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The Isotopic Analysis of Water from the Henderson Mine,  
Clear Creek County, Colorado

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For several years, the U. S. Geological Survey has been conducting an investigation into the isotopic composition of surface and ground waters in the Rocky Mountain area of Colorado, Wyoming, Montana, and New Mexico. In March of 1970, an interesting occurrence of ground water was brought to the attention of the author by Mr. Jack Bright and Mr. Willis White of the Climax Molybdenum Company. Mr. White has been working as a geologist at the Henderson property of the Climax Molybdenum Company and mentioned to the author the occurrence of a large amount of water that was flowing into the Henderson mine workings at an elevation of approximately 2,500 feet below the valley floor. Ten samples of water were collected by the author in various places in the Henderson workings. The deuterium analyses of these samples varied from -138 to -144 permil D/H (fig. 1). Samples of snow cores collected at various places in Butler Gulch in an area overlooking the mine on April 6, 1970, gave analyses of -175 to -182 permil (table 1). The west fork of Clear Creek, sampled at the same time, just above the mine workings, gave analyses of -145. On July 15, 1970, samples of various creeks heading on the west side of Jones Pass were sampled and analyzed for deuterium. Their analyses varied from -138 to -146 permil (table 1). The water collected in the mine, therefore, could very easily have originated as surface water providing that the meteorological conditions that prevailed at the time the water fell on the surface were similar to those of today. In the summer of 1970 Mr. White mentioned that a large amount of gas of unknown composition was being emitted from orifices within the mine workings. Most of the gas emissions were occurring together with water either from fractures or from drill holes in the mine workings. Mr. White was of the opinion that much of the gas coming out was carbon dioxide. Since the author has been involved in investigations of the isotopic composition of carbon dioxide from natural sources, he thought that it might be of interest to collect a sample for  $C^{13}/C^{12}$  and also for  $C^{14}$  analyses. Accordingly, some samples were collected on May 28, 1970, July 15, 1970, and February 17, 1972. These first

samples were collected by allowing the gas to be sucked through absorbers which converted the carbon dioxide to strontium carbonate. The strontium carbonate was later filtered and analyzed for both its  $C^{13}/C^{12}$  and for its  $C^{14}$  content. The analyses of these samples are given in Table 2.

The  $C^{14}$  result of approximately 17 percent of modern, or an equivalent age of approximately 14,000 years, was for the sample collected on July 15, 1970. There was some question as to the possibility of contamination from atmospheric  $CO_2$  by the collection technique, and further samples of water and  $CO_2$  were collected by Mr. White, according to directions and in bottles furnished to him by the author. Immediately upon filling the bottles with water from a small geyser erupting from the floor of the drift in the Henderson Mine, Mr. White added strontium chloride-ammonia reagent, also furnished by the author, and sealed the bottles. The author then collected the bottles, and the strontium carbonate was filtered and analyzed in the laboratory in Denver. The  $C^{14}$  of this sample (W-2617), determined by Meyer Rubin in the U. S. Geological Survey's  $C^{14}$  laboratory in Washington, D. C., gave a  $C^{14}$  date of greater than 39,000 years.

A year and a half later a third sample was collected by Mr. Willis White on February 17, 1972 from the same site. The  $C^{14}$  value for this sample was 1 percent of modern carbon, equivalent to 36,600 years old. It is difficult to assess the significance of this 1 percent of modern carbon value. If no contamination during sample collection and handling occurred, we could be seeing the influence of a small amount of modern carbon in this water. Further  $C^{14}$  monitoring over a period of five or more years will be necessary to decide whether a small amount of modern carbon is present in the  $CO_2$ .

The source of the  $CO_2$  is still problematical. The  $C^{13}/C^{12}$  analysis of the  $CO_2$  extracted from the water has a delta value of between -4 and -6 permil PDB.

Various assumptions can be made as to the sources of the carbon that is now found in the  $\text{CO}_2$  gas coming out from the mine. The various possibilities are listed below:

(1)  $\text{CO}_2$  originated as soil-air carbon dioxide that had dissolved in the water at the time the water was percolating through the soil zone at the surface. This carbon dioxide charged water would then need additional carbon added to it from one or more sources. The above is true, since the  $\text{C}^{13}/\text{C}^{12}$  of soil-air  $\text{CO}_2$  dissolved in water should give a value of between -20 and -25 permil PDB, while the actual  $\delta\text{C}^{13}$  of the  $\text{CO}_2$  in the water is about -5 permil. The various sources of carbon that might find their way into the ground water can be tabulated as follows:

(a) *Volcanic  $\text{CO}_2$ .*--Since there are no active volcanoes in the immediate area and there has been no activity for many millions of years, this source of carbon is unlikely.

(b) *Carbon dioxide that was associated with the Tertiary intrusion that underlies Red Mountain.*--This source of carbon would be very old, and cannot be eliminated as a possibility.

(c) *Carbon dioxide derived from limestone.*--There are no sedimentary limestones immediately overlying Red Mountain, but there is always a possibility of some wind-blown carbonate being present in the soil.

(d) *Carbon dioxide from possible carbonate in Precambrian rocks of Red Mountain.*--Samples of the Urad porphyry containing microscopic calcite and rhodochrosite from the Urad Mine and carbonate deposited in the Vasquez fault in the Henderson Mine all give  $\delta\text{C}^{13}$  of -3.8 to -6.6 permil.

As long as some of the carbon dioxide in the mine has been derived from soil-air  $\text{CO}_2$ , it is possible to derive a  $\text{C}^{14}$  age for the water. The only problem would be to determine the amount of dead carbon added from one of the sources in paragraphs (a)-(d). The more dead carbon that is added from these other sources, the younger the actual age of the water. Conversely, the smaller the amount of dead carbon added from these sources, the greater the age of the water.

(2) The carbon dioxide in the mine might have been derived entirely from one of the sources listed in paragraphs (a)-(d) above, and none of it might have originated from soil-air  $\text{CO}_2$ . In this case, there is no possibility of dating the ground water by C determination of the carbon dioxide dissolved in it.

The agreement between the deuterium hydrogen ratios in the Henderson Mine water and present-day surface waters suggests that the source of the mine water was surface (meteoric) water. Since the isotopic composition of the surface waters in the region probably has not changed by more than a few permil since Miocene time, we cannot use the D/H ratio to determine when the water collected in the mine had been at the surface. The variations in D/H between various samples, and the variations in temperature between collection sites in the mine, suggest that the mine waters are a mixture of at least two waters differing in their isotopic composition and previous history.

If the water originated at the surface, it would have dissolved  $\text{CO}_2$ , both from the atmosphere and from soil  $\text{CO}_2$ . The exact amount of soil  $\text{CO}_2$  dissolved would have depended on many factors, such as thickness of soil, organic content of soil, temperature, etc. The water may have either taken on additional  $\text{CO}_2$  or exchanged its  $\text{CO}_2$  with carbonate in the fractured rock through which it passed. The gas pressure observed in the mine can be explained by heating of water that was saturated with  $\text{CO}_2$  at low temperature. The hot water would be supersaturated with gas, which would be released when the pressure was decreased as the water reached the mine.

The ambiguity regarding the sources of the  $\text{CO}_2$  in the mine water makes a  $\text{C}^{14}$  age determination of the water difficult. From the above considerations it is apparent that there are still problems associated with the dating of this water by the  $\text{C}^{14}$  method.

Table 1.--Location and results of analyses for deuterium on water samples  
collected in the area of the Henderson Mine

Location	Date	I. F. No.	D/H (permil, SMOW)
Butler Gulch, 8 ft. of snow core, 11,700 ft. elevation	April 6, 1970	3346- 8	-175
Do.	do.	9	-182
Snow above Clear Creek, west side of road across from explosive depot, 10,400 ft. elevation	do.	12	-180
West fork of Clear Creek, above Henderson Mine	do.	13	-145
Steelman Creek	July 15, 1970	17	-144
Bobtail Creek	do.	18	-138
McQueary Creek	do.	19	-146
Jones Creek	do.	20	-142
West fork of Clear Creek, above Henderson Mine	do.	21	-146
Butler Gulch Creek, near junction of Clear Creek	do.	22	-145

Table 2.--Location and results of  $C^{13}$  analyses on samples collected in the area of the Henderson Mine

Location	Date	I. F. No.	$C^{13}$ (permil, PDB)
CO <sub>2</sub> from Henderson Mine, 2X drift (5871N, 4180E), bubbled through SrCl <sub>2</sub>	May 28, 1970	3346-15	-13.3
Do.	do.	16	-14.3
Do.	July 15, 1970	23	-12.8
Do., but direct precipitation with SrCl <sub>2</sub>	do.	24	-5.9
Calcite formation, 2X drift (5871N, 4180E)	do.	25	+1.7
Carbonate from Vasquez fault, Henderson Mine	do.	44	-3.8
CO <sub>2</sub> by direct precipitation with SrCl <sub>2</sub> , CX-110 in 45C, 8035 level	do.	45	-5.5
CO <sub>2</sub> by direct precipitation, west trending drift that connects electrical and settlers with #2 shaft run-around drift, 8035 level	do.	46	-5.6
Do.	Feb. 17, 1972	49a (3 bottles)	-4.8
Do.	do.	49b (3 bottles)	-4.8
Carbonate #72-19, rhodochrosite from Urad Mine	do.	47	-6.6
Carbonate #72-21, Urad porphyry with microscopic calcite--from contact in 424X drift, 8035 level, Henderson Mine	do.	48	-4.1



