

## **Elemental Content Of Mineral Licks In The Klamath Mountains, Siskiyou County, California**

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Mineral licks are important components of terrestrial ecosystems that have special value in the annual life cycle of deer and elk. Lick use helps herbivores maintain a proper electrolyte balance even as forage quality changes seasonally. In this study, 5 lick sites, mostly in soft weathered rock or deep soil exposed in roadcuts, were sampled on the Klamath National Forest in northwestern California. Lick samples were analyzed for pH, electrical conductivity (reflective of salinity), and 10 water-extractable elements (Ca, Na, K, Mg, Mn, Fe, I, Cl, S as SO<sub>4</sub>, and N as NO<sub>3</sub>). Soil textures varied from sand to silty clay. Lick pH varied from 3.6 to 9.8. Electrical conductivities of the saturated paste extracts varied from 0.2 to 16.7 dS m<sup>-1</sup>. While iodine is the element that is most often higher in lick samples compared to non-lick materials, no single and consistent soil attribute was overwhelmingly enhanced at the lick sites. Each site had at least one chemical condition that was different from the non-lick comparison samples, so the individual licks may provide different nutrient supplements.

Key words: deer licks, elk licks, geophagy, Klamath Mountains

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Mineral licks are important components of terrestrial ecosystems, in particular because of their significant contributions to the life cycle of herbivores (Heimer 1973, Weeks and Kirkpatrick 1976, Weeks 1978). Research as far back as the 1950s indicates that herbivores have reduced access to high concentrations of mineral elements, such as sodium and calcium, compared to carnivores and omnivores (Rea and Rea 2005). While ungulates often incidentally ingest soil adhering to plant roots (Healy et al., 1972; Arthur and Alldredge, 1979), purposeful ingestion of soil (geophagy) by herbivores can be a symptom indicating deficiency in various nutritional elements, such as phosphorus, calcium, and sodium, and to a lesser degree, magnesium, sulfate, and the micro-elements cobalt and copper (Eksteen and Bornman 1990, Jones and Hanson 1985).

In North America, plants may provide insufficient levels of nutrients during certain times of the year (Belovsky and Jordan 1981). Animals use natural mineral licks predominately in the spring and early summer months during gestation and lactation (Jones and Hanson 1985, Robbins 1993, Ayotte et al. 2008). The use of natural mineral licks can help maintain a positive balance for sodium during these critical periods (Weeks and Kirkpatrick 1976).

Other elements (Mg and Ca) consumed at mineral licks may be more important to ungulates than sodium. High concentrations of magnesium and calcium are associated with optimum development of antlers and body weight of white-tailed deer (Jones and Hanson 1985). Frequent use of mineral licks in spring has been attributed to a high intake of potassium in forage, which interferes with essential absorption of magnesium in the ruminant digestive tract and causes grass tetany (Weeks and Kirkpatrick 1976, Jones and Hanson 1985, Schultz et al. 1988). As with sodium, supplementing magnesium intake can counter high potassium ingestion during spring (Schultz et al. 1988). The literature indicates that sodium chloride is the most probable attractant, while a strong nutritional need is for calcium and magnesium (Jones and Hanson 1985, Moe 1993, Kennedy et al. 1995).

Mineral licks used by deer were noted a century ago in the Klamath Mountains of northern California, where they were favored sites for deer hunting until protected by a game refuge (Bryant, 1918). Deer and elk licks are commonly observed on the Klamath National Forest, but have not been described, analyzed, and classified. The objectives of this study were to begin identifying known locations of mineral lick sites, to determine their physical and chemical properties, and to create a useful classification system to communicate information about them to wildlife biologists and land managers.

## MATERIALS AND METHODS

*Study area.*—The study area is located on the Klamath National Forest within the Klamath Mountains physiographic province in western Siskiyou County, California. The general locations of sampled lick sites are indicated in Figure 1. The sites are within a 50-km radius of 41° 31' N, 123° 10' W. The climate is Mediterranean with cool, wet winters and hot, relatively dry summers. The mean annual precipitation of the sampled sites varies between 787 and 1651 mm with most of the precipitation occurring as rain between October and April (Table 1) (Rantz 1968). Elevations of the lick sites range from 220 to 1459 m. All of the licks are located in coniferous forest vegetative types. Douglas fir [*Pseudotsuga menziesii* (Mirbel) Franco] dominates on most sites, with white fir [*Abies concolor* (Gordon and Glend.) Lindley], ponderosa pine (*Pinus ponderosa* Laws), incense cedar [*Calocedrus decurrens* (Torrey) Florin], tanoak [*Lithocarpus densiflorus* (Hook. & Arn.) Rehd.], and black oak (*Quercus kelloggii* Newb.) on some sites (Table 1). Soils at the sites are mapped as Haploxerults, Haploxeralfs, Dystroxerepts, and Humixerepts (Table 1). Lick materials are from metavolcanic, serpentinite/talc, diorite, and quartz diorite lithologies (Table 2) (Wagner and Saucedo 1987).

*Sample collection.*—The lick sites sampled for this study were being used by California black-tail deer (*Odocoileus hemionus columbianus*) (all sites; Figure 2) and Roosevelt elk (*Cervus canadensis roosevelti*) (Sites 1 and 7). Lick samples were taken where actual ingestion was indicated by teeth and tongue marks (Figures 3 and 4) in the dry or wet soil or soft rock material (i.e., regolith). The actual lick ingestion spots varied from less than 1 m<sup>2</sup> to several m<sup>2</sup> in size. Sites 1, 2, 6, and 7 were originally sampled in 1998. Site 8 was sampled in 2016. Non-lick soil samples for comparison were collected in 2016 near the licks (within 1-10 m) at Sites 1, 2, 6, and 8, but in places that showed no

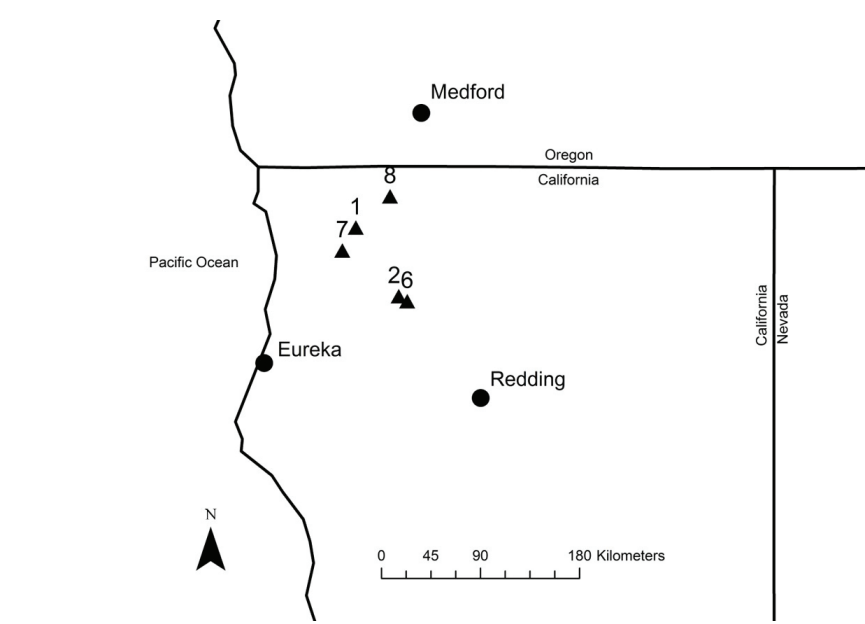


Figure 1.—Locations of sampled mineral lick sites.

Table 1.—Environmental descriptions of mineral lick sites.

Site	Elevation (m)	Mean annual pre- cipitation (mm)	Exposure	Summer moisture	Vegetation	Soil classifica- tion
1	730	1650	Road cut	dry	Douglas fir, tan oak	Haploxerults
2	973	1143	Road cut	dry	Douglas fir, mixed conifer	Haploxeralfs
6	1459	1397	Road cut	dry	White fir, mixed conifer	Dystroxerepts
7	220	1651	Landslide	dry	Douglas fir, tan oak	Haploxerults
8	640	787	Landslide	wet	Douglas fir, ponderosa pine, black oak	Dystroxerepts, Humixerepts

concentrated hoof prints or marks of gnawing or licking. Replicate non-lick samples were taken at all sites, except Site 7. Lick sample replicates were obtained at Sites 2, 6, and 8.

Sampled lick sites occurred mostly in road cutbanks (Table 1, Figure 2). Roadcuts generally expose regolith materials that are located one to several meters below the soil surface, which would not normally be accessible to animals. In the Klamath Mountains, 4,000 miles of roads increase the occurrence of roadcut lick sites compared to natural surface-occurring lick sites. The lick at Site 1 is in a deep soil exposed in a roadcut. The licks at Sites 2 and 6 are in soft, weathered bedrock (known as saprock; Graham et al. 2010). Site 7 is in saprock exposed in a landslide scarp. Site 8 is at a wet seepage area associated with a small, stabilized landslide. Eight sites were investigated, but only five (Sites 1, 2, 6, 7, and 8) were used in this study because the others could not be found when revisited in 2016 for additional sampling.



Figure 2.—Doe and fawn using lick at Site 1.

*Laboratory methods.*—Materials from lick and non-lick sites were sampled, air-dried, gently crushed, and sieved to remove coarse fragments ( $>2$  mm). Soil textural classes of the regolith materials were determined by tactile evaluation (Thien 1979). The pH of the materials was determined on a 1:1 ratio of regolith/distilled water. Saturation paste extracts, using distilled water, were obtained and electrical conductivity (EC), an indicator of overall salt content (Soil Survey Staff 1993), was immediately measured (Burt 2004).

No consistent chemical extraction method has been adopted for compositional analysis of mineral licks. Extractants include water, acid extracts of varying strengths, and other methods typically used in soil fertility assessments (e.g., Arthur and Alldredge 1979, Kennedy et al. 1995, Dormaar and Walker 1996, Ayotte et al. 2006). The wide variety of methods makes it difficult to compare values among studies reported in the literature. In this study, water-soluble components were extracted from the saturated pastes of regolith (soil or thoroughly crushed saprock) and distilled water. Elemental analysis (Ca, Na, K, Mg, Mn, Fe) of the solutions (acidified with 2%  $\text{HNO}_3$  after extraction) was performed using an ICP-OES. Chloride, nitrate, sulfate, and iodine were analyzed by ion chromatography. The chemical compositions reported are concentrations (mg L<sup>-1</sup>) in the regolith extract solutions, not as concentrations in the solid phase, so they can only be used for comparison of similarly analyzed samples.

## RESULTS

*Use of licks.*—All of the lick sites have evidence of heavy traffic by deer (and elk in the case of Sites 1 and 7); i.e., hoof prints and droppings. Beyond this, the soil or soft rock of the dry licks have tooth marks (Figure 3) and smooth surfaces (Figure 4) where the deer have gnawed and licked the earthen materials. This activity has produced concavities in roadcut escarpments ranging in size from no wider than a deer's tongue to holes large enough for the deer to enter (Figure 3). The wet lick at Site 8 is on more level ground rather than an escarpment, and the deer consume the mud near a seep (Figure 5). We were able to place a game camera at Site 1 for three days in early August 2016. The lick was visited for 19 minutes by a doe and two fawns on the first morning (Figure 2), a single doe for four minutes the second morning and a single doe for 10 minutes late that afternoon, and two does for six minutes the third morning.

*Physical properties.*—Most of the licks (Sites 2, 6, 7) were in saprock, one was in a deep subsoil (Site 1), one was in a surface soil (Site 8). The textural classes of the lick regoliths ranged from sand to silty clay (Table 2). Regolith textures for metavolcanic, argillite, and serpentinite lick sites were loam and finer, while quartz diorite and diorite lick samples had loam and sandy loam textures. One sample from the quartz diorite (6L-c) was finer textured (silt loam) because it was weathered from a xenolith, an inclusion of finer-grained, more mafic rock.

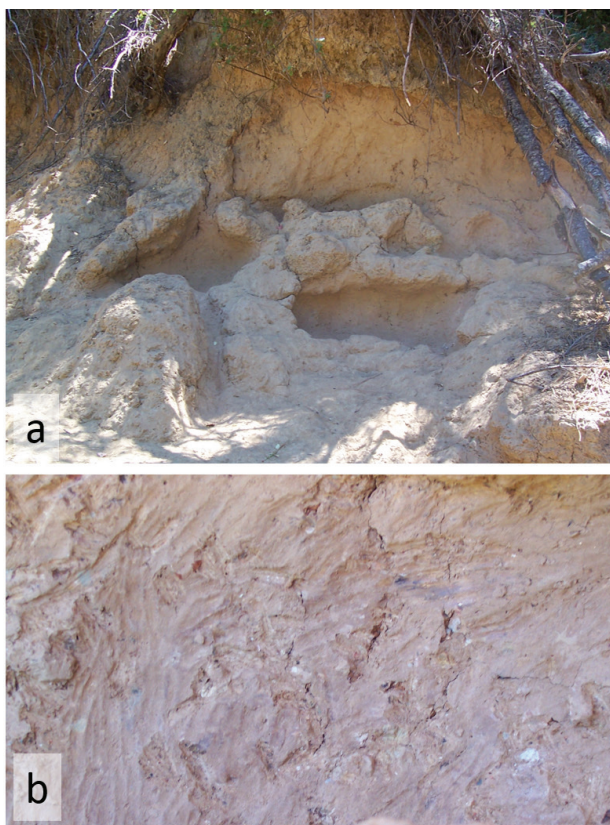


Figure 3.—Site 1 (a) roadcut with holes produced by deer and elk eating soil, (b) close up showing teeth marks in the soil. Horizontal field of view in (a) is 2.75 m.



Figure 4.—Site 2 (a) rock vein in road cut being used as a lick by deer, (b) close up showing rock surface smoothed by licking.



Figure 5.—Site 8, wet lick at a seep. Note the tile spade blade (40 cm long) at right for scale.

Table 2.—Rock type and physical properties of lick materials.

Site/sample ID <sup>a</sup>	Rock type at site	Sample regolith type, texture	Lick material dry color (Munsell notation) <sup>b</sup>	Depth below surface (m)
1L	Metavolcanic	Soil, silty clay loam	Brown (7.5YR5/4)	1.5 - 2.0
1NL	Metavolcanic	Soil, silty clay loam	Reddish yellow (7.5YR 6/6 - 7/6)	1.5
2L-a	Metavolcanic	Saprock, clay loam	Very pale brown (10YR8/2)	2.0
2L-b	Metavolcanic	Saprock, clay loam	Light gray (2.5Y7/1)	3.5
2NL	Metavolcanic	Fine material in rock fractures, loam - sandy clay loam	Pale - very pale brown (10YR 7/3)	3.5
6L-b	Quartz diorite with iron oxide stains	Saprock, fine sandy loam	Strong brown (7.5YR5/6)	4.0 - 6.0
6L-c	Xenolith	Saprock, silt loam	Light olive gray (5Y6/2)	4.0 - 6.0
6NL	Quartz diorite	Saprock, Sand	Light gray (10YR 7/2)	3.0 - 6.0
7L	Serpentinite/talc	Saprock, silty clay	Light greenish gray (5GY7/1)	2.0+
8L	Diorite	Soil, loam - sandy loam	Gray - pale brown (10YR5/1 - 6/3)	0-0.05
8NL	Diorite	Soil, loam - sandy loam	Grayish brown (10YR5/2)	0-0.05

<sup>a</sup>Samples from mineral licks are indicated with “L”, those from non-lick samples for comparison are indicated with “NL”.

<sup>b</sup>GretagMacbeth. 2000.

*Chemical properties.*—The pH of lick regolith material varied from 3.6 to 9.8 (Table 3). These samples were divided into three pH groups: acidic (<6.6), neutral (6.6-7.3), and alkaline (>7.4) (Soil Survey Staff 1993). Most of the lick samples were alkaline (Sites 1, 7, and 8), some were neutral (Site 6) or acid (Site 2).

The EC of lick materials varied from 0.2 to 16.7 dS m<sup>-1</sup> (Table 3). For reference, seawater has an EC of 55 dS m<sup>-1</sup> and soils are considered saline when the EC is  $\geq 4$  dS m<sup>-1</sup> (Soil Survey Staff 1993). While only two sites had mean EC values that indicated them to be saline (samples from Sites 2-b and 8), lick samples had higher EC values than associated non-lick samples at every site except Site 6.

Sodium was the most abundant water-soluble cation in most of the lick samples, usually by an order of magnitude (Table 3), but it was undetectable in lick samples at Sites 2-b and 8. Despite its general abundance, sodium concentrations were not higher in lick samples than in associated non-lick samples, except at Site 1. Magnesium in lick samples ranged from abundant (Site 8) to undetectable (Site 2-b), and was not consistently more or less than in associated non-lick samples. Potassium was present in all lick samples, though more abundant than in non-lick samples at only one site (Site 2-b).

Concentrations of manganese and iron were less than 1 mg L<sup>-1</sup>, except at Site 2 (Mn in lick and non-lick samples and Fe in lick samples), and only at Site 2 were concentrations greater in lick than in non-lick samples (Table 3). Samples from Site 2 had the lowest pH values in this study and manganese and iron become more soluble under these more acidic conditions (Brady and Weil 2007).

Chloride was the most abundant water-soluble anion in lick samples at all sites except Site 2 (Table 3). Chloride concentrations were not consistently higher in lick samples compared to non-lick samples. At Site 2, sulfate was the most abundant anion in both lick and non-lick samples, but was not consistently higher in one or the other. Nitrate concentrations ranged widely (undetectable to 1285 mg L<sup>-1</sup>) with no consistent trend between lick and non-lick samples. Iodine concentrations were mostly less than 1 mg L<sup>-1</sup> (the Site 1 lick sample had 1.4 mg L<sup>-1</sup>), but were higher in lick samples compared to non-lick.

## DISCUSSION

Clays have been hypothesized to promote digestion in ungulates by buffering the rumen pH, absorbing secondary plant compounds (e.g., tannins) that impede digestion, and ameliorating digestive ailments such as diarrhea (Ayotte et al., 2006). Ingested coarse soil material (sand) may also provide an abrasive action that is beneficial to digestion in ruminants (Cooley and Burroughs 1962). Regoliths at the lick sites we sampled span from sand- to clay-rich, and non-lick sites spanned the same range, so animal selection based solely on soil texture is not obvious.

Alkaline lick materials can help to buffer rumen pH from becoming too acidic (Ayotte et al. 2006), yet the wide range in pH of the lick sites suggests that deer are not consistently seeking material of a restricted pH range.

While no single water-soluble component is consistently higher in the lick samples than the non-lick samples, most of the licks do have at least one strongly differentiated property. At Site 1, the pH, sodium, and chloride are elevated; at Site 2-a, the lick is enriched in acidity, salinity, sulfate, manganese, and iron, while Site 2-b is enriched in calcium, potassium, manganese, and iron and is even more acidic and saline; Site 7 is highly alkaline; and at Site 8 the lick has especially elevated levels of calcium, magnesium, and chloride. All of the lick materials are more saline (higher EC) than the associated non-lick material, except at Site

Table 3.—Selected chemical analyses of saturated paste extracts from mineral licks and associated non-lick material.

Sample	pH	EC dS m <sup>-1</sup>	Ca	Na	K	Mg	Cl	SO <sub>4</sub>	NO <sub>3</sub>	I	Mn	Fe
----- mg L <sup>-1</sup> -----												
<i>Site 1</i>												
Lick	8.2	0.5	8	104	1	9	34	2	0.1	1.4	0.03	0.05
Nonlick n=3	5.4 5.1-5.5	≤0.08	35 27-41	32 19-55	10 7-12	21 14-33	5 4-6	7 6-9	ND <sup>a</sup>	0.02 ND-0.05	.04 0.02-0.07	0.03 0.03-0.04
<i>Site 2</i>												
Lick - a	4.6	1.3	100	306	14	202	162	2030	21	0.4	11.0	3.0
Lick - b n=3	3.7 3.6-3.7	12.7 9.7-16.7	458 409-517	ND	427 388-483	ND	18 5-25	450 90-698	ND	0.2 ND-0.6	65.3 57.1-71.2	6.7 2.5-11.9
Nonlick n=3	5.3 5.1-5.5	0.3 0.2-0.5	133 58-194	314 193-498	41 27-48	101 43-171	168 48-317	542 28-1254	13 5-30	0.01 ND-0.03	3.44 1.34-7.30	0.07 0.03-0.11
<i>Site 6</i>												
Lick n=2	6.7 6.6-6.7	0.3 0.2-0.3	6 5-7	28 23-33	1 1-1	2 2-2	17 14-20	2 1-2	7 6-7	0.4 0.3-0.5	0.03 0.02-0.03	0.2 0.1-0.2
Nonlick n=4	6.6 5.7-7.1	0.1 0.1-0.3	22 5-35	96 29-156	3 1-5	6 1-9	30 4-68	55 5-132	ND	0.02 ND-0.06	0.11 0.01-0.4	0.07 0.02-0.22
<i>Site 7</i>												
Lick	9.8	1.1	10	409	10	4	201	76	36	0.5	0.03	0.02
<i>Site 8</i>												
Lick n=3	8.1 8.0-8.1	8.2 5.1-13.7	1924 695- 4196	ND	128 93-158	1071 506- 2059	897 103- 1946	15 7-21	≤8	0.4 ND-0.9	0.10 0.06-0.17	0.68 0.36-1.28
Nonlick n=3	6.00 5.6-6.6	0.7 0.3-1.4	447 255-579	54 36-66	810 240- 1929	312 119- 527	196 25-525	102 22-244	1285 2-3835	ND	0.06 <0.01- 0.16	1.00 0.49-2.02

<sup>a</sup>ND = none detected

6, and this salinity may be what attracts the deer and elk to the sites. The potential mineral nutrient benefit must vary from site to site depending on the unique compositions of the licks.

The lick samples from Site 6 are the least extreme in all respects in that they have neutral pH, relatively low EC, and generally low concentrations of cations and anions compared to the other lick samples. Furthermore, the composition of the lick samples at Site 6 is not much different from the non-lick samples, so it is not clear why the deer are ingesting mineral matter at the site. The only element that is appreciably higher than in the non-lick samples is iodine, so perhaps the deer can detect this difference.

Of the 10 elements reported here, iodine is the one that is most often higher in lick samples compared to non-lick materials. Iodine is an essential nutrient for animals (Whitehead, 1984), as it is required for the synthesis of growth-regulating thyroid hormones. The main source of iodine in soils is atmospheric deposition of sea-water-derived iodine, but certain types of rocks and soils derived from them can be enriched in iodine (Whitehead, 1984). Ingested soil was found to be a major source of iodine for lambs in a New Zealand study (Healy et al., 1972).

In summary, no single and consistent regolith attribute was overwhelmingly enhanced at the lick sites, but each site had at least one chemical condition that was different from the non-lick comparison samples. The individual licks may provide different nutrient supplements.

*Lick classification.*—Classifying mineral lick sites aids in communicating site characteristics useful to wildlife biologists and land managers. Dormaar and Walker (1996) used physical site characteristics to classify lick sites in southern Alberta, Canada. They classified sites as dry earth licks, muck licks, and rock face licks. We incorporated elements of their system by specifying regolith type (soil or saprock) and whether it is dry or wet during the summer dry season (wet is reflective of groundwater seepage at the surface). We also felt it was important to indicate the type of exposure, since licks on roadcuts have different management concerns than naturally exposed lick sites. Reaction class (pH) and alkalinity (EC) are relatively simple to measure, but reflect concentrations of ions and do not necessarily relate to which nutrient ions are present. The chemical enhancement class, indicating the increase in ion concentrations above background (non-lick) levels, provides a better descriptor of potential nutrient value to animals, but requires extensive laboratory analyses. The six factors listed in Table 4 (exposure, regolith, dry/wet, reaction class, salinity, and chemical enhancement) provide useful information to understand lick sites in the Klamath Mountains.

Table 4.—Classification of mineral lick samples from the Klamath Mountains. Chemical components (cations and anions) present at levels elevated above those of non-lick samples are listed with enhancement factor in parentheses; e.g., I(28x) indicates average iodine levels from lick sample are increased by 28 times relative to highest value of nearby non-lick samples.

Site	Exposure	Regolith	Dry/ wet	Reaction class	Salinity	Chemical enhancement above non-lick levels
1	Roadcut	Soil	Dry	Alkaline	Nonsaline	I(28x), Cl(6x), Na(2x)
2	Roadcut	Saprock	Dry	Acid	Nonsaline	Fe(27x), I(13x), Mn(2x), SO <sub>4</sub> (2x)
2	Roadcut	Saprock	Dry	Acid	Saline	Fe(61x), Mn(9x), K(9x), I(7x), Ca(2x)
6	Roadcut	Saprock	Dry	Neutral	Nonsaline	I(7x)
7	Natural	Saprock	Dry	Alkaline	Nonsaline	ND
8	Natural	Soil	Wet	Alkaline	Saline	I(>40x), Ca(3x), Mg(2x), Cl(2x)

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