

Lithium in Tufas of the Great Basin: Exploration Implications for Geothermal Energy and Lithium Resources

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ABSTRACT

Lithium/magnesium, lithium/sodium, and to a lesser extent, potassium/magnesium ratios in calcium carbonate tufa columns provide a fingerprint for distinguishing tufa columns formed from thermal spring waters versus those formed from non-thermal spring waters. These ratios form the basis of the Mg/Li, Na/Li, and K/Mg fluid geothermometers commonly used in geothermal exploration, which are based on the fact that at elevated temperatures, due to mineral-fluid equilibria, lithium preferentially partitions into thermal waters relative to magnesium. Cooling of thermal waters during their ascent to the surface can lead to an imbalance in Li/Mg, Li/Na, and K/Mg ratios between fluids and host rocks which in turn can lead to preferential precipitation of lithium and potassium relative to magnesium and sodium in host minerals, thus increasing the Li/Mg and K/Mg ratios of mineral precipitates to levels higher than that normally seen in the surface environment.

These lithogeochemical trace element ratios have significance for geothermal exploration, because tufa columns potentially overlie electricity grade geothermal resources at depth. As defined here, tufa columns form in lacustrine lakes. Lakes were abundant in the Great Basin in wetter periods of the Pleistocene to Recent Epochs, but as the lakes dried up, the springs also dried up, leaving the tufa towers behind as the only physical evidence in many cases that thermal waters might still be present in the subsurface.

In addition to providing a potentially diagnostic lithogeochemical tool for geothermal exploration, the analysis of lithium and other elements in tufa deposits could serve as exploration guides for hot spring lithium deposits. Even though lithium clays such as those at McDermitt, Nevada occur at shallow depths, they are easily eroded and/or covered by thin layers of post-mineral sediments or colluvium. Tufa columns, because of their vertical height and greater degree of lithification, offer more resistance

to erosion and are more likely to remain exposed, where they can be mapped and sampled.

Introduction

This manuscript is the second of two papers describing the geochemistry of tufa columns and their associated spring waters. The first paper (Coolbaugh et al., 2009) discussed the mode of occurrence of tufa columns, their relevance to geothermal exploration, water geochemistries of associated springs, and provided a preliminary review of the lithogeochemistry of tufa columns. This second paper provides more detailed documentation on water and rock geochemistries and describes diagnostic major and trace element ratios and concentrations that can be used to distinguish tufa columns formed from thermal waters from those that formed from non-thermal waters.

Background and Relevance

Several recent discoveries of thermal groundwater beneath calcium carbonate tufa columns in Nevada underscore the geothermal exploration significance of tufa columns. No thermal springs are currently associated with these tufa columns, thus, the presence of the tufa columns provided the most visible evidence that thermal waters are still present in the subsurface. These discoveries occurred at Astor Pass, Nevada (Coolbaugh, et al., 2006), in the southwestern Smoke Creek Desert, Nevada (Coolbaugh, et al., 2006), and at Emerson Pass, Nevada (Kratt et al., 2010).

Calcium carbonate tufa columns, as defined here, form around subaqueous springs that discharge into lakes. Dissolved calcium in the spring water reacts with atmospherically derived CO₂ in the lake water to form vertical columns of calcium carbonate (calcite) that in extreme cases, as at Pyramid Lake, Nevada, rise as much as 100-200 meters above the lake bed (Benson, 1994; Coolbaugh et al., 2009). The chemical process that forms tufa columns is different than that which produces subaerial calcium carbonate travertine deposits on the land surface. Travertine deposits form when CaCO₃ reaches saturation in spring waters due to depressurization and loss of CO₂ as spring waters approach the surface.

The effervescence of CO₂ raises the pH in the spring waters, which reduces calcium carbonate solubility, which in turn leads to calcium carbonate deposition.

The fact that different chemical processes are involved in the formation of subaqueous tufa deposits and subaerial travertine deposits has significance for geothermal exploration. Electricity grade geothermal resources are not usually associated with large travertine terraces because of the inverse solubility of CaCO₃ with temperature. Thermal waters with a high-temperature parentage typically do not have sufficient dissolved carbonate/bicarbonate to form significant carbonate terraces on land. However, high-enthalpy-parentage fluids can produce large tufa columns in lakes, if sufficient concentrations of calcium in the springs waters are available to combine with CO₂ derived from lake water. The chemical differences between thermal waters associated with tufa columns versus those associated with travertine deposits are illustrated in Figures. 1-3.

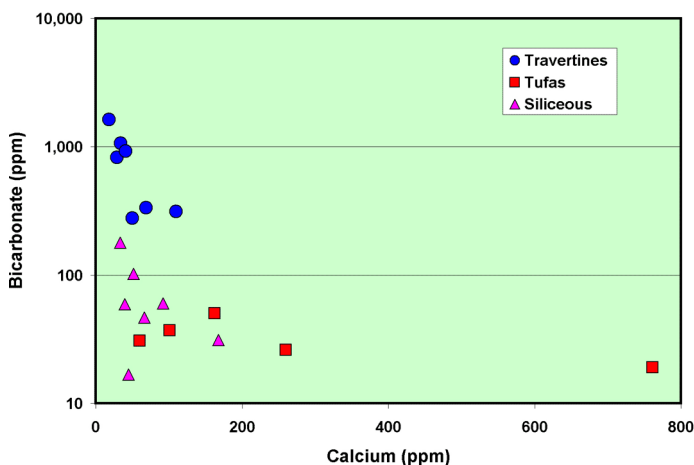


Figure 1. Bicarbonate and calcium concentrations of thermal waters associated with large travertine domes (blue circles), large tufa columns (red squares), and lacustrine opalized sediments (purple triangles) in NV and eastern CA. Tufa waters have higher Ca contents and lower HCO₃ contents compared to travertine waters.

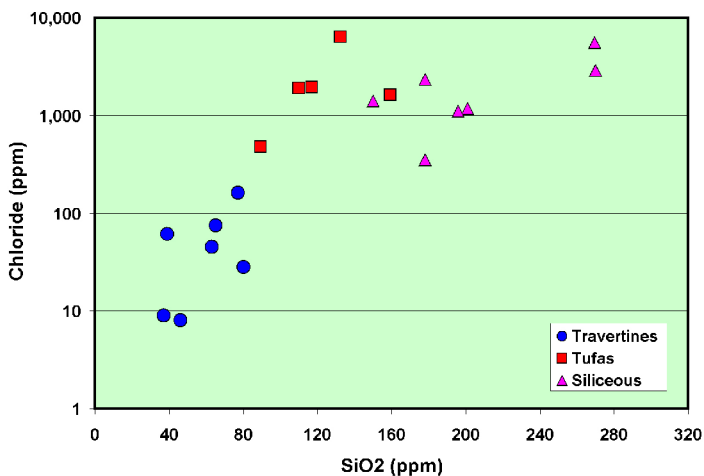


Figure 2. Chloride and silica concentrations of thermal waters associated with large travertine domes (blue circles), large tufa columns (red squares), and lacustrine opalized sediments (purple triangles) in NV and eastern CA. Tufa waters have higher Cl and silica contents compared to travertine waters.

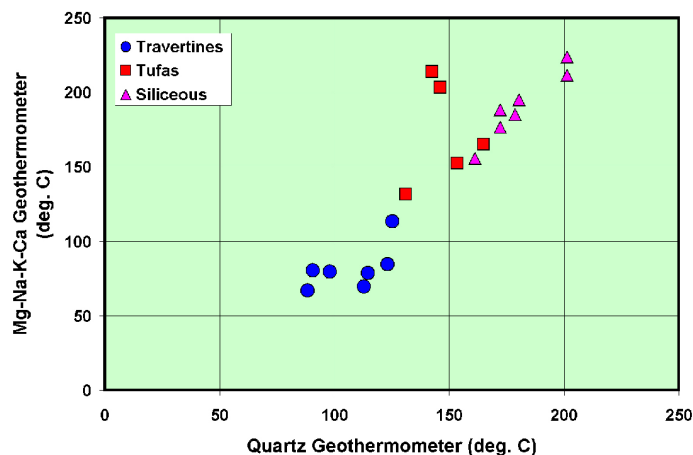


Figure 3. Fluid geothermometers for thermal waters associated with large travertine domes (blue circles), large tufa columns (red squares), and lacustrine opalized sediments (purple triangles). Thermal waters associated with large tufa columns yield higher geothermometer temperatures than thermal waters associated with large travertine domes from western NV and eastern CA. Tufa waters are from Pyramid Rock, Astor Pass, Needle Rocks (2 samples), and the southwest Smoke Creek Desert (Coolbaugh et al., 2006). Travertine waters are from Bartine Hot Springs, Diana's Punch Bowl, Hyder Hot Springs, Hot Pot, and Sou Hot Springs, NV. and Fales Hot Spring, CA. The chalcedony geothermometer was used for silica if the Mg-Na-K-Ca geothermometer was less than 100°C, and the quartz geothermometer was used if the Mg-Na-K-Ca geothermometer was greater than 100°C, following the procedure of Mariner et al. (1983). References for geothermometer equations are: quartz (no steam loss) and chalcedony (Fournier, 1981); and Na-K-Ca-Mg (Fournier and Truesdell, 1973; Fournier and Potter, 1979).

Where lakes are still present in the Great Basin, active springs are still found at tufa towers. Examples at Pyramid Lake in west-central Nevada include hot springs at Needle Rocks (with tufa columns up to 100 meters high), hot springs at Pyramid Rock (a large tufa column projecting 100 meters above the water surface and another 100 meters below the water surface), and cold springs at Popcorn Rocks. Tufa columns occur over much of the northwestern Great Basin where lakes are not present. Their widespread occurrence is evidence of the presence of large bodies of water (e.g. former Lake Lahontan) in the geologically recent past. However, in stark contrast to tufa columns at Pyramid Lake, to the authors' knowledge, none of the tufa towers standing on dry lake beds are associated with active springs. Evidently, when Lake Lahontan and other lakes in Nevada dried up, the lowered water table led to the disappearance of springs as well, leaving behind the tufa towers as the main surface evidence that thermal groundwaters might still be present in the subsurface today.

Not all tufa columns owe their existence to thermal springs, however. Cold springs can also precipitate tufa, as long as sufficient calcium is present in spring waters to react with CO₂-saturated lake waters. It is for this reason that the ability to distinguish between thermal and non-thermal tufa columns becomes important. Shallow temperature surveys have been used to distinguish geothermal heat flux at several tufa columns, including at Astor Pass and the southwestern Smoke Creek Desert (Coolbaugh et al., 2006) and at Emerson Pass (Kratt et al., 2010). However, shallow cold groundwater could interfere with the ability of shallow temperature surveys to detect deeper thermal aquifers at some localities. Drilling is a more reliable method, but is also more expensive.

Lithochemochemistry

The current geochemical research project was borne out of a desire to determine if lithochemochemical analyses of tufa towers could identify distinctive geochemical fingerprints of thermal spring activity. It is logical that such geochemical fingerprints or markers could exist, since geothermal waters are known to have distinctive chemical compositions, and higher concentrations of most solutes in general, compared to shallower, colder waters. To assess this possibility, 36 samples of carbonate deposits were taken from northwestern Nevada and easternmost California (Figure 4): 27 samples come from tufas, 8 samples come from travertines, and one sample comes from a calcite-chalcedony vein. Samples were selected to enable distinctions between thermal and non-thermal tufa columns, thermal travertines, distal versus proximally precipitated travertine, and tufa columns versus more regionally precipitated wave tufa or shoreline tufa. Wave tufa (shoreline tufa) is calcium carbonate that precipitated directly (without spring activity) from lake waters that were saturated in calcium carbonate, as was the case for former Lake Lahontan in northwestern Nevada. In contrast to spring-related tufa columns, which form distinctive tower-like edifices (Figure 3 in Coolbaugh et al., 2009), wave tufa occurs as relatively thin, widely dispersed crusts along shorelines and lake bottoms. Such calcium carbonate deposits are thinnest on the former lake bottom, and thickest along shorelines and on projecting near-surface promontories where dissolved CO₂ concentrations are highest due to wave enhanced interaction of lake waters with the atmosphere. Most tufa column samples were taken from centrally located, sub-vertical tubular structures that represent the original conduits for spring waters flowing into the lake (Figures 3, 5 in Coolbaugh et al., 2009). These tubular structures were further sub-sampled to form groups representing tube centers, inner tube walls, and outer tube borders or peripheries.

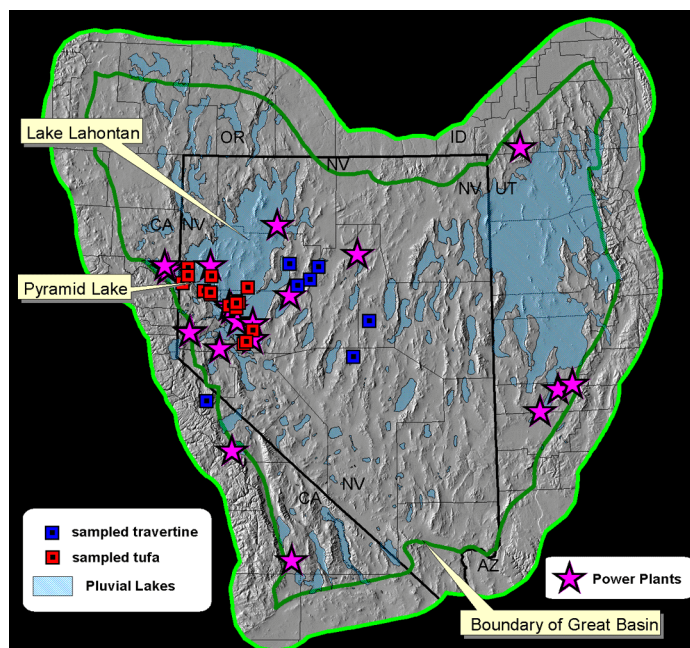


Figure 4. Locations of carbonate tufa and travertine samples analyzed in this study.

Sampling and Analytical Procedure

The samples were analyzed at the Nevada Bureau of Mines and Geology. After crushing and grinding, 400 mg samples were dissolved in a mixture of 2 ml concentrated nitric acid, 6 ml concentrated hydrochloric acid, and 2 ml concentrated hydrofluoric acid, heated for one hour at 100°C, cooled, and brought to a total volume of 500 ml. Trace elements were determined with an ICP-MS (Micromass Platform) using USGS standards GXR-1, GXR-2 and GXR-5 for calibration. Calcium was determined using the ICP-OES (Varian Vista AX) using USGS standards GXR-1, GXR-5, and NIST-88a for calibration. The ICP-OES was used for Mg and Si determinations using GXR-1, GXR-2, GXR-5 standards for calibration. A table of the results will be provided upon request from the authors.

Results

Many chemical constituents and ratios, including the Sr/Ca ratio, do not appear, at least with the present data set, to provide useful information pertaining to the thermal history of tufa columns. However, several geochemical criteria have been identified that appear capable of distinguishing “thermal” from “non-thermal” tufa in most cases. They include:

1. Magnesium concentrations
2. A summed metal loading factor
3. Lithium/magnesium ratios
4. Lithium/sodium ratios, and,
5. Potassium/magnesium ratios.

Results - Mg

Magnesium concentrations are distinctly higher in wave-form (non-spring-related or shoreline) carbonate tufa compared to spring-related tufas (Figure 5). Some samples of the peripheries

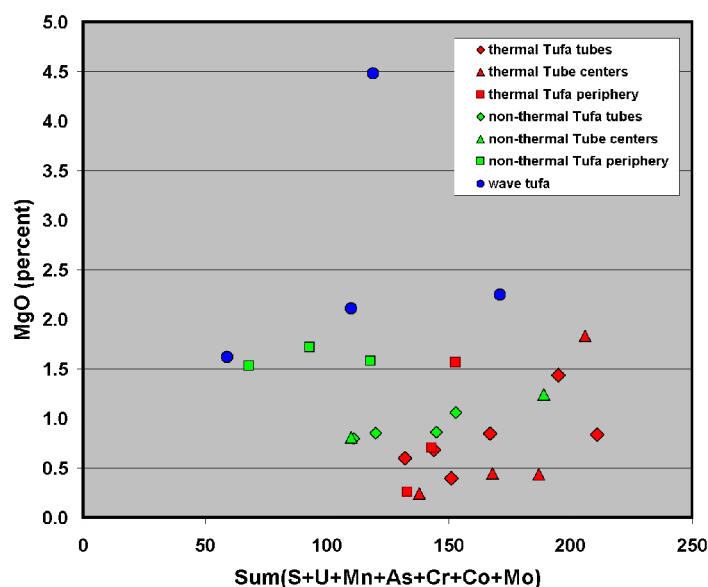


Figure 5. Magnesium concentrations plotted against a summed rank index of sulfur, uranium, manganese, arsenic, chromium, cobalt, and molybdenum for tufa columns. Tufa columns associated with geothermal activity tend to have higher values of the metal index, and lower concentrations of Mg compared to non-thermal tufas and wave-form (shoreline) tufas. Sample locations are shown on Figure 4.

or margins of tufa columns also have elevated Mg concentrations compared to the interior of tufa columns (Figure 5), suggesting that some wave-form or non-spring tufa may form as crusts on the outer margins of spring-related tufa columns, in a manner analogous to the tendency of wave-form tufa to form thicker crusts on ridges projecting into lakes. The high Mg concentrations in wave-form tufa may be related to relatively high Mg concentrations in lake waters; Pyramid Lake currently has Mg concentrations ranging from 96-106 ppm (Poulson et al., 2007), which is orders of magnitude higher than concentrations normally found in thermal waters, and also higher than concentrations found in most cold, shallow groundwaters. The correlation of Mg concentrations with tufa type lends credence to the concept that minor or trace cationic component concentrations of tufa columns can indeed be influenced by fluid source (spring vs lake).

Results - Metals

Trace metals, most of which have a positive charge in surface waters and groundwater, typically occur in higher concentrations in thermal groundwater than in shallow cold groundwater or lake waters. Subject to the ability of such metals to either substitute into the carbonate lattice of tufa columns or to precipitate as metal carbonates or substitute into other mineral species such as clays, one might expect to find higher metal concentrations in thermally derived tufa columns relative to non-thermally derived tufa columns. An inspection of the database reveals clues that this may indeed be the case, because thermally derived tufa columns at some locations have relatively high concentrations of some metals, but the correlation of any single metal with all thermal spring-related tufas is not consistent. This lack of consistency could be caused by the variable composition of host rock through which groundwater flows in different parts of Nevada where the samples were taken. Volcanic rocks, sedimentary rocks, metamorphic rocks, and plutonic rocks of various compositions will tend to generate distinctive fluid trace element signatures.

A combined metal loading factor correlates more consistently with thermal tufas than any single metal (Figure 5). After inspection of the data, six metals (U, Mn, As, Cr, Co, and Mo) plus sulfur were combined together into an overall metal index. A simple sum of metal concentrations for each sample is not appropriate for such an index since each metal has its own range of concentrations, which can differ from that of other metals by orders of magnitude. Consequently a ranking system was employed. The concentration of each metal was ranked numerically from 1 to n, where n represents the highest concentration of that metal in the database, and 1 represents the lowest concentration. Rankings for each of the seven constituents were then summed to yield an overall "metal factor" for each sample. Higher metal factors reflect greater overall metal loadings (plus sulfur). A metal index calculated in this manner, although somewhat qualitative, attempts to measure the overall degree to which tufa columns are enriched in trace metals, on the premise that thermal groundwaters will tend to be more enriched in such elements than colder groundwaters, because of longer fluid flow paths in bedrock, higher temperatures, and more reactive fluid compositions.

The chemical distinction of thermal tufas from non-thermal tufas is clearer when the metal loading factor is plotted against Mg

concentrations (Figure 5). For a specified Mg concentration, higher metal indices correlate with thermal tufas, but the index threshold varies as a function of Mg concentration (Figure 5). Perhaps it is easier for metals to substitute into near-surface Mg-bearing minerals (e.g. clays), which may be more abundant in non-thermal tufas (because of the high Mg-content of lake waters), thus giving rise to a bias which is partially compensated for by calculating the ratio of the metal factor to Mg concentration.

Elemental Ratios Related to Fluid Geothermometry

Some major and trace elements ratios have analogues in fluid geothermometry; these ratios were evaluated for their ability to distinguish thermal from non-thermal tufa columns. Upon examination, it was found that, indeed, the ratios Li/Mg (which forms the basis of the Mg-Li geothermometer, Kharaka and Mariner, 1989), Li/Na (which forms the basis of the Na-Li geothermometer, Fouillac and Michard, 1981) and to some extent, K/Mg (which forms the basis of the K-Mg geothermometer, Giggenbach, 1988) can be used to discriminate thermally derived tufas from non-thermally derived tufas (Figures 6-8). The ratio of K/Na, related to the well known K-Na geothermometer, does not work as well in this regard.

The Mg-Li, Na-Li, and K-Mg fluid geothermometers are based on the fact that at elevated temperatures, due to mineral-fluid equilibria, lithium and potassium preferentially partition into thermal waters relative to magnesium and sodium, respectively. If mineral-rock re-equilibration is suppressed during the ascent (and cooling) of thermal waters to the surface, it leads to an imbalance in Li/Mg, Li/Na, and K/Mg ratios between fluids and host rocks which in turn can lead to preferential precipitation of lithium and potassium relative to magnesium, and of lithium relative to sodium, in host minerals, thus increasing the Li/Mg, Li/Na, and K/Mg ratios of mineral precipitates to levels higher than

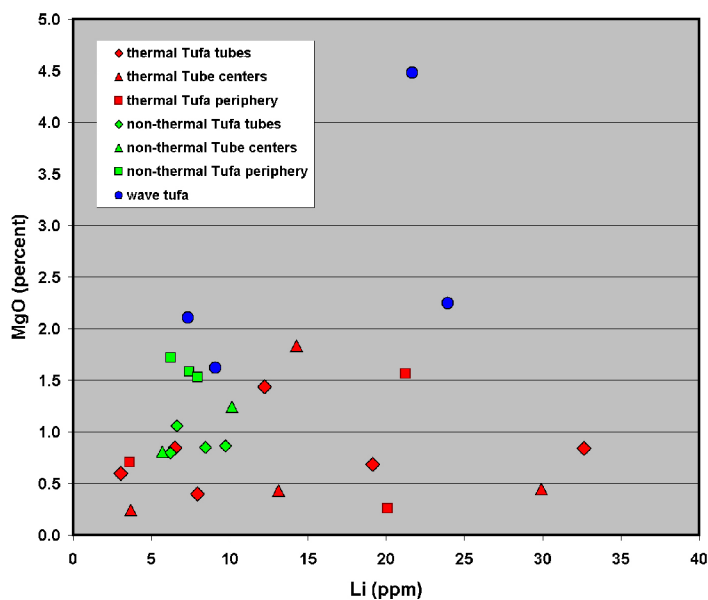


Figure 6. Magnesium concentrations plotted against lithium concentrations for tufa columns. For a given Mg concentration, tufa columns associated with geothermal activity tend to have higher lithium concentrations than non-thermal tufas and wave-form (shoreline) tufas. Sample locations are shown on Figure 4.

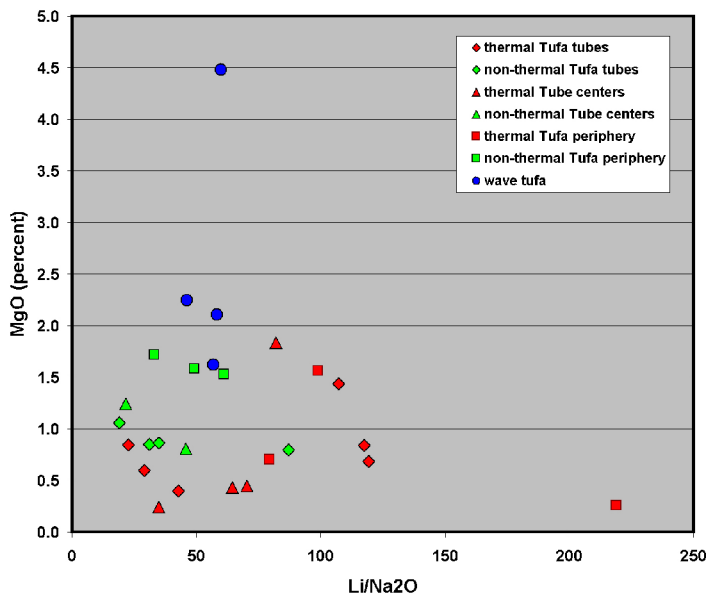


Figure 7. Magnesium concentrations plotted against lithium/sodium ratios for tufa columns. For a given Mg concentration, tufa columns associated with geothermal activity tend to have higher lithium/sodium ratios than non-thermal tufas and wave-form (shoreline) tufas. Sample locations are shown on Figure 4.

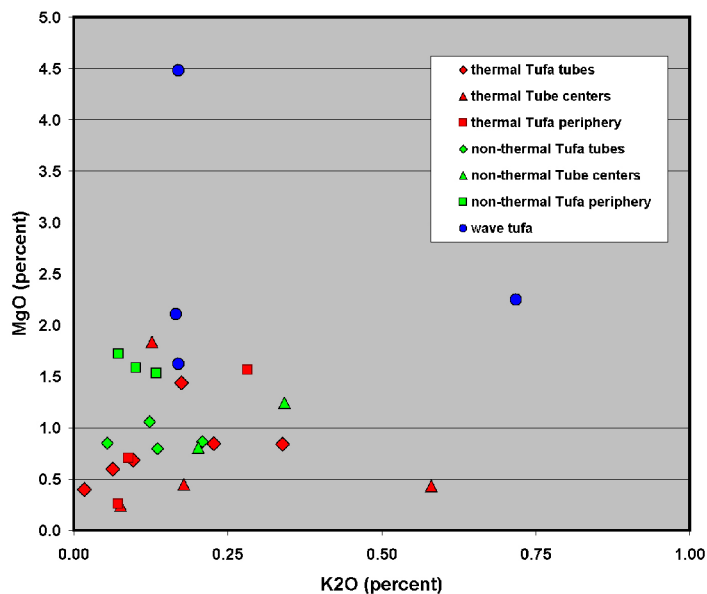


Figure 8. Magnesium concentrations plotted against potassium concentrations for tufa columns. For a given Mg concentration, tufa columns associated with geothermal activity tend to have higher potassium concentrations than non-thermal tufas and wave-form (shoreline) tufas. Sample locations are shown on Figure 4.

that normally seen in the surface environment. This relationship is potentially complicated by the presence of multiple mineral species in tufa columns, each of which are likely to have its own partitioning factors. X-ray diffraction (XRD) analysis verifies that calcite is the predominant component in these tufas, but small amounts clays, sulfates, and silica could be present and would not be detected by XRD.

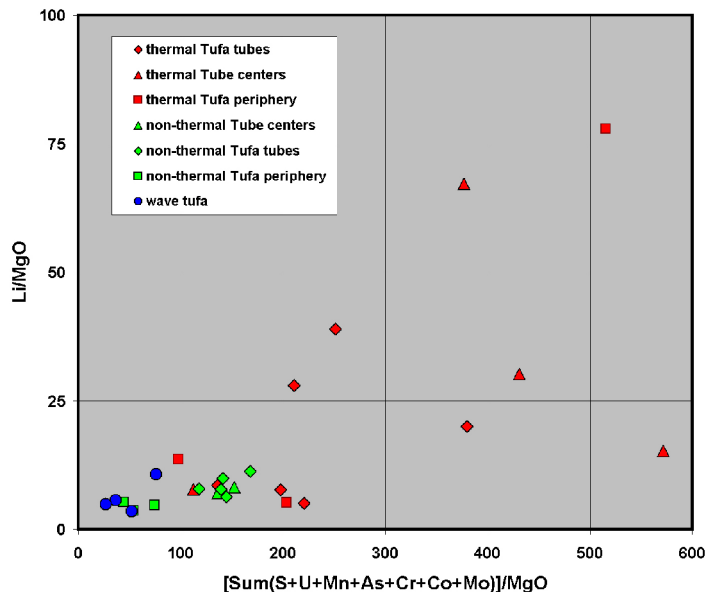


Figure 9. Lithium/magnesium ratios plotted against a summed ranking index of sulfur, uranium, manganese, arsenic, chromium, cobalt, and molybdenum (normalized by Mg concentrations) for tufa columns. Tufa columns associated with geothermal activity tend to have higher values of the metal index, and higher lithium/magnesium ratios, compared to non-thermal tufas and wave-form (shoreline) tufas. Sample locations are shown on Figure 4.

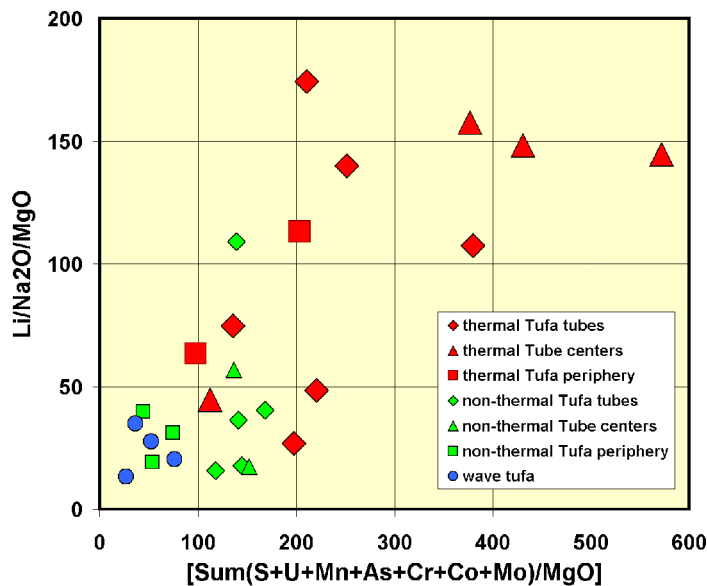


Figure 10. Lithium/sodium ratios, normalized by magnesium, plotted against a summed ranking index of sulfur, uranium, manganese, arsenic, chromium, cobalt, and molybdenum (also normalized by Mg concentrations) for tufa columns. Tufa columns associated with geothermal activity tend to have higher values of the Li/Na/Mg ratio, and higher values of the Mg-normalized metal index, compared to non-thermal tufas and wave-form (shoreline) tufas. Sample locations are shown on Figure 4.

The chemical distinction of thermal vs. non-thermal tufas that is provided by Li/Mg and Li/Na ratios is similar to, and reinforces, the distinction made with the previously described metal index (Figures 9-10). The correlation of Li/Na ratios with tufa types

is improved further when the Li/Na ratio is divided by the Mg concentration (Figure 10), perhaps because the presence of Mg in component minerals, such as carbonates or clays, facilitates lithium substitution to levels higher than normally possible without it (lithium substitutes for magnesium in many minerals).

Discussion and Link to Lithium Clay Resources

The association of elevated lithium/magnesium and lithium/sodium ratios with thermal-spring tufa columns is indirectly corroborated by the occurrence of lithium-rich lacustrine clay (hectorite) deposits, whose formation has been attributed to thermal spring activity, as at Hector, California (Ames, *et al.*, 1958) and within the McDermitt Caldera in northern Nevada (Eggleston and Hertel, 2008). The substitution of lithium for magnesium in hectorite (a magnesium-rich smectite clay) is facilitated by other ionic substitutions in the clay mineral that provide a charge balance. This helps explain why the Li/Mg ratio in hectorite can reach potentially economic concentrations (for lithium mining) compared to other magnesium-bearing minerals where charge-balancing substitutions are not as readily available. The magnesium in hectorite is believed to be supplied by lake waters at Hector, California (Ames *et al.*, 1958). This is consistent with relatively high Mg concentrations found in Pyramid Lake in western Nevada (~ 100 ppm, Poulson *et al.*, 2007) and is consistent with the fact that Mg concentrations in geothermal waters are typically low.

In addition to providing a potentially diagnostic lithochemical tool for geothermal exploration, the analysis of lithium and other elements in tufa deposits could serve as exploration guides for hot spring lithium deposits. The lithium deposits at McDermitt are currently being evaluated as an economic source of lithium for the rapidly developing lithium battery market. Even though lithium clays such as those at McDermitt occur at shallow depths, they are easily eroded and/or covered by thin layers of post-mineral sediments or colluvium. Tufa columns, because of their vertical height and greater degree of lithification, offer more resistance to erosion and are more likely to remain exposed, where they can be mapped and sampled.

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