the basin. The extensive thickness of salt present in the basin indicates that saturation with respect to sodium chloride was predominant during most of the subsidence history of this basin. There are no beaches or algal reef complexes which would suggest desiccation from a much larger body of water. The ancestral chemical system was probably very high in solutes.

The source of the lithium in the basin is volcanic in origin. It enters the basin from two major directions. One is from the north where the El Tatio geothermal field is known to contain approximately 47 ppm of lithium, one of the highest recorded. The other source is very likely from the saline lakes located in the Andean Cordillera to the east of the salar. Structural interpretations suggest the presence of numerous east-west lineaments which may provide the conduits through which lithium-bearing solutions discharge into the salar.

Silver Peak—Clayton Valley, Nevada. The Silver Peak salt marsh is more complex, possibly because we know much more about it, having produced lithium over some 13 years. The Clayton Valley system can be considered as an intermediate between Salar de Uyuni and Salar de

Atacama as it incorporates the structural elements of the Salar de Atacama and it underwent fluctuating arid wet climatic cycles. The basin consists of interbedded fine grained sediments and halite. This is consistent with the proposed Quaternary cyclical climate for the Western U.S., although obvious breaks such as those reported by G.I. Smith at Searles Lake have not been yet recognized. Although the halite layers in the section contain large lithium reserves, production comes mainly from an unconsolidated volcanic ash aquifer. Structure maps of the volcanic ash indicates that some portions of the basin subsided as much as 150 meters during sedimentation.

COMPOSITION

All three basins contain abnormal lithium concentrations. As mentioned previously, the lithium must be attributed directly or indirectly to volcanic-geothermal activity of recent or older age. However, there is no doubt that the strength recorded today in the brine is the direct result of an intense concentration mechanism resulting from natural solar evaporation. Figure 2 shows some partial chemical analyses of the major cations contained in the three brines. All analyses represent the averages of several samples collected in each of the basins and for Silver Peak represent the production averages from the well field. It can be seen that the Salar de Atacama contains the highest lithium, potassium as well as magnesium concentrations. Concentrations as high as 5,000 ppm Li have been recorded at Atacama. This can be the result of either a richer source material such as for example the geothermal brines of El Tatio or, if we assume a similar source material for all three basins, that the evaporation-concentration mechanism was the most intense for the Atacama basin. The figure also indicates that ratios between various cations are significantly different between all three basins.

	Silver Peak	Atacama	Uyuni
Li	.023	.14	.025
K	.53	1.87	.62
Na	4.43	6.92	9.1
Mg	.033	.91	.54
Mg/Li	1.5	6.6	21.5

Figure 2. Partial chemical analysis (%) for three lithium bearing saline basins.

CONCLUSION

Silver Peak is presently the sole producer of lithium from a brine. The Salar de Atacama is presently under evaluation by Foote Mineral Company and the Chilean government as a source of lithium, potassium and possibly other chemicals. Salar de Uyuni is now another potential candidate. These three salars contain large potential resources of lithium that can satisfy any conceivable future demand for lithium.

The salars discussed in this paper are only three of the great number of salars existing along the North American and South American Cordillera. Not all will contain lithium, but many must certainly contain abnormal concentrations of lithium and other cations. Under the proper demand stimulus, more exploration will be conducted in various salars. The results of this exploration will most certainly reveal that lithium is not as rare an element as it was once thought to be.

DISCUSSION

H. Borchert:

Question. Is it possible to roughly quantify the parts of lithium in brines which are connected with 1) volcanic exhalations of thermal springs, 2) solar concentration processes, and 3) solutions of oil-field facies derivation?

Answer. I believe the question asks for lithium concentrations of brines of various origins.

1) Brines of volcanic origin (which result from solar evaporation as evidenced by salt bed occurrences in the section) vary in strength. At Silver Peak, Nevada, the strength is about 300 ppm Li (100–500), Atacama, Chile, 1,500 ppm Li (1,000–5,000), Uyuni, Bolivia, 100–700 ppm Li. 2) Brines of marine origin contain about 20 ppm (i.e. Dead Sea brine). 3) Oil-field brines vary from 100–700 ppm in areas from Arkansas, Texas (Collins, 1976).