The Role of Clays in Fixing Lithium

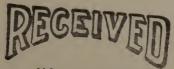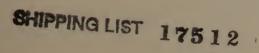# The Role of Clays in Fixing Lithium

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CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

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A study of some methods by which lithium is retained in clay minerals

CONTENTS

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By Harry C. Starkey

ABSTRACT

Lithium, in small amounts, is widespread in clay minerals. It may be present in clays as impurities, as inclusions, in lattice cavities, adsorbed on the surface, or by isomorphous substitution. Isomorphous substitution is the most common occurrence. The clay containing the largest amount of lithium is swinefordite, but this mineral is found in only one location. Hectorite, a trioctahedral smectite, can contain a large amount of lithium and is not uncommon in arid regions.

Two types of origin have been postulated for hectorite: hydrothermal alteration of a montmorillonite, which was suggested first and is valid in some cases, and direct precipitation in saline lakes, which has gained support in recent years.

INTRODUCTION

Lithium has been reported to be widespread in small amounts in soils and sediments of the United States, especially in the arid Southwest (Shacklette and others, 1973; Cannon and others, 1975). This lithium is probably associated with the clay minerals (Horstman, 1957; Tardy and others, 1972). Siroonian and others (1959) pointed out that minor elements such as lithium may occur in minerals in one or more of several ways, such as in admixed impurities, in inclusions or alteration products, in lattice cavities, adsorbed at the surface or in structural imperfections, or by isomorphous replacement in the structure. We are primarily interested in the last two methods, but the others also pertain to the investigation of the presence of lithium in clays.

Lithium has not been routinely reported in clays because the analyst was not looking for it specifically and because its determination is not part of a routine chemical analysis. Because lithium has a low atomic weight (6.9), the weight percentage is small when compared with that of other elements, and its absence from an analysis would not be noticeable in the summation of the elements.

Horstman (1957) and Ashry (1973) reported lithium in various clay minerals. Tardy and others (1972) showed lithium contents of clay minerals ranging from as low as 7 ppm in some montmorillonites and some kaolinites to as high as 6,000 ppm in hectorites. Villumsen and Nielsen (1976), in their study of the Quaternary sediments of eastern Jutland, found that most of the lithium in the sediments was located in the clay-size fraction.

This report reviews some of the occurrences of lithium in clays and discusses possible means by which lithium is bound to the clays.

CLAYS CONTAINING LITHIUM

KAOLINITES

There are conflicting views concerning the presence of lithium in kaolinites, although it has been reported many times. Mason (1958) stated that kaolinite consists of one Si_4O_{10} sheet and one aluminum-hydroxyl sheet and that the aluminum and silicon are not replaced by other elements. Therefore, pure kaolinite analyses are close to the ideal formula, which would indicate that most, if not all, lithium in kaolinites is present as impurities. Horstman (1957), however, stated that magnesium may substitute for aluminum in kaolinite, creating a charge deficiency that is satisfied by a lithium ion moving into one of the vacant octahedral sites. He further stated that one lithium ion may enter for each magnesium ion present, giving a Mg/Li weight ratio of 3.5. Some natural samples approach that value.

McLaughlin (1959) reported 3 ppm lithium or less in two samples of dickite, and 12 ppm or less in two samples of halloysite. He reported a range from 0 to 100 ppm in six samples of kaolinite. Another sample of kaolinite had 220 ppm lithium in the sand-size fraction, but the sample reportedly contains micaceous material.

Ronov and others (1970) reported that kaolinite that formed from granodiorite contained about 45 ppm lithium, but kaolinite that formed from amphibolite contained as much as 118 ppm lithium. These determinations, however, were made on whole rocks; the purest sample was listed as ≈100 percent kaolinite, which indicates the possible presence of minor impurities.

Ashry (1973) concluded that the lithium present in river sediments was located in the kaolinites, probably in the octahedral lattice vacancies to compensate for magnesium substitution. No analyses were made of kaolinite separates. His conclusion is based on a correlation between the quantity of kaolinite present and the lithium content. The lithium could be in some mineral associated with the kaolinite.

In their studies of kaolinites from altered schists and granites, Mosser and others (1974) observed that the amounts of trace elements in these kaolinites were rather small and that lithium was more plentiful in the kaolinites from the granites than in those from the schists.

Samples of flint clays showed lithium contents of more than 2,000 ppm (Tourtelot and Brenner-Tourtelot, 1978), but the lithium was thought to be located in a small amount of a dioctahedral chlorite similar to cookeite, which had not been recognized previously in sedimentary rocks.

H. A. Tourtelot and Meier (1976) mentioned three possible modes of occurrence of lithium in kaolinitic clays of western Pennsylvania: (1) substitution (possibly with magnesium) in the structure; (2) presence in detrital minerals from the same source area as the kaolinite; (3) presence in previously unrecognized authigenic minerals that formed under conditions similar to those in which kaolinite was formed. In most of these cases, it is possible that the lithium exists in minerals other than in the kaolinite.

The possibility that lithium exists in the structure of kaolin minerals seems poor to most people involved in clay studies. Brindley (1951) stated that mineralogical and chemical studies indicate little variation in the composition of kaolin minerals. This is supported by Grim (1968), who stated that analyses of many kaolinites have shown very little lattice substitution, except for the substitution of very small amounts of iron and titanium in poorly crystalline varieties. Although analyses indicate some substitution in the structure, the fine-grained nature of the samples makes it difficult to be certain that all of the impurities have been removed from kaolinites (Deer and others, 1965). When analyzing kaolinites, one must make certain that all impurities are eliminated or identified.

MICAS AND ILLITES

Lithium is widespread in micas (Stevens and Schaller, 1942; Foster, 1960; Zawidzki, 1976). This is of great importance in the study of clay minerals because of the degradation of the micas, by weathering, through illite to mixed-layer clays and then to smectites. The lithium is not carried to the montmorillonites during this transformation; because it is highly mobile, it is soon weathered out of the mica and either is carried away in solution or remains to be incorporated into the structure of newly formed clay minerals (Ronov and others, 1970). The ubiquity of micas suggests that they should be considered as the carriers of lithium in clay mixtures. The micas may be so fine grained that they cannot be separated from other clay minerals and may not be recognized, unless the clays are given a very close examination by X-ray powder diffractometry and other methods.

Lithium is concentrated in the late stages of pegmatite formation and consequently is found in such minerals as spodumene, lepidolite, and petalite (Ahrens and Liebenberg, 1946). When not enough lithium

is present to form these minerals, the lithium moves into the structure of other micas, where sites of 6-fold coordination are available and where it is associated with ions of similar size, such as Mg^{+2}, Fe^{+2}, and Al^{+3}.

SMECTITES

The trioctahedral smectites contain the largest amounts of lithium; dioctahedral smectites contain little lithium. Hectorite is the lithium-bearing trioctahedral smectite reported first by Foshag and Woodford (1936). This clay has been reported by various researchers to have Li_2O contents of more than 1.0 percent (Ross and Hendricks, 1945; Starkey and others, 1977). No lower limit has been defined for the lithium content of hectorite; clays containing less than 1.0 percent Li_2O have been called hectorite also (Dyni, 1976; Brenner-Tourtelot and Glanzman, 1978).

Two types of genesis exist for lithium-bearing trioctahedral smectites: (1) hydrothermal alteration and (2) precipitation in high-alkali lacustrine deposits. Regarding the first, Ames and others (1958) stated that the hectorite at the type locality at Hector, Calif., was formed by the action of solutions containing fluorine and lithium in the last stages of hot-spring activity. Sand and Regis (1960) reported on a lithium-bearing montmorillonite from the Spider Uranium Mine, Honeycomb Cliffs, Tooele County, Utah, that is identical to hectorite but contains more lithium and fluorine. They attributed its formation to the action of Li-Mg-F solutions. Shawe and others (1964) reported on a lithium-bearing montmorillonite in a hydrothermally altered tuff. Later, Starkey and Mountjoy (1973) identified this clay as a mixture of montmorillonite and hectorite.

Faust and others (1959) demonstrated that ghassoulite from the Djebel Ghassouel (Rhassoul) mine in Morocco is the same as hectorite, and that it was formed under conditions similar to those described by Millot and others (1957), who had postulated formation by precipitation in a lacustrine environment. Dyni (1976) described a trioctahedral lithium-bearing smectite from the Green River Formation in Utah that is of probable lacustrine origin. Glanzman and others (1978) described lithium-rich fluviatile-lacustrine sediments near McDermitt, Nev., which contained clays with as much as 0.65 percent lithium.

Norton (1965) reported a lithium-bearing montmorillonite from Yavapai County, Ariz. He stated that the beds were originally formed as a lake sediment but indicated that the beds were later altered to a bentonitic clay in part by hydrothermal solutions. These smectites are found primarily in arid regions (Harder, 1972; Tardy and others, 1972;

Vine, 1975; Brenner-Tourtelot and Glanzman, 1978). Other areas of the arid southwestern part of the United States also contain lithium-bearing smectites (Cannon and others, 1975; Vine and others, 1975, E. B. Tourtelot and Meier, 1976; Starkey and Blackmon, 1979).

The lithium-bearing smectites from Pleistocene Lake Tecopa in southeastern California that were reported by Starkey and Blackmon (1979) are detrital. The origin of these clays was not determined, although it is possible that they were formed in lakes in the Ash Meadows region to the north.

One occurrence is known of a lithium-bearing smectite that is not found in an arid environment. This is a dioctahedral-trioctahedral smectite that has been given the name swinefordite (Tien and others, 1975). This clay is formed as a weathering product of spodumene and as pseudomorphs after spodumene. It is found in an open-pit mine at Kings Mountain, N.C., along quarry walls and along fissures. When hydrated, it looks like petroleum jelly and feels like grease; it has the highest lithium content known in clays. Five analyses reported by the authors show values for Li_2O that range from 4.29 to 5.66 weight percent.

FIBROUS CLAYS

Although the fibrous clays are not as common as the smectites and kaolinites, they have been reported to contain significant amounts of lithium. Tardy and others (1972) reported ranges from 19 to 90 ppm lithium in palygorskite, and from 370 to 1,000 ppm lithium in sepiolites. They stated that sepiolites were precipitated in lagoonal environments during arid periods. Velde (1977) also stated that sepiolites could be formed chemically in a saline environment. Millot (1970) and Tardy and others (1972) have shown that palygorskite can be precipitated in lacustrine or lagoonal environments.

SOURCES OF LITHIUM IN CLAYS

Mason (1958) reported that during magmatic crystallization, lithium is incorporated into pyroxenes, amphiboles, and micas, although a considerable amount remains until the last stages of differentiation. Ronov and others (1970) also stated that during magmatic differentiation lithium replaces magnesium, ferrous iron, and aluminum in silicates and aluminosilicates, and a small portion accumulates in residual melts to form lepidolites and spodumenes.

Weathering removes lithium from the above named minerals (Zawidzki, 1976). According to Heier and Billings (1969), the lithium extracted by weathering is removed with the soil solution or is incorporated into clay minerals. The lithium removed with the soil solution may be incor-

porated into the ground water or may be carried off in streams. The water carried off by streams will eventually reach the oceans or it may accumulate in closed basins, such as those in the Basin and Range province of the Southwestern United States. In such basins, lithium, as well as other minerals, would be concentrated through evaporation. If the proper conditions of high pH and sufficient amounts of silica and magnesium are present, trioctahedral smectites or sepiolite may be formed (Tardy and others, 1972; Starkey and Blackmon, 1979).

Hydrothermal waters may not only pick up lithium from downward-percolating surface waters but may also leach lithium from the underground rocks through which they pass. Lithium from these waters may be incorporated into preexisting clays.

Lithium-bearing waters from springs are thought by some to be the source of lithium in clays, especially in the case of trioctahedral smectites (Ames and others, 1958; Norton, 1965). Brenner-Tourtelot and Glanzman (1978) acknowledged the possible presence of thermal springs in the Horse Spring Formation of Miocene age in southern Nevada, but they suggested that the waters from these springs may have actually freshened the playa waters and lowered the content of lithium in clays.

DISCUSSION

Lithium that is found in the clay mineral itself, rather than being present as impurities, most likely is incorporated into the structure during the formation of the clay. It also may be added to the clay by hydrothermal alteration, although this method apparently is not as common as the inclusion of lithium along with magnesium in the precipitation of the clay.

In nature, lithium is rarely, if ever, found on the exchange sites of clays, although Lombardi (1963) claimed that lithium is removed rapidly from water by clay minerals and that 98 percent of the lithium in the waters of Vega Spring in the Saline Valley of California was removed in the 2 mi from the spring to the salt deposits of Saline Valley. He suggested no method by which the lithium could be removed from the water by clays.

The lithium could not be removed from the water by clays through cation exchange because a variety of cations other than lithium are present in these waters. Any of these cations would be adsorbed by the clays in preference to lithium. Lithium, because of its size and charge (Heier and Adams, 1964), is at the bottom of the cation-replacement series (Lawrence, 1958; Carroll, 1959) and can be replaced by any of the competing cations in the waters.

Lithium can enter into the montmorillonite structure if the montmorillonite first is saturated with lithium ions and then is heated (Greene-Kelly, 1955). In the laboratory, lithium-saturated clay can be prepared because the exchanging solution contains only lithium cations, which, because of their preponderance, can replace the cations originally on the exchange sites. If this is done, a question still exists as to where the lithium goes when it enters the clay structure.

Many investigators (Greene-Kelly, 1955; White and others, 1961; Glaeser and Mering, 1967; Mering and Glaeser, 1967; Schultz, 1969) believe that when a lithium-saturated montmorillonite is prepared in the laboratory and heated, the lithium is driven into vacant sites in the octahedral layer if the layer charge is in the octahedral layer. This neutralizes the montmorillonite and makes it nonexpanding. With trioctahedral smectites, no reduction of expansibility takes place because the octahedral sites are filled at the time of formation and no place remains in the octahedral layer for the lithium ions to enter. If the lithium does enter the octahedral layer of a dioctahedral smectite, the clay is not converted into a trioctahedral clay. This is illustrated by the fact that a lithium-treated dioctahedral clay will not expand with glycerol, whereas a natural lithium-bearing trioctahedral clay will expand with glycerol. Dyni (1976) stated that he knew of no experimental demonstration of the transformation of a dioctahedral smectite to a trioctahedral one.

Russell and Farmer (1964), and Ertem (1972) suggested that although some lithium may migrate into vacant octahedral sites upon heating lithium-saturated montmorillonite, the remainder reacts with the lattice hydroxyls or interlayer water to yield protons. Heller and Kalman (1961) had previously concluded that the lithium entered the octahedral layer and lodged somewhere between the zero plane (the plane of the octahedral cation) and the adjacent oxygen sheet. Heller and others (1962) reported that the lithium does not enter into the octahedral layer because such entry would produce a pyrophyllite structure, and the obtained infrared data do not match those of pyrophyllite. Others believe that most, or all, of the lithium enters into the hexagonal holes in the structure (Tettenhorst, 1962; Calvet and Prost, 1971).

Ostrom (1960) identified a mixed-layer phase in hectorite from Hector, Calif., and deduced that it was an intermediate phase between phlogopite and hectorite. He suggested that hectorite is the product of the action of hot springs on a nonexpanding trioctahedral magnesium-silicate mineral, such as phlogopite. To my knowledge this is the only suggestion that hectorite is formed by the alteration of a mica.

In conclusion, the data show that lithium is not readily incorporated into the structures of existing smectites. This is borne out by the conclusions of Tardy and others (1972), which show that, in altered clay

minerals, little lithium is present; in detrital clay minerals, lithium content is moderate; and, in magnesian clay minerals formed in a dolomitic or sulfate facies, lithium is greatly enhanced. Tardy and others (1972) stated that the amount of lithium may serve as an indicator of the detrital or authigenic origin of clays. Heier and Billings (1969) also stated that lithium from soil solutions is incorporated into "precipitation clay minerals." Lithium substitutes for magnesium or Fe^{+2} in the formation of minerals (Heier and Adams, 1964), and magnesium is essential for the formation of smectites (Harder, 1972).

LITHIUM-FLUORINE RELATIONS

A relation may exist between the content of lithium and the content of fluorine in smectites. Foster (1960) showed that a 1:1 ratio between Li_2O and fluorine existed in aluminum-lithium mica. E. B. Tourtelot and Meier (1976) noted that in samples of smectite containing less than 1 percent fluorine, the lithium content increased with the fluorine content; but, in samples containing more than 1 percent fluorine, the lithium content tended to decrease as the fluorine content increased.

Granquist and Pollack (1960) synthesized hectorite with and without the use of any fluoride, but their best results were obtained with a mix that included LiF as one of the starting materials. Laponite, a commercially synthesized hectorite, also contains fluorine (Neumann, 1965). The Li_2O/F ratio of natural hectorite is 5.0, and the ratio for Laponite is 4.4. Although these two ratios are similar, it is still unclear whether or not fluorine is necessary for the incorporation of lithium into the smectite structure.

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