

TRACE ELEMENT LEVELS IN MONTANA BIGHORN SHEEP HORNS

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Abstract: In an effort to develop a tool for law enforcement use, multi-element scans were done on 112 bighorn sheep horn samples from 21 Montana hunting districts. The hunting districts were grouped into 8 geological regions for comparison. A total of 16 different elements were recorded from the samples. The mineral contents of individual samples were not specific enough to allow definite pinpointing of their area of origin. However, a key was developed which allowed samples from hunting areas having an unlimited number of permits to be separated from districts having limited numbers of permits with a 99.2% efficiency. A comparison of the element data with published horn size data for the areas gave a significant inverse correlation between magnesium levels and horn size as well as with the combined aluminum and magnesium levels. Grass tetany, atmospheric acid deposition ("acid rain"), soil infertility and bound phosphorus appear to be hypotheses tenable with this horn size and mineral relationship.

Mineral analysis of hair samples from a variety of big game mammals gave rise to the hypothesis that it might be possible to analyze samples from sheep horns for trace minerals and identify the area from which the animal came. Similar analysis of feathers from waterfowl has enabled researchers to identify their areas of geographical origin. It was hoped that this would serve as an aid in law enforcement and in the control of bighorn sheep harvest.

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METHODS

Montana law requires that all bighorn sheep ram heads taken in Montana be registered and marked with a metal plug. The drill

shavings were collected from most sheep hunting areas in Montana during the 1984 hunting season.

A standard 250 mg aliquot was weighed out from each sample. Any obvious contamination was removed and the sample was submitted for analysis.

Originally it was felt that the small size of samples would only permit the use of the very sensitive and expensive neutron activation analysis technique. However, after the samples had been obtained, it was found that they were large enough to permit multiple element scans by an atomic emission spectrum technique. This much cheaper technique permitted a ten fold increase in the number of samples that could be analyzed.

Spectra Inc. of San Diego, CA. analyzed the samples. They were charred, vaporized and their atomic emission spectra was photographically recorded. This technique permits small samples to be scanned simultaneously for the presence of 45 separate elements. The concentrations measured were accurate to within a factor of two.

The results were grouped according to the hunting area of origin. These were then grouped on the basis of the geology of the region of the state in which the hunting area was located.

RESULTS

A total of 112 samples from 21 hunting districts were analyzed (Fig. 1). These were grouped into 8 geological regions for comparison. Six to 12 different elements were identified in individual samples with 8 being the most common number. A total of 16 different elements were recorded from the samples (Al, Bo, Ca, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Ti, Zn).

The concentrations of Ca and Na were too high to be used for comparisons while still obtaining adequate information about less abundant elements using this atomic emission technique. Seven elements had a high enough frequency of occurrence to allow meaningful comparisons (Al, Cu, Fe, Mg, P, Si, Zn). Table 1 summarizes the analytical results from this study.

The mineral contents of individual samples were not specific enough to allow definite pinpointing of their area of origin. However, the composite data indicates that various areas do tend to have distinctive tendencies in their element contents.

Rank comparisons for the means of the seven commonly occurring elements indicated that the Prairie-Breaks (hunting districts 620 and 760) tended to have the lowest overall concentrations of minerals. Six (Al, Cu, Fe, Mg, Si, Zn) of the seven common elements were recorded for the area and one (P) was not found. The mean levels of iron and zinc were the lowest of any of the areas. No trace elements other than these common ones were found in the samples. Since only four samples were

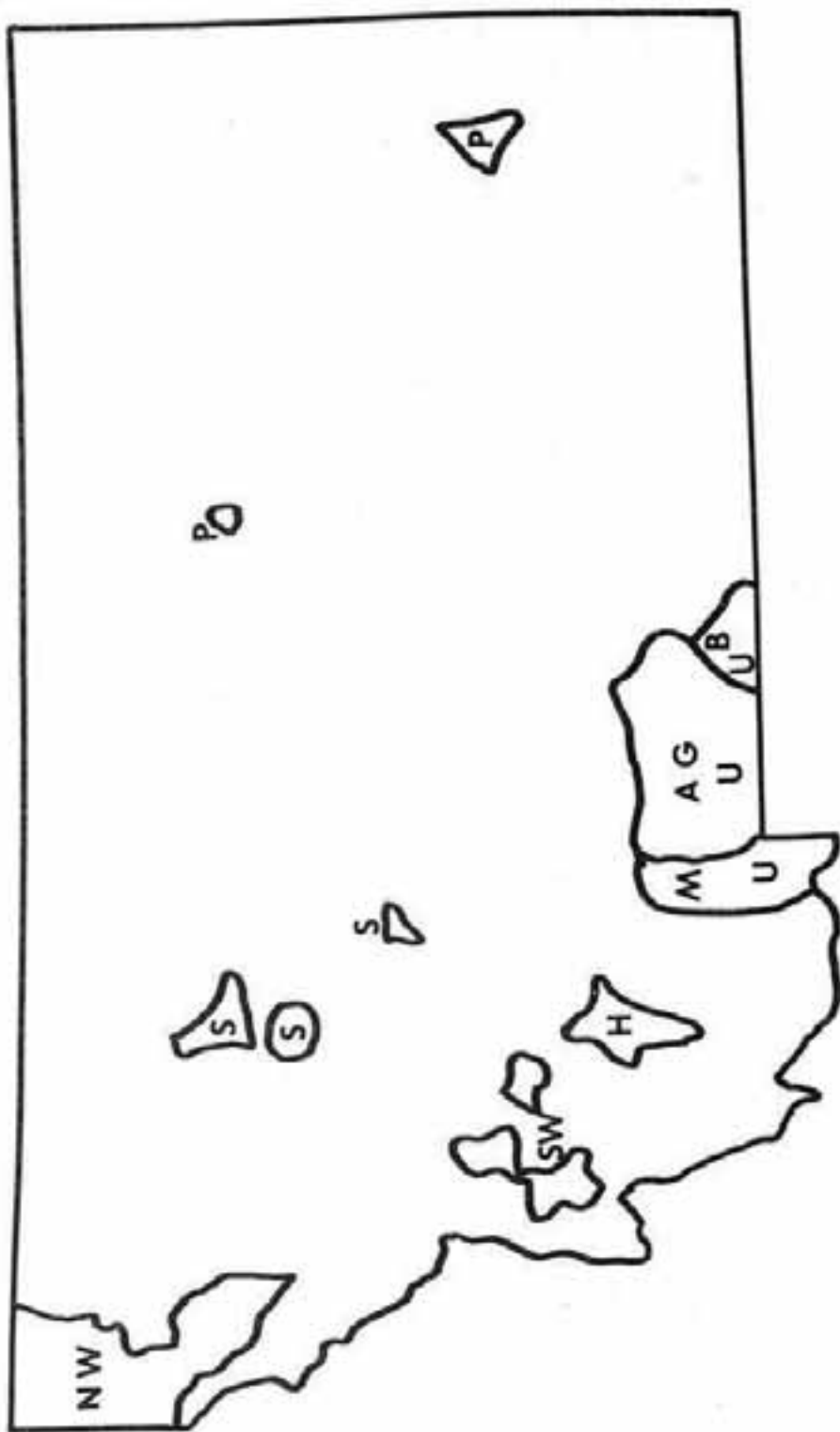


Fig. 1. A map of Montana showing the bighorn sheep hunting areas from which samples were obtained. All areas had a limited number of hunting permits except those designated for unlimited. P = prairie-breaks; S = Sun River-Belts; NW = Northwest; SW = Southwest; H = Highland; M = Madison; AB = Absaroka-Gallatin; B = Beartooth.

Table 1. A summary of the trace elements found in Montana bighorn sheep horns by region.

Mean Concentrations in Parts per Million								
AREAS	North west	South west	Highland	Madison	Absaroka Gallatin	Sun River	Bear tooth	Prairie Breaks
n	17	18	12	12	25	17	7	4
ELEMENTS								
Al	9	20	71	65	77	5	80	15
Ca	All samples had over 1000 ppm							
Cu	4	6	4	6	4	3	6	4
Fe	36	12	14	25	20	26	14	11
Mg	17	172	35	179	156	79	279	138
Na	All samples had over 1000 ppm							
P	94	194	188	292	210	44	179	0
Si	113	51	30	73	121	19	48	39
Zn	112	325	346	254	300	79	279	38
OTHER ELEMENTS								
Freq.	59%	61%	17%	8%	32%	12%	29%	0%
	Bo	Bo	Bo	Pb	Bo	Ti	Pb	none
	Mo	Mn	Ni		Mn	Cr		
	Ti	Ni			Ni			
		Pb			Pb			
HORN VOLUME (as calculated from Stewart and Butts 1982)								
	198	196	192	135	161	174	125	---

available from these small hunting districts, the results should be interpreted with caution.

The Sun River-Belts area (hunting districts 421,424,441,455) was ranked second lowest in the overall abundance of the seven common elements. The levels of Cu and Si were the lowest of any of the areas. The mean levels of phosphorus were quite low and the area has sometimes been regarded as having soils low in this element. All seven common elements were present in samples from the area. Only 12% of the samples contained elements (Cr, Ti) other than the common ones.

While the Prairie-Breaks and Sun River-Belts areas were really fairly similar in overall mineral content, there was a substantial jump in the mineral contents of the next lowest area (Northwest Montana) over these two low ranked areas.

The third lowest ranked area in the mean concentration levels of the major seven elements was Northwest Montana (100 numbered hunting districts). All seven elements were found. These districts ranked lower than any other area in mean level of Al and Mg but highest in iron and second highest in silicon. Other elements were frequent (Bo, Mn, Mo, Ti) in these samples, occurring in 59% of the samples.

The Highland (hunting district 340) was the fourth ranked area. All common elements were present. The area ranked second lowest in mean silicon and magnesium levels and highest in the level of zinc. Other elements (Bo, Ni) were found in 17% of the samples.

The southwestern Montana area (200 numbered hunting districts) fell in fifth place in overall mean element abundance. The area ranked second lowest in iron levels and second highest in zinc levels. Other elements were found with greater frequency than in any other area (61%; Bo, Mn, Ni, Pb).

The sixth ranked area (Beartooth, hunting district 502) had the highest mean levels of Al and Mg and the second highest level of Cu. None of the seven common elements were particularly low. Other elements had a 29% frequency of occurrence (Pb).

The Absaroka-Gallatin area (hunting districts 300, 303, 500, 501) had the second highest mean levels of the more common elements. It showed the highest mean levels of silicon and the second highest of aluminum and phosphorus. Only iron was relatively low (3rd ranked). The frequency of occurrence of other elements was 32% (Bo, Mn, Ni, Pb).

The Madison area (hunting districts 301 and 302) showed the highest mean levels of the common elements. It ranked highest in phosphorus and second highest in copper, iron and magnesium. Only the Prairie-Breaks ranked lower in the occurrence of other elements (8%; Pb).

A binary key of the type often used for the identification of biological materials was developed and is presented in table 2. This key was developed to permit the separation of samples obtained in hunting areas having an unlimited number of bighorn permits (Beartooth, Absaroka-Gallatin, Madison) from all areas having a limited number of permits. One sample was found not to be correctly classified by using this key giving a classification efficiency of 99.1%.

DISCUSSION

The areas of the state which included geological substrates of primarily sedimentary origins tended to have the lowest occurrences of mineral elements in the horn samples. These included the Prairie-Breaks, the Sun River - Big Belts, and Northwest Montana (Alt and Hyndman 1972). Northwest Montana does have some mineral deposits of sedimentary origin and includes some mineralized areas on the edge of the Idaho batholith. It also includes the site of the largest silver producing mine in North America.

Areas whose geological substrates which include igneous base materials tended to have higher mineral levels. Many of these have had metal mining operations in them historically. These include the Southwest Montana, Highland and the Absaroka-Gallatin areas. The Beartooth area contains very old igneous rock. Mineralized zones are present but it should be noted that some of these sheep herds migrate to summer ranges in the Absaroka mountains (Martin 1985; Stewart 1975).

The Madison range contains primarily metamorphic and sedimentary rocks. Some igneous rocks are found in the portion of the range adjacent to Yellowstone Park. Little in the way of economic minerals have been found in the area. The element levels recorded for this area were quite similar to those for adjacent Absaroka-Gallatin region.

Comparison of the ranking of the areas according to overall mineral levels with the data for horn volumes of 3 year old rams (Stewart and Butts 1982) did not reveal a significant relation ($r=.57$, $n=7$). The two areas with the largest horns also had the highest mineral levels.

When horn size was compared with the levels of individual elements a significant negative correlation was found with Mg levels ($r=-.790$, $P=.025$). Combined aluminum and magnesium levels were also negatively correlated with horn size ($r=-.831$; $P=.015$). Magnesium imbalances, particularly low levels are associated with the "grass tetany" syndrome (Robbins 1983; Jones and Hanson 1985). This condition is encouraged by cool weather and reduced food intake (Church 1972). Its effects are pictured as producing episodes of illness and malnutrition during the spring periods critical for horn growth. Magnesium imbalance is also associated with eclampsia which could cause a loss of the fetus and mother with no effect upon horn growth. Magnesium and

Table 2. A key for classifying bighorn sheep horn samples as to their origin from unlimited permit hunting areas (Beartooth, Absaroka-Callatin, Madison) or from limited permit hunting areas based upon mineral composition.

A.	Have Mg levels of 500 ppm or more	-- 1	
	Have Mg levels under 500 ppm	-- B	
	1. Al level or Si level at or over 50 ppm		-- Unlimited
	Al or Si level under 50 ppm		-- Limited
B.	Have Si level at or over 250 ppm	-- 2	
	Have Si level under 250 ppm	-- C	
	2. Al level at or over 50 ppm		-- Unlimited
	Al level under 50 ppm		-- Limited
C.	Al level at or over 250 ppm	-- 3	
	Al level under 250 ppm	-- D	
	3. Zn level under 500 ppm		-- Limited
	Zn level at or over 500 ppm	-- 4	
	4. Fe level 50 ppm or more		-- Unlimited
	Fe level below 50 ppm		-- Limited
D.	Zn level 500 ppm or over	-- 5	
	Zn level under 500 ppm	-- E	
	5. Al level 100 ppm or more		-- Limited
	Al level under 100 ppm	-- 6	
	6. Si level under 50 ppm		-- Limited
	Si level 50 ppm or over	-- 7	
	7. Cu level of 10 ppm or over		-- Limited
	Cu level under 10 ppm	-- 8	
	8. Al level of 10 ppm or over		-- Limited
	Al level under 10 ppm		-- Unlimited
E.	Cu level of 0		-- Limited
	Cu level not 0	-- F	
F.	Fe level of 0	-- 9	
	Fe level not 0	-- G	
	9. Si level of 50 ppm or more		-- Limited
	Si level of under 50 ppm	-- 10	

Table 2 continued.

	10. Al level 25 ppm or more		-- Unlimited
	Al level under 25 ppm	-- 11	
	11. Ni present		-- Unlimited
	Ni absent		-- Limited
G.	Zn level of 0	-- 12	
	Zn level not 0	-- H	
	12. Cu level under 10 ppm		-- Limited
	Cu level of 10 ppm or more	-- 13	
	13. Mg level under 100 ppm		-- Limited
	Mg level 100 ppm or over	-- 14	
	14. Fe level under 10 ppm		-- Unlimited
	Fe 10 ppm or over	-- 15	
	15. Pb present		-- Unlimited
	Pb absent	--	May be either limited or unlimited.
H.	Zn level 250 ppm or more	-- 16	
	Zn level under 250 ppm	-- I	
	16. Cu level 3 ppm or more	-- 17	
	Cu level under 3 ppm	-- 21	
	17. Al level under 50 ppm		-- Limited
	Al level 50 ppm or over	-- 18	
	18. Fe under 10 ppm		-- Unlimited
	Fe 10 ppm or over	-- 19	
	19. Si 50 ppm or over		-- Limited
	Si under 50 ppm	-- 20	
	20. Fe 25 ppm		-- Unlimited
	Fe 10 ppm		-- Limited
	21. Al under 10 ppm		-- Limited
	Al 10 ppm or over	-- 22	
	22. Fe level over 5 ppm		-- Limited
	Fe level 5 ppm or under	-- 23	
	23. Al over 50 ppm; Mg under 100 ppm		-- Unlimited
	Al at 50 ppm; Mg at 100 ppm		-- Limited

Table 2. Concluded.

I.	Al level of 5 ppm	-- 24	
	Al level over 5 ppm	-- J	
24.	Si level is 0	-- 25	
	Si level is not 0	-- 27	
25.	Fe level under 50 ppm		-- Limited
	Fe level 50 ppm or over	-- 26	
26.	Fe level of 250 ppm		-- Limited
	Fe level not 250 ppm		-- Unlimited
27.	Si level of 5 ppm		-- Limited
	Si level not 5 ppm	-- 28	
28.	Zn level of 100 ppm		-- Limited
	Zn Level not 100 ppm	-- 29	
29.	Mg level of 100 ppm		-- Limited
	Mg level not 100 ppm		-- Unlimited
J.	Si level under 10 ppm	-- 30	
	Si level 10 ppm or over		-- Limited
30.	Fe 5 ppm or over		-- Limited
	Fe under 5 ppm	-- 31	
31.	Cu 3 ppm or over.		-- Unlimited
	Cu under 3 ppm	-- 32	
32.	Al at or over 100 ppm		-- Unlimited
	Al under 100 ppm		-- Limited

aluminum are often the last elements leached from soils. High altitude soils are often heavily leached by snowpack melt. It also been noted that magnesium, aluminum and iron often form insoluble complexes with phosphorus and thus limit its availability (Robbins 1983). Phosphorus deficiency is a world wide problem and most of the forage that ungulates consume is of marginal adequacy (Church 1972). Phosphatases are important in cellular energy transfer and in the synthesis of keratin (Fraser et al 1972). It should also be noted that atmospheric acid deposition tends to mobilize Al and Mg to the point of toxicity to plants. Thus it is reasonably possible to hypothesize an involvement of "acid rain" in the horn size of bighorn sheep in Montana. It is uncertain at the present time which of these four hypotheses (grass tetany, acid rain, soil infertility, bound phosphorus) represent the best explanation for this negative correlation. The last three, separately or in combination, are the most likely. Management strategies ranging from range manipulation to provision of mineral supplements probably could be developed to counter these nutritional problems if it can be shown that they exist.

An unlimited number of bighorn sheep permits are sold for certain hunting areas in southern Montana (Beartooth, Absaroka-Gallatin, Madison). It is important to prevent hunters from killing an animal in a limited area under a permit for an unlimited area. This could result in a decrease in hunting opportunity and, in some situations, an overharvest in a limited area. The key (table 2), based upon grouping the unlimited areas together and then all limited areas together had good discrimination. The primary difficulty in its development was in distinguishing the Highland and Southwest Montana areas from the unlimited ones. It is important to test the key using another similar set of samples before it can be considered validated.

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QUESTIONS AND ANSWERS

Wayne Heimer, Alaska: I'm interested in arsenic. We've been working with the mineral industry in our country which is interested in gold. Gold and arsenic are chemically similar. They found some arsenic in some of our sensitive areas, and it wasn't in the places we thought it would be. We have, maybe, an interesting correlation between arsenic concentration and mineral licks and horn size. Arsenic, of course, is related to hair coat in low amounts. Did you find any arsenic?

Picton: No, the problem is that this particular method of analysis cannot identify arsenic. Arsenic is quite volatile, so when you run the sample it boils off before the other elements, so you have the choice of running for arsenic or running for the other elements. As a matter of fact, I've had some interest in arsenic too, but to run it you have to have enough material for duplicate samples, and the same thing would apply to mercury. Now there are some areas, for example, Yellowstone Park where you could conceivably have mercury influencing small horn size in some of these unlimited areas. But the problem is you can't test for mercury at the same time you test for these other elements. It would require a separate analysis and there are some areas in which mercury reaches levels which could be toxic.

No Name: Is there any correlation between the abundance, or presence or absence of mineral licks in some of these regions showing a relationship between magnesium and low horn size?

Picton: I'm not sure, that's something I haven't really looked at. It's an interesting question. My impression (now this is strictly off the cuff) is that there's almost a negative correlation, in that some of the areas that had relatively larger horns and low concentrations of minerals, had quite a number of licks in them. But in these southern unlimited permit areas, which are the areas that tend toward the small horns, we don't find much in the way of mineral licks. Very few in the Yellowstone area quite frankly. Dick Knight and I have spent a lot of time flying, and a lot of time trying to see evidence of licks in these areas. There are some, but they don't seem to be very extensive.

Jim Ford: Are you planning a study to show a correlation between the minerals and horn size?

Picton: I guess Charlie and I haven't really talked about it yet. I think that's the obvious thing to do, and I really would like to investigate it further. We had not prepared a proposal, but we have talked about it, and we'd like to do some actual soil fertility measurements and a few things like that to go along with this work.