A Strategic Metal for Green Technology:
The Geologic Occurrence and Global Life Cycle of Lithium

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Abstract

As technological demand for materials with specific physical properties has increased, the importance of strategic metals cannot be ignored. Strategic metals are those materials that have high economic value, are used in a variety of applications, and have few or no viable substitutions; supply may face the risk of restriction due to various technical, economic, or social factors. Mainly due to the growing demand for lightweight and powerful batteries, lithium has become such a metal.

While supplies of lithium have historically been mined from pegmatites, brine extraction from salars, or salt flats, has become the dominant source for lithium within the past decade. These salars are found in continental, volcanogenic highlands in arid regions of the world with internal drainage basins; the most noticeable exist in the Andean Altiplano. The lithium in the brines originates from the alteration and weathering of volcanic rocks. The South American salars can be classified by their morphology and by their chemistry. More importantly, the origin and evolution of the brines within these salars can be qualitatively analyzed using the concept of the chemical divide, which determines changing solute concentrations as water evaporates.

To quantify the stocks and flows of lithium at present, a global life cycle tracking the metal through its anthropogenic life stages (production, fabrication and manufacturing, use, and waste management) was developed. This life cycle appears to be the first of its kind for lithium and will begin to quantify the rates and types of use of lithium, as well as its potential for recycling. The combination of analysis of both the supply and demand sides of lithium gives a comprehensive picture of the current status of lithium, which is vital to understanding the future of this strategic metal.

Introduction

The incredible advancement in technology over the past several decades has radically changed human demand for metals. Traditionally, industry and consumers required high quantities of commodity metals such as steel, copper, and aluminum. Technological advances made in every major industry increasingly demand rarer metals with specific physical properties. While high volume production of metals like iron is not yet a thing of the past, platinum group metals and rare earth elements are becoming just as important in products that are taken for granted today. The transition from demand for bulk metals to scarcer metals has created some concern in political and industrial circles about adequate, reliable supplies of the rarer elements.

In 1981, a cooperative program called the International Strategic Minerals Inventory (ISMI) was formed by government officials from the United States, Canada, the Federal Republic of Germany, the Republic of South Africa, Australia, and the United Kingdom to address these concerns. The purpose of this organization was to publish publicly available and nonproprietary data about the short-term, medium-term, and long-term supplies of specific minerals for policy considerations. Although ISMI acknowledged that technical, financial, and political complications may interfere with supplies of these minerals, their focus was on deposits and on demand. ISMI evaluated minerals such as chromium, manganese, nickel, phosphate, platinum-group metals, cobalt, titanium, graphite, vanadium, tungsten, tin, zirconium, and lithium (Andstett et al. 1990).

ISMI referred to the minerals of concern as "strategic." This term, they acknowledged, was imprecise; they used it to refer to minerals that come largely from

foreign sources, that are difficult to replace, and that are important to a nation's economy (especially in its defense industry): Andstett writes, "Usually, the term implies a nation's perception of vulnerability to supply disruptions and of a need to safeguard its industries from the repercussions of a loss of supplies" (1990). Describing minerals as strategic therefore implies that modern society or industry has become dependent on them.

While there is some disagreement about the specific definition of a strategic material, the general consensus is that these qualities that make a certain metal strategic (Weil et al. 2009):

1) The metal is used in several important industry sectors

2) It may be difficult to find adequate substitutes for the metal in one or more important applications

3) The number of applications is large and is increasing over time

4) The metal is used in applications in which it is dissipated, meaning that recycling potential is limited

5) The metal has high economic value

6) Production and/or reserves of the metal are geographically concentrated

There is some recent disagreement as to the difference between strategic and critical metals. Strategic metals are usually associated with national security or military needs, while supply restrictions of critical metals can cause economic damage. Because critical has broader connotations than strategic, all strategic metals are critical, whereas not all critical metals are strategic (Committee on Critical Mineral Impacts on the U.S. Economy 2008). Throughout this paper, the two terms will be used interchangeably.

Lithium fulfills all of the requirements to be considered a strategic metal. Lithium is used in a variety of industries, including ceramics and glass, batteries, lubricating greases, air treatment, in the production of primary aluminum, and alloys. Only lithium in batteries and air conditioning systems can be recovered and recycled; the rest of the uses are dissipative. The amount of lithium used in batteries has increased 20% annually over the past few years and shows no signs of slowing down, as lithium-ion batteries may be ideal for use in electric and hybrid vehicles. Substitutes for lithium in most of its major applications have compromised performance (Jaskula 2010). The lithium production industry is extremely concentrated, with four companies producing 90% of the world's supply. One deposit, the Salar de Atacama, produces over 60% of the world's lithium, and there are only ten other deposits that are currently being exploited (Ebensperger et al. 2005); few other deposits have been identified (Figure 1).

Lithium was traditionally mined from pegmatite deposits, which may be zoned or unzoned. These pegmatite deposits are usually mined from the surface, and generally contain 0.59 to 1.36 percent lithium and contain between one and 50 million metric tons of ore. Zoned deposits contain lithium minerals such as spodumene, petalite, lepidolite, eucryptite, and amblygonite (Table 1). Unzoned deposits contain spodumene throughout the rock, which is homogenous. Spodumene may account for 25% of the rock; unzoned deposits tend to be the most important source of pegmatitic spodumene (Anstett et al. 1990).

However, brine extraction has become the dominant source of lithium within the past decade. Lithium is dissolved by chemical weathering like all other alkali metals; these weathering waters can become concentrated into lithium-rich brines if they are in

closed basins where evaporation exceeds precipitation (Anstett et al. 1990). These lithium brines commonly occur in the internal drainage basins in continental, volcanogenic highlands with arid climates. In South America, these salt flats are called salars and are an important feature of the Andean Altiplano (Warren 2010).

Although some research regarding the morphology and geochemistry of these salars has been done, few scholars have attempted to place these brine deposits within the context of the ever-expanding lithium industry. The predominant purpose of this paper, therefore, is to develop a comprehensive and multidisciplinary understanding of the lithium brine deposits. Towards that end, the geologic occurrence of the salars, the methods of extraction and beneficiation used to produce lithium from them, and the potential geopolitical and environmental consequences of brine mining in South America will be explored. Additionally, this supply-oriented research will be complemented by exploring the demand side of the lithium industry by evaluating the use of lithium in batteries and through the creation of a global anthropogenic life cycle for lithium. This life cycle will track the stocks and flows of lithium worldwide during 2007 through its life cycle stages of production, fabrication and manufacturing, use, and waste management.

The goal is to develop a broad yet rigorous understanding of the status and potential future of lithium. Lithium has gotten significant political and media attention in the past few years due to its potential use in electric and hybrid vehicles. Lithium batteries are ideal for vehicles because they have the greatest energy density of all batteries; this combination of power and low weight is vital to the development of electric and hybrid vehicles to replace traditional fossil fuel-driven vehicles. It seems likely that

lithium's application in a variety of "green" products will increase demand throughout the next century. Therefore, it is vital that scientists and design engineers, as well as leaders in government and industry, understand both the supply and demand sides of this strategic metal.

Geologic Occurrence

Origin of the Altiplano and Tectonic Context

Only the Tibetan Plateau is larger and higher than the Andean Altiplano. Stretching 1800 kilometers across northern Peru and Bolivian down through northern Chile and Argentina, the Altiplano exceeds an elevation of three kilometers across a 300 to 400 km wide plateau. What makes this feature even more awe-inspiring is that it did not result from continental collision or accreted terranes; instead, crustal shortening dominated its formation.

The original interpretation of the Altiplano was that it originated from the arc magmatism associated with the subduction of the Nazca Plate beneath the South American Plate: the addition of mantle material would be the cause of crustal thickening. However, it is now argued that magmatic processes were not important in creating the Altiplano. Instead, structural shortening of the crust, causing thickening, and thermal thinning of the lithosphere, causing uplift, are the dominant cause (Allmendinger et al. 1997).

According to Isacks' model for plateau development for the Altiplano, the first stage was a widespread, basin-and-range type shortening that occurred during the late Miocene; the second stage was a foreland fold-thrust belt (Isacks 1988). The foreland compresses and thickens the ductile lower crust, which then lifts up the upper crust into a

plateau. The lithosphere becomes hotter and weaker due to the high rate of convergence and the low angle of subduction. Using currently available information, 70 – 90% of the thickening is accounted for solely by shortening. The "missing" crust may be due to either insufficient data or from an unknown process of magmatic addition. Possibilities include hydration of upper mantle rocks to crustal velocities or local tectonic underplating (Allmendinger et al. 1997).

It should come as no surprise that such a vast feature would be heterogeneous. There are two distinct parts of the plateau: the Bolivian Altiplano and the Puna in Argentina and Chile. While a detailed discussion of their differences in topography, magmatism, and lithospheric structure is beyond the scope of this paper, it is worth noting that the two regions likely underwent the same stages of development at different times. For example, uplift began about 25 Ma in the Bolivian Altiplano compared to 15 – 20 Ma in the Puna; shortening ceased about 6 – 12 Ma in the Altiplano, while it lasted until 1 – 2 Ma in the Puna (Allmendinger et al. 1997). Several notable features in the Altiplano near northern Chile and their topographies are shown in Figure 2.

The Pre-Andean Depression is an intramontane basin in Chile that is at an altitude of 2.5 kilometers and is filled with Tertiary to Holocene continental clastic and evaporite sediments. It contains the Salar de Atacama (which should not be confused with the Atacama Desert) and the Punta Negra salar at its south end. The Salar de Atacama is the largest evaporitic basin in Chile at 3000 square kilometers. The western edge of the Salar de Atacama borders the Cordillera de la Sal, which is the remains of a Tertiary salar deformed during Cenozoic tectonism (Risacher et al. 2003).

The Western Cordillera is an elevated plateau above four kilometers in elevation. It is Miocene to Holocene and consists of rhyolitic ignimbrites and andesitic stratovolcanoes, which may tower as much as 2.5 kilometers above the rest of the plateau. Most of the smaller salars in Chile occupy the interior drainage basins demarcated by these volcanoes (Risacher et al. 2003).

The Bolivian Altiplano is another major intramontane basin; it separates the Western Cordillera from the Eastern Cordillera above 22 °S latitude. The Salar de Uyuni, which is the world's largest salt flat at 10,000 square kilometers, occupies the central trough of the Bolivian Altiplano (Risacher et al. 2003). It is estimated that the Salar de Uyuni may contain almost half of the world's reserve base of lithium (Jaskula 2010).

While the tectonic definition of the Altiplano is the part of the plateau reaching elevations above three kilometers, the more specific alternative definition is that the Altiplano consists of the internally-draining (endorheic) basins within this plateau (Allmendinger et al. 1997). The second definition is more appropriate for discussion of the salars, which inherently depend on closed basins for their origin and evolution.

Evaporite and Brine Deposits

Evaporite deposits are formed from the precipitation of salts when water loss is greater than water gain by the basin. The remaining brine becomes more and more concentrated over time. This process is usually driven by solar evaporation; it is worth noting that aridity is not always dependent on temperature because the driving force for evaporite deposition is the water balance. While some of the most famous evaporite deposits occur in hot deserts, evaporite deposits can also occur in cold, arid climates,

such as the highlands of the Andes. Although precipitation increases to the west (Figure

3), it is greatly exceeded by evaporation across the entire Altiplano (Risacher et al. 2003).

Evaporites are divided by the source of the original brine: they can be thalassic

(marine) or athalassic (nonmarine). Lithium brines in the salars of South America are

athalassic (Warren 2010). Beyond the requirement of the dominance of evaporation over

precipitation, an internal drainage basin is required for salar formation (Risacher and

Fritz 2009).

While the precipitated solid salts are often the target of extraction in evaporite

deposits, lithium brines are becoming the primary feedstock in certain deposits. These

include Clayton Valley in Nevada, Salar de Atacama in Chile, Salar de Hombre Muerto

in Argentina, and Dabuxum Salt Lake and Zhabuye Salt Lake, both in southwestern

China. The lithium in these brines is a result of weathering of volcanic rocks, which also

supply potassium, magnesium, and boron as well as more common ions like sodium and

calcium (Warren 2010). Because of the concentration of lithium in these salars, the

leaching of the rhyolitic rocks in the region likely occurred at temperatures around

400°C. Because lithium salts are highly soluble, lithium ions stay in solution and

concentrate over time (Risacher and Fritz 1990).

These lithium brines are "relatively unmodified pore brines (relict or connate

waters) residing in permeable saline subsurface lithologies" that are found in

"suprasealevel saline lacustrine settings in many arid continental high altitude

volcanogenic terrains" (Warren 2010).   Lithium salts are highly soluble, and so lithium

tends to stay in solution, although sorption onto clays (such as onto hectorite in Clayton

Playa, Nevada) is possible. The common minerals found in the salars are listed in Table 2; no minerals of lithium have ever been found in the South American salars.

Chile, Argentina, and southwestern China currently dominant lithium brine extraction, although Bolivia has the world's largest reserve base. These locations have been able to develop salars because of their history of aridity, which is required for the formation of evaporite deposits. The climate of the Altiplano has remained arid to semi-arid since the Miocene. Large saline lakes were present at various times throughout Chile and Bolivia; in the early Pleistocene, two large lakes in Bolivia were Lake Ballivian and Pre-Minchin. Present day Lake Titicaca is a remnant of the former (Rettig et al. 1980).   The latter lake evolved during the two major lacustrine periods in Bolivia: the Minchin, from 35,000 to 20,000 BP, and the Tauca, from 12,000 to 10,000 BP (Risacher and Fritz 1991); it is likely that Chile also experienced lacustrine phases, as well (Risacher et al. 2003). Fossil salt crusts found throughout the Altiplano are remains of these giant, deep saline lakes.

The variety of salars can be astounding, but some attempt has been made to classify them on the basis of their morphology and chemistry. Researchers have traditionally separated Bolivian salars from Chilean salars for the purpose of analysis, although the differences between the two groups may be less significant than between members of the same group.

Salar Morphology

Salars range in size from 0.03 km^2 to 10,000 km^2 (Figure 4); there are four salars greater in area than 2,000 km^2 while the rest are smaller than 400 km^2 (Risacher and Fritz 2009). Risacher proposed a morphology classification scheme in 1990 that has been

adopted by most researchers; it divides salars into four main types (Figure 5). However, the vast majority of salars exhibit more than one, if not all, of these physical types; the transition can happen laterally (different types in different places) or temporally (different types at different times during the year).

The first type is the saline lake or permanent salt lake. They rarely dry up and consist of relatively deep saline water, up to 10 meters, on top of a substance with low permeability. The precipitation of salts occurs mainly from freeze-out; precipitated solids commonly include natron, mirabilite, and hydrohalite.

The second type is the highly porous salt crust, which is often found in the center of the basin. The pores are usually full of interstitial brine, while the dominant solids are gypsum and halite. This type represents a more complete stage of evaporation where fluid inflow is minimal.

The third type is the playa, which is found at the central depression of the basin. A confined aquifer is saturated by the reduced interstitial brine, commonly a few meters deep. A very shallow pool of water, spring-fed and on the order of a few centimeters to a few decimeters deep, often lies on top of the muddy lacustrine sediments. This surface pool usually dries up annually during the dry season and is not directly related to the brine underneath. If it is above the water table, the brine is affected by oxidation and evaporation. Capillary action draws up the brine into the sediments, and can precipitate gypsum, mirabilite, and ulexite; these minerals can often be found in irregular, unzoned lenses.

The fourth type is an exposed unconfined aquifer. These occur when unconsolidated deposits of gravel and sand fill a basin and the water table is at or higher

than the topographic surface; a very shallow lake is produced. Salts freeze out or evaporate.

Salar Chemistry

There are two classes of solutes in the Andean salars: those derived from alternation of volcanic rocks, which produce dilute inflows, and those resulting from brine recycling, which produce brackish water. These waters have historically been referred to as ALT (alteration) and EVA (evaporite leaching) waters, respectively (Risacher and Fritz 1990).

Risacher and Fritz (1990, 2009) compared the composition of these dilute inflows to the composition of water in North America that was affected only by the weathering of andesitic to rhyolitic rocks, similar to the igneous petrology of the Andes (White et al. 1963, 1980 as qtd. in Risacher and Fritz 1990, 2009). The similarity of the Bolivian dilute inflows to the North American waters, as illustrated in Table 3, suggests that the Bolivian inflows result only from the alteration of volcanic rocks, without the involvement of hydrothermal activity or evaporite dissolution.

However, Chilean dilute inflows are more concentrated than their Bolivian counterparts. The increasing proportion of concentration is not the same for all solutes; for example, silica is enriched only 1.7 times more than in Bolivian brines, but sulfate is enriched 8.1 times. The source of the extra sulfate is unlikely to be from the dissolution of gypsum and anhydrite, because calcium would be enriched by approximately the same amount of sulfate. The more likely explanation is the oxidation of sulfur in volcanic glass, as Chilean volcanoes are more sulfuric than their Bolivian counterparts (Risacher and Fritz 2009):

$$S + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+$$
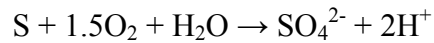
The brackish inflows were once thought to result from the dissolution of halite in ancient salars or from the mixing of waters with brines (Risacher and Fritz 1991). However, it is more likely that brine mixing is the dominant process operating to produce the brackish inflows. While there are large deposits of Neogene evaporites in the Andes that consist mainly of halite and gypsum, the outcrops have very low concentrations of bromine (Pueyo et al. 2001). If the evaporite deposits were the main source of solutes for the brackish waters, the low level of bromine would be preserved in the inflow waters, but this phenomenon is not observed. Instead, the concentration of bromine in the brackish inflows is consistent with dilute inflows mixing with brines. The origin of these unknown, underground brines that mix with dilute waters to produce the brackish inflows is unknown. Two hypotheses seem possible for the origin of the brines:

The first explanation is that the source is ancient salars trapped underneath volcanic formations. The climate of the Altiplano has remained arid to semi-arid since the Miocene, concurrent with volcanic activity. Under the Principle of Uniformitarianism, salars probably existed in the Altiplano throughout this period of aridity. These ancient salars could consequently covered by lava and pyroclastic flows. The brines would then be released and would be available to mix with dilute inflows; however, only very large salars could supply the amount of brine required, as smaller volumes would be quickly exhausted (Risacher and Fritz 2009). The other major problem with this explanation is that the high heat from the volcanic activity would have vaporized surface water; only brines protected by sediments could be preserved (Risacher et al. 2003).

The more likely source is currently existing salars. Because the bottoms of the vast majority of salars are at least somewhat permeable, the salars are in dynamic equilibrium with their surroundings. Leaked solutes are recycled within the same salar or in adjacent ones; this flow may be driven by high heat flow. Outflux of leaking brine is compensated by the influx of brackish waters, which keeps the concentration of solutes relatively constant (Risacher and Fritz 2009).

In this scenario, steady state can be attained in two different scenarios depending upon the permeability of the bottom sediments. If the bottom is impermeable, the concentration of conservative solutes (bromine and lithium) will increase, reducing the brine's rate of evaporation. At a high enough concentration, the vapor pressure of the brine will balance the relative humidity. However, if the bottom is permeable, steady state is achieved when inflow flux balances outflow flux (Risacher et al. 2003).

One way to determine if a lake is at steady state is to take the ratio of a component's total mass in the lake to its annual input; the result has the dimensions of time. If the age of the last event that could have perturbed equilibrium (be it climatic, geologic, or anthropogenic) is known and is greater than this ratio, then the ratio is the residence time of the component in the lake. Residence time and infiltration rate are inversely related (Risacher et al. 2003). The annual flux and concentration of the solutes in the inflow is equal to the annual leakage of waters and the concentration of solutes in the lake in this salt balance.

Ancient trapped salars likely have provided solutes in the past, but their supply has been exhausted. Recycling of brines between and within existing salars accounts for the production of brackish inflows because these brines mix with dilute waters. .

Brine Evolution

Brine evolution is modeled after Hardie and Eugster (1970, 1978; as qtd. in Risacher et al 2003): during evaporation, the concentration of solutes in the brine increases, and the minerals that precipitate out do so in order of increasing solubility. The concept of the chemical divide arises because the ionic activity product must be equal to the solubility product, so when a mineral precipitates, the concentration of all the solutes cannot increase at once. As evaporation continues, the solution becomes enriched in some solutes and depleted in others depending upon the ratio of solute concentrations at the beginning and the minerals that precipitate.

There are two methods to determine brine evolution. The first approach is qualitative; it determines the changing composition of the evaporating solution step-by-step. Its focus is on the pathway, not on the solute composition. The second approach is quantitative; it focuses on the composition of the solution as it evaporates. Risacher and Fritz (2009) use the simulation code EQL/EVP, which is based upon the ion-interaction model and calculates the composition of an evaporating solution step-by-step. Another method is based upon Al-Droubi et al (1980; as qtd. in Risacher et al. 2003), which is valid for solutions with carbonate and silicate species. Throughout the discussion of these methods, the square brackets refer to total concentrations in mol/l or mmol/l.

The Chemical Divide Model

While there can be dozens of minerals in an evaporating basin, only a handful of them control the evaporative pathways. Therefore, these minerals are the focus of analysis of brine evolution, as shown in the qualitative modeling approach summarized here (after Risacher and Fritz 2009). Sodium and chlorine dominate most brines in terms

of concentration, but they do not affect the evaporation pathways because both solutes are conservative until extreme stages of evaporation. Therefore, brine evolution is characterized by calcium, sulfate, and carbonate, even though these ions are less concentrated in solution. This method is not meant to actually predict the evaporative evolution that creates a brine, but is instead meant as an educational tool.

The first mineral to precipitate out of a solution is usually calcite, $CaCO_3$:

$$[Ca^{2+}] * [CO_3^{2-}] = K_{calcite}$$

Because the ion activity product must remain constant, calcium and carbonate cannot increase simultaneously; instead, the concentration of one ion will increase and the other will decrease. This is the first chemical divide and it determines two pathways: the alkaline path (carbonate increases while calcium decreases) and the neutral path (calcium increases and carbonate decreases). Which pathway a brine will follow depends on the relative concentrations of calcium and carbonate in the water.

If the brine follows the neutral pathway after the first chemical divide, the concentration of calcium increases and the next mineral to precipitate is gypsum, $CaSO_4 \cdot 2H_2O$:

$$[Ca^{2+}] * [SO_4^{2-}] * [H_2O]^2 = K_{gypsum}$$

Once again, the concentrations of calcium and sulfate ions cannot both increase at the same time. This represents the second chemical divide for the neutral pathway: the two possible pathways are the calcium-rich, sulfate-poor path and the calcium-poor, sulfate-rich path. Because some of the initial concentration of calcium was used up in precipitating calcite, the pathway the brine takes after the second chemical divide depends on the concentrations of calcium and sulfate at the beginning of gypsum

precipitation and not on the initial concentrations of the brine. The sulfate-rich pathway produces sulfate-rich ($Na-SO_4-Cl$) brines; the calcium-rich pathway produces calcium-rich ($Na-Ca-Cl$) brines.

If, however, the brine follows the alkaline pathway after the first chemical divide, pH controls the precipitation of magnesium salts, which can be either carbonates or silicates:

$$Mg^{2+} + nH_4SiO_4 \rightarrow Mg\text{-silicates} + 2H^+$$

$$2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2$$

$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3$$
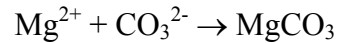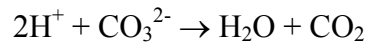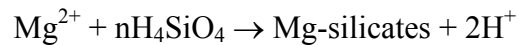
Because both possibilities utilize carbonate, it is possible to reverse the alkaline path to the neutral path if the decrease of carbonate is sufficient. These magnesium salts control the second chemical divide for the alkaline pathway: one produces $Na-CO_3-Cl$ brines and the other produces $Na-SO_4-Cl$ brines.

The Alkalinity Approach

The alkalinity approach (Al-Droubi et al. 1980, as qtd. in Risacher et al. 2003) to brine evolution is more useful than the concept of the chemical divide in predicting pathway, and can be performed without computer modeling. The same general concept is the same as the above method, but the alkalinity approach is more rigorous. The total alkalinity of a solution is:

$$\text{Alkalinity} = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] + [B(OH)_4^-] - [H^+]$$

Because all of these terms are interdependent and therefore difficult to manipulate, this operational definition of alkalinity is combined with the electro-neutrality equation.

Alkalinity is therefore defined as the difference between the conjugate cations of the strong bases and the conjugate anions of the strong acids:

$$\text{Alkalinity} = [Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] - [Cl^-] - 2[SO_4^{2-}]$$

When calcite precipitates, this equation can be rewritten:

$$\text{Alkalinity} - 2[Ca^{2+}] = [Na^+] + [K^+] + 2[Mg^{2+}] - [Cl^-] - 2[SO_4^{2-}]$$

As long as calcite is the only mineral that precipitates, the concentrations of the solutes on the right hand side of the above equation increase linearly with the concentrating factor, F, of the solution that is evaporating. Using sodium as an example and with the subscript $_0$ symbolizing the concentration of the initial solution,

$$[Na^+] = F * [Na^+]_0$$

Where F = mole number of water in initial solution / mole number of water in solution, such that:

$$F = (H_2O)_0 / (H_20)$$

Therefore, the alkalinity equations for calcite precipitation can be rewritten as:

$$\text{Alkalinity} - 2[Ca^{2+}] = F * \{[Na^+]_0 + [K^+]_0 + 2[Mg^{2+}]_0 - [Cl^-]_0 - 2[SO_4^{2-}]_0\}$$

Which can be simplified to:

$$\text{Alkalinity} - 2[Ca^{2+}] = F * (\text{Alkalinity}_0 - 2[Ca^{2+}]_0)$$

If the initial solution has more alkalinity than twice its calcium concentration ($\text{Alkalinity}_0 > 2[Ca^{2+}]_0$), as the solution evaporates, the difference between alkalinity and calcium concentration will increase and alkalinity will dominate. If the initial solution has less alkalinity than twice its calcium concentration, then calcium will dominate alkalinity as evaporation continues. Comparing alkalinity to twice the calcium

concentration will therefore allow determination of what pathway a solution will follow after this first chemical divide.

Magnesium silicates or carbonates precipitate in the early stages of evaporation like calcite: if both calcite and magnesium minerals are precipitating, the alkalinity equation is rewritten:

$$\text{Alkalinity} - 2[Ca^{2+}] - 2[Mg^{2+}] = [Na^+] + [K^+] - [Cl^-] - 2[SO_4^{2-}]$$

$$\text{Alkalinity} - 2[Ca^{2+}] - 2[Mg^{2+}] = F * \{[Na^+]_0 + [K^+]_0 - [Cl^-]_0 - 2[SO_4^{2-}]_0\}$$

If the initial solution as more alkalinity than twice its calcium and magnesium concentrations (in other words, if the left hand side of the above equation is positive), then the evaporating water becomes an alkaline brine enriched in carbonates and depleted in calcium and magnesium. If the opposite is true, the solution will follow the neutral pathway and will be depleted in carbonate. If alkalinity is greater than twice the calcium concentration but less than twice the calcium and magnesium concentrations, it will follow the alkaline pathway while calcite is precipitating and will then follow the neutral path once magnesium salts begin to precipitate.

If the solution is following the neutral path, it will become more and more enriched with calcium and may precipitate gypsum. The precipitation of gypsum is the second chemical divide in the evolution of a neutral brine; either brines that are calcium-rich/sulfate-poor or calcium-poor/sulfate-rich are produced according to the ratio of calcium to sulfate at the beginning of gypsum precipitation, not of the initial solution. Figure 6 provides a schematic to summarize the brine evolution pathways.

The brine evolution process results in three major groups of brines: alkaline, sulfate-rich, and calcium-rich. The alkaline brines are $Na/HCO_3 - CO_3 - Cl$ and follow

the alkaline I – IA pathway. The sulfate-rich brines are Na/SO$_4$ – Cl and follow either the

sulfate-alkaline I – IIA – III pathway or the sulfate-neutral II – III pathway. The calcium-

rich brines are Na – Ca/Cl and follow the calcic pathway II – IV. While theoretically

possible, the pathways I – IIA – IV and II – (Na/CO$_3$-Cl) have not been observed in any

natural evaporating solution (Risacher et al. 2003).

It should be apparent from this analysis that even a small variability in calcium,

magnesium, or alkalinity in the initial water can change the resulting brine dramatically

(Risacher et al 2003). Because the solute concentration in the dilute water is mainly due

to rock alteration, the lithology of the region is the dominant control in brine evolution

and fate. Moderately mineralized igneous rocks that are weathered tend to produce

waters that follow the sulfate alkaline pathway; highly mineralized igneous rocks' waters

follow the sulfate-neutral pathway. Sedimentary rocks, which usually contain high levels

of calcium, tend to produce calcic brines (Risacher et al. 2003).

Additional Variables in Brine Evolution

The brine evolution model described above operates under the assumption that the

evaporating basin is essentially a closed system that is not affected by other

environmental factors. Risacher et al. explain that the discrepancies between the brines

predicted by the model and the brines that are actually observed in the Altiplano are due

to these other variables that affect the evaporation pathway. These variables have the

most impact if they affect a solution in the early stages of evaporation (Risacher et al.

2003).

For example, wind-blown dust and salts may enter the water from the atmosphere,

potassium can partake in exchange reactions with clay minerals, and sulfate

concentrations can decrease from bacterial reduction. All of these scenarios have the potential to change the evaporation pathway a solution will follow. Additionally, inflow waters that are following different evaporation pathways may mix in a large basin with complex lithology (Risacher et al. 2003).

These "disturbing forces" account for the reason why Chile only has one alkaline salar out of more than 200 observed. This unexpected deficiency is due to the high concentrations of native sulfur in the Western Cordillera and the deposition of gypsum-rich dust. The sulfur is oxidized and thereby acidifies the water, reducing its carbonate concentration significantly. The gypsum enriches the waters with calcium, but because of calcite's low solubility, carbonate concentrations decrease.

In summary, South American salars occupy the internal drainage basins of the Altiplano where evaporation exceeds precipitation. The lithium in these salars that makes them of economic interest originates from the weathering of volcanic rocks. While the variety of salars in terms of their size, chemistry, and morphology is astounding, some classification is possible. It is also possible to predict the type of brines produced and the evaporation pathway followed by a solution. All the information that is required is the alkalinity and the concentrations of solutes like calcium, magnesium, sulfate, and carbonate; however, environmental contamination may change the composition of a solution significantly and thus change the type of brine it produces.

Extraction and Beneficiation

Hard Rock

In 1978, Averill and Olson argued that extraction technology for pegmatites was well-developed, and further research and development would not be cost-effective;

however, researching methods of extraction from clays and, more importantly, brines should be a priority. They also acknowledged that currently available reduction and refining methods may not be suitable for large-scale operations.

At the time of their paper, hard rock mining for lithium dominated the supply. Pegmatite ore bodies are the most common type of ore deposit for lithium; the lithium is most commonly found in the minerals lepidolite, petalite, and spodumene.

Lithium from pegmatites is recovered and concentrated by froth flotation, hydrometallurgical extraction, and precipitation from aqueous solution (Averill and Olson 1978). It is crushed to finer than 0.3 mm, cleared with caustic and sometimes sodium sulfide, and then conditioned with oleic acid, a collector (Figure 7).

To extract lithium from spodumene (which is usually 2% lithium), one of two processes is used. The first process, called the acid process, uses heat to convert spodumene from its alpha to beta structure, which is then ground to 0.15 mm and treated with sulfuric acid. With the addition of heat, the lithium becomes lithium sulfate, which is soluble. Magnesium, calcium, aluminum, and iron are removed before the lithium is precipitated with sodium carbonate. The second process, called the alkaline process, requires heating spodumene or lepidolite with limestone. The lithium silicates become lithium hydroxides after leaching the lithium aluminates. This hydroxide solution is processed with evaporators, which crystallizes lithium hydroxide monohydrate.

Lithium chloride is used as the source material for the production of lithium metal in a process similar to the production of sodium: through molten salt electrolysis. It is electrolytically reduced from a fused salt that is a mix of potassium chloride and lithium chloride; this is a low volume and high energy process. A steel box in a refractory-lined

fire box is heated to 500 °C, and is typically 3 cubic meters in size. Lithium metal is

reduced at the steel cathodes and chlorine is oxidized at the graphite anodes, as shown in

the following reactions:

Anode reaction: $2Cl^- \rightarrow Cl_2 + 2e^-$

Cathode reaction: $Li^+ + e^- \rightarrow Li^0$
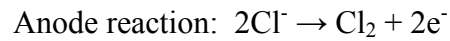
Five kilograms of chlorine gas are produced for each kilogram of lithium metal,

which presents an environmental and worker health challenge; it also makes fire control

equipment mandatory. This process is also extremely energy-intensive: one kilogram of

lithium metal requires about 46 kWh of energy, not including heating. Processing

minerals from hard rock sources also has high transport costs and because the deposits

tend to be relatively small, hard rock production is not often able to take advantage of

economies of scale (Ebensperger et al. 2005).

Two decades later, little progress had been made towards reducing the

environmental impact and increasing the production of lithium metal, which is used

primarily as the anode in lithium ion batteries and in alloys with magnesium and

aluminum (Kipouros and Sadoway 1998). The electrolytic reduction process now

requires a central mild steel cathode with opposing graphite plates, which serve as the

anode. A bell-like structure prevents the mixing of the liquid lithium and chlorine gas.

Anhydrous lithium chloride is the source of lithium, and potassium chloride is used as the

solvent.

Potential ways to reduce the environmental impact of this process include

replacing electrode materials; the authors suggest titanium diboride as a replacement for

graphite. This material has been proved in the laboratory setting and is now being used

in a few industrial applications. There are several emerging technologies that may provide alternatives to the currently-used process, although all are economically unviable currently (Kipouros and Sadoway 1998).

Brines

While oceans contain 0.2 ppm lithium and some clays, such as hectorite, may contain appreciable amounts of lithium, exploiting these potential sources is both technologically and economically infeasible at present, although increasing demand and value may spur further exploration in this area. Therefore, brines are the only true alternative to hard rock mining.

Production of lithium from brines has an inherently smaller environmental impact than hardrock mining, although lithium brines also require extensive processing. In addition to less impact, brine extraction is also less expensive, and is increasingly driving pegmatite producers out of competition (Warren 2010).

In 1978, Averill and Olson argued that the two factors that were the dominant controls on lithium production from brines were the grade of the brine and the concentration of calcium and magnesium. Lithium has traditionally been recovered using solar evaporation or flotation, which is ineffective for dilute brines. Averill and Olson suggested ion exchange or liquid-liquid extraction to concentrate lithium from more dilute brines and to reduce concentrations of calcium and magnesium.

When concentrations of calcium and magnesium are low, operators have traditionally treated the brine with lime to precipitate magnesium. The brines can be evaporated to recover commodities such as potash, borax, salt cake, soda ash, and dilithium sodium phosphate. Froth flotation is utilized to extract the phosphate from

these materials; the dilithium sodium phosphate is treated with sulfuric acid and sodium carbonate to recover the lithium, as was done in the 1970s in Searles Lake, California (Averill and Olson 1978).

Brines that contain enough lithium to be economically exploited are mostly found in arid, high altitude, continental volcanogenic terrains (Warren 2010). Beyond concentration of lithium in the brines and the chemical constraints of calcium and magnesium contamination, there is a major physical constraint on brine extraction: the porosity of the salt crust. As depth of the host aquifer increases, effective porosity and permeability approach zero at about 50 m depth. Because of this constraint, there is a limit to economic brine recovery to these shallower regions (Figure 8).

Current Brine Operations

Different operators use different methods to produce lithium. In the Salar de Hombre Muerto in Argentina, FMC uses a proprietary alumina adsorption system to extract lithium directly from the brine. The Salar de Atacama in Chile produces lithium carbonate from solar evaporation ponds. This facility is able to produce lithium carbonate with 90 ha of evaporation ponds, which is only 1/20th of the area required at Clayton Valley, Nevada due to the extreme aridity of the climate (Warren 2010). Zabuye Salt Lake and Dabuxum/East Taijinier Lakes in China both produce lithium carbonate from extraction and solar evaporation. In the US, the plant at Searles Lake was in operation from 1961 – 1978 and produced lithium carbonate as a byproduct of salt cake and soda ash production, although the source is likely too depleted to become viable again; Clayton Valley in Nevada may be viable (Warren 2010).

The Salar de Uyuni in Bolivia, which contains almost half of the world's reserve base of lithium (Jaskula 2010) may come on line in the next decade. However, production from this salar is currently limited to 40 metric tonnes each month from a state-run pilot plant; it also has very high Mg:Li ratios and therefore would require pretreatment with calcium hydroxide before evaporation. High Mg:Li ratios drive up the price of production (Figure 9).

The lithium industry's moment of truth was in 1997, when Sociedad Quimica y Minera de Chila S.A. (SQM) began to produce lithium chloride from the Salar de Atacama and processed this material into lithium carbonate in Antofagasta. SQM capitalized on the fact that brine extraction was high volume and low cost, and it managed to drive down the market price of lithium by 50% in 1998 (Table 4). Facilities in the US, Russia, Australia, Argentina, and China reduced production or shut down entirely; they produced lithium hydroxide from spodumene, petalite, and lepidolite, which is simply not cost effective when competing with brine extraction (Ebensperger et al. 2005). This is the most recent paper summarizing the state of the industry.

Since 2002, the companies producing lithium from brines are SQM in Chile, Chemetall (in Chile and the US), and the FMC Corporation in Argentina. In China, the China Xinjuang Nonferrous Metals Corporation of Mingyuan produces lithium carbonate from brines as well as from domestic and imported ores. Chemetall and SQM accounted for 75% of the market in 2002. It is important to note that while the Salar de Atacama produced 60% of the world's lithium in 2003, the total value of the industry to Chile is just over 1% of the revenues they receive from copper mining. It is also interesting to

note that the industry is highly concentrated, as four companies produce 90% of the world's supply of lithium (Ebensperger et al. 2005).

Chile is likely to continue to dominate the world's supply of lithium for decades, at least while the Salar de Uyuni remains essentially unexploited. It therefore seems likely that the Chilean government will find that promoting sustainable development will be a priority in this century. The traditional way that governments "share" the benefits of a mining project are through company taxation and royalty payments, which may affect the operations of SQM depending upon the political climate in the country (Ebensperger et al., 2005). The demand for lithium brines will likely be driven by increased use of lithium-ion batteries in technologies such as electric and hybrid vehicles, as well as in consumer electronics (Yaksic and Tilton 2009).

Lithium Batteries

Introduction

As part of the American Recovery and Reinvestment Act of 2009, the US Department of Energy gave lithium battery suppliers and manufacturers a $930 million grant to promote research on lithium-ion battery technology (Jaskula 2010); an additional $10 million was granted to Toxco, the recycling company planning to build the first lithium battery recycling facility in the United States (Hamilton 2009). This staggering amount was a part of a $2.4 billion dollar grant to develop the American capacity for electric drive vehicles through both manufacturing and deployment. This sum, combined with the $25 billion of direct loans as part of the Advanced Technology Vehicles Manufacturing Incentive Program in 2008, illustrates the ever-increasing importance of lithium, which is apparent even to politicians.

This governmental commitment is a reflection of recent trends: the amount of lithium consumed for battery manufacturing has increased by 20% each year during the latter half of the decade. In 2008, lithium ion batteries accounted for 70% of the global rechargeable battery market, which was worth $7.4 billion that year (Jaskula 2010). As concerns over America's dependence on foreign oil and the consequences of climate change grow more serious, consumers, politicians, and scientists are all looking for easy solutions. Lithium-ion batteries, which may be ideal for electric, hybrid electric, and plug-in hybrid vehicles, are becoming an increasingly attractive technology.

Types of Lithium Batteries

Lithium is suitable for batteries because of its physical properties: it is the most electropositive metal (Table 5). It is also the lightest metal (M_W = 6.84 g/mol and ρ = 0.53 g/cm^3); therefore, it has the highest energy density (Figure 10). This combination of power and low weight makes it ideal for applications in which portability or mobility is a top priority; an excellent example is electric vehicles. Lithium has been used to make batteries for decades; consequently, there are dozens of types of lithium batteries. However, all lithium batteries fall into three general categories: lithium anode batteries, lithium ion batteries, and lithium air batteries.

All batteries have the same basic components: an anode, a cathode, and an electrolyte solution containing dissolved salts. During discharge – when the battery is converting its chemical energy into electrical energy – ions move from the negative electrode (anode) to the positive electrode (cathode). Oxidation occurs at the anode, and reduction occurs at the cathode. The difference between batteries is the type of material

that is used in each of these three components and their configuration. Electrolytes can act as a buffer for ion flow or can participate in the reaction (Brain and Bryant 2000).

Lithium anode batteries, or lithium batteries, were the earliest lithium-based batteries to be developed and commercialized. They are primary batteries; primary batteries are not rechargeable because one or more of their electrodes is depleted as the battery is used. Lithium batteries utilize lithium metal or lithium compounds as anodes. Because lithium is the most electropositive metal, these batteries produce roughly double the voltage of traditional alkaline batteries. They are often used in smaller consumer devices such as clocks, calculators, and cameras. Lithium batteries have a lifespan of 15 or more years, and thus are often used in implanted medical devices such as pacemakers (Protomatic 2010).

The second class of lithium batteries is lithium-ion batteries, which are rechargeable (also called secondary batteries). When they are charging, lithium ions move from the positive to the negative electrode, which is the reverse of the discharge reaction. Lithium-ion batteries have many advantages over older battery technology. Lithium-ion batteries can store the same amount of energy as a lead-acid battery with one-sixth of the mass, they lose only 5% of their charge each month (versus 20% for nickel-metal hydride batteries), and they can withstand hundreds of cycles of charging and discharging. However, many lithium-ion batteries currently on the market have a lifespan of less than five years and have been known to ignite (Brain 2006).

The rechargeable nature of lithium-ion batteries is due to intercalation compounds, which let lithium to move into the anode or cathode. Intercalation compounds allow the reversible insertion of a molecule between two other molecules;

several inorganic compounds allow alkali metals to react reversibly in this manner (Tarascon and Armand 2001). During discharge, lithium ions move from the anode into the cathode; during charging, lithium ions move from the cathode into the anode.

There are many different types of lithium-ion batteries that use different materials for the electrodes and electrolyte. Cathode material is usually a lithium oxide, such as $LiCoO_2$ or $LiMn_2O_4$; the anode is often graphite; and the electrolyte consists of lithium salts, such as $LiClO_4$, in an organic solvent. Lithium-ion batteries therefore have extensive material demands beyond that for lithium – for example, batteries account for 25% of global cobalt demand. Using recycled cobalt and nickel in lithium-ion batteries represents a 51.3% savings in natural resources and a 45.3% savings in fossil fuel requirements (Dewulf et al. 2010).

Lithium air batteries, or lithium metal-air batteries, are a developing technology that may be feasible within the decade (Luoma 2009). If they are successful, they will have the energy density of gasoline. They utilize a lithium anode and a porous carbonate cathode, in which oxygen molecules are reduced by lithium ions during discharge to form lithium oxide or lithium peroxide. The electrolyte has been demonstrated with a gel polymer (Abraham and Jiang 1996). One of the current research challenges is finding a membrane that allows oxygen in but keeps moisture out, since lithium can ignite when exposed to water.

Battery Recycling

As lithium batteries become more widely used, they will become a larger proportion and quantity of the waste stream. It is important that waste management practices, whether they be landfilling or recycling, must be safe as well as economical.

Fortunately, the lack of metallic lithium in lithium-ion batteries gives recyclers more flexibility in cell disassembly and processing (Lain 2001). It is estimated that up to 98% of lithium can be recovered from battery recycling (Jungst 1999).

There are two recycling processes that are currently in use for the recycling of lithium-ion batteries. The first type, the so-called Toxco process, can be used to process any type of lithium waste products. The material is first cooled in liquid nitrogen and is then shredded and mixed with water. This process usually produces lithium hydroxide. The second type, the so-called Sony process, incinerates the cells. While lithium is lost, cobalt can be recovered (Lain 2001).

A process that utilized emerging technology is being developed at AEA Technology Batteries in the UK and is effective for lithium-ion batteries that use cobalt. First, the batteries are shredded mechanically without being exposed to water, with which lithium violently reacts. The electrolyte is separated from the solids with a suitable solvent, which is then evaporated away at a reduced pressure. The boiling point at this reduced pressure must be below the decomposition temperature of lithium (80 °C). A different solvent is used to recover pieces of the electrode (Lain 2001). The residual electrode particles are lithium cobalt oxide, which is electrochemically reduced in the following reaction:

$$2LiCoO_2 \text{ (s)} + H_2O \rightarrow 2CoO \text{ (s)} + 2LiOH \text{ (aq)} + \tfrac{1}{2}O_2 \text{ (g)}$$

Lain suggests that the recycling of lithium-ion batteries will be profitable because most of the income will come from selling the products, not charging the disposers. While lithium battery recycling is still in its infancy, it should be a priority for research and development funding both from industry and from the government; as will be

demonstrated later, recycling of lithium-ion batteries may significantly reduce the amount of primary lithium that must be extracted to meet increasing demand.

Beyond the requirement of adequate recycling facilities, it is necessary for programs to recover batteries to be created. If lithium battery manufacturers or companies that use lithium batteries in their products (such as car and computer companies) implement programs to help consumers and industries give their used batteries back at the end-of-life, battery recycling will be much more successful. A combination of corporate and social infrastructure to retrieve batteries, combined with advanced recycling technology, may result in a significant supply of secondary lithium. A large secondary reserve base may alleviate some concerns over supply restrictions of primary lithium.

Geopolitical and Environmental Complications

The stark beauty of the Salar de Uyuni, the world's largest salt flat, seems unlikely to inspire the kind of fervent political debate currently raging about the future of Bolivian lithium. While Bolivia has almost half of the world's estimated reserve base of lithium, it produces only about 40 metric tonnes each month from a pilot plant on the Salar de Uyuni. The pilot plant is operated by the Corporación Minera de Bolivia (Comibol), which is the state-run mining company. It built and operates the plant from a $6 million investment; significantly more funding would be required to produce enough lithium to affect world supply (Jaskula 2010).

A long history of resource extraction by foreigners has left the Bolivian government and public suspicious at best of attempts made by international mining companies to extract lithium. One Comibol supervisor said, "The previous imperialist

model of exploitation of our natural resources will never be repeated in Bolivia. Maybe further down the line there could be the possibility of foreigners accepted as minority partners, or better yet, as our clients. This is our ideal. We will supply them with lithium with no middlemen" (McDougall 2009).

The current Bolivian president, Evo Morales of the Movimiento al Socialismo (MAS) party, has capitalized on this feeling to maintain popularly through his term. He nationalized the natural gas industry in 2006 by marching with troops to occupy the gas fields (Zississ 2006). His approval rating increased 80% after doing so, indicating the disdain most Bolivians hold for foreign extraction companies (Lehoucq 2008). While the public seems to support Morales' reversal of market-friendly policies, the international community has reacted less positively, often claiming that President Morales is compromising the free market and democracy in Bolivia mainly out of concern for his party's power, rather than being driven by a genuine concern for the public. During Morales' presidency, Bolivia has fallen from 31st to 74th on the Bertelsmann Management Index, which evaluates a country's ability to achieve development goals within a stable democratic framework (Lehoucq 2008).

Oil and gas extraction, as well as metals mining, has resulted in significant environmental damage and social disruption, but with a small fraction of the profits staying within Bolivian borders. There is a general feeling within South America's poorest country that they are not seeing enough benefits, be the economic or social, from foreign exploitation of their resources. The Bolivian Minister of Mining, Luis Alberto Echazu, said, "We want to send a message to the industrialized countries and their companies: we will not repeat the historical experience since the fifteenth century: raw

materials exported for the industrialization of the west that has left us poor" (Kahya 2008).

On top of the loss of profits from its resources to international mining companies, the Bolivian economy is affected by the volatility of mineral and oil and gas prices, which may have ramifications for all of its industries. The political scientist Fabrice Lehoucq argues that Bolivia's riches in mineral and hydrocarbon resources are ironically undermining its development: "Bolivia's dependence on resource rents and mineral exports has often exposed the country to booms as commodity prices rise, followed by disastrous busts…that undermine the profitability of other exports because of exchange-rate appreciation" (2008).

Bolivia has been called the Saudi Arabia of lithium by many commentators (Romero 2009), but thus far, pressure from Japanese and European companies to make deals for extraction have been thoroughly rebuffed. The new Bolivian constitution that came into law last year has a provision that gives indigenous groups control over the natural resources in their territory, which may allow tribes to block mining companies entirely. However, in the past, Bolivia has allowed international companies to stay on as minority partners, so Bolivia continues to be courted by companies like Mitsubishi hoping to persuade Morales to give them a guaranteed piece of the lithium pie. While government officials and many of its people do not look kindly upon foreign companies having anything to do with lithium extraction, some Bolivians are rooting for development, which they view as an opportunity to improve economic and social conditions in this struggling country. A Bolivian economist, Juan Carlos Zuleta, said, "We have the most magnificent lithium reserves on the planet, but if we don't step into

the race now, we will lose this chance. The market will find other solutions for the world's battery needs" (Romero 2009). While a few indigenous people manage to eke out a living on the Salar de Uyuni by selling salt they dig by hand, there are limited economic opportunities in the highlands, and some locals feel like lithium extraction may be their best bet to improve their lot. Pedro Camata, a teenager who lives near the salar, said, "I've heard of the lithium, but I only hope it creates work for us. Without work here, one is dead" (Romero 2009).

Beyond the geopolitical complications that may affect Bolivia's desire and ability to export lithium, significant environmental damage from extraction may threaten future lithium supply, as well. Opponents to development claim that lithium extraction will disturb huge areas of the salar permanently and will demand large quantities of water, which may threaten supplies to the arid region's inhabitants (McDougall 2009). However, Marco Octavio Rivera of Bolivia's Environmental Defense League notes that brine extraction of lithium is one of the least environmental harmful methods of mining (Friedman-Rudovsky 2009).

In the end, of course, the Bolivian government will control the fate of the lithium extraction industry in the country. It is important for international companies, from those in the mining industry to those manufacturing hybrid vehicles, to realize that while lithium-ion batteries may lessen the industrialized world's dependence on Middle Eastern oil, they may cause a dependence on the Saudi Arabia of lithium. Trading one dependence for another in the name of green technology may not be as green as it first appears.

The Global Anthropogenic Life Cycle of Lithium

Introduction

      The global anthropogenic life cycle of lithium is inspired by the methodology developed by the Stocks and Flows (STAF) project at the Yale Center for Industrial Ecology. The STAF project has produced life cycles for a variety of commodity metals, including copper, zinc, iron, silver, and nickel. The STAF methodology focuses on the four stages of a metal's life cycle (production, fabrication and manufacturing, use, and end-of-life) at three geographic levels (country, regional, and global). While the STAF methodology aggregates the country data into regional cycles and then aggregates the regional cycles into the global life cycle, there is not sufficient information available for lithium to easily generate the country and regional level cycles. Unlike these major commodity metals, lithium is not used in such great quantities. Therefore, a global basis was developed for lithium; hopefully it will be used as a stepping-stone for top-down analyses in the future.

      The STAF methodology is an example of material flow analysis; the focus can be anthropogenic or natural cycles. Anthropogenic material flow analyses track the flows and stocks of the material through four life phases: production, fabrication and manufacturing (F&M), use, and waste management and recycling (WM). The spatial and temporal boundary conditions for an MFA can be quite variable, but the fundamental time and space units for the STAF analyses are by country and by year. Because this is a global life cycle, the country level is not the fundamental space unit for the lithium cycle. Import and export trade is important for the country and regional cycles, but has a net zero impact for the global cycle. In more detailed cycles for lithium in the future,

databases like the UN Comtrade Database will be useful for import/export information, but trade not an issue at the global level.

The STAF team was also able to assign confidence levels, based upon the Bayesian probability approach, to indicate the reliability and accuracy of the data collected. While the mathematical rigor of Moss and Schneider (2000, as qtd. in Graedel et al. 2005) is outside of the scope of this paper, a more general discussion of the reliability and limitations of the data will be discussed.

While the results of these life cycles are interesting unto themselves, they can also be used to explore the effects of future changes in supply, demand, and/or product applications. They may also be used to estimate the size of the secondary reserve base, or the stocks currently in use that have the potential to be recovered and recycled. For strategic metals such as lithium, where the risk and impact of supply restriction may be a concern, the potential to recycle in-use stocks may alleviate some concern about supply of primary material.

Building the Life Cycle

The mantra of the STAF project might as well be "never correct and never finished"; because of sometimes severely restricted availability of necessary data, assumptions must be made and sometimes proxy data must be used. The purpose of generating this life cycle for lithium is to produce a first estimate of the stocks and flows in 2007 using readily available information applied with reasonable assumptions.

The easiest way to create the life cycle is to focus on the inflows and outflows for one life cycle stage at a time. Because the quality and availability of the data tends to

decrease from production to waste management, it is advisable to start at the beginning of the life cycle. The sources of the data and any assumptions made will be explained here.

All calculations are done in metric tonnes of lithium and are rounded to two significant digits. Data from the year 2007 is used, except where noted. The life cycle that was generated is found in the Life Cycle and Future Scenarios section at the end of this paper.

Production

The inflow to the production life cycle stage is from the lithosphere; the outflow is processing losses. Yaksic and Tilton (2009) assumed recovery rates based upon the source of lithium:

- 50% recovery rate for hectorites

- 50% recovery rate for pegmatites

- 45% recovery rate for brines

- 20% recovery rate for ocean water

Pegmatites and brines currently produce the vast majority of lithium supplies each year; recovery of lithium from clays and ocean water is economically unfeasible currently. Operations in Argentina, Chile, and China exploit brines, while other countries mine pegmatites. Because the USGS Mineral Yearbook (Jaskula 2010) provides production data, not extraction data, the production of lithium must be divided by the applicable recovery rate to determine the approximate amount of lithium that was extracted to produce the specified amount. The 45% brine recovery rate was applied to Argentina, Chile, and China; the 50% pegmatite recovery rate was applied to all other countries.

The inflow of lithium from the lithosphere to the production stage is 55,000 metric tonnes; the total outflow of lithium from the production life cycle to the fabrication and manufacturing stage is 26,000 metric tonnes. The outflow of lithium from the production life cycle to the environment ("repository") is 30,000 metric tonnes; this outflow represents the lithium that is lost during processing. It was assumed that the waste was not reprocessed to recover more lithium.

Fabrication and Manufacturing

The total inflow of lithium to the fabrication and manufacturing (F&M) stage is the amount of lithium coming out of the production stage; traditionally, this flow is divided into intermediate lithium products. The total outflow of lithium from the F&M stage to the use stage is divided into product flows. No information was available for manufacturing losses; therefore, it was assumed that the loss of lithium during F&M was 10% of incoming flows. This value is typical for metal flows analyzed by the STAF team (Johnson et al., 2005). Therefore, the total outflow of lithium from F&M to use is 23,000 metric tonnes.

The amount of lithium in each intermediate product is extrapolated from the percent of lithium that is used in each application and the form of lithium the application requires. SQM, a Chilean chemical company, estimated the main applications for lithium in their Annual Report from 2007 (Figure 11), as shown. The dominant applications for lithium are batteries, ceramics and glass, lubricating greases, and in air conditioning. The other uses category includes alloys, construction, dyes, industrial bleaching and sanitation, pool chemicals, and specialty inorganics (Jaskula 2010).

The dominant lithium intermediate product for each application is sometimes difficult to determine; the range of products within each product category may be quite variable. The product category, the dominant intermediate (either known or assumed), and the source of the data is displayed in the table below.

Product Category	Intermediate Product	Status	Source[*]
Batteries	lithium carbonate	Assumed; lithium metal and hydroxide may be used, but in relatively small quantities	Y&T 09; EM&M 05
Lubricating Greases	lithium hydroxide	Known	Y&T 09; EM&M 05
Frits	lithium carbonate	Known	Y&T 09
Glass	lithium carbonate	Assumed; lithium metal is used to control melting points, but the larger use is lithium carbonate for glazing	EM&M 05
Air Conditioning	lithium bromide	Known	EM&M 05
Aluminum	lithium carbonate	Known	Y&T 09; EM&M 05
Polymers	lithium carbonate; butylithium	Butylithium given by Y&T 09; lithium carbonate given by EM&M 05. Assume 50% of each intermediate product	Conflict
Continuous Casting	lithium carbonate	Known	Y&T 09
Chemical Processing	butylithium	Assumed; organic derivatives require butylithium (Y&T 09)	Y&T 09
Pharmaceuticals	butylithium; lithium carbonate; lithium metal	Butylithium given by EM&M 05; lithium metal and carbonate given by Y&T 09. Assume 33% of each intermediate	Conflict
Other	lithium carbonate	Assumed; no information is available. Without breaking this product category down further, cannot predict intermediate. Assume carbonate, as it is most widely used; amount of lithium is often expressed in lithium carbonate equivalents.	

[*]Guide to abbreviations: Y&T 09 refers to Yaksic and Tilton, 2009.
EM&M 05 refers to Ebensperger, Maxwell, and Moscoso, 2005.

Using this information, it is possible to calculate the amount of the F&M inflow that is in the form of each intermediate product in the 26,000 metric tonnes flow.

Intermediate Product	Fraction of Inflow (%)	Total Mass of Inflow (metric tonnes)
Lithium carbonate	75	19,000
Lithium hydroxide	12	3,100
Lithium bromide	6	1,500
Butylithium	6	1,500
Lithium Metal	1	260

The outflow, which is 23,000 metric tonnes after the assumed 10% manufacturing loss rate, is divided by the fraction of the product category (SQM, 2007) to calculate the mass flow of lithium in each type of product that enters the use stage.

Product Category	Market Share	Amount Entering Use (metric tonnes)
Batteries	25	5,800
Lubricating Greases	12	2,800
Frits	10	2,300
Glass	8	1,800
Air Conditioning	6	1,400
Aluminum	4	930
Polymers	4	930
Continuous Casting	3	700
Chemical Processing	3	700
Pharmaceuticals	3	700
Other	22	5,100

Use

The inflows to the use stage are divided by product category. The outflows to waste management (WM) include only those products in which potential recovery is conceivably possible; they may be either landfilled or recycled. All of the products in which lithium is dissipative are not included in the inflows to the WM stage; instead, they go to the repository.

Because the global life cycle is a snapshot of a single year, the outflows from the use stage include lithium in products were manufactured earlier (which are coming to the end of their lifetime) and lithium that is dissipated. Lithium is dissipated in most of its applications, including greases, frits, glass, polymers, chemical processing, pharmaceuticals, and production of primary aluminum, where it is used to lower the melting point of the cryolite bath in the Hall-Héroult process (Ebensperger et al. 2005).

The majority of possible applications in the "other" product category – including dyestuffs, industrial bleaching and sanitation, pool chemicals, and specialty inorganics (Jaskula 2010) – are also dissipative. While the lithium used in alloys and construction, which are both listed in this "other" category, is not dissipative, no information is available on the percent of lithium used in these applications, and so it is assumed that the entire "other" category will be dissipated and will flow into the repository.

Lithium is not dissipated when it is used in batteries, air conditioning systems, and continuous casting, which are the remaining three production application categories. Metals that were continuously cast have the potential to be recovered and recycled, but they will be reused as the alloy or metal; their lithium content will not be recovered independently. These product categories enter their own metal scrap cycles after the use life cycle stage, and are no longer a part of the lithium life cycle recoverable flow. Therefore, the only two types of products in which lithium has the potential to be recovered are batteries and air conditioners (Chemetall 2010).

Batteries, air conditioners, and metals that were continuously cast do not enter the waste management stage during the year in which they were produced. Instead, they stay in the use stage during their lifetime. Because this life cycle is a 2007 snapshot of the

lithium life cycle, the lithium in these three product categories that is coming out of the use stage is lithium that entered the use stage in the past. Typical product lifetimes are used to determine the approximate year in which the product that is now existing the use stage entered it.

Ideally, it would be possible to know the lifetime distribution for a particular product; however, this information was not available for any of the three relevant product categories; it was assumed that all of the products exit the use stage at their average lifetime.

The database LiVES (Lifespan database for Vehicles, Equipment, and Structures) from the National Institute for Environmental Studies of the Ministry of the Environment of Japan was used to find literature that gave lifetime estimates for the product categories. It is accessible at http://www.nies.go.jp/lifespan/. Batteries had an average lifetime of 10.9 years and air conditioners had an average lifetime of 15.3 years (Nomura 2005).

Because continuous casting refers to a process rather than a product, metals that were continuously cast may be used in any number of applications that may have dramatically different lifetimes. Without more detailed information, an informed guess must be made as to the average lifetime. The estimated lifetime is 25 years, which is intermediate between products with shorter lifetimes, such as appliances and consumer products, and structure and equipment lifetimes, which are significantly longer.

Based upon these lifetime estimates, the batteries that are coming out of the use stage in 2007 are from 1996, the air conditioning units are from 1992, and the continuous casting metal is from 1982.

In 1996, batteries represented approximately 7% of annual lithium use (Ober 1996). The world production of lithium in 1996 was 11,000 metric tonnes (Ober 1998). Therefore, the flow of lithium in batteries exiting the use stage in 2007 was approximately 770 metric tonnes.

In 1992, air treatment represented approximately 4% of annual lithium use (Ober 1992). No information on the world production of lithium in terms of mass of lithium produced was available for this year; instead, information regarding the production of lithium minerals and brines was available; 160,000 metric tonnes of lithium ore were produced in 1992 (Ober 1994).

The production of minerals and brines is available for the year 1996, as is the production of lithium itself. By dividing the production of lithium by the production of minerals and brines, the ratio of lithium in minerals and brines can be estimated; it is approximately 5.2%. Therefore, this ratio can be used to estimate lithium production for 1992. 5.2% of 160,000 metric tonnes is 8,300 metric tonnes. Therefore, the flow of lithium in air conditioners exiting the use stage in 2007 is 330 metric tonnes.

In 1982, the world production of lithium minerals was 92,000 metric tonnes (Ferrell 1984). Using the same ratio of lithium to minerals, the world production was 4,800 metric tonnes of lithium in 1982. However, no information is available on the lithium used for continuous casting in any USGS publication during the 1970s and 1980s. Continuous casting is also not mentioned in any of the papers published in *Energy* after the 1976 USGS Symposium on Lithium Resources and Requirements by the Year 2000. Because continuous casting is not mentioned in any major publication from the period, it

can be assumed that the amount of lithium used in continuous casting in 1982 is negligible and therefore this flow will be discounted.

In summary, one outflow from the use stage is to the WM stage and includes the battery, air conditioning, and casting product streams – although the latter is negligible – and totals 1,100 metric tonnes. Another outflow goes from the use stage into the repository and totals 15,000 metric tonnes. It was assumed that no significant amount of lithium is lost in the use of batteries and air conditioners, which is reasonable because these devices tend to be closed systems. Because the inflow of the use stage in 2007 was 23,000 metric tonnes and 15,000 metric tonnes was dissipated within the year, the addition of lithium to stock in use was 8,000 metric tonnes globally.

Waste Management

The waste management life cycle stage refers both to products that are landfilled and products that are recycled; the WM stage only includes the products that are theoretically recoverable. In the case of lithium, only lithium in batteries and air conditioning units is potentially recoverable. Because the lithium in casting applications is not recoverable but there is potential for metal to be recycled, this product waste stream enters a scrap cycle. No scrap from continuous casting is leaving the use stage in 2007, but it may exit the use stage in the future.

Potential for Recycling

Some lithium bromide is currently recycled; for example, the companies Refrigerant Exchange Inc. and LBD Associates, LLC both offer recycling services. However, the volume of lithium bromide solution that is recycled each year is proprietary and unknown. It is assumed that this flow is relatively insignificant.

A similar situation exists for lithium battery recycling. Toxco is the only facility in North America that can recycle both primary and secondary lithium batteries; they have patented a cryogenic lithium battery recycling process. They store batteries in underground concrete structures, where residual electrical energy is discharged from the larger batteries. The batteries are cooled to – 325 °F to minimize the risk of explosion. They are then shredded and separated; the lithium components are converted to lithium carbonate (Toxco 2003). One of their clients is Tesla Motors, which sends Toxco its lithium-ion batteries (Sibley 2009).

The Department of Energy awarded Toxco 9.5 million dollars to expand their recycling operations to Ohio from British Columbia; the DOE emphasized that more recycling infrastructure will be required for the projected growth of hybrid and electric vehicle industry (Toxco 2009). Other American companies that recycle some types of lithium batteries are Kinsbursky Brothers, a partner of Toxco, and Battery Solutions. International companies that recycle some lithium batteries include Belgium's Umicore and Japan's Nippon Mining & Metals and GS Yuasa.

Because few companies recycle lithium batteries, most information on battery recycling is proprietary. It is difficult even to make an order of magnitude estimate with essentially no available and accessible data. Due to the fact that only a handful of facilities are currently in operation, and all recycle dozens of other kinds of batteries, it is reasonable to assume that the current recycle flow for lithium is negligible in comparison with the other flows. Therefore, there is no significant flow of lithium from WM back to F&M.

However, as the financial services firm Canaccord Adams reports, almost 97% of lead-acid batteries are now recycled, suggesting that as the industry develops, most lithium batteries will be recycled (Sibley 2009). The issue of future changes in recycling, as well as in demand and application market share, will be discussed in greater detail in the next section.

Future Demand and Scenarios

The Lithium Industry: Then and Now

In 1976, the U.S. Geological Survey held the Symposium on Lithium Resources and Requirements by the Year 2000 in Golden, Colorado. Representatives from the lithium industry argued that there would be no shortage of lithium by 2000, while government scientists maintained that there would be a serious shortfall. All present agreed that pegmatite resources would be sufficient over the short term, while brines would potentially be a long-term resource (Edwards 1978).

During the late 1970s, the largest use of lithium was in the aluminum industry, where it is used in the cryolite bath in the Hall-Héroult process; it was estimated that 25 – 30% of the aluminum produced in the US at the time used lithium carbonate. The second largest use was in glass and ceramics to make products such as Corningware, black and white television tubes, and fiberglass insulation. Less significant uses included lithium hydroxide greases (which accounted for 55% of greases manufactured in industrialized countries), butylithium in the production of synthetic rubber, and lithium bromide used in large industrial air conditioners. One conference attendant noted that the lithium battery industry was "the most talked about and highly publicized" but, in terms of amount of lithium used, was essentially negligible (Comer 1978).

A representative from the Foote Mineral Company, which was a subsidiary of Newmont Mining, and operated a spodumene mine in Kings Mountain, North Carolina and a brine extraction operation in Clayton Valley, Nevada, scoffed at the idea of a shortage. Between 1955 and 1960, the US Atomic Energy Commission required enormous amounts of lithium hydroxide for the hydrogen bomb program; when the program ended, the lithium industry had enough extraction and processing facilities for supply to overwhelm demand by 500%. The lithium industry took 13 years to recover from minimal profits due to this overcapacity.

The industry representative wrote, "To whose who expressed this concern about the unavailability of lithium, I am prepared at this meeting or any time to take your orders for lithium ores, lithium chemicals or lithium metal in whatever form you wish to have it." He continues, "I believe that those individuals who continue to express unrealistic concern about the supply of lithium resources and the ability of the lithium industry to convert these resources into useable forms of lithium, should behave more responsibly" (Comer 1978).

Other participants suggested that the newly-discovered Salar de Atacama might reduce the predicted gap between supply and demand (Kunasz 1978); of course, they have subsequently been proven correct – this Chilean salar now accounts for over 60% of the world's lithium production (Ebensperger et al. 2005).

The Future of the Lithium Industry

Some predictions from 1977 have shown remarkable consistency with the current situation: most notably, that lithium batteries would become a dominant product application and that lithium would be supplied from the South American salars.

However, the sense of concern over the future of lithium has not abated over time; headlines like "In Search of Lithium: The Battle for the 3rd Element" (McDougall 2009) abound. Most of this apprehension originates from the predicted gap between the limited supply of lithium and the increased demand for lithium-ion batteries for hybrid and electric vehicles.

This concern is compounded by the fact that Bolivia, which has the world's largest reserve base of lithium at 5,400,000 metric tonnes (Jaskula 2009), may not extract and export enough lithium to keep up with demand due to geopolitical conflict, as described previously. Bolivia's supply of lithium accounts for nearly half of the world's total reserve base but only produces about 40 metric tonnes per month from a pilot plant in the Salar de Uyuni that is operated by the state company Corporación Minera de Bolivia, otherwise known as Comibol (Jaskula 2010). If the Bolivian government continues to strangle the lithium extraction industry within its borders, we may face a serious limit to the growth of electric and hybrid vehicles.

However, most workers have attempted to make predictions about the future of the lithium industry while ignoring potential geopolitical supply restrictions. They have operated under the assumption that the Bolivian government will change its mind about lithium extraction once it becomes sufficiently valuable, and therefore brine extraction will increase significantly over the next decades.

The predicted driving force for increased lithium demand is the growing industry of electric and hybrid vehicles, for which lithium-ion batteries seem ideal due to their high energy density and low weight. All of the major car companies have released or are planning to release models using lithium-ion batteries in the next few years (Jaskula

2010), although few models utilizing the technology are currently on the road. The other field that may see significant growth is nuclear fusion, although this is far more uncertain.

Predictions for Future Growth

Two papers have attempted to quantitatively analyze the future of the industry and are worth a short discussion. Ebensperger et al. (2005) offered three growth scenarios based upon current trends, which they termed low growth, likely growth, and high growth; this was an attempt to predict upper and lower boundaries on the growth of lithium (Table 6). They noted that glass and ceramics, aluminum, lubricants, pharmaceuticals, and polymers were all proven technologies that had entered their full maturity phase and were therefore unlikely to experience significant growth (less than 5% annually). Air conditioning is also a mature technology, but installation is increasing in developing countries as income levels rise, and therefore may experience relatively higher growth. They predicted that primary batteries, used in consumer electronic devices, would grow between 6 – 10% annually; they predicted that secondary batteries, used in electric and hybrid vehicles, would grow between 10 to 15% annually. However, in the past few years, the amount of lithium used in batteries has increased 20% annually (Jaskula 2010).

Yaksic and Tilton (2009) made predictions about future lithium demand in their creation of a cumulative availability curve for lithium. A cumulative availability curve is an alternative to the fixed-stock approach, which assumes that there is a nonrenewable, fixed stock of a mineral (which may be resources, reserves, or reserve base) that society can exploit. However, none of these stocks are actually fixed, as new deposits are discovered and advanced extraction technologies emerge. As Yaksic and Tilton write,

"Long before the last barrel of oil or the last ton of copper were extracted from the earth's crust, the cost of production would become prohibitive, causing demand to decline to zero" (2009).

The cumulative availability curve, on the other hand, shows the quantities of a material that can be recovered under current conditions (including current technology, labor and input prices, etc.) from known resources at different prices. The cumulative output of the material is plotted against the cost of producing it. Some curves are able to capture known and unknown deposits, although Yaksic and Tilton were not able to do so for lithium; they were able to create high-cost (pessimistic) and low-cost (optimistic) curves (Figure 12).

The availability of a mineral depends on three aspects of the curve. The first is the shape of the curve, which is determined by geologic factors such as the nature and occurrence of deposits. The second is the speed at which society moves up the curve, which depends on demand. Demand can be affected by population growth, per capita income growth, and rates of recycling. The third is shifts in the curve, which reflect technological advances that reduce cost of production.

In order to model the second aspect of the curve, the speed at which society moves up the curve, Yaksic and Tilton created a high-growth, worst case prediction for future demand in 2100; the details can be seen in Table 7. Under these conditions, the required cumulative output of lithium from 2008 to 2100 to meet future demand is 17.5 million metric tonnes of primary lithium production. It is important to note that their scenario does not take recycling into account, because recycling does not deplete resources and move society up the curve.

The Importance of Recycling to Meet Future Demand

High rates of recycling may go a long way to meet future demands. To model the effect of recycling on lithium demand, the life cycle generated for 2007 was expanded. It is important to note that these models are not predictions of future demand; instead, they are mean to illustrate possible scenarios of the lithium industry in the future. Although great care was taken to make reasonable assumptions, these scenarios are by no means an attempt to make accurate predictions of the future. Life cycle diagrams of each scenario can be found in the Life Cycle and Future Scenarios section.

Scenario A assumes 20% annual growth in batteries from 2007 to 2025, with demand for all other product categories remaining equal to their 2007 values. It is assumed that the increase in required lithium comes from brines, which is reasonable because this source has the greatest expansion potential. It is assumed that recycling continues to contribute negligible flows of lithium from use to F&M.

Scenario B is similar to Scenario A, except it is assumed that 50% of the inflow to the waste management stream is recycled and the other half is landfilled. Scenario B may be regarded as the optimistic version of Scenario A.

Scenario C is mean to have a longer timescale than A and B. It is assumed that batteries experience an annual growth of 20% until 2025, at which point the growth rate drops to 10% through 2050. This is reasonable because it is unlikely for any product to maintain such high levels of growth for decades on end, especially when it may be replaced by newer technologies. It is assumed that all other product categories remain equal to their 2007 values, and that recycling is negligible.

Scenario D is similar to Scenario C, except it is assumed that 50% of the inflow to the waste management stream is recycled and the other half is landfilled. Scenario D may be regarded as the optimistic version of Scenario C.

Scenario E is the most optimistic of all; it assumes an 80% rate of recycling from 2007 – 2050 with the same trends in battery growth as Scenario C.

While it is known that the average electric or hybrid vehicle uses a 9 kWh battery, which uses 6.25 kg of lithium carbonate equivalent, it should be apparent from the Yaksic and Tilton (2009) prediction that estimating growth of vehicles is extremely complicated; for simplicity's sake, a growth rate in the product category of batteries was used. For the scope of the modeling, which is to investigate the effect of recycling on demand for primary lithium, this approximation is sufficient. The results from the modeling are shown below.

Scenario	Assumptions	Lithium Extracted (metric tonnes)	Lithium Recycled (metric tonnes)
A	In 2025 20% annual growth No recycling	420,000	Negligible
B	in 2025 20% annual growth 50% recycling	400,000	11,000
C	In 2050 20% annual growth from 2007 – 2025 10% annual growth from 2025 – 2050 No recycling	4,200,000	Negligible
D	In 2050 20% annual growth from 2007 – 2025 10% annual growth from 2025 – 2050 50% recycling	3,500,000	290,000
E	In 2050 20% annual growth from 2007 – 2025 10% annual growth from 2025 – 2050 80% recycling	3,100,000	470,000

Comparing Scenarios A and B reveals that a recycling rate of 50% of batteries decreased the amount of primary lithium that must be extracted by 5% for 2025. Comparing Scenarios C and D reveals that a recycling rate of 50% decreased the amount of primary lithium that must be extracted by 18%; comparing Scenarios C and E reveals that a recycling rate of 80% decreased the amount primary lithium that must be extracted by 30%.

These models illustrate the significant effect that recycling of batteries may play in reducing the amount of primary lithium that must be produced each year. Because serious geopolitical issues may present a risk to the supply of brines, funding research and development of recycling technology and recycling facilities should be a priority for the industry. Additionally, corporate policies such as incentives or manufacturing take-back programs to encourage consumer recycling should be implemented as the use of lithium-ion batteries begins to take off. These measures may help counteract limits to the supply of primary lithium from geopolitical conflicts, price volatility, environmental restrictions, and changing technological demands.

Conclusion

Traditional hard rock mining of lithium from pegmatite ore bodies has become dominated by brine extraction within the past two decades. Extracting lithium from brine is a lower cost and high volume process that requires less energy and fewer chemicals than its hard rock predecessor. This reason, combined with the fact that salars in South America and southwestern China hold most of the reserve base of lithium, has put increasing scientific and political attention onto these brine deposits. However, few scholars have tried to place these salars into the context of the industry as a whole,

although analysis both of the supply and demand side of lithium is essential to understanding and preparing for its future.

Lithium enters solution during the weathering of volcanic rocks; in the Andean Altiplano, these volcanoes delineate the boundaries of a series of internal drainage basins. Because they exist in an extremely arid climate, evaporation exceeds precipitation and evaporitic brine deposits called salars form. Some workers have attempted to classify these salars by their morphology and their chemistry; however, the former is quite variable and may not yield much useful information.

Evaluating the geochemical evolution of a weathering solution in these salars is possible using the didactic concept of the chemical divide. Because the ionic activity product of a mineral must remain equal, concentrations of solutes cannot all change at the same time. Therefore, in the case of the South American salars, the precipitation of calcite, magnesium salts, and gypsum controls the evaporative pathway of a brine. Even small changes in the concentrations of calcium, magnesium, sulfate, and carbonate in the initial solution can have a dramatic effect on the type of brine that results; consequently, external environmental factors, such as wind-blown dust or bacterial activity, can also affect the geochemical evolution of a brine.

The Salar de Uyuni in Bolivia, which has almost half of the world's reserve base of lithium, is currently only producing 40 metric tonnes of lithium per month from a state-run pilot plant, but private company is currently operating on the Chilean Salar de Atacama, which now supplies 60% of the world's lithium. Brine extraction of lithium is the future for the industry, despite potential geopolitical complications.

The lithium industry is growing rapidly, thanks many to ever-increasing demand for lightweight, powerful batteries in products ranging from iPods and laptops to electric and hybrid vehicles. Lithium batteries have the highest density (provide the most electricity in the smallest mass) of any battery currently in development. Many of the applications of lithium-ion batteries fit under the "green design" umbrella, although little work has been done to evaluate the long-term social and environmental consequences of large-scale production from brines.

This understanding of both the supply and the demand side of the industry was synthesized in creating the first known global life cycle for lithium. This life cycle tracks lithium through its four life cycle stages in 2007; it is hoped that it is used as a basis for future, more in-depth study. The life cycle reveals that because the majority of lithium is used in dissipative uses and because there are few currently operating companies to recover and recycle lithium from batteries and air conditioning fluid, demand for primary lithium is overwhelming dominant.

A series of future scenarios (which were not meant as predictions but instead examples of how the future market may behave under certain circumstances to understand its sensitivity to various factors) reveals that high rates of recycling of consumer and vehicle batteries would greatly decrease demand for primary lithium, as there would be a substantial, recoverable secondary reserve base of lithium. Both government and industry should encourage recycling development now, both in technological advances and in take-back programs to increase recovery of batteries at their end-of-life. This secondary reserve base is likely to reduce demand for primary lithium, and consequently may ease concern about the potential disruption of the supply

of lithium. While geopolitical complications are out of the hands of geologists, the situation may not be as dire as it first appears.

However, we must be careful that we do not trade our dependence on Middle Eastern oil for a dependence on South American lithium, because we will not escape the problems of the past by doing so. As politicians and consumers grow increasingly concerned about our dependence on foreign oil and the potential impacts of global climate change, electric and hybrid vehicles begin to seem like a viable replacement for fossil fuel-burning vehicles throughout the industrialized world. Lithium batteries have potential to be used in many different "green" products, but without careful consideration of the true impacts of lithium extraction, we may be trading one set of problems for another.

Lithium is but one of the many metals that are likely to be vital for continued technological advances and economic growth over the next century. Based on current trends, the demand for rare metals will increase more than the demand for bulk metals in the coming decades. These rare metals may face significant complications and limitations in their supply due to technical, economic, geopolitical, and environmental concerns. Therefore, we cannot focus only on the impact of a product during its use stage; the entire life cycle must be considered.

It is, therefore, of upmost importance that we have a strategy for our strategic metals. Recycling may be a way to reduce our demand for primary material and may partially free us from the potential technological, geopolitical, and environmental factors that may restrict trade. Both recycling technology and recycling take-back program will help us create and use genuinely green technology.

<u>Acknowledgments</u>

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Lithium Global Life Cycle, 2007

Batteries, 5800

Greases, 2800

Frits, 2300

Alloy/Metal scrap cycles

Carbonate, 19000	Glass, 1900
Hydroxide, 3100	Air Conditioning, 1400
Bromide, 1500	Aluminum, 930
Butyl-, 1500	Polymers, 930
Metal, 260	Casting, 700

Production

Fabrication And Manufacturing

Use

8,000

1100

Waste Management

Chem. Processing, 700

Pharmaceuticals, 700

Other, 5100

Lithosphere

55000

30000

2,600

Recycle

15,000

1100

Repository

Landfills

Life Cycle and Future Scenarios

Scenario A: Global Life Cycle in 2025

Assuming 20% annual battery growth, no recycling
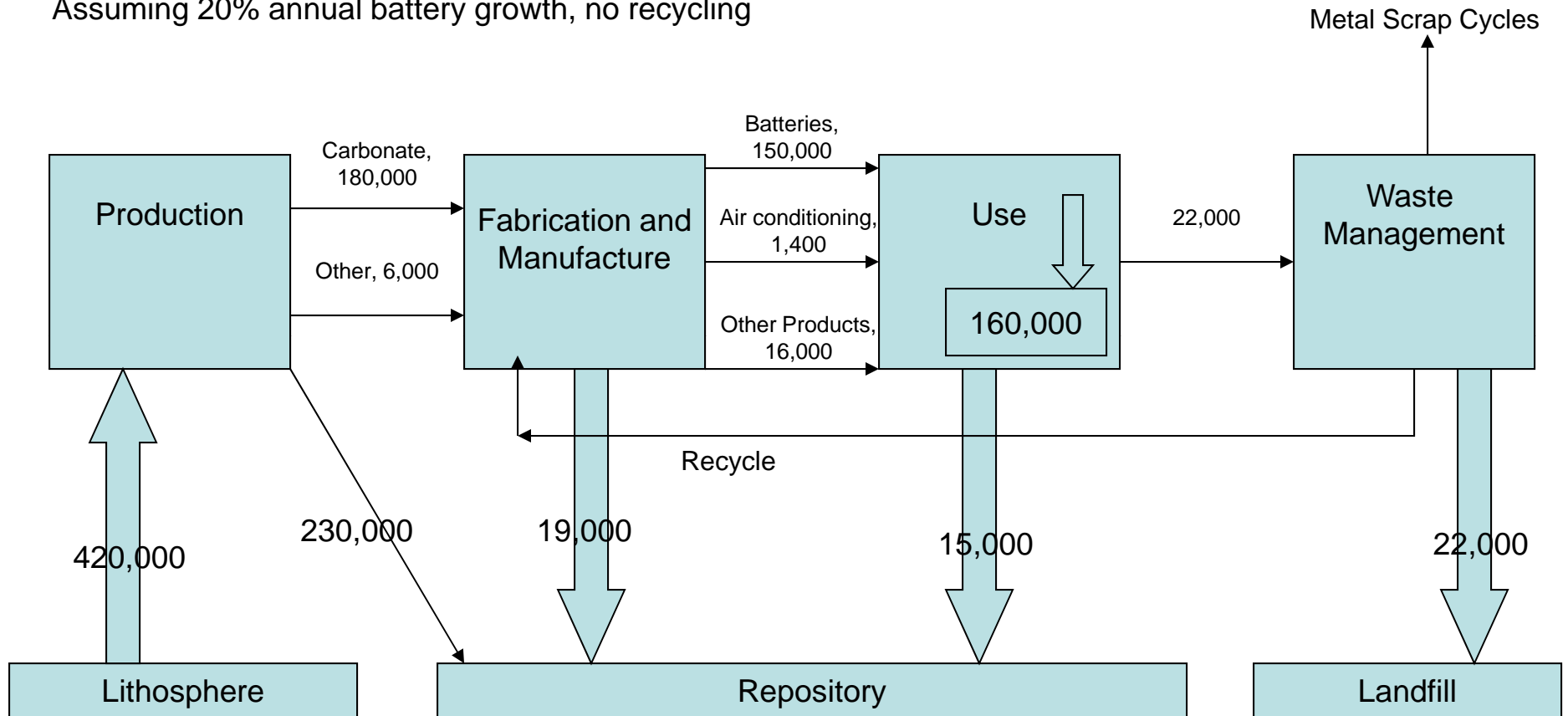
Scenario B: Global Life Cycle in 2025

Assuming 20% annual battery growth, 50% recycling

Production → Carbonate, 170,000 → **Fabrication and Manufacture**

Production → Other, 6,000 → **Fabrication and Manufacture**

Fabrication and Manufacture → Batteries, 150,000 → **Use**

Fabrication and Manufacture → Air conditioning, 1,400 → **Use**

Fabrication and Manufacture → Other Products, 16,000 → **Use**

Use — 160,000

Use → 22,000 → **Waste Management**

Waste Management → Metal Scrap Cycles

Waste Management → Recycle, 11,000 → **Fabrication and Manufacture**

Lithosphere → 400,000 → **Production**

Production → 220,000 → **Repository**

Fabrication and Manufacture → 8,000 → **Repository**

Use → 15,000 → **Repository**

Waste Management → 11,000 → **Landfill**

Scenario C: Global Life Cycle in 2050

Assuming no recycling

Metal Scrap Cycles

Production

Carbonate, 1,900,000

Other, 6,000

Fabrication and Manufacture

Batteries, 1,700,000

Air conditioning, 1,400

Other Products, 16,000

Use

1,700,000

590,000

Waste Management

Recycle

4,200,000

2,300,000

190,000

15,000

590,000

Lithosphere

Repository

Landfill
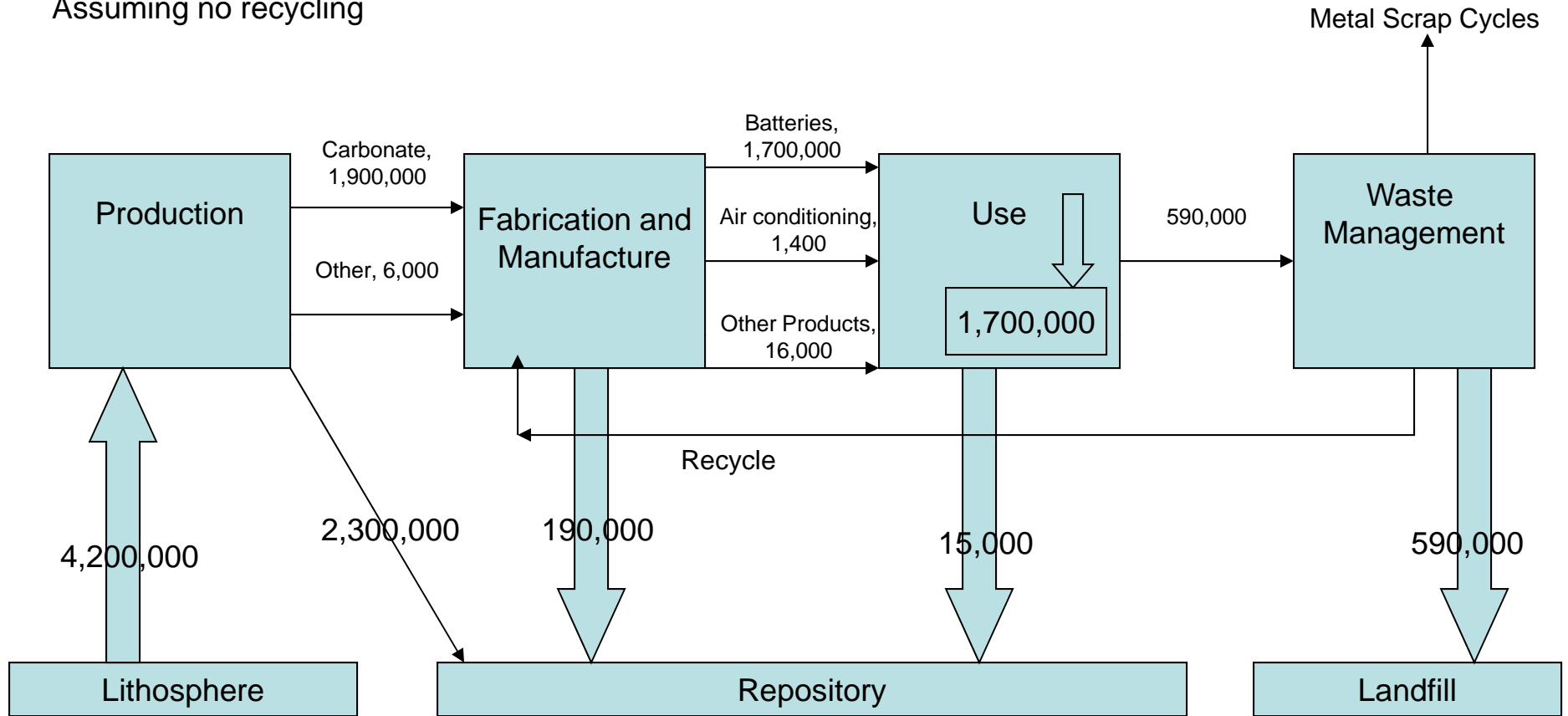
Scenario D: Global Life Cycle in 2050

Assuming 50% recycling

Metal Scrap Cycles

Production		**Fabrication and Manufacture**	**Use**	**Waste Management**

Carbonate, 1,600,000

Other, 6000

Batteries, 1,700,000

Air conditioning, 1,400

Other Products, 16,000

1,700,000

590,000

Recycle, 290,000

3,500,000

1,900,000

160,000

15,000

290,000

Lithosphere

Repository

Landfill
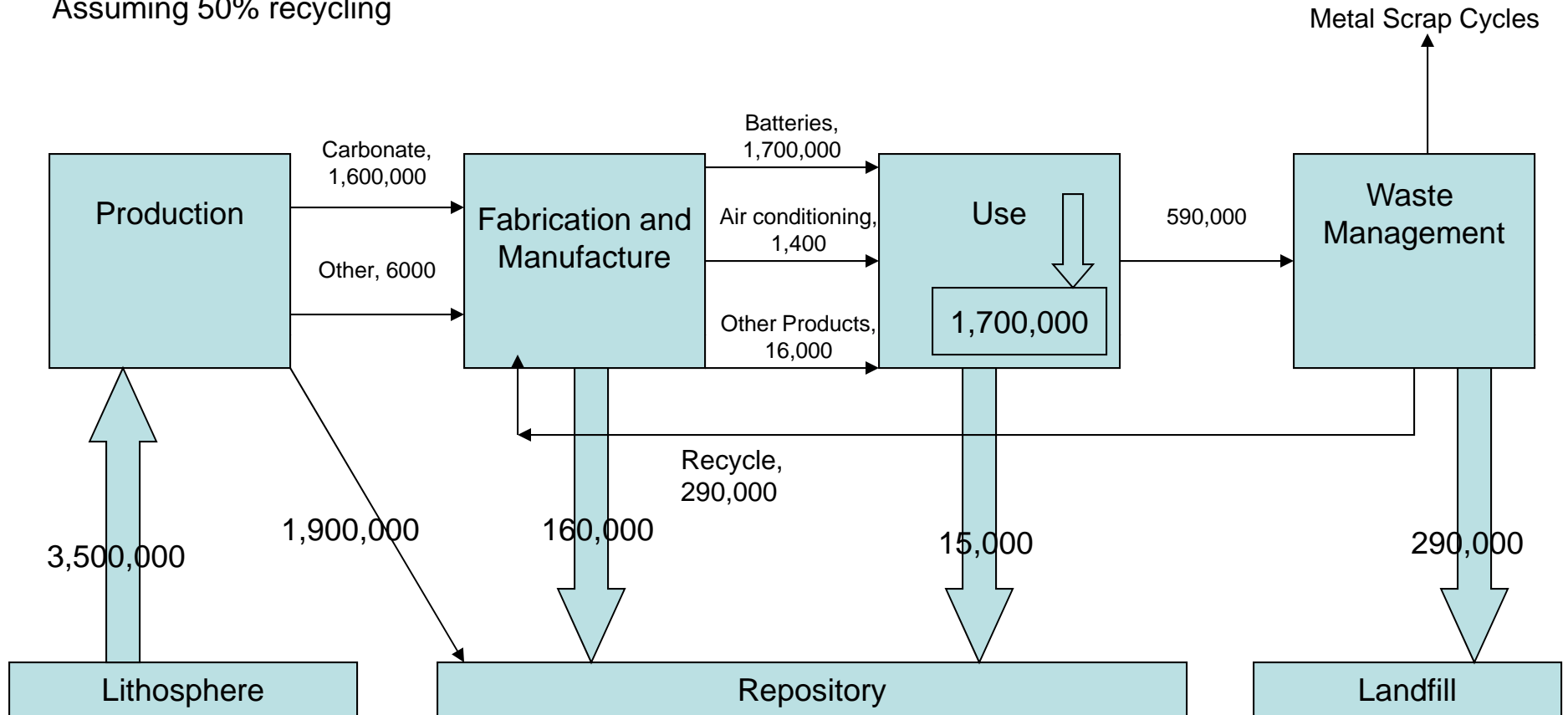
Scenario E: Global Life Cycle in 2050

Assuming 80% recycling

Metal Scrap Cycles

Production		Fabrication and Manufacture		Use		Waste Management

Carbonate,
1,400,000

Other, 6,000

Batteries,
1,700,000

Air conditioning,
1,400

Other Products,
16,000

1,700,000

590,000

Recycle,
470,000

3,100,000

1,700,000

140,000

15,000

120,000

Lithosphere		Repository		Landfill
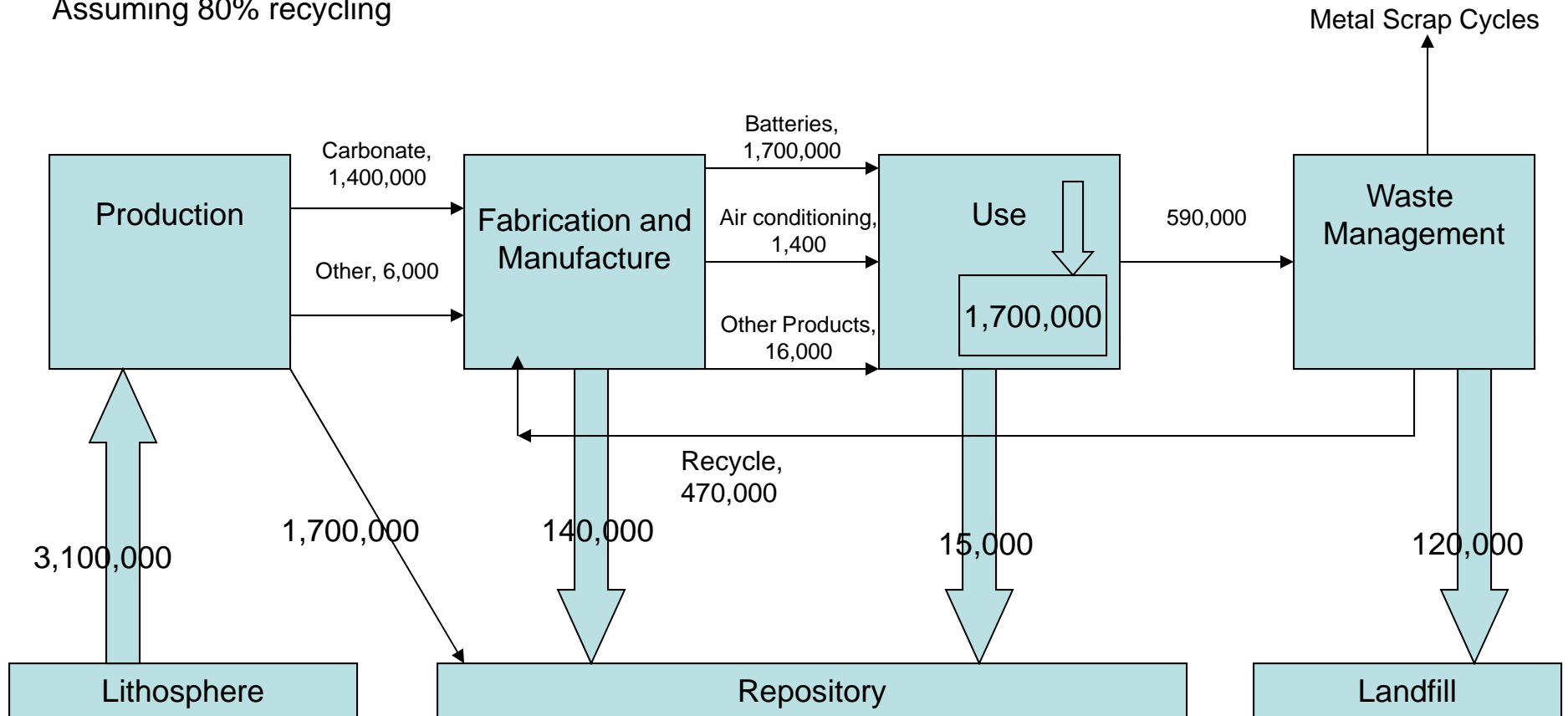
Tables

Table 1 – Common Lithium-Bearing Minerals (after Anstett et al. 1990)

Mineral	Chemical Formula	Theoretical Content (%)		Content of Commercial Concentrates (%)	
		Li	Li_2O	Li	Li_2O
Spodumene	$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	3.73	8.03	2.6 – 3.5	5.5 – 7.5
Petalite	$Li_2O \cdot Al_2O_3 \cdot 8SiO_2$	2.27	4.88	1.7 – 2.2	3.6 – 4. 7
Eucryptite	$Li_2O \cdot Al_2O_3 \cdot 2SiO_2$	5.51	11.86	2.1 – 3.0	5.5 – 6.5
Amblygonite	$2Li(F,OH) \cdot Al_2O_3 \cdot P_2O5$	4.96 – 4.76	10.1 – 10.24	3.5 – 4.4	7.5 – 9.5
Lepidolite	$KLi_2AlSi_4O_{10}(F,OH,O)$	≤ 3.58	≤ 7.70	1.5 – 3.3	3.3 – 7.0

Table 2 – Common Minerals in South American Salars (Risacher et al. 2003)

Amorpous silica	SiO_2
Antarcticite	$CaCl_2 \cdot 6H_2O$
Bischofite	$MgCl_2 \cdot 6H_2O$
Calcite	$CaCO_3$
Gypsum	$CaSO_4 \cdot 2H_2O$
Halite	$NaCl$
Mirabilite	$Na_2SO_4 \cdot 10H_2O$
Natron	$Na_2CO_3 \cdot 10H_2O$
Thenardite	Na_2SO_4
Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$
Ulexite	$NaCaB_5O_9 \cdot 8H_2O$

Table 3 – Comparison of Waters Resulting from the Weathering of Intermediate to Felsic Rocks in North America, Bolivia, and Chile (Risacher and Fritz 2009)

	USA	Range	Bolivia	Range	Chile	Range	Chi/Bol
PH	7.5	6.6–8.3	7.9	3.8–10.4	7.8	3.9–9.8	*
Na	1.51	0.08–3.09	0.93	0.072–2.87	4.03	0.112–22.9	4.3
K	0.13	0.01–0.49	0.13	0.032–0.46	0.32	0.017–2.15	2.5
Ca	0.24	0.005–1.15	0.32	0.038–0.763	1.50	0.004–12.2	4.7
Mg	0.10	0.004–0.34	0.17	0.006–0.807	0.70	0.001–7.51	4.1
Alk	1.42	0.34–3.62	1.13	−0.064–4.88	1.92	−0.11–9.2	1.7
SO4	0.23	0.001–0.87	0.28	0.021–1.72	2.27	0.04–28.6	8.1
Cl	0.39	0.04–1.75	0.35	0.024–1.49	2.26	0.007–9.93	6.5
Si	0.89	0.15–1.35	0.74	0.052–1.6	0.90	0.052–1.72	1.2
TDS	224	70–479	196	51–501	636	47.4–4050	3.2

USA analyses from White et al. 1963 and White et al. 1980. Average values of 62 USA waters, 54 Bolivian waters and 187 Chilean waters. Chi/Bol is the ratio between Chilean and Bolivian concentrations. In mmol/l except Alk in meq/l and TDS in mg/l. (Modified from Risacher and Fritz 1991)

Table 4 – Effect of SQM Entering Market on Price of Lithium (Ebensperger et al. 2005)

Year	Price per kilogram ($US)
1996	2.70
1998	1.39
2000	1.45
2001	1.48
2002	1.59
2003	1.70[a]
2004	1.87[b]

Table 5 – Standard Electrode Potential Table

Electrode	Half-Equation	$E°$/V
$F^-\|F_2(g)$, Pt	$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
$H^+, H_2O_2\|Pt$	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O$	+1.77
$H^+, MnO_4^-, Mn^{2+}\|Pt$	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.52
$Cl^-\|Cl_2(g)$, Pt	$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}, Cr^{3+}\|Pt$	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$H^+, H_2O\|O_2(g)$, Pt	$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.19
$Br^-\|Br_2(l)$, Pt	$Br_2(l) + 2e^- \rightarrow 2Br^-$	+1.07
$OCl^-, Cl^-\|Pt$	$OCl^-(aq) + H_2O + 2e^- \rightarrow Cl^-(aq) + 2OH^-(aq)$	+0.89
$Hg^{2+}\|Hg$	$Hg^{2+} + 2e^- \rightarrow Hg$	+0.85
$Ag^+\|Ag$	$Ag^+ + e^- \rightarrow Ag$	+0.80
$Fe^{3+}, Fe^{2+}\|Pt$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$I^-\|I_2(s)$, Pt	$I_2(s) + 2e^- \rightarrow 2I^-$	+0.54
$cu^e\|Cu$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Cl^-\|Agcl$, Ag	$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$Sn^{4+}, Sn^{2+}\|Ft$	$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}$	+0.15
$H^+\|H_2(g)$, Pt	$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$	0.00
$Pb^{2+}\|Pb$	$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	−0.13
$Sn^{2+}\|Sn$	$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.14
$Fe^{2+}\|Fe$	$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.44
$Zn^{2+}\|Zn$	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Al^{3+}\|Al$	$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.66
$Mg^{2+}\|Mg$	$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.36
$Na^+\|Na$	$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71
$Li^+\|Li$	$Li^+(aq) + e^- \rightarrow Li(s)$	−3.05

Table 6 – Future Demand Predictions for Lithium (Ebensperger et al. 2005)

Predicted world lithium consumption in 2010

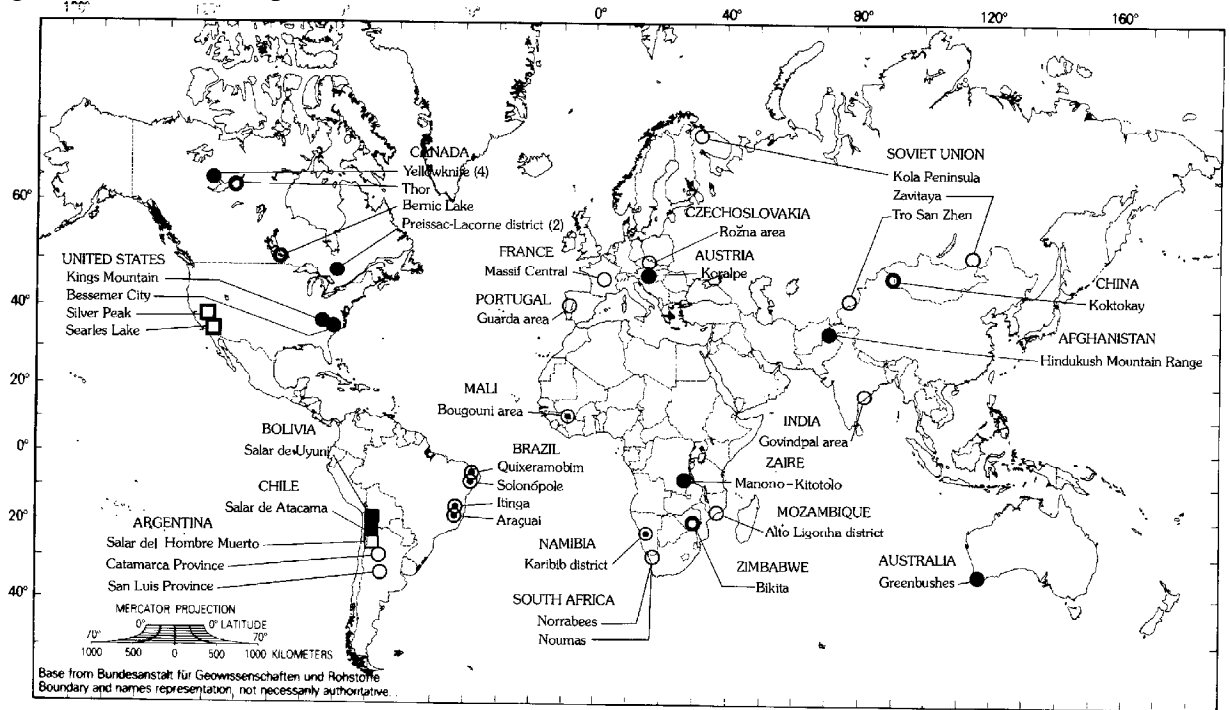| Application	Use in 2003			Projected Scenarios-2010		
	%	LCE	Li metal	Low growth	Likely	High growth
Batteries	19	14.252	2.679	27.774	31.507	37.911
Lubricants	16	12.002	2.256	13.786	15.167	16.888
Frits	12	9.001	1.692	11.845	12.666	13.535
Glass	9	6.751	1.269	8.884	9.499	10.151
Air conditioning	8	6.001	1.128	7.380	8.166	9.023
Aluminium	6	4.501	846	3.637	5.170	5.697
Pharmaceuticals	5	3.751	705	4.936	5.640	6.309
Polymers	4	3.000	564	3.217	3.690	4.262
Other uses	21	15.753	2.961	18.095	19.374	21.128
Total	100	75.012	14.100	99.553	110.879	124.904

Table 7 – Assumptions for 2100 Demand Forecast (Yaksic and Tilton 2009)

Lithium 2008–2100 demand forecast assumptions by major end-use markets

End-use market	Assumptions
Automobile batteries	(1) World population will grow according to UN estimations from 6.5 billion people in 2008 to 9.0 billion people in 2100. (2) The global ratio of people per automobile will fall from 8 in 2008 to 3 in 2100. (3) Annual battery production equals the growth in the world vehicle fleet plus the replacement of old car batteries (10-year average life assumed). (4) The percentage of hybrid and fully electric automobiles will increase from its 2008 level of under 1 percent to 100 percent by 2050 where it will remain for the rest of the century. (5) Hybrid and fully electric automobiles on average will use 9 kWh lithium batteries. (6) Lithium batteries will on average last for 10 years. (7) Lithium batteries will be recycled, recovering 80% of the lithium.
Secondary batteries (rechargeable portable devices)	15% growth for ten years; then 10% growth for ten years more; 3% growth until 2050; 1% growth from 2051 to 2100.
Primary batteries (non-rechargeable portable devices)	8% growth for ten years; then 5% growth for ten years more; 3% growth until 2050; 1% growth from 2051 to 2100.
Lubricating greases	5% growth for next ten years; then 3% growth for the next twenty years; finally 1% growth until 2100.
Frits and glass	3% growth for ten years; then 2% growth for the next twenty years; finally 0.5% growth until 2100.
Air conditioning	5% growth for ten years; 3% growth for the next ten years; finally 1% growth until 2100.
Aluminum	0% growth for ten years; 5% reduction over the next ten years; no lithium consumption after 20 years.
Others	4% growth for ten years; 2% growth in the next ten years, finally 1% growth until 2100.

Notes: ªThese assumptions are likely to produce demand forecasts that exceed the actual growth in lithium consumption over the 21st century for the following reasons: (1) the ratio of people per automobile is unlike to reach 3 by the end of the century. (2) The assumed rate of growth of hybrid and electric vehicles – 4.5 million by 2010, 27 million by 2020, 146 million by 2050, and 308 million by 2100 – is optimistic, in part because all automobiles may not be hybrid or fully electric by 2050. (3) Some hybrid automobiles may use smaller batteries than the assumed 9 kWh battery, containing less lithium. For example, the Toyota Prius HEV uses a battery of 1.3 kWh. (4) New technologies may reduce the amount of lithium needed per battery. (5) The assumption that the use of lithium in secondary batteries, which are used in portable devices such as cell phones, will grow between 10 and 15 percent per year over the next 20 years is optimistic. (6) The forecasts only consider the recycling of automobile batteries, though other lithium batteries may be recycled as well. (7) The forecasts assume that demand for the other lithium applications (excluding aluminum production) will grow for more than 90 years without leveling off.

Figures

Figure 1 – Lithium Deposits and Estimated Resources Worldwide (Anstett et al. 1990)

Figure 2 – The Main Morphostructural Units and the Locations of Salars (Risacher et al. 2003)

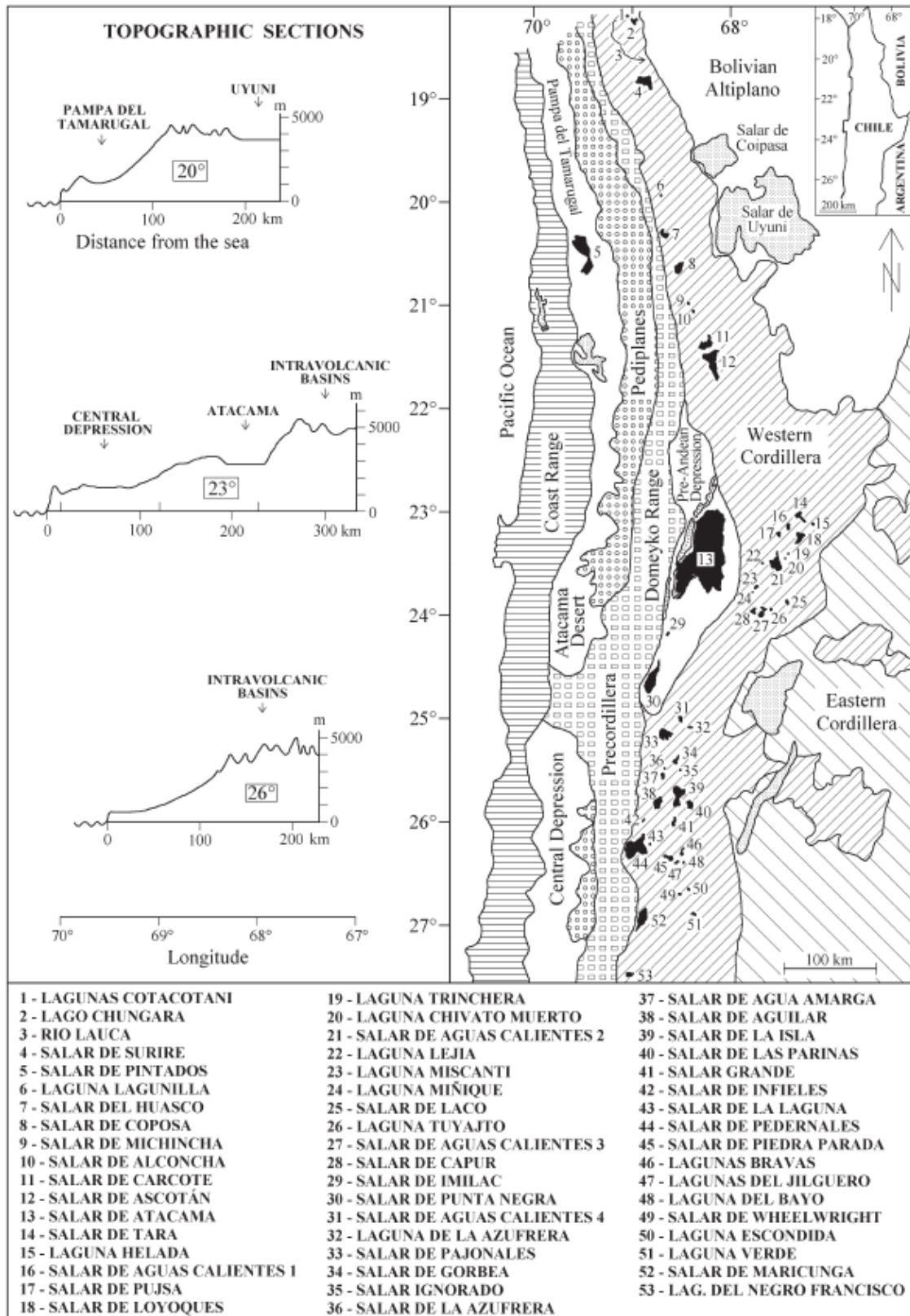|		
1 - LAGUNAS COTACOTANI	19 - LAGUNA TRINCHERA	37 - SALAR DE AGUA AMARGA
2 - LAGO CHUNGARA	20 - LAGUNA CHIVATO MUERTO	38 - SALAR DE AGUILAR
3 - RIO LAUCA	21 - SALAR DE AGUAS CALIENTES 2	39 - SALAR DE LA ISLA
4 - SALAR DE SURIRE	22 - LAGUNA LEJIA	40 - SALAR DE LAS PARINAS
5 - SALAR DE PINTADOS	23 - LAGUNA MISCANTI	41 - SALAR GRANDE
6 - LAGUNA LAGUNILLA	24 - LAGUNA MIÑIQUE	42 - SALAR DE INFIELES
7 - SALAR DEL HUASCO	25 - SALAR DE LACO	43 - SALAR DE LA LAGUNA
8 - SALAR DE COPOSA	26 - LAGUNA TUYAJTO	44 - SALAR DE PEDERNALES
9 - SALAR DE MICHINCHA	27 - SALAR DE AGUAS CALIENTES 3	45 - SALAR DE PIEDRA PARADA
10 - SALAR DE ALCONCHA	28 - SALAR DE CAPUR	46 - LAGUNAS BRAVAS
11 - SALAR DE CARCOTE	29 - SALAR DE IMILAC	47 - LAGUNAS DEL JILGUERO
12 - SALAR DE ASCOTÁN	30 - SALAR DE PUNTA NEGRA	48 - LAGUNA DEL BAYO
13 - SALAR DE ATACAMA	31 - SALAR DE AGUAS CALIENTES 4	49 - SALAR DE WHEELWRIGHT
14 - SALAR DE TARA	32 - LAGUNA DE LA AZUFRERA	50 - LAGUNA ESCONDIDA
15 - LAGUNA HELADA	33 - SALAR DE PAJONALES	51 - LAGUNA VERDE
16 - SALAR DE AGUAS CALIENTES 1	34 - SALAR DE GORBEA	52 - SALAR DE MARICUNGA
17 - SALAR DE PUJSA	35 - SALAR IGNORADO	53 - LAG. DEL NEGRO FRANCISCO
18 - SALAR DE LOYOQUES	36 - SALAR DE LA AZUFRERA	

Figure 3 – Increasing Precipitation, as shown along a Cross-section of the Altiplano (Risacher and Fritz 2009)
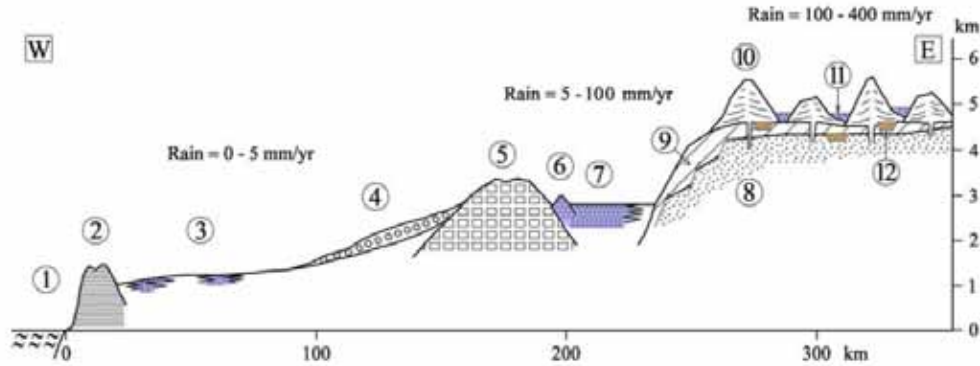

Fig. 2 Cross section from the Pacific Ocean through the Andes Cordillera (at latitude UTM northing 7400000). 1: Pacific Ocean; 2: Coast Range; 3 and 4: Central Valley or Atacama Desert (3: fossil salars, 4: pediplanes or alluvial fans); 5: Precordillera (Domeyko Range); 6 and 7: Pre-Andean Depression (6: Cordillera de la Sal, 7: salar de Atacama); 8, 9, and 10: Andes Cordillera (8: basement, 9: ignimbrite plateau, 10: stratovolcanoes); 11: present salars; 12: hypothetical ancient buried salars

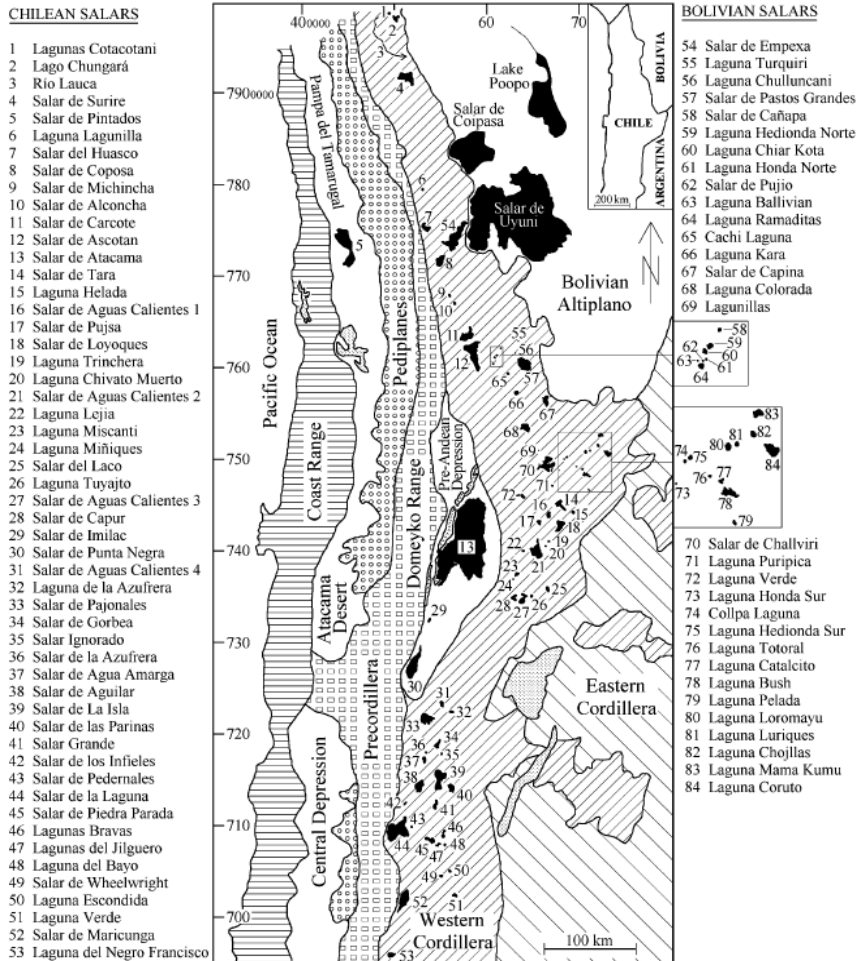Figure 4 – Major Central Andean Salars (Risacher and Fritz 2009)

CHILEAN SALARS

1 Lagunas Cotacotani
2 Lago Chungará
3 Río Lauca
4 Salar de Surire
5 Salar de Pintados
6 Laguna Lagunilla
7 Salar del Huasco
8 Salar de Coposa
9 Salar de Michincha
10 Salar de Alconcha
11 Salar de Carcote
12 Salar de Ascotan
13 Salar de Atacama
14 Salar de Tara
15 Laguna Helada
16 Salar de Aguas Calientes 1
17 Salar de Pujsa
18 Salar de Loyoques
19 Laguna Trinchera
20 Laguna Chivato Muerto
21 Salar de Aguas Calientes 2
22 Laguna Lejia
23 Laguna Miscanti
24 Laguna Miñiques
25 Salar del Laco
26 Laguna Tuyajto
27 Salar de Aguas Calientes 3
28 Salar de Capur
29 Salar de Imilac
30 Salar de Punta Negra
31 Salar de Aguas Calientes 4
32 Laguna de la Azufrera
33 Salar de Pajonales
34 Salar de Gorbea
35 Salar Ignorado
36 Salar de la Azufrera
37 Salar de Agua Amarga
38 Salar de Aguilar
39 Salar de La Isla
40 Salar de las Parinas
41 Salar Grande
42 Salar de los Infieles
43 Salar de Pedernales
44 Salar de la Laguna
45 Salar de Piedra Parada
46 Lagunas Bravas
47 Lagunas del Jilguero
48 Laguna del Bayo
49 Salar de Wheelwright
50 Laguna Escondida
51 Laguna Verde
52 Salar de Maricunga
53 Laguna del Negro Francisco

BOLIVIAN SALARS

54 Salar de Empexa
55 Laguna Turquiri
56 Laguna Chulluncani
57 Salar de Pastos Grandes
58 Salar de Cañapa
59 Laguna Hedionda Norte
60 Laguna Chiar Kota
61 Laguna Honda Norte
62 Salar de Pujio
63 Laguna Ballivian
64 Laguna Ramaditas
65 Cachi Laguna
66 Laguna Kara
67 Salar de Capina
68 Laguna Colorada
69 Lagunillas

70 Salar de Challviri
71 Laguna Puripica
72 Laguna Verde
73 Laguna Honda Sur
74 Collpa Laguna
75 Laguna Hedionda Sur
76 Laguna Totoral
77 Laguna Catalcito
78 Laguna Bush
79 Laguna Pelada
80 Laguna Loromayu
81 Laguna Luriques
82 Laguna Chojllas
83 Laguna Mama Kumu
84 Laguna Coruto

Figure 5 – Morphology of Andean Salars (Risacher and Fritz 2009)

Figure 6 – Brine Evolution (Risacher and Fritz 2009)

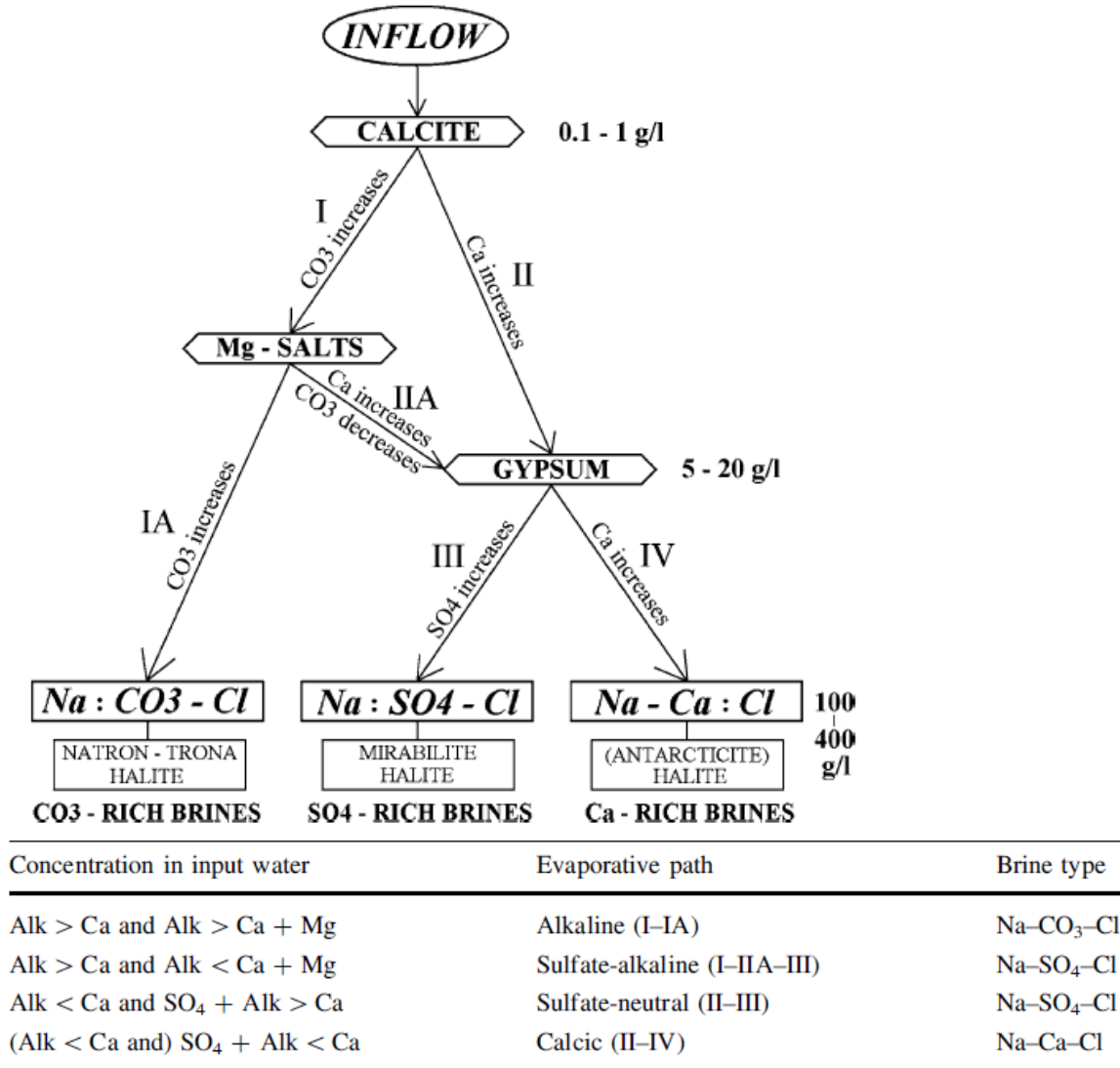| Concentration in input water	Evaporative path	Brine type
Alk > Ca and Alk > Ca + Mg	Alkaline (I–IA)	Na–CO$_3$–Cl
Alk > Ca and Alk < Ca + Mg	Sulfate-alkaline (I–IIA–III)	Na–SO$_4$–Cl
Alk < Ca and SO$_4$ + Alk > Ca	Sulfate-neutral (II–III)	Na–SO$_4$–Cl
(Alk < Ca and) SO$_4$ + Alk < Ca	Calcic (II–IV)	Na–Ca–Cl

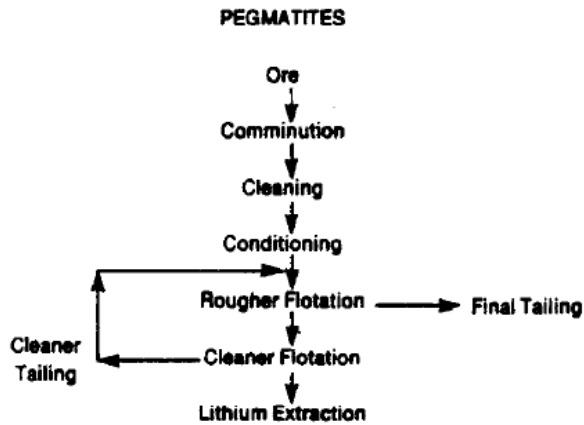Figure 7 – Pegmatite Process (Averill and Olson 1978)

Fig. 3. The flowsheet for lithium production from pegmatites.

Figure 8 – Effect of Depth on Porosity in Saline Pans and Salar Deposits (Warren 2010)
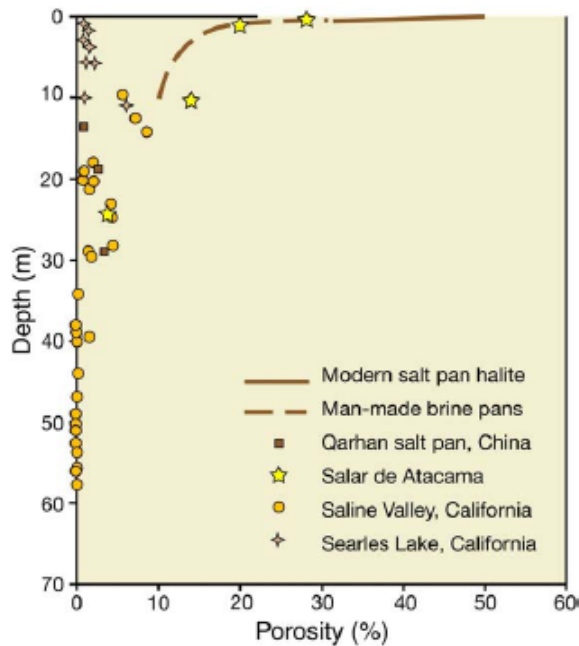

Figure 9 – Effect of Mg:Li Ratios on Production Costs (Yaksic and Tilton 2009)

Ranking	Deposit, province or country	Country	Grade (percent lithium)	Ratios (magnesium to lithium)	Evaporation rate (mm per year)	Range of costs (dollars per pound)
1	Atacama	Chile	0.15	6.4	3700	0.70–1.00
2	DXC	China (Tibet)	0.04–0.05	0.22	2300	1.00–1.20
	Zhabuye	China (Tibet)	0.05–0.1	0.001	2300	1.00–1.20
4	Taijinaier	China	0.03	34	3560	1.10–1.30
	Hombre Muerto	Argentina	0.06	1.37	2600	1.10–1.30
	Olaroz	Argentina	0.09	2	2600	1.10–1.30
	Silver Peak	USA	0.023	1.5	1000	1.10–1.30
8	Rincon	Argentina	0.04	8.5	2600	1.20–1.50
	Maricunga	Chile	0.092	8	2600	1.20–1.50
	Greenbushes	Australia	1.36	n/a	n/a	1.20–1.50
11	Uyuni	Bolivia	0.04	19	1500	1.30–1.80
	Masvingo (Bikita)	Zimbabwe	1.4	n/a	n/a	1.30–1.80
	Bernic Lake	Canada	1.28	n/a	n/a	1.30–1.80
	Cherryville	USA	0.68	n/a	n/a	1.30–1.80
15	Barroso-Alvao and Covas de Barroso	Portugal	0.37–0.77 and 0.72	n/a	n/a	1.40–2.00
	Gajika	China	n/d	n/a	n/a	1.40–2.00
	Maerkang	China	n/d	n/a	n/a	1.40–2.00
18	Brazil	Brazil	n/d	n/a	n/a	1.50–2.00
19	Separation Rapids	Canada	0.62	n/a	n/a	1.80–2.20
20	Quebec	Canada	0.53	n/a	n/a	1.90–2.30
	Jaijika	China	0.59	n/a	n/a	1.90–2.30
22	Qaidam Basin	China	n/d	n/d	n/d	1.50–2.50
23	Searles Lake	USA	0.0065	125	1000	2.00–2.50
	Kings Mountain	USA	0.69	n/a	n/a	2.00–2.50
25	Etykinskoe	Russia	0.23–0.79	n/a	n/a	2.10–2.70
26	Namibia	Namibia	n/d	n/a	n/a	2.20–2.80
	Salton Sea	USA	0.022	1.3	1800	2.20–2.80
	Great Salt Lake	USA	0.004	250	1800	2.20–2.80
29	Dead Sea	Israel-Jordan	0.002	2,000	n/d	2.40–3.00
	Manono-Kitololo	Zaire	0.58	n/a	n/a	2.40–3.00
	Bougouni Area	Mali	1.4	n/a	n/a	2.40–3.00
32	Yellowknife	Canada	0.66	n/a	n/a	2.50–3.00
33	McDermitt	USA	0.24–0.53	n/a	n/a	3.50–4.70
	North Carolina	USA	n/d	n/a	n/a	3.50–4.70
	Russian pegmatites	Russia	n/d	n/a	n/a	3.50–4.70
36	Smackover	USA	0.0386/0.0365	20	n/d	5.00–6.40
37	Oceans	n/a	0.000017	n/a	n/a	7.00–10.00

Notes: n/d = no data are available.

n/a = not applicable, either because the evaporation rate and ratio of magnesium to lithium are not relevant for lithium extracted from hard-rock mineral deposits or for other reasons.

Source: Yaksic (2008) and the sources cited there. Production costs are estimates by Yaksic (2008) based on a variety of industry sources.

Figure 10 – Comparison of Battery Technologies by Volumetric and Gravimetric Energy Density (Tarascon and Armand 2001)
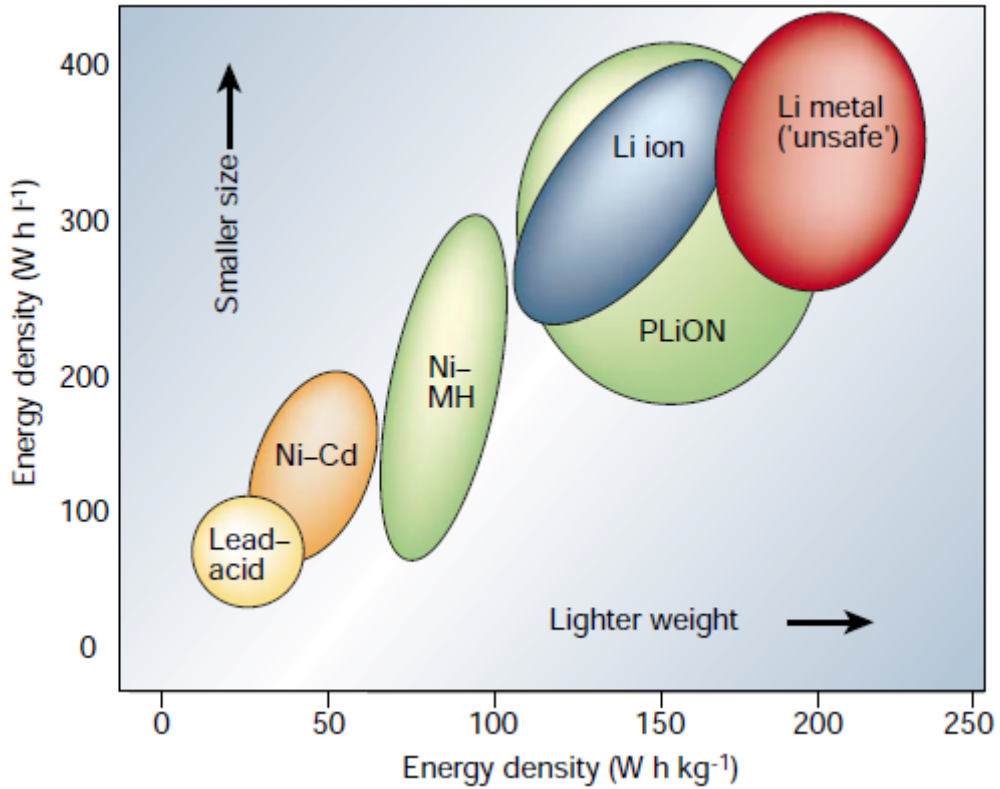

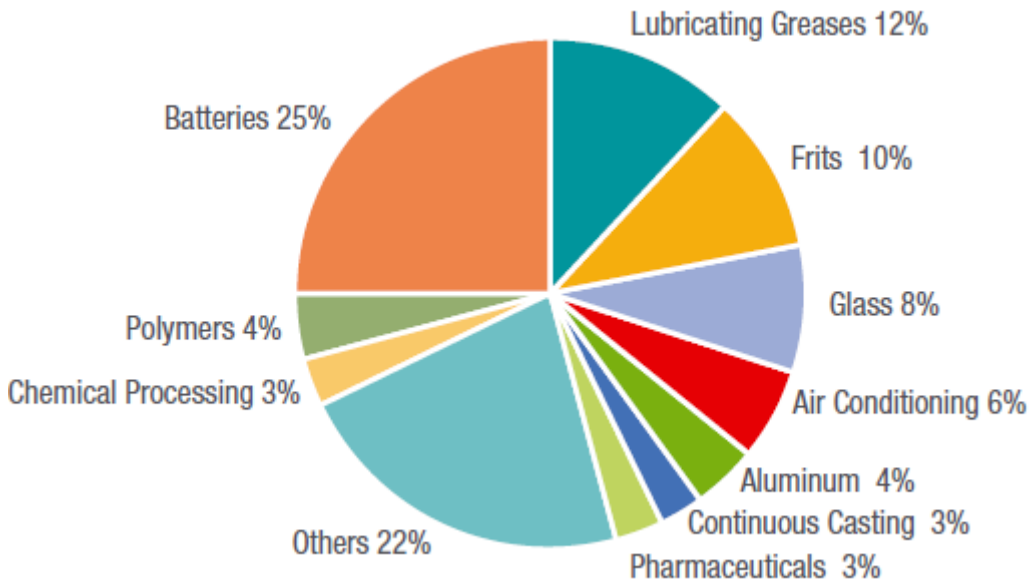Figure 11 – Main Uses of Lithium, as of 2007 (SQM 2007)

Figure 12 – Cumulative Availability Curves for Lithium (Yaksic and Tilton 2009)