Li-rich Claystone in the McDermitt Caldera, Nevada: Characteristics and Possible Origin

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November 24, 2022

Abstract

The Lithium Nevada Corp. Thacker Pass Project has a measured resource of 242M tonnes at 0.29% Li (~0.7M tonnes Li). The deposit is the southernmost of five known lenses hosted within intracaldera tuffaceous sediments along the west side of the McDermitt caldera, which formed by eruption of 16.4 Ma peralkaline-metaluminous tuff. Analyses of 9880 core samples (~1.5-m thick) give a mean of ~ 2500 ppm Li, with some >8800 ppm. Entire sedimentary sections in the southern and western parts of the caldera basin have high Li (1500+ ppm). Pre-caldera rocks, the McDermitt Tuff, late caldera volcanics, and unaltered tuffaceous sediments have relatively low Li (5 -140 ppm). Sediment deposition was mainly subaqueous in the closed caldera basin. Li-rich fill may have been deposited from airborne sources. Claystone comprises most of the Thacker Pass deposit and dominates Li-rich intervals. The rest is mostly feldspar-rich ash. X-ray diffraction (XRD) data from six core holes across the deposit show consistent lateral mineral zoning. A Li-rich zone (mean >4,000 ppm) mainly contains illitic clay and underlies a zone of lower Li with smectite + analcime. Based on XRD peak locations and chemistry, the closest analogs to the illitic clay are Li micas (e.g. tainiolite). Montmorillonitic clay and a basal silicified zone underlie the illitic zone. Some transitional rock of mixed-layer clay between the illite and smectite zones also has high Li. All clay has similar optical properties but SEM images show illite forms tiny hexagonal plates and smectite has no resolvable crystallinity. Calcite, albite, K-feldspar, and quartz occur in all zones, dolomite and fluorite near the top of the illite zone, and pyrite and bitumen in unoxidized rock. The Li-rich zone has relatively high K, Rb, Mo, As, and Sb. Secondary Kspar in the Li-rich zone gave an 40Ar/39Ar age of 14.87±0.05 Ma. No origin fully explains known characteristics. The presence of illite suggests a moderate temperature hydrothermal system. Release of Li from tuffaceous sediments and transport by alkaline groundwater are consistent with most mineralogy (characteristic of closed hydrologic system diagenesis) and with the Kspar date that long postdates caldera magmatism. Release of 10 ppm Li from the likely 50-200 km3 of intracaldera sediments would contribute ~1-4M tonnes Li.

Li-rich Claystone in the McDermitt Caldera, Nevada: Characteristics and Possible Origin
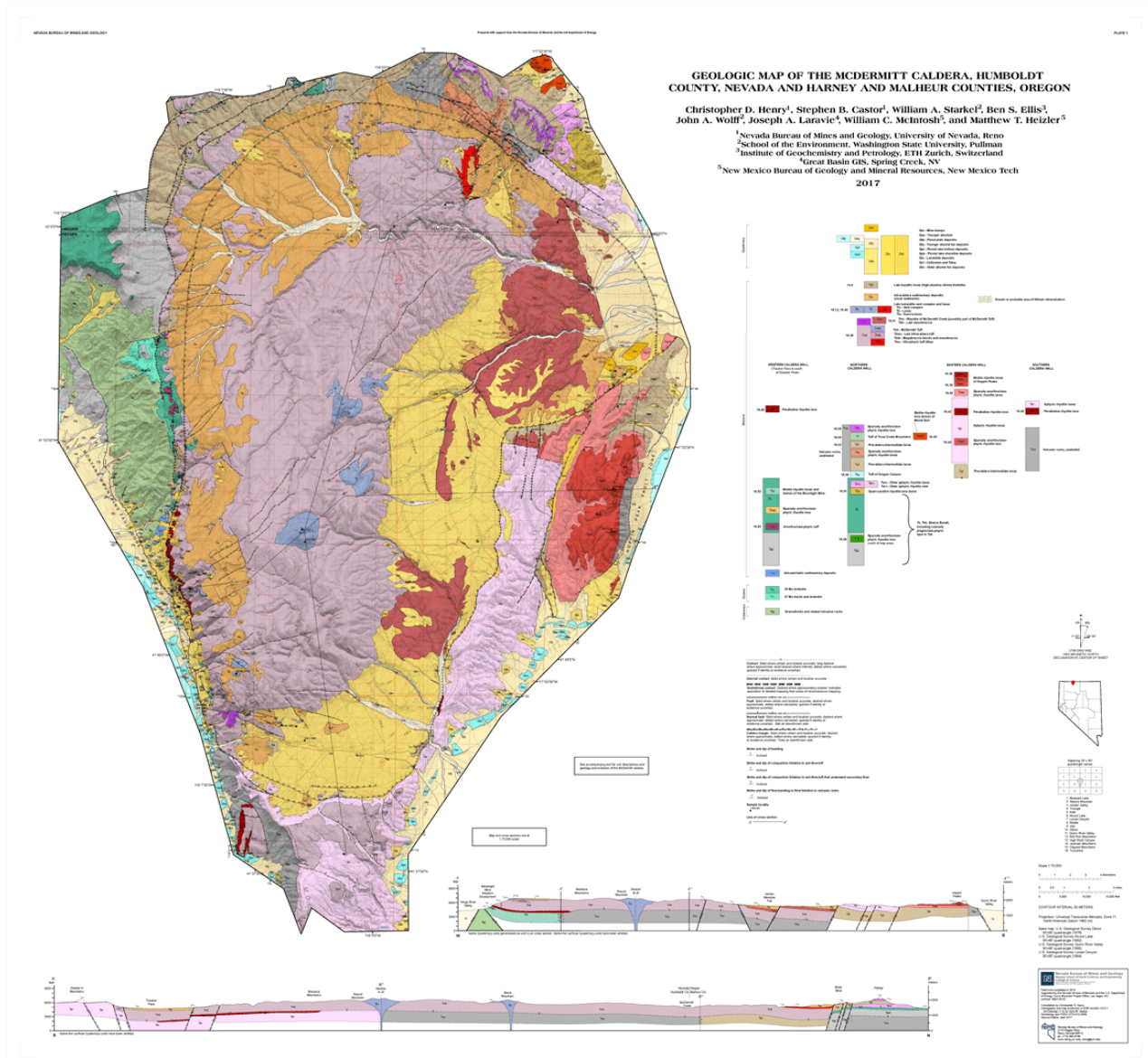
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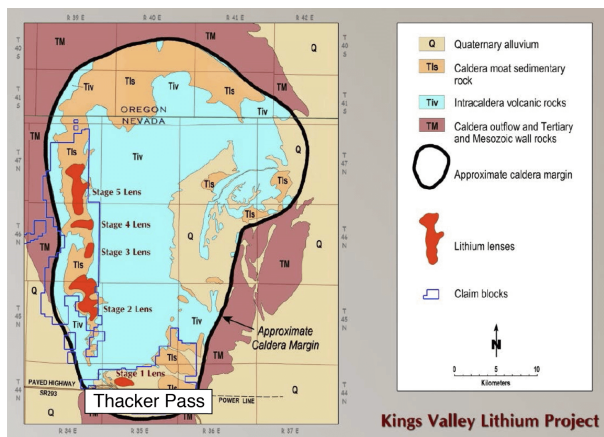U.S. Geological Survey, Reno, NV 89557
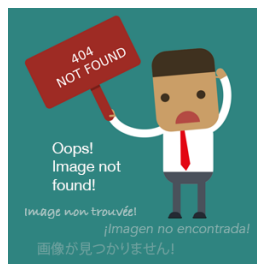
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CALDERA GEOLOGY

Lithium mineralization is widespread in post-collapse, intracaldera tuffaceous sediments that occupy the "moat" of the McDermitt caldera, a doughnut-shaped area surrounding the central resurgent dome (Henry et al., 2017; this paper and full map can be downloaded for free from GSA Geosphere; https://pubs.geoscienceworld.org/gsa/geosphere/article/13/4/1066/350213/geology-and-evolution-of-the-mcdermitt-caldera (https://pubs.geoscienceworld.org/gsa/geosphere/article/13/4/1066/350213/geology-and-evolution-of-the-mcdermitt-caldera)). The tuffaceous sediments accumulated in small part from post-collapse tuff eruptions at McDermitt and largely from regional tuff eruptions elsewhere along the Yellowstone hotspot. Our work focuses on the Thacker Pass deposit, southmost part of the caldera (below), which alone contains ~1.12 million tonnes, measured and indicated Lithium (~6Mt LiCarbonateEquivalent, LithiumAmericas, 2018). Additional known areas of minerallization (Stages 2-5 lenses) and widespread anomalies vastly increase the total Li in tuffaceous sediments in the caldera.

Q	Quaternary alluvium
Tls	Caldera moat sedimentary rock
Tiv	Intracaldera volcanic rocks
TM	Caldera outflow and Tertiary and Mesozoic wall rocks
⬭	Approximate caldera margin
	Lithium lenses
▱	Claim blocks

N

0   5   10
Kilometers

Kings Valley Lithium Project

Major Events: Cenozoic Volcanism and Development of the McDermitt Caldera

14.87±0.05 Ma (n=1). Formation of secondary Kspar in Li-rich zone. Marks at least part of time of diagenesis and probably part of Li mineralization.

≤16.4 to ~14.9 Ma?. Closed-hydrologic system diagenesis of the intracaldera tuffaceous sediment sequence. Diagenesis may have started at beginning of sediment deposition and was almost certainly occurring at 14.87±0.05 Ma, the age of secondary Kspar that is part of diagenesis.

≤15.69±0.04 to ≥16.26±0.04 Ma (n=7). Deposition of as much as 200 m (200 km^3) of tuffaceous sediments in caldera basin based on dating of 7 interbedded tephra. Deposition probably began pre-resurgence and

16.41±0.02 Ma (n=3). Post-collapse lavas and domes of icelandite lavas and lesser dacite and rhyolite lavas were extruded widely in the caldera. Broad resurgent uplift of the southwestern and northern parts of the caldera probably mostly postdated this magmatism.

16.39±0.02 Ma (n = 3). Eruption of ~1000 km^3 of strongly zoned, peralkaline aphyric high-Si rhyolite to anorthoclase-rich Fe-rich dacite McDermitt Tuff and collapse of the McDermitt caldera. Most tuff ponded in the caldera. McDermitt Tuff, our proposed formal name, includes at least part of the tuff of Double H (Rytuba and McKee, 1984) as well as variably named and correlated tuffs (Greene, 1972, 1976; Minor et al., 1988; and Peterson et al., 1988)

16.38±0.07 to 16.36±0.02 Ma (n = 2). Eruption of at least three biotite-sanidine-quartz-plagioclase rhyolite lavas (rhyolites of Hoppin Peak) outside of what was to become the eastern margin of the caldera.

16.49±0.02 Ma (n = 1). Biotite-quartz-sanidine-plagioclase rhyolite was emplaced as several shallow intrusions ~5 km northeast of the caldera.

16.62±0.02 Ma (n = 1). The first of many biotite-quartz-sanidine-plagioclase, metaluminous rhyolites were emplaced as several lava domes along what became the southwestern margin of the caldera.

≥16.69±0.02 Ma. Steens Basalt lavas began to erupt from unknown sources and flowed into what became the northwestern part of the caldera. Eruptions were nearly continuous until caldera formation. These flows became more silicic with time, progressing irregularly through icelandite (Fe-rich andesite; Wallace et al., 1980) and anorthoclase-phyric rhyolite to aphyric high-Si rhyolite. At least the more silicic rocks had local sources. Ages of anorthoclase rhyolites range from 16.69±0.02 Ma on the lowest exposed unit underlying icelandites north of the caldera to 16.35±0.04 Ma on a flow in the northern caldera wall. Aphyric rhyolites are undated but probably emplaced mostly during the later parts of this time range..

IGNEOUS GEOCHEMISTRY AND LI ENRICHMENT
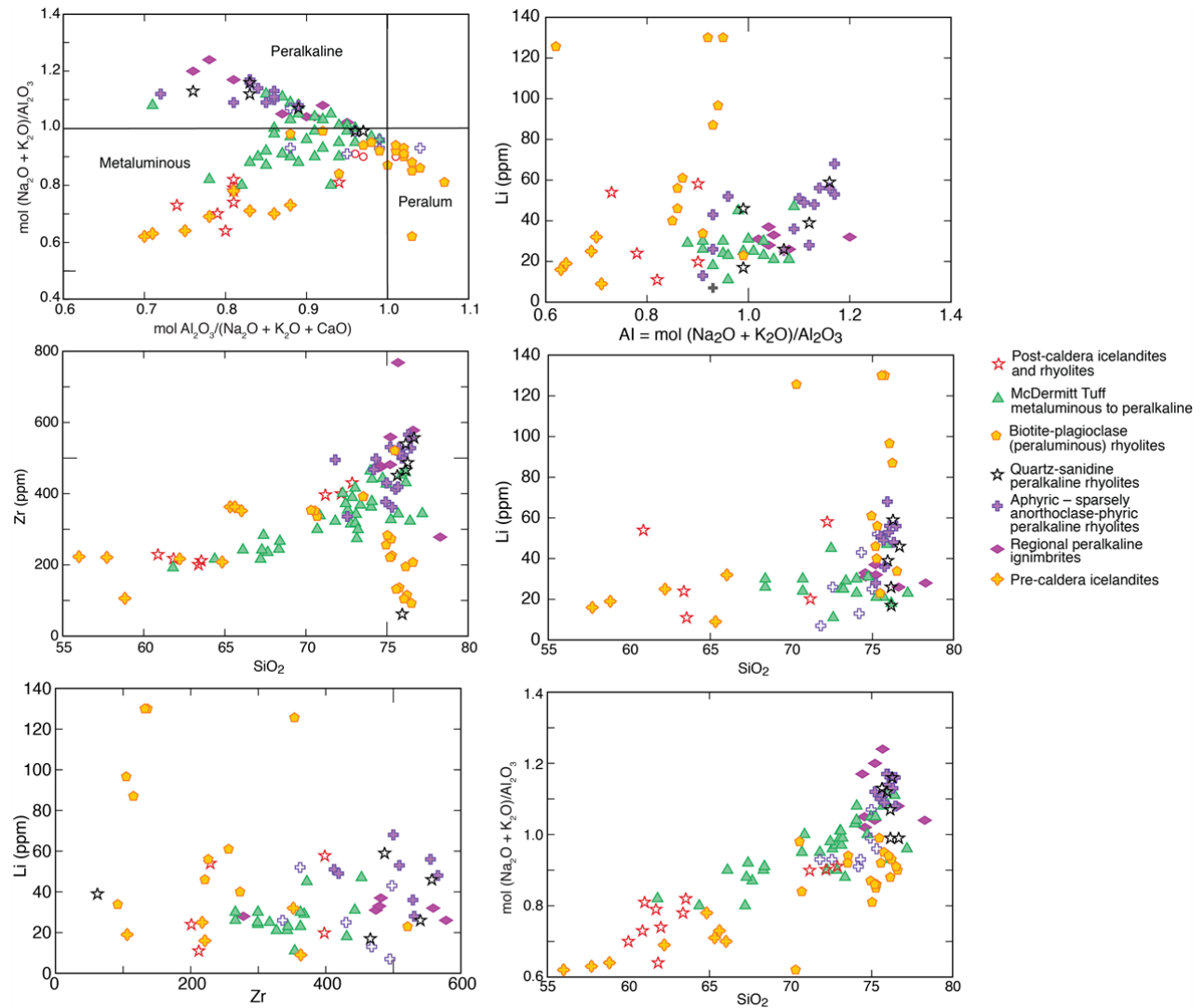
The caldera-forming McDermitt Tuff is zoned from metaluminous, low-Si dacite to peralkaline, high-Si rhyolite. Other middle Miocene igneous rocks include several peralkaline suites as well as biotite-bearing metaluminous to peraluminous rocks. The biotite-bearing rocks (Li=71±37 ppm, max 130, n=12) contain twice as much Li as do the peralkaline rocks (McDermitt Tuff Li=27±9 ppm, max 47, n = 17 or other peralkaline rocks Li=33±16 ppm, max 61, n=37). Li increases only slightly with increasing SiO_2 except in high-Si rhyolites, where Li increases more strongly in peraluminous than in peralkaline suites. This relative enrichment is consistent with observations of Benson et al (2017) and Hofstra et al. (2013) that Li is more eriched in rhyolites that have a substantial continental crustal component.

# LITHIUM DEPOSIT MINERALOGY, CHEMISTRY

Thacker Pass Li Deposit
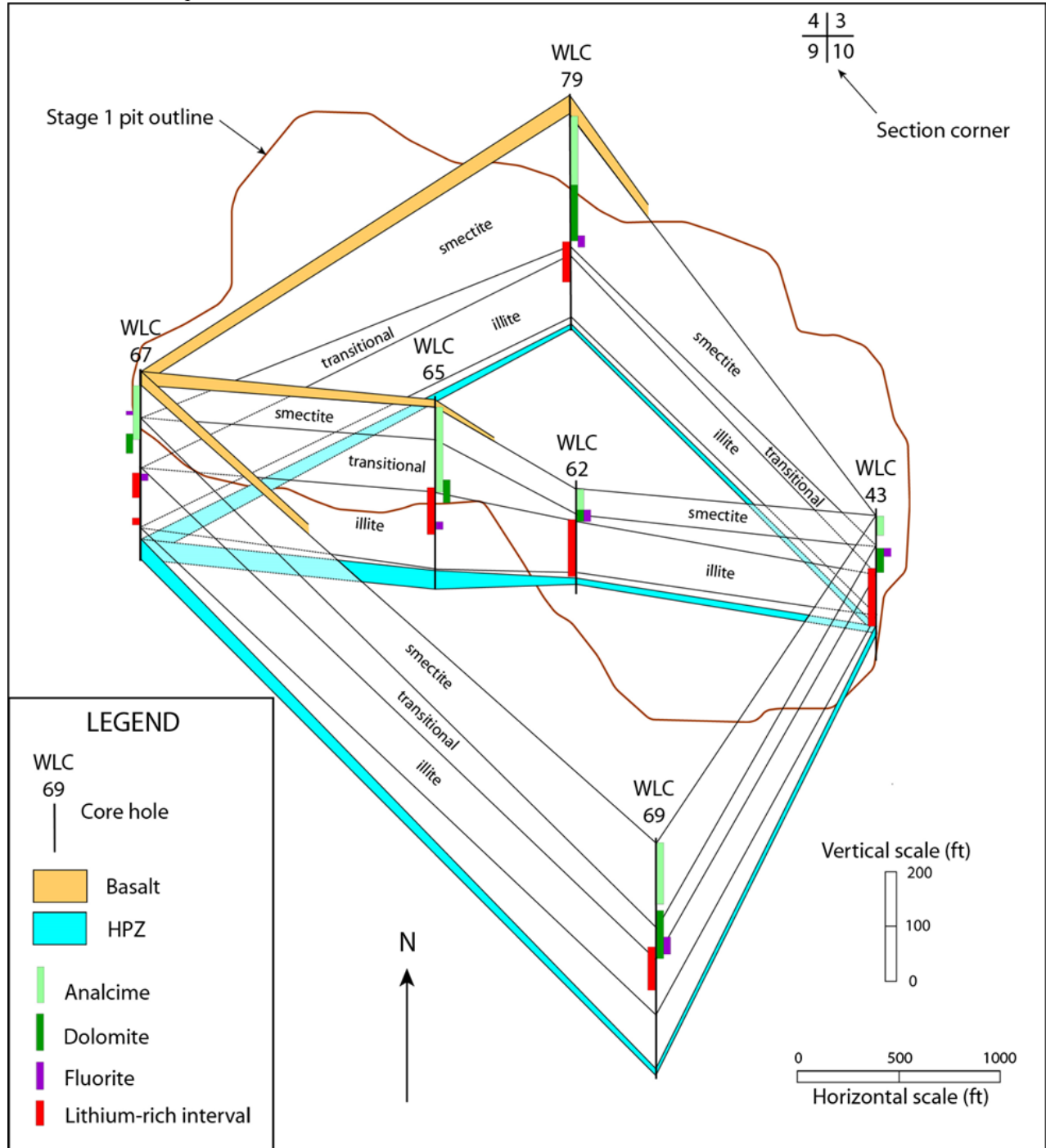
Li minerallization forms stratiform lenses containing Li-enriched illite and smectite in the tuffaceous sediments. Bulk samples contain as much as 7500 ppm Li, and entire sections up to 60 m thick contain a minimum of 1000 ppm (see below). The highest Li zones, with the greatest potential for mining, generally contain more than 4000 ppm.

The relative contribution of low-temperature diagenetic versus high-temperature hydrothermal fluids in concentrating lithium is uncertain (Henry et al., 2017). Alteration progresses from almost fresh glass, to a mix of zeolites, to analcime, and to potassium feldspar; interbedded mudstones are altered to dioctahedral smectite and trioctahedral smectite including hectorite (cf. Glanzman and Rytuba, 1979; Rytuba and Glanzman, 1979). Rytuba and Glanzman found a correlaton between Li with analcime-bearing samples. We also find interlayered illite/smectite, illite, and minor dolomite and fluorite.

Except for illite, this mineral assemblage is typical of low-T (≤50°C), closed hydrologic system diagenesis, where groundwater evolves through rock-water interaction and evaporation in a closed basin such as in the McDermitt caldera to become highly alkaline and saline (Surdam, 1977; Langella et al., 2001). Based on studies of diagenesis of Tertiary deposits of the Gulf Coast, the presence of illite could indicate temperatures of 100°C or more (Boles and Franks, 1979; Bourdelle et al., 2013). However, Turner and Fishman (1991) found that pore-water chemistry can be more important than temperature in illite formation and that illite can form at near-surface temperatures in saline, alkaline lakes similar to the McDermitt caldera setting.
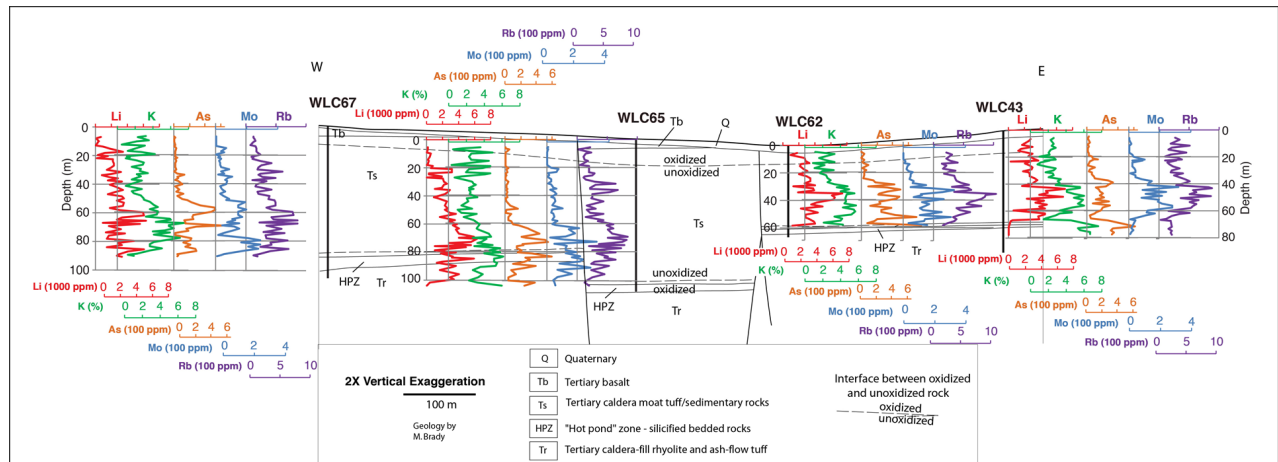

This west-east cross section through the deposit demonstrates parallel enrichment in Li, K, As, Rb, and Mo (and Sb, F, not shown).
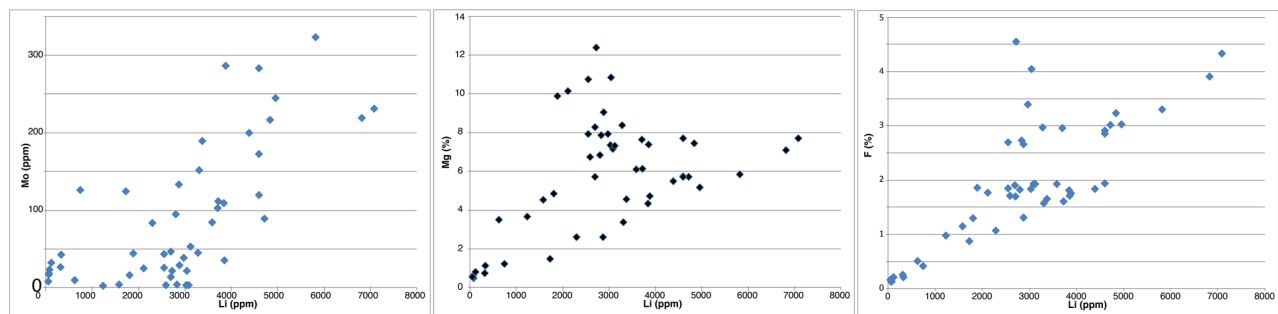

Plots of Li vs Mo, Mg, and F show their correlation (bulk samples from drillhole WLC43). Strong linear correlation of Li-F and Li-Mg suggest their presence in the same mineral. High, uncorrelated Mg and F values indicate presence of dolomite and fluorite, confirmed by XRD and thin sections (See Mineralogy). Mineral site of Mo currently unknown.

LI MINERALOGY

The following four, unfortunately fuzzy plots are of bulk samples that show presence of Li smectite (hectorite), Li-bearing mixed-layer smectite-illite, Li-bearing illite (polylithionite?), and Li mica (tainiolite?).
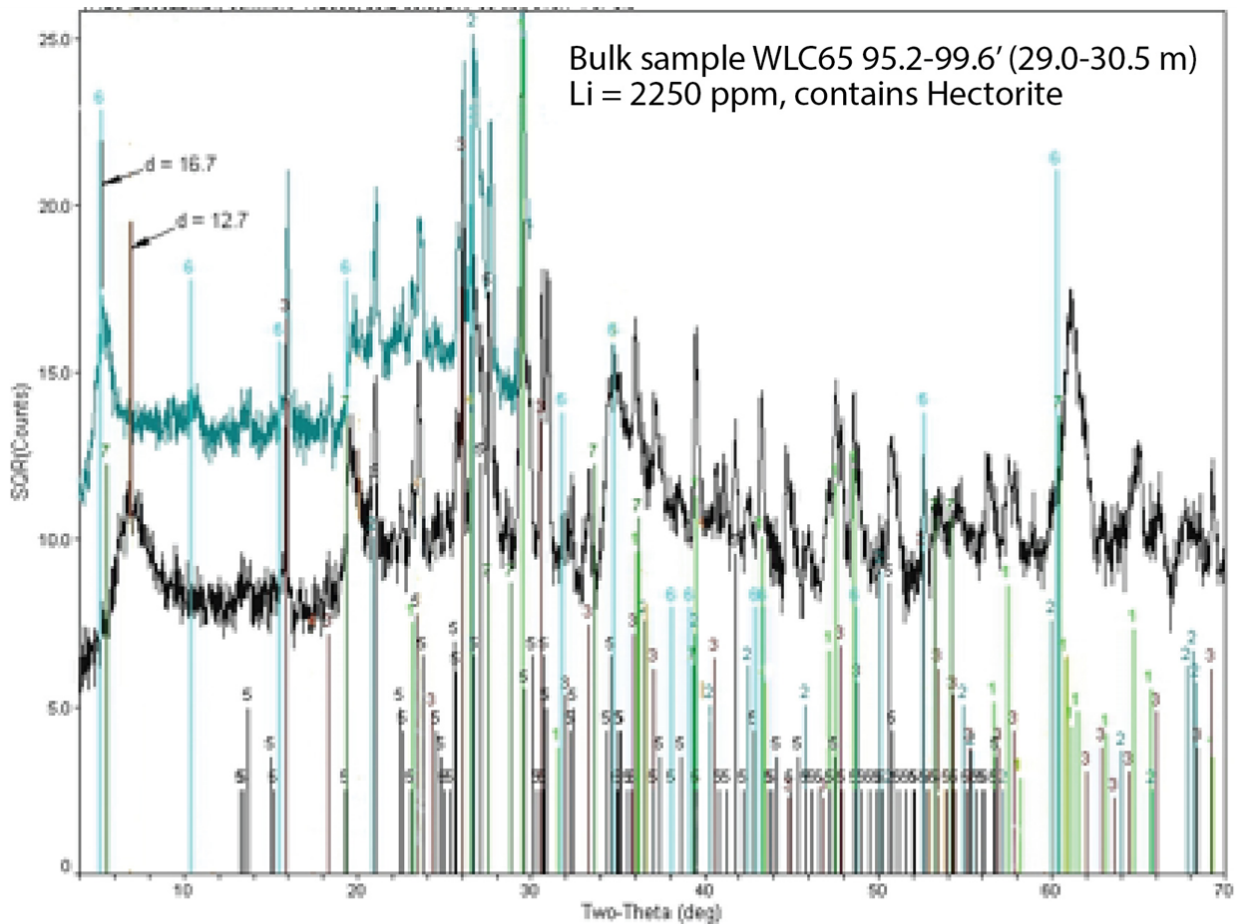
Powder XRD scan of bulk sample WLC65 95.2-99.6' (29.0-30.5 m). Li = 2250 ppm. Lower trace oven dried, upper trace glycolated. ICDD standard peaks shown as numbered bars for calcite (1), quartz (2), analcime (3), K-feldspar (5), saponite 17A glycol (6), and hectorite (7).
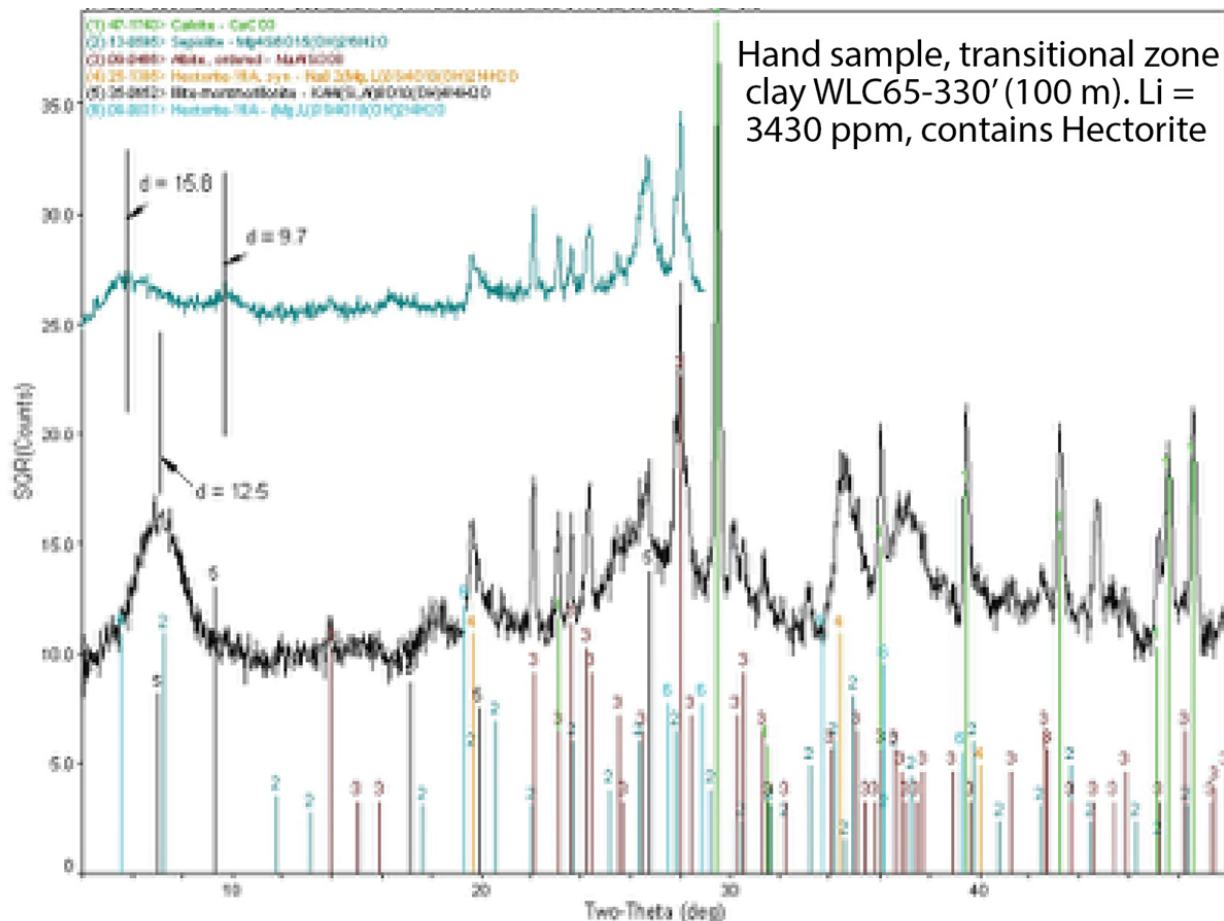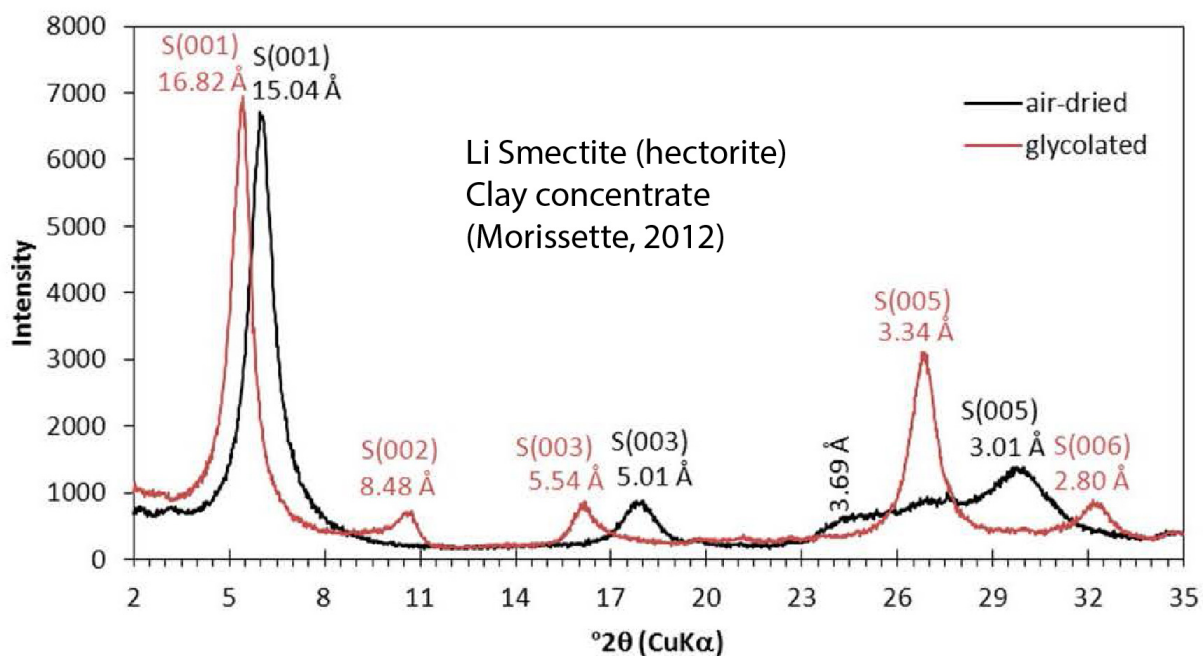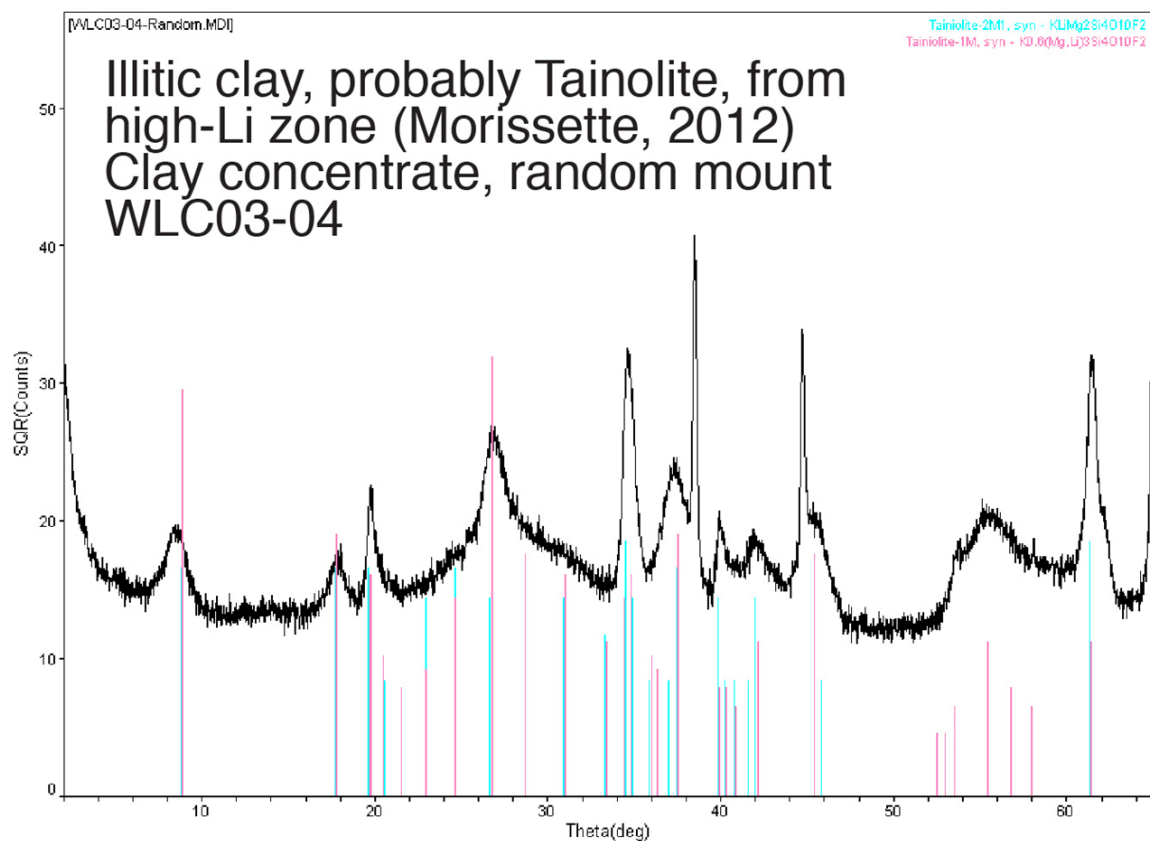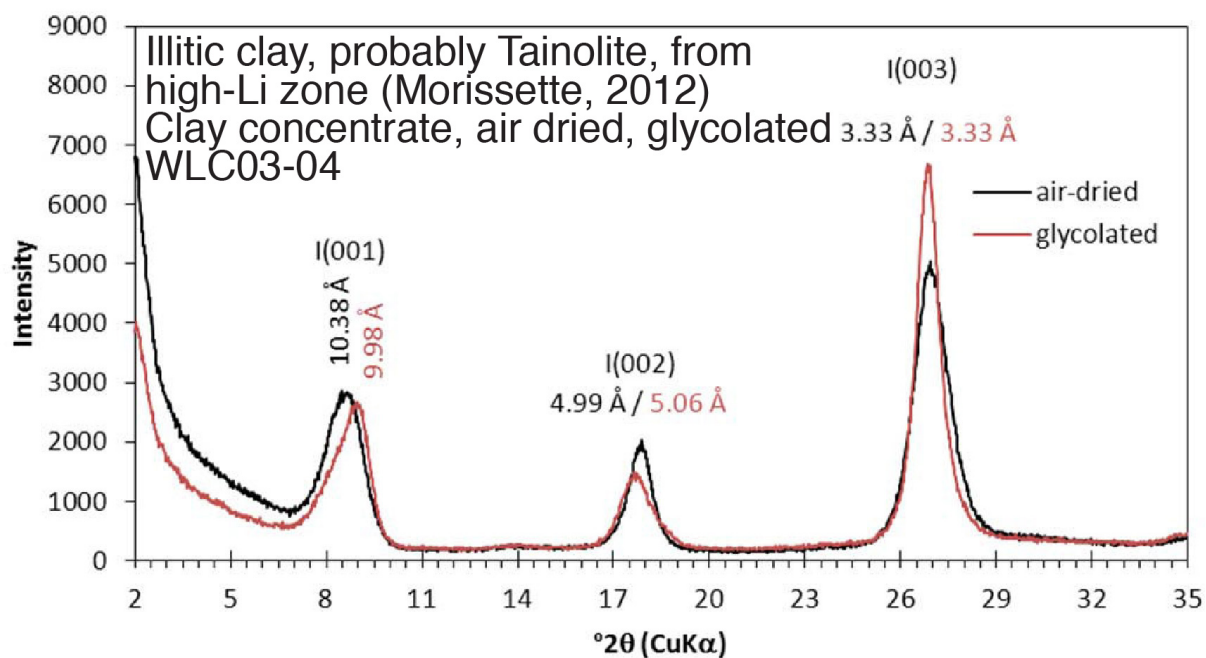
Powder XRD scan of hand sample of dark brown transitional zone clay WLC65-330′ (100 m) with Li = 3430 ppm. Lower trace oven dried; upper trace glycolated. ICDD standard peaks shown as numbered bars for calcite (1), sepiolite (2), albite (3), hectorite-16 A synthetic (4), illite-montmorillonite (5), and hectorite-16 A (6).
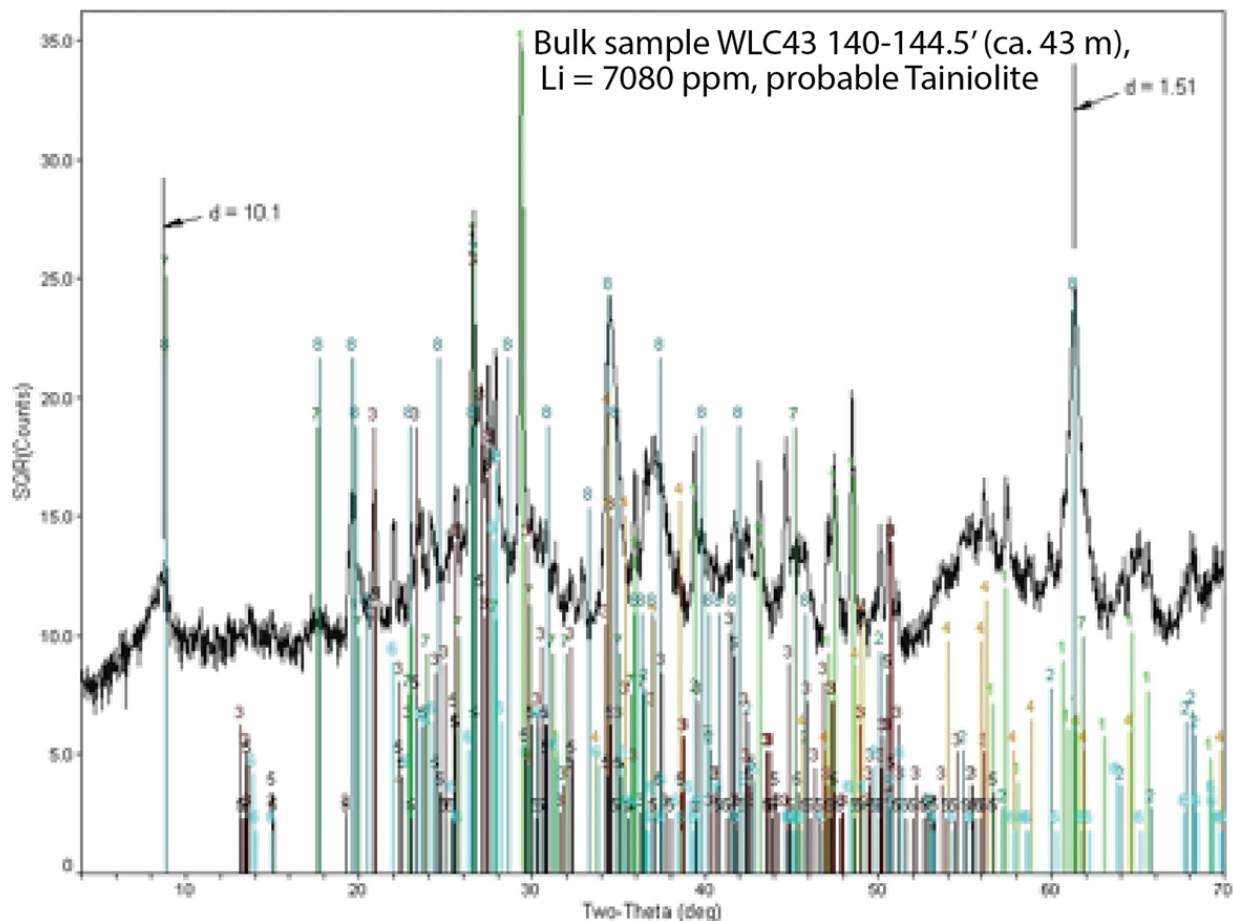
Powder XRD scan of oven-dried bulk sample WLC43 140-144.5' (ca. 43 m) with Li = 7080 ppm. Interval includes hand sample WLC 43 141.1. Most intense peaks correspond to ICDD standard for calcite (1) and illite (7) or tainiolite (8). The tainiolite standard is a better fit for the diffuse clay peaks in some cases than illite, particularly the intense peak at 2theta = ca. 61 deg (d = 1.51). Moderate quartz (2) and K-feldspar (3) peaks present.

The following three plots are of clay separates that further support presence of hectorite and tainiolite(?). X-ray peak locations best fit tainiolite, which, however, is a Li-mica, whereas broad peaks suggest a clay mineral.

Li Smectite (hectorite)
Clay concentrate
(Morissette, 2012)

Illitic clay, probably Tainolite, from
high-Li zone (Morissette, 2012)
Clay concentrate, air dried, glycolated 3.33 Å / 3.33 Å
WLC03-04

I(003)

I(001)
10.38 Å
9.98 Å

I(002)
4.99 Å / 5.06 Å

air-dried
glycolated

[WLC03-04-Random.MDI]

Tainolite-2M1, syn - KLiMg2Si4O10F2
Tainolite-1M, syn - K0.8(Mg,Li)3Si4O10F2

Illitic clay, probably Tainolite, from
high-Li zone (Morissette, 2012)
Clay concentrate, random mount
WLC03-04

MSESE

[XRD\cmoris]<c:\Documents and Settings\cmoris\MDI\DataScan\Controllers\Goniom1\data-2010> Tuesday, Mar 20, 2012 11:18a (MDI/JADE6)

LI MINERAL COMPOSITION AND IMAGES
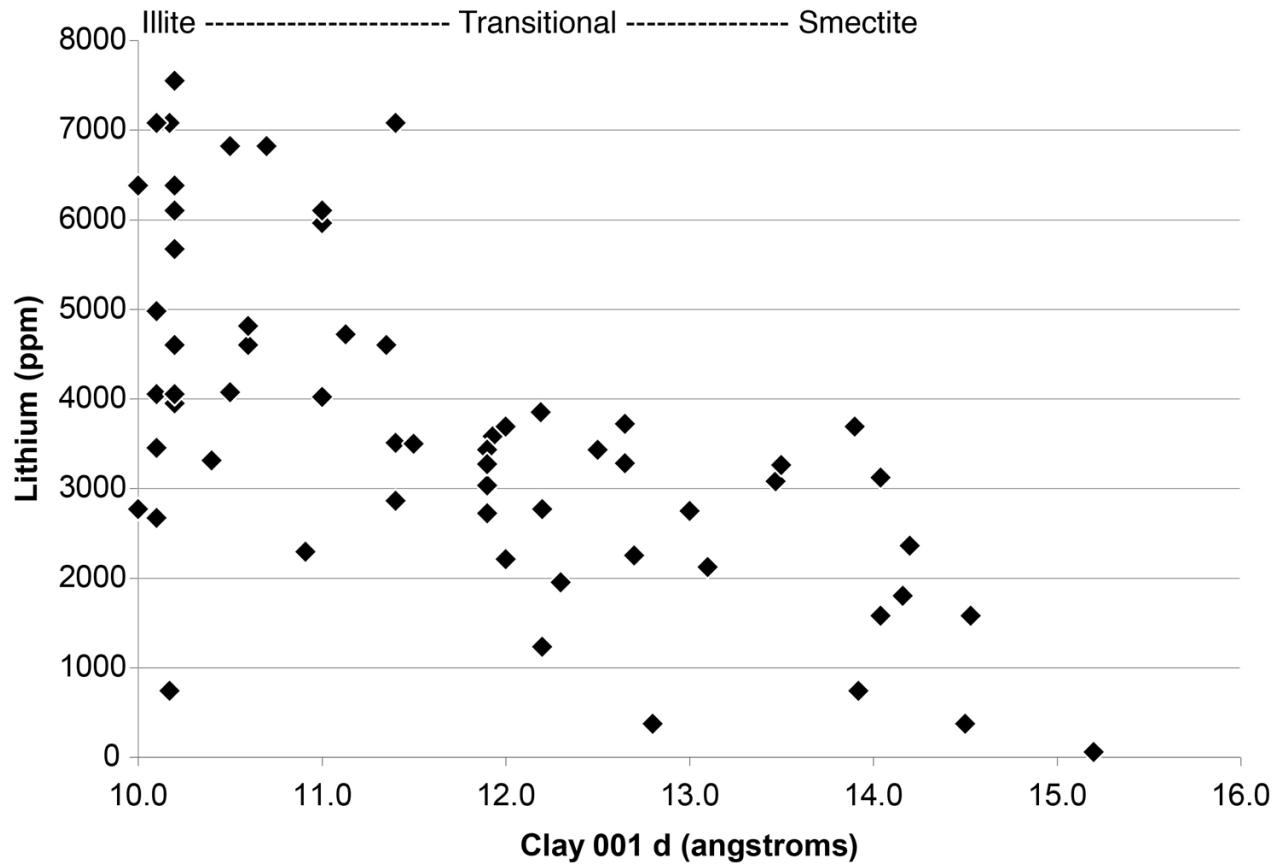
Lithium content plotted against d spacing for the 001 peak of clay from hand specimens and pulps for drill holes WLC-43, WLC-62, WLC-65, and WLC-67.

Correlation of Li concentration with clay d spacing supports the presence of Li-rich illite (tainiolite?) and Li-rich smectite (hectorite).

	lepidolite	polylithionite	trilithionite	tainiolite	WLC03-05	illite
SiO2	47.81	60.32	46.44	52.77	56.00	47.53
TiO2		trace		2.00		0.67
Al2O3	28.47	13.00	27.20	trace	2.40	23.57
FeO	0.04			1.89		3.24
Fe2O3		0.18	0.44		1.97	7.83
MnO	0.91	0.12	0.80	1.38	0.03	
MgO	0.00	0.24		17.38	17.70	1.72
CaO	trace	0.72			0.11	0.19
Li2O	3.64	6.18	5.51	2.43	2.75	
Na2O	0.86	2.04	0.55	1.22	0.49	0.14
K2O	9.86	11.04	9.95	11.36	7.55	6.77
Rb2O	0.90				0.10	
Cs2O	0.16				0.07	
H20+	2.52	1.70	2.00	4.23	4.12	8.34
F	4.85	4.46	7.10	5.35	6.71	
	100.00	100.00	100.00	100.00	100.00	100.00
Location	California	Russia	unknown	Russia	McDermitt	Illinois
Data source	1	1	2	1	3	4

Chemical composition of lithium micas, McDermitt Li-rich clay (WLC03-05), and illite. Analysis sources: 1. Handbook of Mineralogy, v. 2 (lepidolite, polylithionite, and tainiolite); 2. Mineralianatlas website (trilithionite), 3. Morissette, 2012 (WLC03-05); and 4. Gaudette et al., 1966 (illite). Analyses normalized to 100% after subtracting H2O-.

Composition of Li-rich illite at McDermitt best matches tainiolite (e.g., low Al, high Mg, and reasonable Li).

Clay from the highest Li zone ($\geq$4000 ppm) at Thacker Pass gives XRD patterns with diffuse peaks with maxima at 2theta locations corresponding to illite and the Li mica species polylithionite, trilithionite, and tainiolite (also taeniolite). On the basis of analyses in Morissette, 2012, the Thacker Pass illitic clay corresponds most closely to that of tainiolite, a lithium mica with relatively high MgO that generally occurs as a late stage mineral in alkaline igneous rocks. However, its K_2O content is most like that of illite. On the basis of XRD and chemistry, Thacker Pass high-Li clay could be described as illitic clay that has the same relationship to tainiolite as illite does to muscovite.
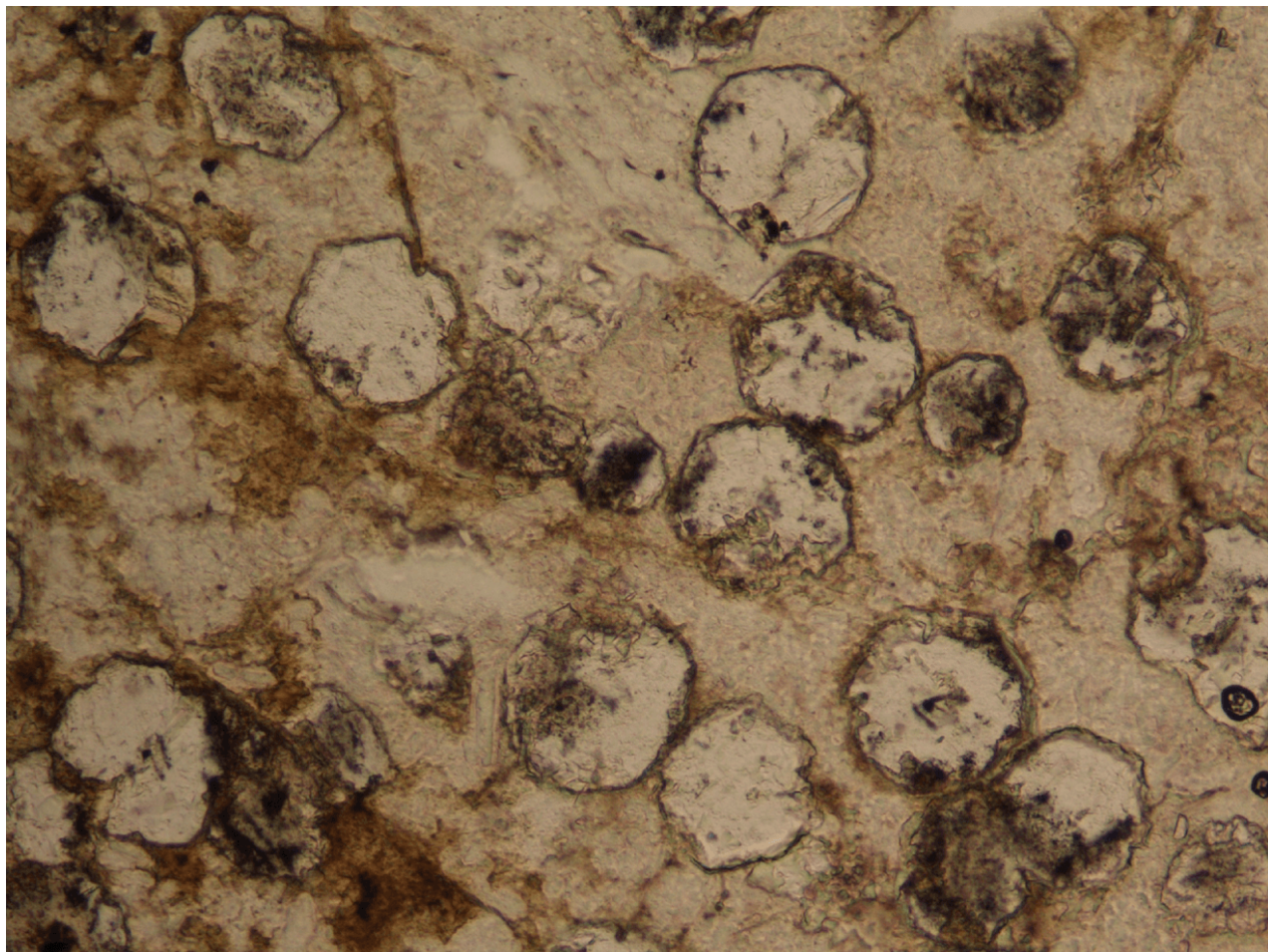
Analcime crystals in tuffaceous sediment, sample WLC43-36.5, horizontal field = 0.8 mm. Matrix includes quartz and smectite (brown). 141.5 ppm Li.
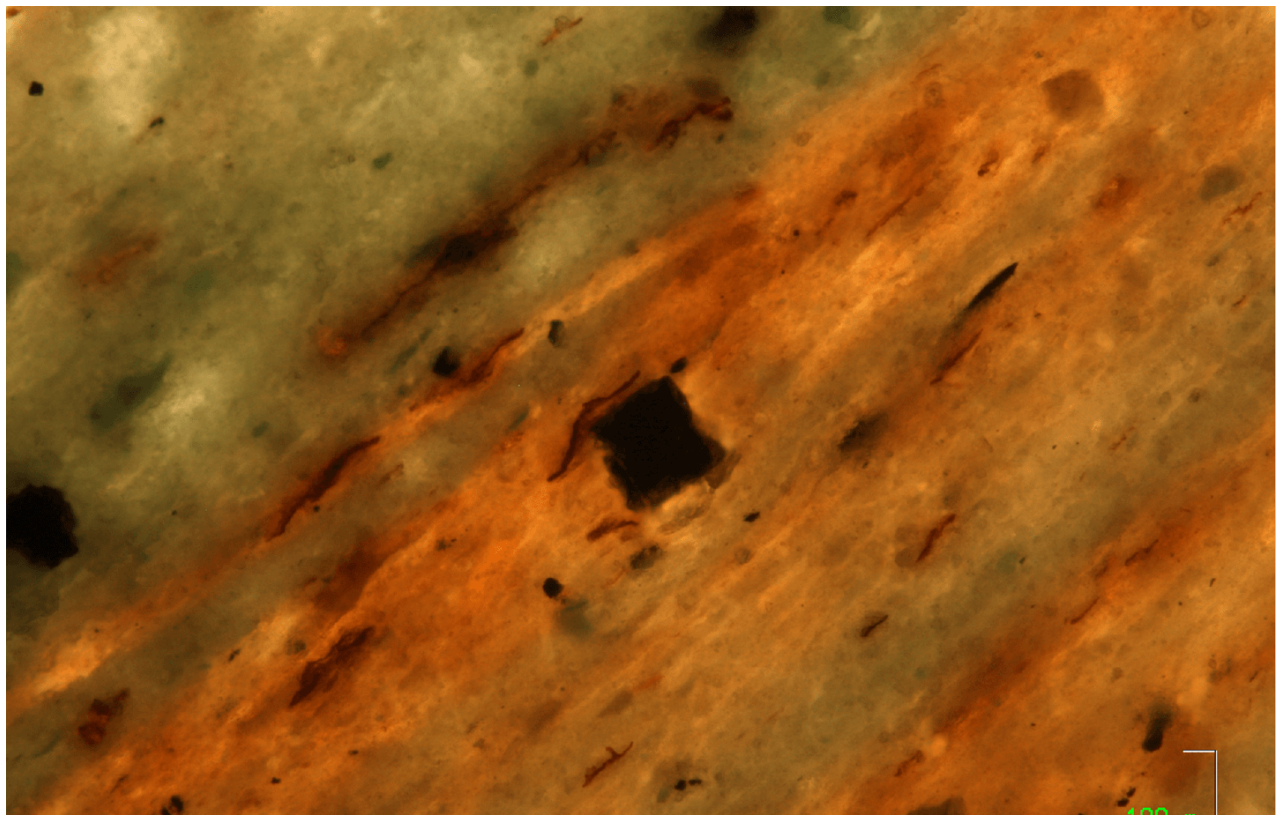
Laminated clay with pyrite cubes and bitumen shards, sample WLC43-141.1, plane polarized light, 6920 ppm Li. Pyrite indicates deposit was underwater and not oxidized.
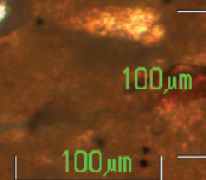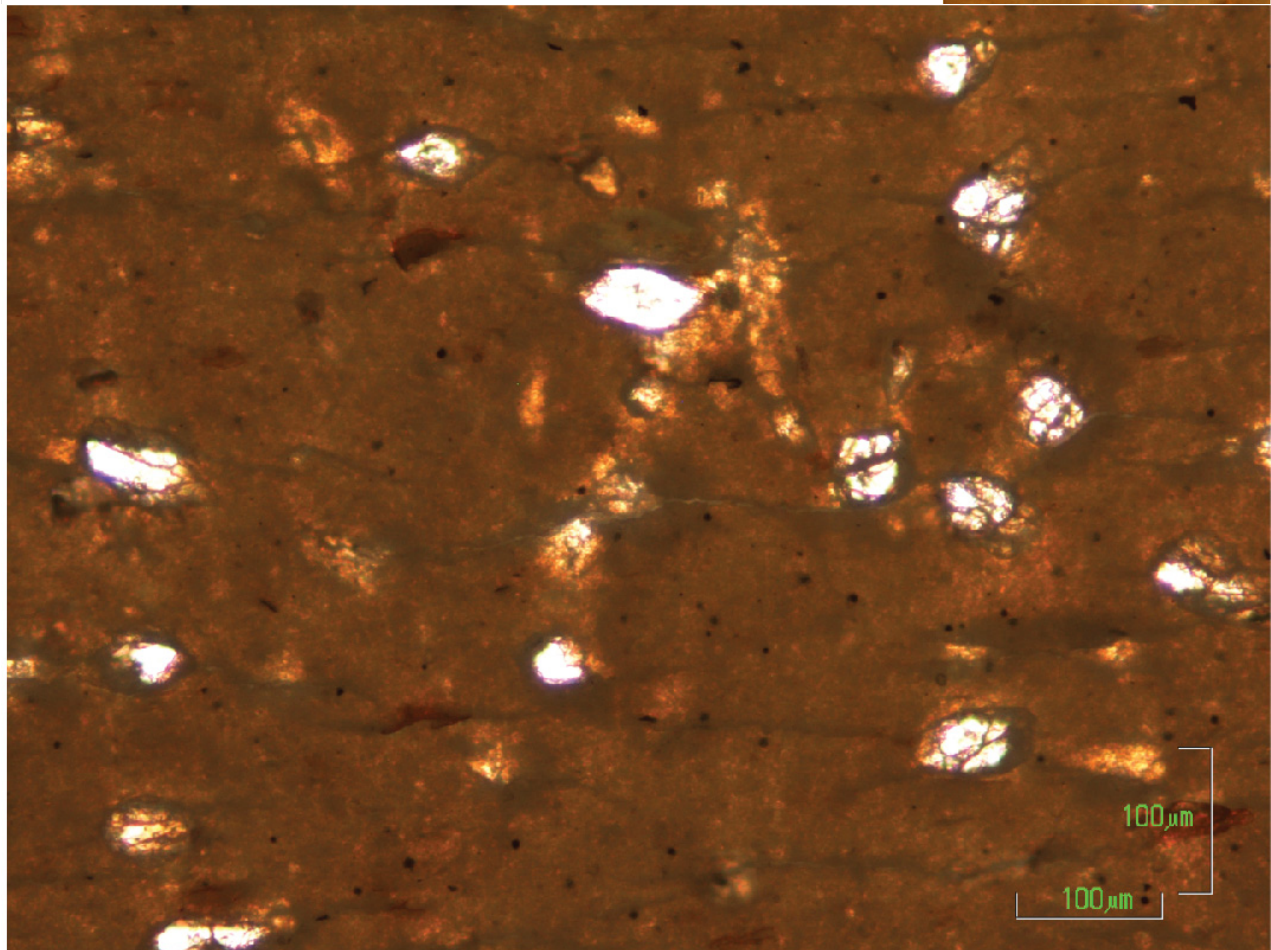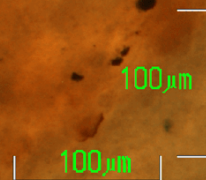
Tuffaceous mudstone with shattered dipyramidal quartz grains, bitumen

flakes, and fine pyrite, sample WLC43-70.2. (4630 ppm Li), plane polarized light. Presence of quartz demonstrates the tuff component is unrelated to the McDermitt Tuff, which lacks quartz.

WLC43-141 20.0kV 11.9mm x5.00k SE(M) 6/16/11   10.0um
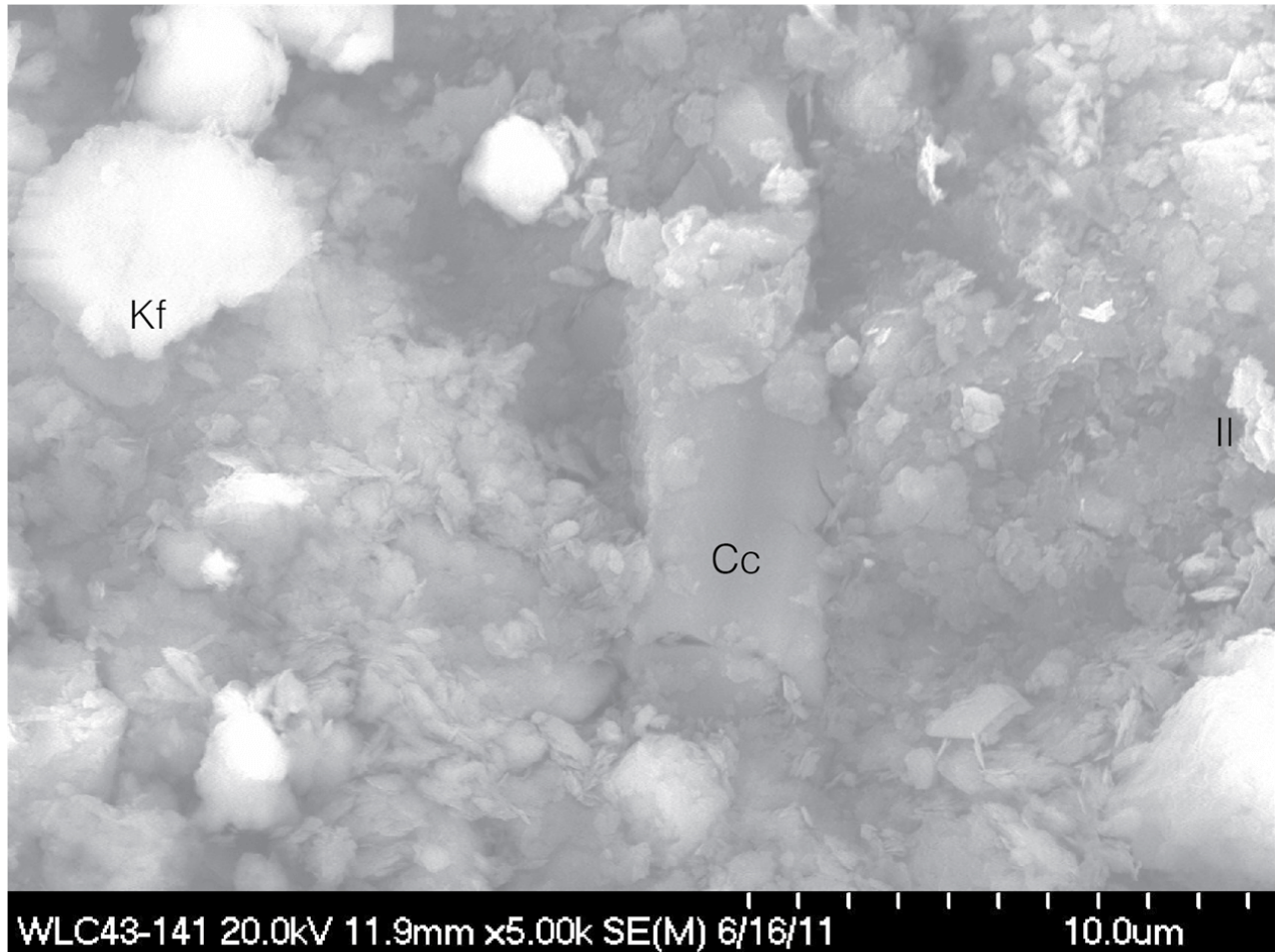
Calcite lozenge, bright Kspar, and illite flakes. Kspar concentrate from a sample with much more abundant Kspar gives an 40Ar/39Ar date of 14.87±0.05 Ma, which is ~1.2 Ma after igneous activity in caldera.

WLC65-176c 20.0kV 11.7mm ×10.0k SE(M) 5/24/11   5.00um
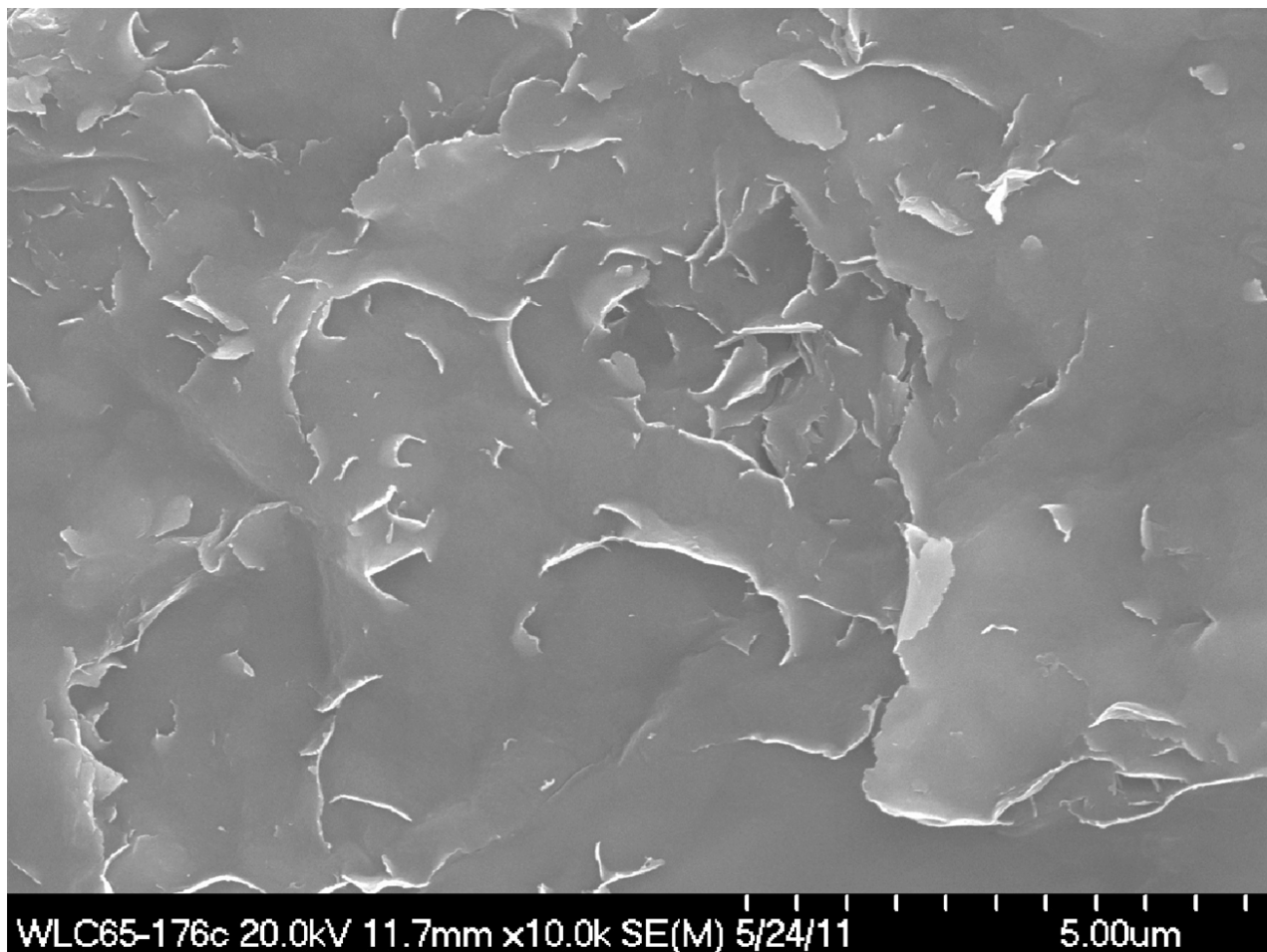
WLC65-176.6 smectite, secondary electron image, showing ultra fine
   crystallinity. From interval with 3690 ppm Li.

Thin-bedded white tuff layer in dark gray clay of Li-rich zone. Tuff layer cut and deformed along high-angle faults. Light-gray chalcedonic quartz occurs along fault planes and some laminae in the tuff and suggests moderately high temperature deposition.

CONCLUSIONS AND ORIGIN OF LI MINERALIZATION

CONCLUSIONS

Post-collapse, intracaldera tuffaceous sediments in the McDermitt caldera contain large Li resources, at least 1.1 Mt Li in Thacker Pass alone.

Development at Thacker Pass is focused on a Li-rich (≥4000 ppm) zone, in which Li resides in illitic clay and transitional illite-smectite. Although the presence of Li-smectite (hectorite) in the caldera has long been known, the illitic clay chemically and structurally resembles tainiolite (a Li-mica).

Unaltered, middle Miocene peraluminous volcanic rocks around the caldera have relatively high primary Li contents (71±37 ppm), whereas peralkaline rocks, including the McDermitt Tuff, have relatively low Li contents (27±9 ppm), which suggests peralkaline rocks were not important to Li mineralization. The intracaldera tuffaceous sediments probably originated by reworking of ash-fall deposits from eruptions outside the McDermitt caldera, and this ash could have been an important source of Li in the deposits.

ORIGIN OF LI DEPOSITS

Evidence supporting high-T, hydrothermal origin

The presence of illite, including tainiolite(?), and rare chalcedony suggests moderately high temperature.

Contemporaneous(?) mafic volcanism may have provided a heat source.

Evidence supporting low-T, diagenetic origin

The zoned mineral assemblage (smectite, zeolite, Kspar) forms by low-T, closed hydrologic system diagenesis in an alkaline, saline lake, consistent with the closed McDermitt caldera basin. Illite can also form at low T in such an environment.

$_{40}Ar/_{39}Ar$ age of Kspar (14.87±0.05 Ma) in the deposit long postdates 16.7-16.0 Ma igneous activity, the obvious possible heat source to drive hydrothermal flow.

Lithium is easily leached from calc-alkaline rhyolite glass (Zielinski et al., 1977), although equivalent studies have not been made of peralkaline rhyolites.

The presence of widespread Li enrichment in the caldera suggests a large-scale process that operated throughout the caldera, in contrast to a more localized, concentrated hydrothermal process.

Known hydrothermal deposits of Hg and U in the McDermitt caldera are not enriched in Li, although Li data are sparse and in part ambiguous (Glanzman and Rytuba, 1979; Rytuba and Glanzman, 1979; Castor and Henry, 2000; Kotlyar et al., 2000; Rytuba et al., 2003).

Evidence that can go either way

Both high- and low-T processes can transport and deposit Mo, As, and Sb. E.g., hydrothermal U deposits in the caldera and low-T, roll-front U deposits in general are enriched in the three elements. Notably, U is not enriched with Li at McDermitt. Significance of K, Rb, and F enrichment is unknown.

Major questions for any origin are: what is the total endowment of Li in mineralized zones of the caldera, and can either leaching of the intracaldera sediments or a widespread hydrothermal system provide what is clearly a huge amount of Li?

A FINAL WORD

These alternative possibilities have major implications for Li exploration and potential resources. If Li deposits formed from Li leached from tuffaceous sediments that accumulated in the McDermitt caldera, then other calderas in the region have potential for similar deposits. If Li was introduced hydrothermally, then the McDermitt deposits may be unique. Could more than one process have contributed? More data are needed on caldera-wide mineral zoning and Li concentrations in the intracaldera sediments, the temperature of formation of the mineral assemblages, and the presence, or lack of, post-caldera collapse heat sources.

ABSTRACT

The Lithium Nevada Corp. Thacker Pass Project has a measured resource of 242M tonnes at 0.29% Li (~0.7M tonnes Li). The deposit is the southernmost of five known lenses hosted within intracaldera tuffaceous sediments along the west side of the McDermitt caldera, which formed by eruption of 16.4 Ma peralkaline-metaluminous tuff. Analyses of 9880 core samples (~1.5-m thick) give a mean of ~ 2500 ppm Li, with some >8800 ppm. Entire sedimentary sections in the southern and western parts of the caldera basin have high Li (1500+ ppm). Pre-caldera rocks, the McDermitt Tuff, late caldera volcanics, and unaltered tuffaceous sediments have relatively low Li (5 -140 ppm). Sediment deposition was mainly subaqueous in the closed caldera basin. Li-rich fill may have been deposited from airborne sources.

Claystone comprises most of the Thacker Pass deposit and dominates Li-rich intervals. The rest is mostly feldspar-rich ash. X-ray diffraction (XRD) data from six core holes across the deposit show consistent lateral mineral zoning. A Li-rich zone (mean >4,000 ppm) mainly contains illitic clay and underlies a zone of lower Li with smectite + analcime. Based on XRD peak locations and chemistry, the closest analogs to the illitic clay are Li micas (e.g. tainiolite). Montmorillonitic clay and a basal silicified zone underlie the illitic zone. Some transitional rock of mixed-layer clay between the illite and smectite zones also has high Li. All clay has similar optical properties but SEM images show illite forms tiny hexagonal plates and smectite has no resolvable crystallinity. Calcite, albite, K-feldspar, and quartz occur in all zones, dolomite and fluorite near the top of the illite zone, and pyrite and bitumen in unoxidized rock. The Li-rich zone has relatively high K, Rb, Mo, As, and Sb. Secondary Kspar in the Li-rich zone gave an 40Ar/39Ar age of 14.87±0.05 Ma.

No origin fully explains known characteristics. The presence of illite suggests a moderate temperature hydrothermal system. Release of Li from tuffaceous sediments and transport by alkaline groundwater are consistent with most mineralogy (characteristic of closed hydrologic system diagenesis) and with the Kspar date that long postdates caldera magmatism. Release of 10 ppm Li from the likely 50-200 km3 of intracaldera sediments would contribute ~1-4M tonnes Li.

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