X-Ray Diffraction Analysis of Samples Rocky Mountain National Park Final Report March 18, 2009

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TITLE OF PROJECT: Testing Mineral Licks Used by Bighorn Sheep in RMNP

NAME OF PARK/NPS UNIT: Rocky Mountain National Park

NAME OF UNIVERSITY PARTNER: University of Colorado at Boulder

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Introduction

Big Horn Sheep in RMNP use two well known mineral licks within the park. The herd on the west side of the park utilizes a mineral lick in the crater on Specimen Mountain. The Mummy herd uses a mineral lick at The Sheep Lakes in Horseshoe Park. The western herd is stable while the eastern herd has been slowly declining for 25 years. The two mineral licks are formed by very different geological processes and from previous studies we see that the mineral content is indeed different.

Research Questions/Objectives:

12) What role do these minerals play in the biological and physiological processes of sheep which may benefit or harm sheep?

1) What is the chemical make-up of each mineral lick? Why do sheep use the mineral licks, are the two licks being used for the same purpose?

Mammals utilize mineral licks to fulfill a number of dietary restrictions. The most common element that sheep seek out is sodium, which is generally in low concentrations in vegetation. Other common elements such as magnesium and calcium may be sought out. In some cases mammals are seek out mineral licks for trace elements such as selenium. Clays may even be utilized to help counter the effects of toxic anti-herbivore compounds in plants. Mammals use mineral licks for most of the year, though pregnant ewes and calf's visit the mineral licks most often. Pregnant and lactating females need to provide nutrients for both themselves and calf's necessitating frequent visits to mineral licks. In addition, Big Horn males use the mineral lick in early summer to recover from the fall rutting period.

The two mineral licks in RMNP are in areas with vastly different bedrock geology. Therefore the mineral content is probably very different in these two licks. Indeed the bedrock for in the west and east is different enough that it may cause forage to differ in its nutritional profile. Therefore the two herds may visit the mineral licks to fulfill different nutritional requirements.

2) What role do these minerals play in the biological and physiological processes of sheep which may benefit or harm sheep? Is the mineral lick at sheep lakes tied with the decline of the mummy herd?

Because both herds utilize mineral licks, detrimental changes in the chemical composition may cause a decline in the herd's population. If the mineral lick in implicated in the decline of the mummy herd, it may not be easily detected, even with careful chemical analysis. A systematic change in the bid horn's diet, whether from forage sources or from the mineral lick could contribute to the Big Horn decline. Declines in nutrients may explain the problem of yearling recruitment. The contamination of the mineral lick may also explain the decline of the big horn herd. A number of changes, mostly anthropogenic have the right timeframe to explain the decline of the herd: Changes in precipitation and temperature related to global warming may change vegetation growth and nutritional profile; the failure of the dam that created the fall river flood may have removed some of the material from the sheep lakes; Atmospheric acid deposition may have leached some of the calcium from the sheep lakes; Atmospheric deposition of heavy metals from anthropogenic sources may accumulate in the sheep lakes (A phenomenon that is well documented in ombrotrophic bogs)

3) How did these mineral deposits form?

The formation of the two mineral deposits is undoubtedly different: The sheep lakes probably fill kettle holes and are underlain by an impermeable layer of glacial till thus acting as a bog in the accumulation of minerals; The crater is composed of volcanic rock and the mineral licks are within a layer of tuff where there may be hydrothermal alteration. Understanding the formation of these two deposits will be aided by chemical analysis but will remain incomplete until physical investigations are carried out. This question is not the main focus of this study, though it is worth addressing to the extent possible.

Methods and Testing Procedure

Phase 1: Chemical analysis of both mineral licks: Park staff will take samples from both mineral licks including the soil from the sheep lakes and the volcanic rock from the crater. Two samples will be taken from each lake and the control samples will be taken from the nearby till and alluvium. Two samples will be taken from the crater mineral lick and two from the nearby volcanic rock. The LEGS lab at CU Boulder will test samples with ICP-MS to determine the elemental composition. The exchangeable ions will be tested by digesting the soil and analyzing with ICP-AES, this will include a limited selection of elements that are likely to be nutritionally important to Big Horn Sheep. In addition, the clay mineralogy will be determined with XRD.

Introduction

Twenty-four samples were sent to the laboratory for trace and major elemental analyses. Most of the samples appear to be soils, while six of the samples are rocks. All samples come from unknown

localities. It is unknown as to if these samples represent identified, classified, or mapped soil units or multiple soil horizons within a soil unit. The origins of the rock samples are also unknown and without thin sections of the rocks any descriptions provided are only based on hand specimen observations.

Methods

The samples were placed on new paper plates and air-dried. Approximately, 0.1 grams of sample was weighed using an Ohaus Analytical *Plus* ® scale. The weight was recorded to 0.00001 grams. The sample was then placed in polypropylene digest tubes (Environmental Express.)

The samples were dissolved using a modified technique developed by Farrell, Matthes and Mackie (1980). This procedure starts by adding 5 ml of a 7:3 mixture of hydrochloric acid and hydrofluoric acid and then 2 ml of nitric acid to the digestion tubes and heated to 95° C in a digestion block (HotBlock by Environmental Express) for about 15 minutes. The samples were cooled and 5 ml of 60% H_2O_2 (30%) and 40% water was added to each sample. The samples were again heated to 95° C until there was no more reaction. Samples were then cooled and brought up to 50 ml with a 1.5% by weight boric acid solution. The samples were then reheated to 95° C for about 15 minutes, then cooled for analysis.

The major elements were analyzed by means of an inductively coupled plasma optical emission spectrometer (ICP-OES, manufactured by Applied Research Laboratories, Model 3410+). The ICP-OES was calibrated with 4 standards, a blank and 3 standards prepared with NIST certified standards. The dissolved samples were diluted 1:20 with deionized water to minimize any matrix effect. Two samples were run in duplicate (SL2-1 and CR-1) and an in-house rock standard was run for validation (Valmont Dike).

Forty-five trace elements (see file for complete list) were measured on the Perkin-Elmer inductively coupled plasma mass spectrometer (ICP-MS), model ELAN® DRC-e. The total quantification technique was used. This technique uses one standard with about 20 elements that span the periodic table. The dissolved samples were diluted 1:20 with deionized water to minimize any matrix effect. The concentrations of the other elements are estimated from the raw kilo-counts and the ICP-MS's response to the different isotopes. The results are very useful for determining the abundance of elements in a sample that might be looked at in more detail in later studies. The results are within plus or minus 20% of the true concentrations.

The major and trace results are combined on attached Excel file "RMNP OES and MS final 6-15-09.xls".

References

Farrell R. F., Matthes S. A., and Mackie A. J. (1980) A simple, low-cost method for the dissolution of metal and mineral samples in plastic pressure vessels, Report of investigations - Bureau of Mines 8480, 19 pages.

RESULTS:

Volcanic Rocks

Cr-1 Cr-2 Cr-2c Cr-3 Cr-4

Soils

SLC-1 SL1-5 SL2-3 SL3-2

SL4-1

Sample preparation and data collection;

Volcanic Rocks:

Representative samples were chipped from Cr-1, Cr-2, and Cr-2c. Samples Cr-3 and Cr-4 arrived as small chips from which several chips were selected at random. Samples were crushed to a course sand size using a steel mortar and pestle. Four to five cubic centimeters were separated from each sample for clay analysis. The remainder of each sample was set aside for whole rock analysis.

Soils:

Soil samples were air dried, lightly ground in a steel mortar and pestle to break up clumps and homogenize samples. Each sample was then split multiple times until a reasonable sized portion remained, using a mechanical soil splitter. Visible roots and plant fibers were removed. Samples were then placed in de-ionized water, thoroughly shaken, and centrifuged to float and remove additional plant fibers. Samples were then treated with bleach to break down and remove organic components (which interfere with analysis of mineral components). Samples were centrifuged, the bleach decanted, and then rinsed with de-ionized water, centrifuged, and decanted several times to remove remaining bleach and dissolved organic compounds.

Samples were then dried, de-clumped, and homogenized. Four to five cubic centimeters of each sample was removed for clay analysis, and the remainder set aside for whole rock analysis. The clay separates were further treated with bleach to remove additional organic compounds, which interfere with clay separations, even in minute amounts.

Whole Rock Samples (Volcanic and Soils):

Whole rock samples were ground using a Tungsten carbide shatter box. 3.000 grams from each sample was then mixed with 0.333 grams of zinc oxide, ground, and prepared according to the requirements of the RockJock software (D.Eberel, 2003). Data was collected from each sample using x-ray powder diffraction techniques, again according the requirement of the RockJock software. Mineral phases were identified from each sample.

Clay Samples: Clays were extracted by suspending each sample in a water column, using Sodium Pyrophosphate as a deflocculant, and allowing all particles, coarser than 5 microns to settle. The remaining solution, containing suspended clay minerals was siphoned off. Oriented slides were prepared from the extracted clay suspension X-Rayed four times, under progressive conditions.

Those conditions are 1) air dried, 2) solvated in ethylene glycol fumes, 3) heat treaded for 2 hours at 300 degrees centigrade, and 4) heat treated for 1 hour at 550 degrees centigrade. Resulting data were analyzed and clays were identified from each sample.

Mineral identifications from the whole rock and clay scans were combined for each sample and input into the RockJock software, along with the raw data from each whole rock scan and relative abundances of the mineral phases were calculated and reported as weight percents of the total sample.

Notes:

Cr-1 and Cr-2c; Clay scans indicated possible trace amounts of palygorskite. An additional, randomly oriented, sample mount was prepared from the clay separate of Cr-1 and scanned at high angles (56 to 65 degrees 2-theta) to observe the 060 peaks of the clay minerals in an attempt to confirm or dispute the possible presence of palygorskite. The possible presence of the 060 peak is suggestive only, barely rising above background readings, if it is truly there at all. (see graph Cr-1, clay, 060). Palygorskite is listed as possible trace.

SL2-3 / Illite, Smectite, and mixed layer Illite/Smectite; In most of the soil samples there is no noticeable reduction in the 001 peak (at approximately 8.9 degrees 2-theta) upon ethylene glycol solvation, except for sample SL2-3. In sample SL2-3 there is a noticeable reduction in peak intensity with glycolation, indicating the presence of smectite layers within illite structures. The presence of a broad peak at approximately 6.5 degrees 2-theta, which expands to 5 degrees upon glycolation, and collapses to 8.9 degrees when heated to 300 degrees centigrade, indicates the presence of additional smectite. Therefore clay minerals in SL2-3 are interpreted as mixed layer Illite/Smectite and Smectite, and clays in the other soil samples are interpreted as Smectite and Illite.

D. D. Eberl, 2003, Users Guide to RockJock – A Program for Determining Quantitative Mineralogy From Powder X-Ray Diffraction Data; U.S. Geological Survey, Open File Report 03-78.

Summary Tables

Soils	(weig	;ht %)														
	Quartz	Microcline	Plagioclase	Hornblende	Apatite	Magnetite	Muscovite	Biotite	Kaolinite	Smectite	Illite	Illite/Smec				
SLC-1	42.2	22.6	21.2	0.7	1.2	0.3	2.3	2.4	2.1	4.1	0.9					
SL1-5	22.6	15.5	17.1	1.6	3.2		6.0	5.4	9.5	15.6	3.4					
SL2-3	25.3	21.5	27.0	0.8	1.9		1.5	2.7	3.1	8.3		7.8				
SL3-2	40.3	26.9	18.2	0.2	1.2		2.2	3.8	1.0	4.5	1.8					
SL4-1	24.5	15.7	18.5	0.6	3.3		5.3	2.4	8.8	13.6	7.3					
Volcani	ic Rocks	s (wiegl	nt %)													
	Quartz	Sanadine	Orthoclase	Plagioclase	Hornblende	Olivine	Diopside	Clinoptilolite	Analcima			Cristobalite Muscovite	Biotite	Smectite	Illite	Palygorskite(?)
Cr-1	13.5	18.2		13.9	1.3			32.6		14.	.5 1	.7 3.7	0.3	0.4	trace	trace
Cr-2	19.3		17.7	11.3	2.2	1.3		11.7		8.	.6 1	.7 9.8	2.7	13.8		
Cr-2c	16.8	9.1						39.4	8.	7 13	.5	2.9	0.8	8.8		trace
Cr-3	9.9	13.5		28.2	3.0	2.4	3.4	2.8		22.	.1	3.2	3.5	8.0		
Cr-4	6.9	12.9						43.7		13.	.6	6.3	1.3	15.4		

Sample name:	SLC-1wr	Type of analysis	Constant background
Full pattern degree of fit:	0.1485	2	0.0
Mineral	Weight %	Shifts	Normalized results
NON-CLAYS			
Quartz	56.0	3	42.2
Microcline	30.0	0	22.6
Plagioclase	28.2	0	21.2
Hornblende	0.9	0	0.7
Magnetite	0.5	0	0.3
Apatite	1.5	0	1.2
Total non-clays	117.0		88.1
CLAYS			
Kaolinite	2.8	-1	2.1
Smectite	5.5	0	4.1
Illite	1.2	0	0.9
Biotite	3.2	0	2.4
Muscovite	3.1	1	2.3
Total clays	15.8		11.9
TOTAL	132.8		100.0





Sample name:	SL1-5wr	Type of analysis	Constant background
Full pattern degree of fit:	0.1575	2	0.0
Mineral	Weight %	Shifts	Normalized results
NON-CLAYS			
Quartz	27.7	3	22.6
Microcline	19.0	1	15.5
Plagioclase	21.0	1	17.2
Hornblende	2.0	-1	1.6
Apatite	4.0	-1	3.2
Total non-clays	73.6		60.1
CLAYS			
Kaolinite	11.7	0	9.5
Smectite	19.2	-1	15.6
Illite	4.2	1	3.4
Biotite	6.6	-1	5.4
Muscovite	7.3	0	6.0
Total clays	49.0		39.9
TOTAL	122.6		100.0





Sample name:	SL2-3 wr	Type of analysis	Constant background	
Full pattern degree of fit:	0.1638	2	0.0	
Mineral	Weight %	Shifts	Normalized results	
NON-CLAYS				
Quartz	31.6	2	25.3	
Microcline	26.8	2	21.5	
Plagioclase	33.6	0	27.0	
Hornblende	1.0	-1	0.8	
Apatite	2.4	-1	1.9	
Total non-clays	95.4		76.6	
CLAYS				
Kaolinite	3.9	0	3.1	
Smectite	10.4	-1	8.3	
Mixed layer Illite/Smectite (70-80%I)	9.7	0	7.8	
Biotite	3.3	0	2.7	
Muscovite	1.8	0	1.5	
Total clays	29.2		23.4	
TOTAL	124.5		100.0	



Sample name:	SL3-2 wr	Type of analysis	Constant background
Full pattern degree of fit:	0.1191	2	0.0
Mineral	Weight %	Shifts	Normalized results
NON-CLAYS			
Quartz	47.7	1	40.3
Microcline	31.9	0	26.9
Plagioclase	21.4	0	17.2
Hornblende	0.3	0	0.2
Apatite	1.5	0	1.2
Total non-clays	102.7		86.8
CLAYS			
Kaolinite	1.1	0	1.0
Smectite	5.3	0	4.5
Illite	2.2	0	1.8
Biotite	4.4	-1	3.8
Muscovite	2.6	0	2.2
Total clays	15.7		13.2
TOTAL	118.3		100.0



Sample name:	SLC-1wr	Type of analysis	Constant background
Full pattern degree of fit:	0.1485	2	0.0
Mineral	Weight %	Shifts	Normalized results
NON-CLAYS			
Quartz	56.0	3	42.2
Microcline	30.0	0	22.6
Plagioclase	28.2	0	21.2
Hornblende	0.9	0	0.7
Magnetite	0.5	0	0.3
Apatite	1.5	0	1.2
Total non-clays	117.0		88.1
CLAYS			
Kaolinite	2.8	-1	2.1
Smectite	5.5	0	4.1
Illite	1.2	0	0.9
Biotite	3.2	0	2.4
Muscovite	3.1	1	2.3
Total clays	15.8		11.9
TOTAL	132.8		100.0





Sample name:	Cr-1wr	Type of analysis	Constant background
Full pattern degree of fit:	0.1713	2	0.0
Mineral	Weight %	Shifts	Normalized results
NON-CLAYS			
Quartz	16.0	2	13.5
Sanidine feldspar	21.6	0	18.2
Plagioclase	16.5	-1	13.9
Hornblende	1.5	0	1.3
Clinoptilolite	38.7	0	32.6
Obsidian	17.2	0	14.5
Cristobalite	2.0	-1	1.7
Total non-clays	113.4		95.6
CLAYS			
Biotite	0.4	0	0.3
Muscovite	4.3	0	3.7
Montmorillonite	0.5	0	0.4
Total clays	5.2		4.4
TOTAL	118.6		100.0







Sample name:	Cr-2wr	Type of analysis	Constant background
Full pattern degree of fit:	0.1375	2	0.0
Mineral	Weight %	Shifts	Normalized results
NON-CLAYS			
Quartz	23.7	1	19.3
Orthoclase feldspar	21.8	-1	17.7
Plagioclase	13.9	4	11.3
Hornblende	2.7	-1	2.2
Olivine	1.6	-1	1.3
Clinoptilolite	14.3	0	11.7
Obsidian	10.5	0	8.6
Cristobalite	2.1	-1	1.7
Total non-clays	90.6		73.7
CLAYS			
Biotite	3.3	0	2.7
Muscovite	12.0	0	9.8
Montmoillonite	17.0	0	13.8
Total clays	32.3		26.3
TOTAL	122.9		100.0



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17.0

Sample name:	Cr-2cwr	Type of analysis		Constant background
Full pattern degree of fit:	0.1388		2	0.0
Mineral	Weight %	Shifts		Normalized results
NON-CLAYS				
Quartz	21.5		1	16.8
Sanadine feldspar	11.7		1	9.1
Clinoptilolite	50.5		1	39.4
Volcanic glass	17.2		0	13.5
Analcime	11.1		1	8.7
Total non-clays	112.0			87.5
CLAYS				
Montmorillonite	11.3		0	8.8
Biotite	1.1		0	0.8
Muscovite	3.7		0	2.9
Total clays	16.1			12.5
TOTAL	128.1			100.0



Sample name:	Cr-3wr	Type of analysis	Constant background
Full pattern degree of fit:	0.1857	2	0.0
Mineral	Weight %	Shifts	Normalized results
NON-CLAYS			
Quartz	13.4	1	9.9
Sanadine	18.3	2	13.5
Plagioclase	38.2	-1	28.2
Hornblende	4.1	-1	3.0
Pyroxene	4.6	0	3.4
Olivine	3.3	-1	2.4
Clinoptilolite	3.7	-1	2.8
Volcanic glass	30.0	-1	22.1
Total non-clays	115.6		85.3
CLAYS			
Biotite	4.8	-1	3.5
Muscovite	4.3	1	3.2
Montmorillonite	10.9	0	8.0
Total clays	20.0		14.7
TOTAL	135.6		100.0



Sample name:	Cr-4wr	Type of analysis	Constant background
Full pattern degree of fit:	0.1382	2	0.0
Mineral	Weight %	Shifts	Normalized results
NON-CLAYS			
Quartz	7.3	1	6.9
Sanidine feldspar	13.8	0	12.9
Clinoptilolite	46.8	0	43.7
Volcanic glass	14.5	-1	13.6
Total non-clays	82.5		77.0
CLAYS			
Biotite	1.4	0	1.3
Muscovite	6.7	0	6.3
Smectite	16.5	4	15.4
Total clays	24.6		23.0
TOTAL	107.1		100.0

