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THE MINERALOGY AND GEOCHEMISTRY OF LITHIUM IN THE  
POPOTOSA FORMATION, SOCORRO COUNTY, NEW MEXICO

By

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INTRODUCTION

Samples found to contain anomalous amounts of lithium were collected from the Popotosa Formation of Miocene age in Socorro County, New Mexico, by G. O. Bachman (oral commun., 1976). In 1977 and 1978, additional sampling of the area and subsequent analytical work by the senior author confirmed the lithium anomaly described in this report. In general, clays and shales average 50 to 60 ppm Li (Heier and Billings, 1970), but many claystones of Tertiary lake beds average 20 to 30 ppm (Tourtelot and Meier, 1976; Brenner-Tourtelot and others, 1978). For the purpose of this report, samples containing greater than 300 ppm Li are considered anomalous (Davis, 1976) for these depositional environments. Rocks containing greater than 1,000 ppm (0.1 percent) Li are considered to be of possible future economic interest.

Although the lithium contents in many Tertiary lake beds and volcanoclastic sediments are generally low, anomalous amounts of lithium do occur in some of these deposits where there is a propitious combination of arid conditions resulting in concentrated brines in playa lakes, lithium-bearing water inflow, generally from thermal springs, and abundant volcanoclastic debris. Such anomalies have been demonstrated, for example, in the McDermitt, Nevada, area (Glanzman and others, 1978) and the Lake Mead, Nevada, area (Brenner-Tourtelot and Glanzman, 1978). In the ancient playas and lakes which contain volcanoclastic sediments, the original glassy materials were altered to clay and zeolite minerals. Lithium was liberated by the alteration of volcanoclastic sediments and subsequently incorporated into authigenic clay minerals.

## ACKNOWLEDGMENTS

The senior author is grateful to George O. Bachman for bringing the lithium-rich tuff beds to her attention and for introducing her to the area. Allen L. Meier ran the chemical analyses for Li, K, Ca, Mg, and F, Mollie J. Malcolm the semiquantitative six-step spectrographic analyses, and Robert W. Brown the X-ray diffraction analyses. James M. Nishi helped with preparation and photographing of scanning electron microscope samples.

## GEOLOGY

The Popotosa Formation was originally described and named by Denny (1940) and later assigned as a lower formation of the Santa Fe Group by Machette (1978a). Although the Popotosa is present throughout a wide area of central New Mexico (see Chapin and Seager, 1975, fig. 5), it is well exposed north of Socorro near the Rio Salado (fig. 1). Figure 1 shows the general outcrop pattern of the Popotosa Formation in the study area and the location of sample sites. K-Ar ages of interbedded volcanic rocks suggest an early to late(?) Miocene age for the formation (Machette, 1978a; Chapin and others, 1978). It represents the early basin-fill deposits in the Rio Grande Rift and consists of intertonguing fanglomerates, sandstones, and playa deposits. Near the base, it is interbedded with the andesite at Cerritos de las Minas (26 m.y., Machette, 1978a); elsewhere the Popotosa unconformably overlies or is in fault contact with older rocks ranging in age from middle Tertiary (Oligocene) to Precambrian.

The Popotosa is unconformably overlain and (or) is in fault contact with an upper formation of the Santa Fe Group, locally named the Sierra Ladrones Formation (fig. 1). The Sierra Ladrones consists of piedmont-slope and axial river facies of a through-flowing drainage system, the ancestral Rio Grande, which first became integrated about 4 m.y. ago (Bachman and Mehnert, 1978). Conversely, the Popotosa Formation reflects an earlier closed-basin drainage system that was extensively deformed in late Miocene-early(?) Pliocene time (Chapin and others, 1978). Locally, beds of the Popotosa Formation dip as much as 60°, and faults offsetting these beds have hundreds to thousands of meters of displacement. The Sierra Ladrones Formation is markedly less deformed than the Popotosa although along the margins of the rift; these younger beds are locally deformed and displaced by Pleistocene faulting (Machette, 1978a, 1978b).



The playa facies of the Popotosa Formation is best exposed between the Ladron and Lemitar Mountains, although it crops out from the north end of the Ladrones to the south end of the Socorro Mountains, a distance of about 55 km. The extensive area of playa outcrop suggests a wide and relatively persistent structural low in Miocene time. At the present time, the area of best exposure continues to be structurally low but occupies a horst position between basins to the east and west (Machette, 1978b).

#### MINERALOGY

Whole-rock X-ray diffractometer patterns were run on all of the samples collected in 1977. The patterns were generated by  $\text{CuK}\alpha$  radiation (34 kV, 18 mA) while scanning at  $2^\circ 2\theta$  per minute. Full-scale deflections are 3,000 counts per second. The data from the X-ray analyses are presented on figure 2. The samples from each particular site are listed in stratigraphic order, but stratigraphic correlation between sample sites is uncertain. The samples represent a wide and mixed range of sedimentary rock types; few true end-members are present. For example, many of the altered tuff beds contain clastic debris and, conversely, many of the clastic rocks and claystones

A brief field description of each sample, approximate thickness of the interval sampled, and the site location are listed in table 1. Beds of altered tuff were sampled in detail, but intervening beds were sampled less consistently. The term "altered tuff" describes a rock that, by texture, morphology, and color, appears originally to have been comprised mostly of volcanic ash or pumice. Nontuffaceous strata within, above, and below the altered tuff beds were sampled for comparison. Both air-fall and water-lain tuffs are present. However, some tuff beds are so altered that their original sedimentary structures and textures have been obliterated. In general, the altered tuffs are white to yellow on outcrop, in contrast to the general reddish and brownish hues of the Popotosa Formation. However, some of the red to brown sandstone and siltstone beds contain large (2 cm) altered pumice fragments. Most of the original glassy component of the tuffs has been altered, as shown by X-ray analysis (amorphous, unaltered glass generally shows as a broad hump between  $14^\circ$  and  $25^\circ 2\theta$  on the X-ray pattern).

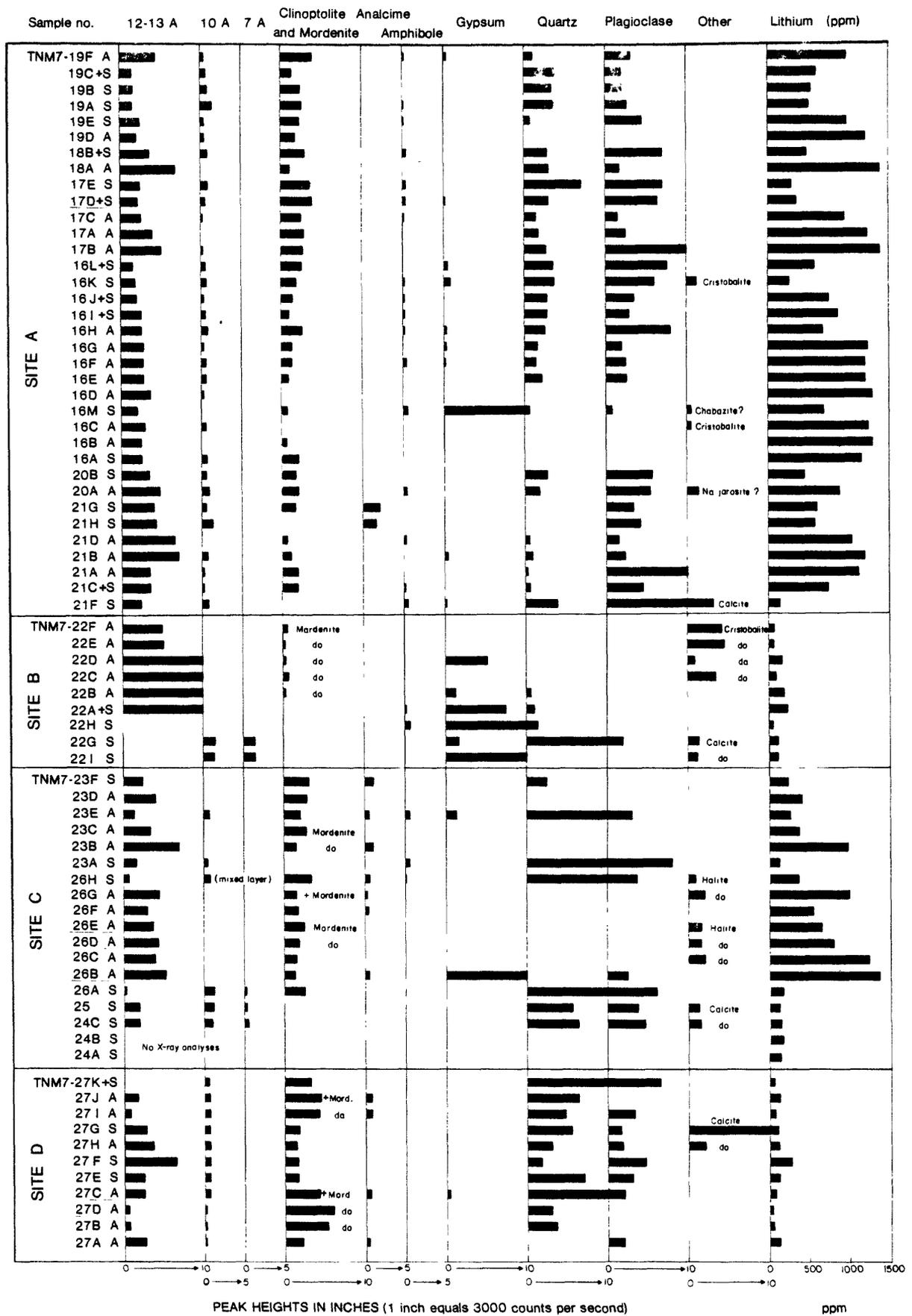


Figure 2.--Mineralogy and lithium contents of samples from the Popotosa Formation. An "A" after the sample number indicates an altered tuff; "+S" indicates tuffaceous sediment; and "S" indicates nontuffaceous sediment. The relative abundance of minerals in whole-rock samples are shown by their X-ray peak heights. A full bar represents a full-scale deflection on the X-ray pattern, 3,000 counts per minute. Lithium contents were determined by atomic absorption spectroscopy.

The nontuffaceous-appearing sediments enclosing the altered tuff beds originally contained some pyroclastic material, which has since been altered to clay and zeolite minerals. As can be seen on figure 2, these sediments contain less lithium and more quartz and feldspar minerals than the interbedded altered tuffs. Amphibole minerals occur in both the altered tuffs and in the sediments. The sediments also contain some calcite or gypsum as cementing material. The discussion that follows briefly describes the mineralogy of the lithium-enriched altered tuff beds, which are composed primarily of clay and zeolite minerals.

Table 1.--Localities of sample sites and description of samples. Samples at each site listed in descending stratigraphic order; correlation of stratigraphic position between sites is uncertain

Sample	Description
Site A: Silver Creek, east side of small unnamed tributary creek, natural exposure, Riley 15' quadrangle, N. Mex., lat 34°18'53", long 107°02'02"	
Fine-grained facies of Popotosa Formation, unconformably overlies andesite	
TNM7-19F	Altered tuff, clayey, pinkish gray-brown; 0.5 m above 19C
19C	Claystone, dark pinkish-gray, hard; mottled with 19B
19B	Claystone, grayish-green; mottles in 19C; also in 6-cm lenses
19A	Altered claystone in units 19B and 19C
19E	Sandstone, pink, fine-grained, tuffaceous; 5 cm thick
19D	Altered tuff, white, dense; 3 cm thick
18B	Claystone, dark pinkish-brown, laminated with white altered tuff; 6 cm thick
18A	Altered tuff, white, coarse-grained; grades up into 18B; 8 cm thick
17E	Claystone, dark-brown, conchoidal fracture
TNM7-17A-D	Altered tuff, white; 0.4 m thick
17D	Contact zone of altered tuff and overlying claystone (17E)
17C	Altered tuff, white, very fine grained
17A	Altered tuff, white, coarse-grained, friable
17B	Altered tuff, white; 3.5 m above 16H
16M	Gypsum, fills joints
16L	Sandstone, gray, pumiceous; 70 cm thick

Table 1.--Localities of sample sites and description of samples. Samples at each site listed in descending stratigraphic order; correlation of stratigraphic position between sites is uncertain--continued

Sample	Description
16K	Shale lens, brown; in gray tuffaceous sandstone
16I	Sandstone, gray, pumiceous, clayey, finely laminated
TMN7-16C-H	Altered tuff; 2 m thick
16H	Altered tuff, brown, clayey; 6 cm thick
16G	Pumice fragments, white; 4 cm thick; occurs in brown claystone; 16G is 80 cm above base of 16B
16F	Altered tuff, gray to brownish-gray, reworked, fluviatile
16E	Altered tuff, gray, fluviatile; manganese staining in joints
16D	Altered tuff, brownish-gray, clayey, slickensided; selenite crystal in joints; 16 m thick
16M	Selenite crystals in 16D
16C	Altered tuff, white; contains remnant glass shards; 6 cm thick
16B	Claystone, gray to light-gray, tuffaceous; selenite crystals in joints; 4-8 cm above brown ash
16A	Claystone, dark-brown, sandy to silty; underlies lowest tuff exposed on north side of ridge. Remainder of section offset to south side of ridge
20B	Claystone, pink; 30 m thick
20A	Altered tuff, white; 8 cm thick
TNM7-21	Interbedded claystones and altered tuffs, 16 m thick, 10 m below base of 20A
21G	Claystone, light yellowish-gray, silty
21H	Claystone, yellow, hard; 2 cm thick
21D	Pumice, very light-gray, altered; occurs in coarse-grained sandstone
21B	Claystone, brown; laminated with white altered tuff
TMN7-21A	Altered tuff, white; occurs in 1 cm pods
21C	Sandstone, pinkish-brown-gray, coarse-grained
21F	Siltstone, slightly pinkish-brown-gray, typical appearance of the finer-grained facies of the Popotosa in this area. Occurs under 0.5-cm-thick limestone

Table 1.--Localities of sample sites and description of samples. Samples at each site listed in descending stratigraphic order; correlation stratigraphic position between sites is uncertain--continued

Site B: Canada Popotosa, ash pit at south end south-trending ridge, San Acacia 7 1/2' quadrangle, N. Mex. lat 34°21'56", long 106°59'27". Fine-grained facies of Popotosa Formation, underlies Precambrian fanglomerate facies (Machette, 1978a)

Sample	Description
TNM7-22	2-m-thick clays (bentonite) interbedded with gypsiferous claystones
22F	Clay, light-yellow, popcorn weathering; top of pit
22E	Clay, light-yellow
22D	Clay, light-yellow; middle of bed
22C	Clay, gray-green, shaley; lens
22B	Clay, light-yellow, blocky-weathering
22A	Claystone, dark gray-green, gypsiferous
22H	Siltstone, yellow-gray, hard, gypsiferous; 1-mm thick beds
22G	Claystone, red-brown, silty
22I	Claystone, dark-green-gray, gypsiferous

Site C: Arroyo Rendija, east side of small north-trending ridge, San Acacia 7 1/2' quadrangle, N. Mex. lat 34°17'20", long 106°58'53". Upper part of lower transitional facies (mostly sandstones) of Popotosa Formation (Machette, 1978a)

TNM7-23	Altered tuff bed 1.2 m thick
TNM7-23F	Siltstone, dark-brown
23D	Altered tuff, light-yellowish-gray, clayey, shaley weathering; 10 cm thick
23E	Altered tuff, light-yellowish-gray, clayey, very hard; 15 cm thick
23C	Altered tuff, light-yellowish-gray, fine-grained, dense; 40 cm thick
23B	Altered tuff, light-yellowish-gray, very clayey; 20 cm thick
23A	Claystone, dark-brown, sandy

Table 1.--Localities of sample sites and description of samples. Samples at each site listed in descending stratigraphic order; correlation of stratigraphic position between sites is uncertain--continued

Sample	Description
TNM7-26	Altered tuff; probably equivalent to unit 23; 1.0 m thick
26H	Siltstone, dark-red-brown, hard
26G	Altered tuff, clayey, dark-yellow-gray
26F	Altered tuff, clayey, dark-yellow, hard, dense, thin-bedded
26E	Altered tuff, light-yellow, silty, hard, gypsiferous
26D	Altered tuff, dark-yellow-green, clayey; weathers to light-yellow blocks
26C	Altered tuff, dark-yellow-gray, very fine grained; weathers to 1-cm thick plates
26B	Altered tuff, dark-yellow, waxy; shaley-weathering
26A	Claystone, dark-red, and medium-red-gray finely-laminated sandstone
25	Claystone, dark-brown, silty, even thin bedding
24A	Claystone, dark red-brown
TNM7-24B	Claystone, dark-red-brown, and yellow, thinly, and irregularly laminated siltstone
24C	Claystone, dark-red-brown, gypsiferous

Site D: Canon del Ojito, south side of north wall of canyon, natural exposure, San Acacia 7 1/2' quadrangle, N. Mex. lat 34°15'59", long 106°57'41". Basal part of Popotosa Formation in this area, rests conformably on 26 m.y. old andesite of Cerritos de las Minas (Machette, 1978a).

TNM7-27	Altered tuffs and volcanoclastic sediments; 6 m thick
27K	Sandstone, pink-gray, medium-grained, tuffaceous, resistant; has black-weathered stain; 70 cm thick
27J	Altered tuff, pinkish-gray, medium-grained
27I	Altered tuff, gray, hard, ledge-forming; 4 cm thick
27G	Clay, stained pink; popcorn texture; a weathering product of 27H
27H	Altered tuff, greenish-white, pumiceous, hard
27F	Conglomerate, white, streaked-pink; contains pebbles of

Table 1.--Localities of sample sites and description of samples. Samples at each site listed in descending stratigraphic order; correlation of stratigraphic position between sites is uncertain--continued

Sample	Description
	volcanic rocks as much as 1 cm in diameter floating in a white clay matrix; 80 cm thick
TNM7-27E	Claystone and siltstone, pink; green along joints; abundant slickensides
27C	Altered tuff, very light gray, medium-grained
27D	Altered tuff, gray, contorted
27B	Altered tuff, pinkish gray, coarse-grained, fluviatile; beds 2-8 cm thick; hard ledge-forming unit
27A	Altered tuff, light-gray, clayey, soft

#### Clay Minerals

A typical X-ray pattern of a white, fine-grained altered tuff (sample TNM7-19D), which contains 1,250 ppm Li is shown on figure 3A. Although the rock appears white, disseminated grains of euhedral, dark-colored biotite can be seen with a hand lens. The main basal (001) reflection of biotite is represented by the peak at  $8.8^\circ 2\theta$ , labeled 10 Å on figure 2. The X-ray pattern also shows the presence of zeolite minerals, most likely clinoptilolite and, possibly a small amount of mordenite (see following section). Additional peaks on the pattern on figure 3A indicate the presence of a clay minerals (labeled C).

The position of the clay mineral 060 reflection at  $61.6^\circ 2\theta$  suggests that this clay is dioctahedral smectite, but the breadth of the peak suggests an admixture of trioctahedral clay. Other elements of this X-ray pattern suggest that this clay is more like a sepiolite than a smectite, but scanning electron (SEM) microphotographs of this sample (fig. 4) and other samples from the area show that the clay is generally platy in habit, not lath-like as sepiolite is commonly described (Millot, 1970). The clay shown in the SEM photographs looks like a smectite. However, it is not hectorite, the lithium-rich smectite, as is evident from the X-ray and chemical analyses. The data on figure 2 suggest that the lithium contents vary with the clay content of the sample; therefore, most of the lithium is probably held in the clay

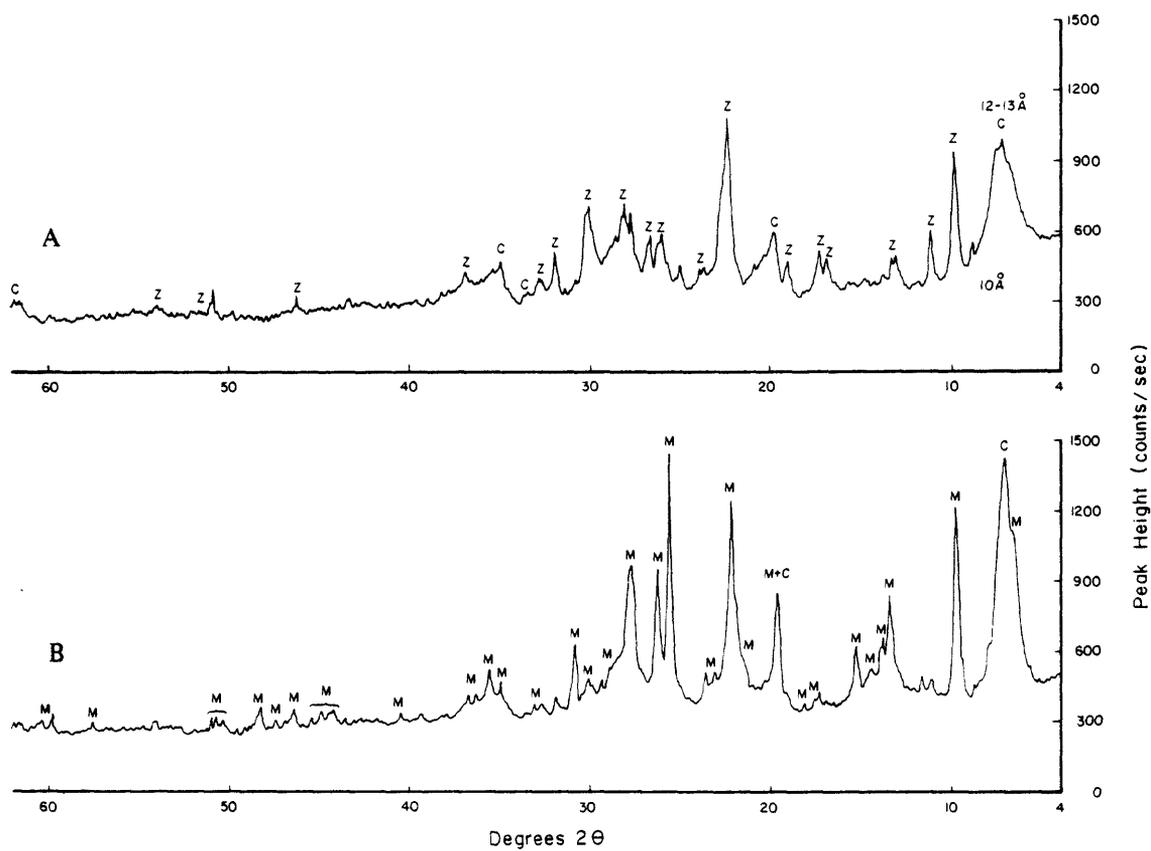


Figure 3.--X-ray diffraction patterns for A, sample TNM7-19D showing clay (C) and clinoptilolite (Z) peaks, and B, sample TNM7-23C showing mordenite (M) and clay (C) peaks.

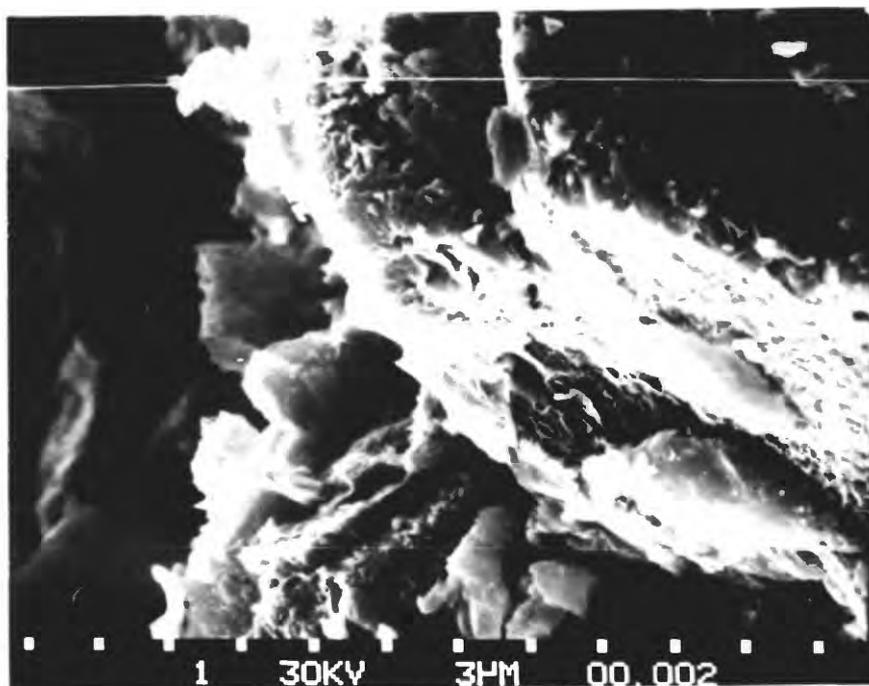


Figure 4.--SEM photograph of clay mineral in sample TM7-19D. Also see X-ray diffraction pattern, figure 3.

minerals in these samples. According to the data we now have, anomalous lithium concentrations in rocks of the Popotosa Formation occur in dioctahedral, or mixed di- and trioctahedral, smectites. A more detailed examination of the clay mineralogy is required to determine the exact species of clay mineral(s) present in the lithium-rich altered tuffs of the Popotosa Formation.

In contrast to the clay minerals just discussed, the clay mineralogy of sample TNM7-22 from a clay pit in the Popotosa (site B, fig. 1) is markedly different. The sampled interval is from an altered tuff that is probably stratigraphically low in the Popotosa. The lithium content (126 ppm) is about twice the average reported for clays. The whole-rock X-ray diffractometer patterns of the sampled interval (TNM7-22A-F, fig. 2) show the presence of cristobalite, gypsum, mordenite, and a smectite, which is most likely montmorillonite. The presence of cristobalite and montmorillonite suggests a slightly different environment of diagenesis from the other altered tuffs sampled.

#### Zeolite Minerals

Zeolite minerals are common in most samples (fig. 2), and clinoptilolite is the most prevalent of those zeolites present. The column on figure 2 labeled "clinoptilolite and mordenite" reports the respective relative abundances of clinoptilolite seen on the X-ray patterns based on the peak height at  $9.9^\circ 2\theta$  and (or) mordenite at  $9.7^\circ 2\theta$ . If mordenite is present in addition to clinoptilolite, its presence is noted as "+mordenite." In these samples mordenite is generally present only in trace amounts. If mordenite is present alone, the sample is labeled "mordenite." Additional zeolites, such as analcime and chabazite, are listed in other columns.

Figure 3B also shows an X-ray pattern of a mordenite-rich sample (TNM7-23C). SEM photographs of the same sample illustrate typical mordenite morphology (fig. 5), and also show that clay minerals are more abundant than the zeolite minerals in this sample. Figure 5A is a view showing the undistinguished morphology of the clay mineral and well-defined mordenite crystals growing in cavities in the clay. Figure 5B is a closeup view of 5A. In the closeup view, both the thin rods of mordenite and some lath-like crystals of clinoptilolite are seen.

It is generally accepted that zeolite minerals can form from the alteration of volcanic glass in alkaline, saline environments (see Mumpton,

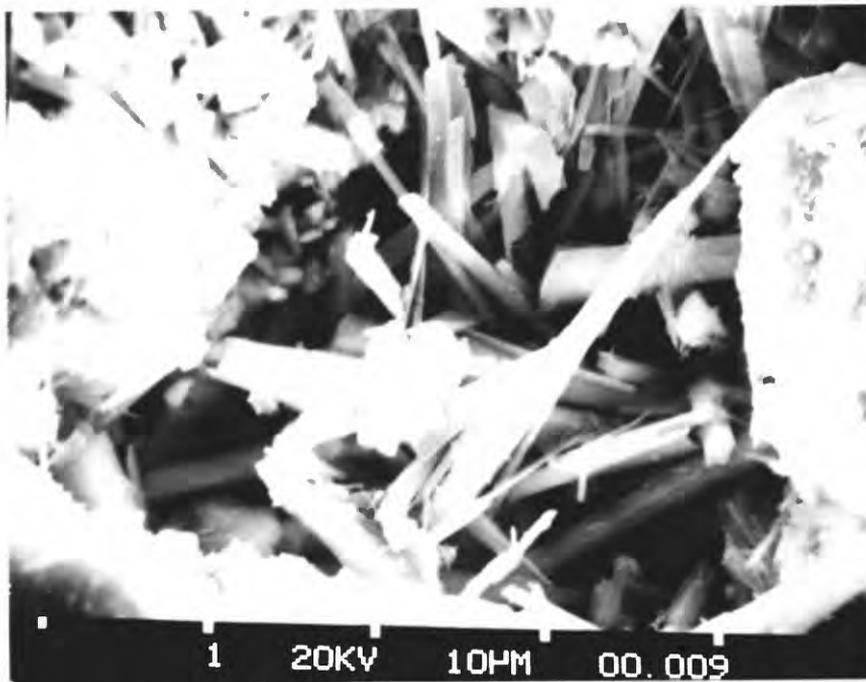
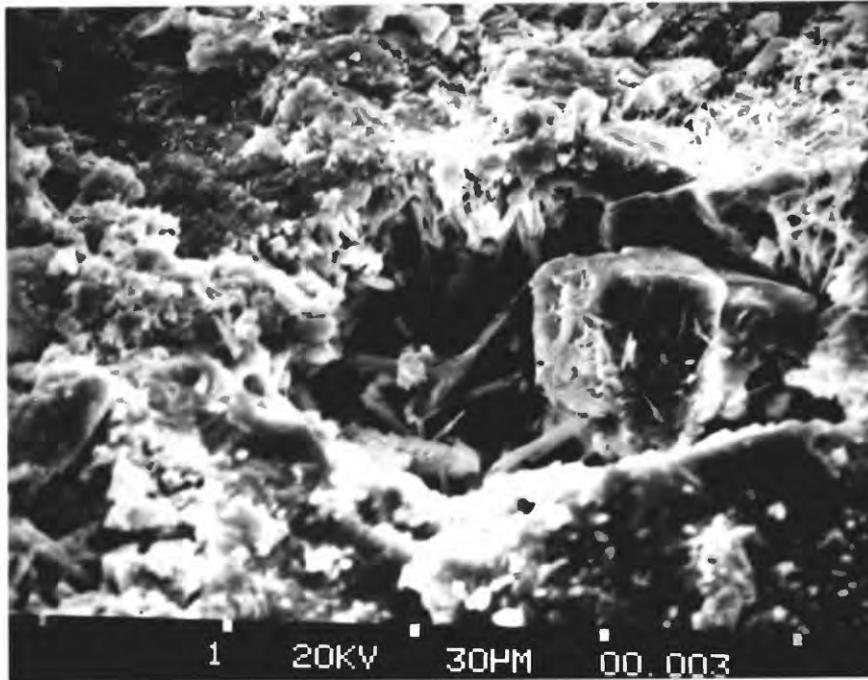


Figure 5.--SEM photographs of sample TNM7-23C showing: A, mordenite needles and clay, and B, a closeup of the cavity in 5A showing lath-like clinoptilolite crystals with the mordenite.

1977; Sand and Mumpton, 1978, for complete discussions). The tuffaceous units, which are interbedded with playa sediments, are more permeable than the claystones of typical playa sediments and, therefore, likely to be minor but geochemically important aquifers (Surdam, 1977). The combination of highly reactive materials such as volcanic glass and its alteration products in a tuff bed, and the tuff bed's enhanced permeability, which allows circulation of ground waters, leads to more pronounced and rapid diagenetic changes than in the less permeable and less reactive claystones of nonpyroclastic playa sediments. The authigenic mineral zonation [fresh glass→montmorillonite+ cristobalite→zeolites (such as clinoptilolite and mordenite→analcime)→ potassium feldspar] is commonly related to increasing alkalinity and salinity of playas and has been well described by Sheppard and Gude (1968, 1969) and Gude and Sheppard (1978).

Some of the pyroclastic beds in the Popotosa Formation contain analcime (fig. 2). The presence of abundant gypsum and lesser amounts of halite also substantiates our interpretation of a playa environment with concentrated brines. At this time, our sampling and knowledge of stratigraphic relationships are not adequate to show whether the previously mentioned mineral zonation is present in specific stratigraphic intervals of the Popotosa Formation, or the zonation is localized by structural control. However, no evidence exists of authigenic potassium feldspar in these samples; therefore, either the chemical environment did not favor its formation or the diagenetic cycle may have been interrupted by tectonic disruption of the ground-water system.

The red to brown colors of most of the sediments of the Popotosa suggest either that most of the formation was deposited in an oxidizing environment, or that the ground-water conditions favored intrastratal oxidation at some later time. A few thin limestones and abundant gypsum beds are present in the playa facies of the Popotosa, but in general, very few carbonate minerals are present. Except for one localized facies, the conglomerates of the Popotosa are generally devoid of or very limited in clasts derived from the Paleozoic and Precambrian rocks. The Paleozoic rocks are the only source for limestones in the area. This suggests that the waters contained little carbonate, and also, that there was not much standing water in the playa. In terms of modern comparisons, the environment of deposition for the Popotosa playa facies would be more like that of the Lower Animas valley, New Mexico, than that of the Great Salt Lake, Utah.

The minerals formed during diagenesis are very sensitive to the chemistry of the intrastratal fluids and to the chemistry and mineralogy of the parent materials. Sample set TNM7-22 (site B, fig. 2) represents a tuff that was altered to clay (samples 22A-F are from tuff; G-I are from the underlying sediments). The altered tuff samples also contain cristobalite and a small amount of mordenite. The mineralogy of these samples can be the result of being either nearer the edge of the playa or higher in a stratigraphic section and thus possibly in fresher water, as in the Sheppard and Gude model (1968, 1969; Gude and Sheppard, 1978). It could also result from the initial alteration of the glass to clay effectively lowering the permeability of the tuff, thereby ceasing alteration by ground-water action.

The lithium contents of sample suite TNM7-22 are also lower than most of the other samples of altered tuff in the Popotosa. The lower lithium contents suggest the same two alternatives as does the mineralogy: (a) the alteration of tuffs and formation of clay took place in fresher water containing less lithium; and (b) the lowered permeability of the beds prevented the subsequent circulation of lithium-rich brine.

#### Mineralogy-Lithium Relationships

The lithium contents of the samples collected are shown graphically on figure 2. The only evident correlation is between lithium and the height of the 12-13 Å clay peaks (that is, relative abundance). This correlation varies between sample sites (for example, compare set TNM7-23 to set TNM7-27) so that if a simple correlation coefficient ( $r$ ) were calculated for all of the samples, it would appear low ( $r < 0.5$ ) even allowing for the qualitative nature of the X-ray diffraction data. However, for samples from a single locality, the correlation coefficient approaches 1 ( $r = 0.96$  in set TNM7-23) indicating a positive correlation between the 12-13 Å clay minerals and lithium.

The lithium contents are not directly related to zeolite content. However, the same conditions that are conducive to the formation of zeolite minerals; that is, the presence of silicic volcanic debris in an alkaline, saline playa, are also conducive to the concentration of lithium and the formation of lithium-rich clays. Zeolites are present in other areas of lithium-rich clays, such as Hector, California (Ames and others, 1958), McDermitt, Nevada (Glanzman, Rytuba, and McCarthy 1978), and Lake Mead, Nevada (Brenner-Tourtelot and Glanzman, 1978). In these areas zeolite and lithium abundance are not necessarily correlative; the most lithium-rich clays and zeolites may not occur in the same bed.

Much has yet to be learned about the various lithium-rich smectites. However, as work progresses on the chemistry of the different water-volcanic glass reactions and the diagenesis of tuffaceous playa sediments, a zonation may be worked out for the different clay minerals similar to the zonation for different zeolite minerals. The significance of such zonations is that the clay mineral suites could be used to predict the occurrence of lithium-rich clays and to predict where in a section of sediments certain minerals should occur (or would have occurred had they not been eroded away). Thus, a reconnaissance sampling from an unstudied basin could suggest whether detailed sampling was worthwhile, and where such sampling should be located.

#### GEOCHEMISTRY

Thirty-eight samples were selected for six-step semiquantitative spectrographic analysis in addition to the atomic absorption and electrode analyses run on all samples. The data from all analyses are presented in table 2. Both results of analysis for lithium--one analysis by atomic absorption spectroscopy (AAS) and one by six-step semiquantitative spectrographic analysis (SSA)--are presented. As can be seen, the average Li content by AAS is higher than SSA by 13 percent. This is due to the lower detection limit and better accuracy of the atomic absorption method (see Meier, 1976, for a discussion of the atomic absorption method). However, the comparison of data for replicate samples shows that the six-step spectrographic method is adequate for most purposes, especially that of reconnaissance work.

The data in table 2 can be divided into a set of lithium-rich altered tuffs (lithium greater than or equal to 1,000 ppm), as well as into a set of all altered tuffs, and into a set of all nontuffaceous sediments, as discussed in the mineralogy section. These three sets of data are summarized in table 3. The arithmetic means of elements in the lithium-rich set and the altered tuff set are almost the same. The average elemental analysis of low-calcium granites, as compiled by Green (1969), is given for comparison because of the overall similarity of the granite's composition with the presumed rhyolitic composition of the altered tuffs. The nontuffaceous sediments were derived from a mixed assemblage of rhyolite ash-flow tuffs and andesites, and should have been considerably more mafic and less potassic than the tuffs.

Magnesium is the only major element significantly enriched in the lithium-rich altered tuffs, relative to the average low-calcium granite



(table 3). Sodium shows a weak tendency to be enriched with lithium while aluminium is unchanged, and the remaining major elements (Ca, K, Fe, and Ti) are significantly depleted. Lithium, in combination with sodium, magnesium, silica, and fluorine, can form the lithium-bearing clay mineral, hectorite. However, the proportions of these elements in these samples, particularly magnesium and fluorine, are too low relative to the lithium content to represent hectorite. Fluorine is enriched by a factor of 1.5 to 2 compared to the average low-calcium granite; but lithium is enriched by a factor of as much as 30, and magnesium is only slightly enriched. The high strontium content (685 ppm, table 3) may indicate the degree of salinity in the original solution that caused the alteration of lithium-rich clay from the glass in the tuffs and tuffaceous sediments.

Among the minor elements, Li and F show strong enrichments, as previously noted. A group of four other elements--cobalt, chromium, copper, and nickel--are enriched among both the Li-rich and normal altered tuffs (columns A and B, table 3). Copper is enriched in all categories compared to the granite, and, as can be seen in table 2, occurs in highly anomalous amounts in the altered tuffs; the tuffaceous sediments, not shown in table 2, average 160 ppm copper. Copper may have been enriched in the same circulating waters that contained high amounts of lithium, but the copper was concentrated by different minerals. Lead contents are close to those of the average granite but beryllium, niobium, and zirconium show slight depletion. Barium, lanthanum, vanadium, and yttrium are strongly depleted in both categories A and B (table 3) by factors of 2 to 5.

The low content of alkali and alkali-earth elements and high contents of mafic elements in the nontuffaceous sediments (column C, table 3) suggest that the source rocks for the sediments may have been more mafic than a standard rhyolite, as we postulated earlier. Because of the alteration and the presence of a brine during diagenesis, it is difficult to say much about the original composition of the sediments based on the present chemistry and mineralogy.

Table 3.--Mean elemental concentrations of sample suites: (A) Altered tuffs with Li $\geq$ 1,000 ppm, (B) all altered tuffs, (C) all nontuffaceous sediments, and (D) the average low-calcium granite (Green, 1969; for comparison with columns A and B).

Significant changes ( $\Delta$ ) relative to column D are noted by  $\emptyset$  (none), + (enriched), or - (depleted)

Element	A			B			C		D
	Mean	SD	$\Delta$	Mean	SD	$\Delta$	Mean	SD	Mean
MAJOR ELEMENTS									
Al	7.5	1.2	$\emptyset$	7.8	1.3	$\emptyset$	9.3	1.3	7.2
Na	2.8	.40	$\emptyset$	2.5	0.7	$\emptyset$	1.9	0.6	2.6
Mg	2.2	.80	+	1.7	.8	$\emptyset$	1.8	.8	1.6
Ca	0.9	.5	-	1.1	.8	-	1.6	.9	2.5
K	.7	.3	-	0.85	.6	-	1.5	1.0	4.2
Fe	1.0	.4	-	1.1	.5	-	2.1	1.2	1.4
Ti	.10	.06	$\emptyset$	.11	.06	$\emptyset$	0.31	.13	0.12
MINOR ELEMENTS									
Li	1250	147	+	770	520	+	250	170	40
F	1370	760	+	1530	880	+	1350	350	850
Mn	124	50	-	132	65	-	230	130	390
Ba	495	400	-	480	425	-	610	410	840
Be	2.3	0.5	-	2.4	.8	-	2.2	.7	3
Co	3.5	2.5	+	3.2	2.6	+	11	5.8	1
Cr	10	15	+	13	22	+	50	44	4.1
Cu	25	29	+	20	20	+	62	56	10
La	15	20	-	35	40	-	39	27	55
Nb	17	3	-	19	5	$\emptyset$	14	5	21
Ni	16	12	+	11	10	+	30	24	4.5
Pb	14	9	$\emptyset$	17	8	$\emptyset$	16	4	19
Sr	685	525		730	460		620	200	
V	22	28	-	20	24	-	70	42	44
Y	11	9	-	20	16	-	28	13	40
Zr	130	85	-	145	77	$\emptyset$	150	35	175

## SUMMARY

The lithium in the Popotosa Formation is associated with the clay minerals, but the lithium-rich clay is not hectorite as might be expected from previous work in other areas. A detailed investigation of the clay mineralogy would be needed to: (a) prove conclusively that the lithium is associated with the clay minerals, (b) discover what species the clay minerals are, and (c) determine how the lithium is held in the clay minerals.

The mineralogy of the samples helps to partially decipher the environment of deposition and the history of diagenesis of the Popotosa Formation. As discussed previously, the presence of clinoptilolite, mordenite, and analcime suggests an alkaline ground-water environment. Gypsum and halite are present as evaporite minerals, so evaporative concentration of the waters produced a brine of unknown salinity. The lithium was probably concentrated in the brine. This brine, moving in the playa sediments, was an agent of diagenesis that produced the lithium-rich clay and zeolite minerals. However, all evidence, such as the color of the sediments, the abundance of sandstones and siltstones, and the sparsity of carbonate beds, suggest that not much water, saline or fresh, was involved in deposition or diagenesis, and that the water probably moved into structurally deeper parts of the Rio Grande Rift fairly early in the history of the sediments.

The geochemical data indicate that the controls on lithium were independent from those on other elements. Because the tuffs are altered, their original composition is uncertain. However, their present chemical composition and their similarity to low-calcium granites suggests that the tuffs were from a magma which was rhyolitic in composition. Major amounts of alkali and alkali-earth elements were leached from the tuffs; mafic elements, such as magnesium, nickel, copper, and cobalt, were added. The lithium and fluorine contents certainly point to movement of elements and concentration of lithium during diagenesis.

The lithium may have been concentrated in playa lake brines and later incorporated into the clay minerals formed during diagenesis of the volcanic glass. We can only speculate on the source of the lithium, however, two sources are likely: (1) the volcanic glass itself, and (2) hot springs discharging lithium-rich water (and some other elements such as copper and strontium) to the playa. For example, at the north edge of the NE 1/4 sec. 19, T. 1 S., R. 1 W. (about 8 km south of site C, figure 1), a series of

altered tuffs in the Popotosa Formation show evidence of hot spring activity-- that is gel-like clays, manganese staining and veining, as well as their general appearance. The hot water in circulation could leach lithium from older rocks and sediments and carry it to the playa. The altered tuffs near this outcrop are not enriched in lithium, but in general, lithium stays in solution longer and travels farther than the other elements (such as manganese) that are brought into the playa.

Based on our present data, it is unlikely that commercial amounts of lithium will be found in the Popotosa Formation although localized concentrations of potential economic grade exist in this area. However, this lithium occurrence does offer an opportunity to study the mineralogy and geochemistry of lithium in detail and hopefully may lead to a better understanding of such lithium deposits.

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