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 Copper River

Gases of mud volcanoes in the Copper River Basin, Alaska

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Abstract—The gases emitted from mud volcanoes in the Copper River Basin of Alaska fall into two distinct types which are not mixed during vertical migration. The gases in the eastern volcanoes are nearly pure carbon dioxide, whereas the western ones contain methane and nitrogen and almost no carbon dioxide. Chemical and carbon isotopic compositions suggest the carbon dioxide rich gases originated by solution of limestones and that methane rich gases probably formed by thermal decomposition of coals.

Permafrost may be a strong factor in separating the Copper River Basin gases. Extending downward for several hundred feet, the permafrost would prevent shallow lateral migration and focus the energy of the gas into occasional mud volcano vents. Soil gas analyses show rapidly decreasing amounts of the methane to about 150 m and of carbon dioxide to about 20–40 m away from the mud volcano pools. Isotopic variations of these natural methane and carbon dioxide gases, which are not intermixed, indicate that calculations of formation temperatures based on $\delta^{13}\text{C}$ ratios cannot be used generally.

INTRODUCTION

MUD VOLCANOES are some of the most spectacular surface manifestations of hydrocarbon seeps. In the Copper River Basin of Alaska (Fig. 1) gas and water rising to the surface have built mounds up to $2\frac{1}{2}$ km in diameter and over 100 m high. It is of particular interest that the gases evolved are of two distinct types with no evidence of mixing of the two.

Descriptions of the volcanoes and chemical analyses of the water and gases evolved by the volcanoes and from some springs in the area have been published (NICHOLS and YEHLE, 1961; GRANTZ *et al.*, 1962). The two Klawasi volcanoes and the Shrub volcano, all east of the Copper River, yield nearly pure carbon dioxide. Some 30–50 km west are three active mud volcanoes with gases that are mainly methane and nitrogen with little carbon dioxide. Between these two groups are springs which also are reported to give off methane–nitrogen gases (GRANTZ *et al.*, 1962). One of these springs is only about 7 kilometers from the Lower Klawasi volcano. This suggests a sharp geographic division between the two types of gases. Chemical compositions of water produced by the volcanoes fall into corresponding distinct groups also. Waters of the eastern region are much richer in bicarbonate.

This paper reports the use of the chemical compositions and carbon isotope ratios to determine the source of the methane and of the carbon dioxide type gases. The absence of lateral migration is discussed. Finally, observations are offered on the use of isotopic ratios of methane and carbon dioxide in deducing subsurface temperatures based on presumed isotopic equilibrium.

EXPERIMENTAL

Gas samples were collected by displacement of mud vol-

cano water from an inverted 250 ml narrow mouth bottle. The bottle was sealed under the pool surface with a screw cap fitted with a Teflon gasket. Soil gas samples were collected by driving a hole into the soil to 1 m or to ice or water. A $\frac{1}{4}$ in. pipe with side holes and fitted with an inflatable packer which was adjustable to be a minimum 20 cm below the surface was then inserted. After sealing the hole from atmosphere and allowing the apparatus to stand ~30 min the gas was pumped from below the packer using a Nalge hand pump. The soil gas sample was pumped through a Teflon septum into a glass bottle from which as much air as possible had been removed with the same hand pump just prior to sample collection. A small positive pressure was left in the bottle after it was filled with soil gas. Soil gas sampling techniques were maintained as uniform as possible, since the air content in a sample is a function of the sampling method, the extent of purging the system, and the time given for the gas in the sampling zone to regenerate itself from the surrounding soils. For guidance in sampling, checks of the gas composition were made on location at the time of sampling using Draeger tubes for methane and for carbon dioxide.

In the laboratory, the inert gas analyses reported in Table 1 were run on a Fisher–Hamilton gas chromatograph using a helium carrier gas flow of 40 ml/min, a column of $2\text{ ft} \times \frac{3}{16}$ in. of 50–80 Poropak R and $15\text{ ft} \times \frac{1}{8}$ in. of 80–100 mesh Molecular Sieve 5A at a temperature of 25°C. Hydrocarbons were analyzed on a flame ionization gas chromatograph using 10% Nujol on a 60–80 mesh alumina column at 80°C and a nitrogen carrier gas flow of 30 ml/min. Methane was converted to carbon dioxide in a combustion train similar to that described by CRAIG (1953). Carbon dioxide was released from carbonate samples by digestion of 0.25 g with 3 ml 100% H_3PO_4 for 3 hr. The evolved gas was isolated under high vacuum in a liquid N_2 trap. The carbon dioxide was cryogenically purified prior to isotope measurements. Carbon isotope ratios were determined on a mass spectrometer using the usual corrections for ^{17}O , mixing and background. NBS Isotopic Reference Material No. 22 with a value of -29.4% on the PDB scale was used as a carbon isotopic reference material for methane, and Solnhofen limestone with a $\delta^{13}\text{C}$ value of -0.64% on the PDB scale was used as a carbon isotopic reference for the carbon dioxide gases. Results are reported as $\delta^{13}\text{C}^{\dagger}$ values relative to the PDB

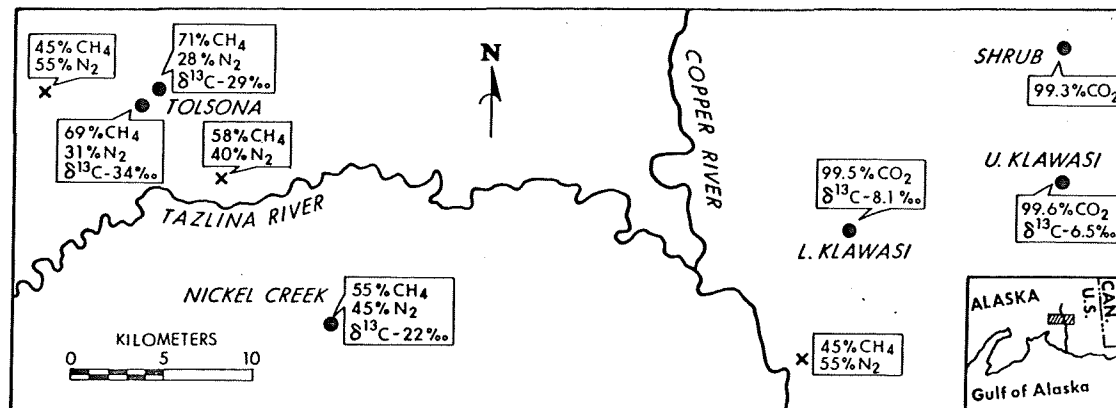


Fig. 1. Composition of gases from mud volcanos and springs; Copper River Basin, Alaska. ● Mud volcano (this study); ×, spring (from GRANTZ *et al.*, 1962).

standard. Duplicate $\delta^{13}C = \{[(^{13}C/^{12}C_{sample}) / (^{13}C/^{12}C_{standard})] - 1\} \times 10^3$ samples of collected gas differed by $\pm 0.4\text{‰}$.

RESULTS AND DISCUSSION

The chemical composition of gas from each sampling locality was similar to that reported for the same locality 15 or more years earlier (NICHOLS and YEHLE, 1961; GRANTZ *et al.*, 1962), despite the variation in amounts of water and gas produced from time to time. Chemical data and stable carbon isotope ratios are shown in Table 1 and summarized in Fig. 1. There was enough ebullition to incorporate some air into the samples, and the analytical results are calculated on an air-free basis by eliminating oxygen along with the corresponding amount of nitrogen found in the atmosphere.

Carbon dioxide gases

The Klawasi volcanoes on the east side of the Copper River Basin produce gases with very low quantities of components other than carbon dioxide. NICHOLS and YEHLE (1961) considered the carbon

dioxide of these mud volcanoes to be "related to Cenozoic volcanic activity from basic igneous bodies". GRANTZ *et al.* (1962) felt that the carbon dioxide could have been derived by diffusion from a volcanic or an inorganic source. Other possible sources of the carbon dioxide include biologic activity and dissolution of limestone by water. The $\delta^{13}C$ values of -6.5 and -8.1‰ for the gases help distinguish among these processes. Although bacterial oxidation of organic materials is a common source of carbon dioxide, that carbon dioxide is normally depleted in ^{13}C compared with the carbon dioxide of the mud volcanoes. Bacterial assimilation of carbon dioxide from a marine source would result in respiration of carbon dioxide enriched in ^{13}C to the same extent as the cell carbon is depleted in ^{13}C (DEGENS, 1969). Such gas would have a more positive $\delta^{13}C$ value than observed.

The carbon isotope ratios are in the range found for carbon in thermal areas (DEGENS, 1969). The Klawasi mud volcanoes are near the apparently extinct volcano, Mt. Drum, which is of Tertiary and Quaternary age (GRANTZ *et al.*, 1962). However, a direct volcanic source is unlikely, since volcanic gases generally contain considerable amounts of nitrogen,

Table 1. Alaska mud volcano gases

	LOWER KLAWASI	UPPER KLAWASI	TOLSONA #1	TOLSONA #2	NICKEL CREEK
Date Collected	June 74	June 75	June 75	June 74	June 74
Methane	.20%	.37%	69.2%	70.6%	54.9%
δ ¹³ C			-33.9‰	-28.2‰	-22.3‰
Ethane	10 ppm	-	-	-	.05%
Propane	2 ppm	-	-	-	-
i-Butane	1.5 ppm	-	-	-	-
n-Butane	-	-	-	-	-
Carbon Dioxide	99.5%	99.6%	.37%	.36%	-
δ ¹³	8.1‰	-6.5‰	-	-	-
Oxygen	.34%	-	-	-	-
Nitrogen	-	.4%	30.5%	28.1%	45.0%
Hydrogen	17 ppm	-	-	-	138 ppm
Helium	258 ppm	97 ppm	612 ppm	1042 ppm	1775 ppm

Table 2. δ¹³C of 3324, S. of Scott

FORMATION
Chitistone (Triassic)
Nelchina (L. Cret.)

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Table 2. $\delta^{13}\text{C}$ of Wrangell carbonates. Sample location: 3324, S. of Scotty Peak; 3329, N.E. of Dixie Pass; 3326, E. of Kuskulana Pass

FORMATION	SAMPLE	$\delta^{13}\text{C}$ (PDB)
Chitistone (Triassic)	3326-19	+2.87
	3329-29	+2.34
Nelchina (L. Cretaceous)	3324-7	- .30
	3324-8	+1.73
	3326-3	+1.83

hydrogen and sulfur gases in addition to carbon dioxide (LYON, 1974). The Lower Klawasi gas contained only 3.4% nitrogen before correction for air, 15 ppm hydrogen and negligible amounts of sulfur containing gases.

Rather pure carbon dioxide gas could be produced through thermal decomposition of limestone by hot volcanic materials. Association of carbon dioxide gases with intrusives and limestones is known in other locations. One is in Northwestern Germany near the Bramscher Massiv (VON BOIGK and STAHL, 1970) where a large carbon dioxide accumulation exists underground. Other carbon dioxide provinces for which a thermal decomposition of limestone by intrusives has been proposed are in New Mexico and Mexico (LEVORSEN, 1967). Carbon dioxide from direct thermal decomposition of limestone by an intrusive would be expected to have a carbon isotopic ratio about 5‰ heavier than the limestone (SHIEH and TAYLOR, 1969). This was confirmed by a value of +5‰ calculated for carbon dioxide in Northwestern Germany (VON BOIGK and STAHL, 1970). $\delta^{13}\text{C}$ of outcrop samples of the underlying Nelchina and Chitistone limestones (Table 2) show that they are typical marine limestones with a $\delta^{13}\text{C}$ value near 0. Since the $\delta^{13}\text{C}$ values of the carbon dioxide gases are negative rather than the +5‰ resulting from direct decomposition of limestones, another process for forming the carbon dioxide must be sought. This is the same situation faced by SHIEH and TAYLOR (1969) for many other thermal gases.

A process by which nearly pure carbon dioxide might have been produced could begin with solution of limestone in water. This could take place over a wider area than direct production of carbon dioxide from heating limestone and could produce very large amounts of carbon dioxide. Solution of limestone would result from both the heat and the water associated with the intrusion. Reaction of magmatic gas with limestone could remove other acidic components such as halogen acids and sulfur dioxide, and at the same time increase the solution of limestone in water. The resulting aqueous solution of carbonate, bicarbonate and carbon dioxide would release carbon dioxide after moving to a zone of lower pressure or greater acidity. Isotopic data are consistent with this mechanism. $\text{CO}_{2(g)}$ is depleted in ^{13}C by about 8‰ relative to the dissolved carbonate with which it is in isotopic equilibrium at 30°C (DEUSER and DEGENS, 1967; MOOK *et al.*, 1974). Limestones in the Copper River Basin area with $\delta^{13}\text{C}$ near 0 and carbon dioxide gas with values of -6.5 and -8.1‰ show this same relationship. This may be a rather general process which is more obvious in the Copper River Basin due to restriction of water flow and in frequency of venting zones.

Methane gases

Gases of the methane-nitrogen type east of the Copper River are strongly depleted in ^{13}C relative to the carbon dioxide gases. The carbon of the methane is enriched in ^{13}C relative to methane formed by biological fermentation which typically has a $\delta^{13}\text{C}$ value of -55‰ or lower. The $\delta^{13}\text{C}$ value does not fit the normal pattern for oil-associated methane which generally has a value more negative than -33‰. One type of methane which would match the observed range of -22 to -33‰ is coal-derived methane. Although methane from coal does vary with the maturity of the coaly material, and gases initially formed tend to be depleted in ^{13}C , the average carbon isotopic ratio of methane ultimately approaches that

Table 3. Soil gases

Area	Distance from Volcano cone (m)	Sample Depth (cm)	CH_4 (ppm)	CO_2 (ppm)
TOLSONA #1	3	75	1188	3100
	6	61	455	800
	20	40	10	2400
	150	30	49	3200
	1000	30	3	300
U. KLAWASI	2	30	2.5	26000
	5	22	2.5	8000
	20	22	2.3	>30000
	40	30	4.6	3000
Reference Points				
1/2 mi. N. Copper Center	-	50	3.7	3000
Glenn Hiway Mile 111	-	50	2.9	4500

of the initial coaly material. A range for Cretaceous coals from about -21 to -28% has been reported (DEGENS, 1969). An outcrop sample of Lower Cretaceous Nelchina Formation coal from the west side of the Copper River Basin had a $\delta^{13}\text{C}$ value of -21.4% . This medium volatile bituminous coal which also underlies the central part of the basin may have lost much of the early generated methane during long periods of relative shallow burial. Although this was an outcrop sample, it supports the hypothesis that methane of the volcanoes originated from coals in the subsurface.

The geology of the western part of the Copper River Basin (FORESMAN, 1970) is consistent with the origins proposed for the methane. Upper Cretaceous shales and sandstones of the Matanuska Formation are overlain by Tertiary sandstone and conglomerates. Although lignitic beds are present and might have served as the source of methane, the $\delta^{13}\text{C}$ values suggest the Cretaceous Nelchina Formation is a more likely source of methane. This is supported by the presence of Cretaceous fossils in the mud volcano cones (GRANTZ *et al.*, 1962). The gas must have come from at least the depth of the Cretaceous section containing these fossils (to 1500 m at the Tolsona volcanoes). An overpressured zone was found at about 1700 m in a well drilled between the Tolsona volcanoes and the Copper River. This overpressuring may have provided the energy for the formation of the mud volcanoes at least in the western part of the basin. HEDBERG (1974) has suggested that generally mud volcanoes are directly related to overpressured zones. In the Caspian Basin, SOKOLOV *et al.* (1969) proposed that the gas must originate at least 10,000–12,000 m deep to account for the formation of cones. This was based on the violent eruptive nature of those mud volcanoes. In the Copper River Basin the overpressured zone and particularly the focusing of the release of gas through infrequent penetrations of the permafrost can account for the mud volcanoes arising from more shallow formations.

Gas migration

The Copper River Basin should be a unique location for study of gas migration. The existence of two types of gases without any apparent mixing suggests that lateral migration at least on a scale of a few kilometers must be essentially absent. To search for evidence of lateral migration of the two types of gases, gas samples were drawn from the shallow subsurface along lines going out from two volcanoes. Results are summarized in Table 3. The soil surrounding the Tolsona volcano pool edge showed higher methane content for at least 150 m. Upper Klawasi gas was detected for 20–40 m from the pool edge. The 'background' level of soil gas was taken as 3 ppm methane and 0.4 ppm carbon dioxide based on soil gas samples from two separate areas away from the volcanoes. Vertical migration was evidently the dominant movement.

Aeromagnetic data and salinity of water of the basin (GRANTZ *et al.*, 1962) correlate with the distinction between the two types of gases. The indications of rather shallow volcanics from the eastern edge of the basin to near the Copper River can account for the formation of carbon dioxide and also provide a barrier to upward migration of methane. Permafrost may be a major factor in focusing the gas into occasional vertical vents resulting in mud volcanoes. The permafrost in the Copper River Basin has been described by NICHOLS and YEHLE (1961). Permafrost is encountered from 0.3 to 3 m beneath the surface and extends to a depth of 40–60 m. It reportedly may be absent under lower terraces, lakes and floodplains of major rivers. The infrequency of venting of the gases through mud volcanoes suggests that permafrost may be nearly continuous. Permafrost would also prevent shallow lateral movement of gas as well as of water carrying dissolved carbon dioxide and help explain the sharp separation of the two gas types. Some lateral migration may be indicated in the methane gas area by the changes in methane to nitrogen ratios shown in Fig. 1. These changes correspond to the reported changes in that ratio in the Delaware-Val Verde Basin (WEISMANN, 1971), but the change in the ratio may also be due to different rates of generation and release of methane and nitrogen.

It has been a frequent practice to use carbon isotope ratios of methane and carbon dioxide mixtures to calculate the temperature at which the gases originated using the methods proposed by BOTTINGA (1969) and CRAIG (1953). The present study demonstrates a practical difficulty with such calculations. There is a range of 12% in carbon isotope ratios even in methanes from the same area which have no carbon dioxide present and therefore no chance for isotopic equilibrium. Similarly, carbon dioxide gases from very similar environment differ by 2%. These variations would give as much as 150°C differences in apparent formation temperatures when used in thermal equilibrium calculations. Differences in the source and even in the time of formation of the methane and its migration history are more evident contributors to isotope ratios than any equilibrium considerations. In the case of carbon dioxide, phase equilibrium of the gas with aqueous carbonate and bicarbonate is much more important than thermal equilibrium. Isotope ratios of methane-carbon dioxide mixtures cannot be used to calculate formation temperatures without first eliminating other more obvious factors controlling isotope ratios.

CONCLUSIONS

The unique gases of the Copper River Basin are products of two different formation mechanisms, even though they are located within a few kilometers of each other. Nearly pure carbon dioxide is available from dissolution of limestone by moisture, heat and acidity of volcanic gases. Methane is probably formed

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by thermal decomposition of coaly materials. There is no evidence for much lateral migration of the gases. Finally, the variations in carbon isotope ratios of each gas show that isotope values of methane-carbon dioxide pairs cannot be used indiscriminantly for calculating of temperatures to which the gases have been exposed.

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