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CARBONATITES AND ALKALIC ROCKS OF THE ARKANSAS RIVER AREA, FREMONT COUNTY, COLORADO. 2. FETID GAS FROM CARBONATITE AND RELATED ROCKS[1]

E. Wm. Heinrich and Raymond J. Anderson
The University of Michigan, Ann Arbor, Michigan
and
The Dow Chemical Company, Midland, Michigan.

Abstract

The Goldie carbonatite of Fremont County, Colorado, and its associated rocks contain a fetid gas shown to consist of a mixture of C_5 and C_6 hydrocarbons, F_2, HF and F_2O. The fluorine has been derived from fluorite. Similar gases are characteristic of thorium veins in the same alkalic igneous district to the east and of various alkalic rocks around the Iron Hill alkalic-carbonatitic complex in Gunnison County, Colorado. These Colorado occurrences are similar to those previously reported from alkalic rocks of the Kola Peninsula, U.S.S.R. The gases are believed to be of magmatic origin.

Introduction

The general geological features of the alkalic igneous province west and southwest of Canon City, Colorado, have been described by Heinrich and Dahlem (1965). The Goldie carbonatite (Heinrich and Quon, 1963) lies in the dike halo of the McClure Mountain-Iron Mountain complex, the largest of the three alkalic intrusive masses in the province. Most of the thorite veins occur east and southeast of the McClure complex, and are genetically associated with the Democrat Creek body (Heinrich, 1958; Christman *et al.*, 1959).

Mineralogically, the Goldie carbonatite is one of the most unusual in the world. Most of it consists of limonite-stained calcite, with local masses of barite. In one of the prospect pits there are exposed replacement nodules of aluminofluoride minerals which consist of various of the assemblage: cryolite, gearksutite(?), pachnolite, weberite, prosopite and ralstonite, together with abundant purple, radioactive fluorite (Heinrich and Quon, 1963).

The sequence of rocks across the carbonatite is:

Hanging wall	1.	Biotite gneiss
	2.	Aplite, 2 ft. thick
	3.	Lamprophyre, 3–3.5 ft. thick
	4.	Carbonatite, 1.5 ft. thick
	5.	Aplite, 1.5 ft. thick
Footwall	6.	Biotite gneiss

[1] Contribution No. 272, the Mineralogical Laboratory, Department of Geology and Mineralogy, The University of Michigan.

Fetid gas occurs in three rocks:

1. Very abundantly in the footwall aplite, in which exomorphic hematite, calcite and minor fluorite have been formed.
2. Locally in the carbonatite.
3. In pegmatite that crops out 50 ft. southeast of the prospect pit. This pod of unzoned granitic pegmatite contains a local vuggy phase in which feldspars have been removed and dusty hematite has been introduced. This porous rock emits a strong fetid odor when broken.

Fetid Gas in Thorite Veins

The thorite district to the east contains numerous fracture-filling and replacement veins of a reddish rock consisting of various combinations of carbonate, alkalic feldspar, barite, hematite and fluorite with lesser amounts of sulfides, quartz and sodic amphibole. The thorium occurs chiefly as thorogummite; brockite and xenotime also are present.

"Most of the mineralized material in the shear zones has a strong fetid odor; it is especially strong in some of the reddish-stained granitic rocks. The odor can be detected only for a few seconds after the rock has been broken. The odor was thought to be caused by selenium compounds but a chemical analysis of the rock showed only traces of selenium. The volatile compounds however may have escaped during grinding of the sample. It also has been suggested that the odor may be due to arsenic or phosphorous compounds. Regardless of its origin the odor is characteristic of the Wet Mountains thorium area and is useful in tracing the shear zones where other evidence of mineralization is lacking" (Christman *et al.*, 1953, p. 7). "The vein rocks at many places emit a strong stinking odor when freshly broken, but the odor disappears in about a minute" (Singewald and Brock, 1955, p. 6). "Many of the veins contain a fetid gas of unknown composition which escapes when the rock is broken; the gas may be a phosphorous compound" (Christman *et al.*, 1959, p. 520).

An olfactory comparison of gas from the Goldie rocks with that from several of the thorium veins makes it noisomely evident that the two, if not identical, are, at least essenceally similar.

A similar stink characterizes some rocks associated with the Iron Hill alkalic carbonatitic complex in Gunnison County, Colorado, about 100 miles to the west:

" . . . a fetid odor like garlic . . . locally characterizes freshly broken rock from thorite veins, trachyte dikes and fenitic rocks . . . " (Hedlund and Olson, 1961, p. B-286).

Composition of the Gas

Analyses of the rocks indicated the essential absence of H_2S, As, Se, Te and P compounds (other than apatite, brockite and xenotime).

Initial attempts to analyze the gas consisted of placing a specimen of the Goldie aplite in an evacuated chamber equipped with a chisel by means of which the specimen was split *in vacuo*. The liberated gas was conducted to a Bendix Time of Flight Mass spectrometer, which unfortunately showed nothing. Rechecking of the specimen by subsequent further splitting in air yielded the characteristic odor, which led us to conclude that the nose is more sensitive than the machine.

Subsequently the specimen was treated as follows:

The rock and a pair of cleaned pliers (acetone, trichloroethylene) were cooled with liquid N_2. The rock was then crushed with the pliers, allowing the fragments to fall into a liquid N_2-bathed beaker. Small samples were then rapidly (1–2 seconds) transferred into the mass spectrometer inlet system. The instrument used was a Bendix Time of Flight Mass spectrometer especially modified to obtain spectra from volatile material in a non-volatile matrix.

The mass spectrometer indicated the presence of:

C_5 hydrocarbons
C_6 hydrocarbons
F_2
HF
F_2O
HCl (possibly a small amount)

The hydrocarbons are present more abundantly than the last four. The C_5's predominate by a factor of 2–3. It is estimated that the total hydrocarbon content is between 10–100 ppm.

Experience at Dow Chemical Company has indicated that on fluorinating hydrocarbons the crude product has an unpleasant odor. This is believed to be due to acid fluorides of the type RCOF. Both F and F_2O have a not entirely unpleasant odor in very low concentration, somewhat resembling that of ozone but more pungent. They can be detected by the nose in extremely small amounts, and an atmosphere containing but 1 ppm is sufficiently disagreeable to induce removal of the nose.

Discussion

Fluorite is an abundant constituent of the Goldie carbonatite; it is present in significant amounts in the adjacent footwall aplite. It is a widespread constituent of the thorium veins, both those of the Wet Mountains and of Gunnison County.

Fetid fluorite (antozonite, Stinkfluss) has recently been found by Greenwood (1964) in the Badu pegmatite, Llano County, Texas. Previously it had been noted in North America in the MacDonald pegmatite near Hybla, Ontario, Canada (Ellsworth, 1932). Its presence elsewhere in the world, *e.g.*, Germany, has been reported by Palache *et al.* (1951).

The free fluorine from fluorite has been formed as the result of partial structural degradation under α-particle bombardment from the accompanying radioactive species, probably mainly thorogummite. The older literature contains repeated references to the liberation of free fluorine when certain fluorites are cleaved or crushed (see, for example, Sine, 1925; Ellsworth, 1932; Palache *et al.*, 1951). The identification of the gas as fluorine was apparently made originally by Becquerel and Moisson in 1891 (Sine, 1925), based on its reaction with water to produce ozone. The information presented here represents analytical confirmation of these old results.

Splitting or grinding may liberate adsorbed H_2O and this, as well as contact with moist air may result in the reaction (Greenwood, 1964):

$$F_2 + 2H_2O = 2HF + H_2O_2$$

Recently, however, Kranz (1965) has studied the composition of gaseous inclusions in fluorite from Wölsendorf, Germany and his results cast doubt on the long-maintained theory that the odor of all fetid fluorite results from the interaction of F_2 with H_2O. Whereas in the lightly colored fluorite from Wölsendorf the gas was mainly inorganic (Ar, N_2, CO_2, H_2S, SO_2, H_2O, HF) with only traces of light hydrocarbons (CH_4-C_3H_8), in the dark violet fluorite (Stinkspat) measurable amounts of fluorinated hydrocarbon compounds also were determined. These include not only light compounds such as $C_2H_4F_2$ but also perfluorinated hydrocarbons with a molecular weight of over 127.

Other Occurrences

Organic compounds, both gaseous and solid, have been found in rocks of the Kola Peninsula, USSR. This unexpected discovery was first described by Petersilie (1958) who found appreciably large amounts of hydrogen, methane and other gaseous hydrocarbon compounds in rocks of the ijolite-urtite series of the Khibina alkalic igneous complex (Voitov, 1962).

Subsequently other discoveries were reported. Petersilie (1963) found that the various rocks of the larger Kola alkalic massifs (Khibina and Lovozero) contain large quantities of hydrocarbon gases in intergranular pores, in microfractures and in vacuoles within minerals. The gases are composed of 70–90% hydrocarbons and 3–10% hydrogen; other constituents are CO and CO_2. In the hydrocarbons methane predominates; also present are ethane, propane, commonly iso-butane, rarely pentane. Volumes up to 243 cm^3/kg were obtained.

Rocks of the two larger massifs (Khibina and Lovozero) are characterized by large amounts of methane and the constant presence of C_2-C_4 gases. These massifs are agpaitic and contain no carbonatites. The smaller miascitic massifs some with carbonatites, Afrikanda, Kovdor and Gremjakha-Virmes, are characterized by a paucity of methane and the absence of the heavier hydrocarbon gases (Petersilie, 1964).

Rocks intruded by the alkalic massifs contain negligible amounts of the gases or only methane in amounts not more than 0.1–0.01 of the content of igneous rocks. Vein rocks and shear zones of post-crystallization age contain no hydrocarbons or only insignificant amounts of them. Petersilie (1963) also shows that the composition of gas from mineral vacuoles varies with the species, and mineral species can be identified by their gas composition irrespective of the massif in which the mineral occurs.

Bitumens of the petroleum type also are present in the alkalic rocks, in carbonatites and some pegmatites (Petersilie, 1963, 1964; Beskrovnyy and Baranova, 1963). The bitumens occur only in those rocks that also contain considerable quantities of the hydrocarbon gases. The bitumens contain relatively large amounts of paraffin hydrocarbons, lesser amounts of naphthene, and usually aromatic hydrocarbons. Bitumens varying from petroleum to asphalt have been found by Beskrovnyy (1958) in the kimberlite pipes of Siberia.

Petersilie (1963, 1964), Zakrzhevskaya (1964) and Ikorskii and Romanikhin (1964) conclude that the gases are of *inorganic magmatic and syngenetic origin;* that they are not the result of emanations escaping from a deep magma chamber but were produced during the process of formation of the intrusive rocks. According to Petersilie (1964) the bitumens likewise are of inorganic origin. In contrast Beskrovnyy and Baranova (1963, p. 621) conclude that their results indicate a migration of petroliferous hydrocarbons along fissures and faults into carbonatite and " . . . that these petroleum bitumens and hydrocarbon gases . . . are the accessories of hydrothermal activity." Florovskaya and Melkov (1962) found that small inclusions of bituminous substances occur only in those grains of nepheline subjected to postmagmatic processes.

Origin

In the Colorado occurrences the hydrocarbon gases have been found in carbonatites, alkalic dike rocks, related thorium veins and their wall rocks. In both Fremont and Gunnison Counties, the geological evidence does not favor any suggestion that these gases migrated into these rocks from previous accumulations in sedimentary rocks. In Fremont County the nearest sediments are in a small down-faulted wedge of Mesozoic sediments about 12 miles to the northeast. In these neither gas nor petroleum occurs, and at least one major fault lies between the wedge and the Precambrian block in which the carbonatites occur. Petroleum occurs at Florence, about 15 miles to the east of the Goldie dike and about 10 miles from the edge of the thorium district. Again several major structural features intervene, and the petroliferous beds emerge into the world of air and light as truncated uptilted hogbacks unconformably overlying the Precambrian rocks along the margin of the Canon City embayment.

In Gunnison County only local remnants of the Morrison sandstone (Jurassic) *overlie* the Precambrian; neither gas nor petroleum is known in this formation here.

White and Waring (1963), in their review on the geochemistry of volcanic exhalations, note that CH_4 is most erratic in occurrence and commonly is not reported; where found, it seldom exceeds 1%. Ellis (1957, p. 424) has discussed the problem of the origin of methane, which " . . . commonly occurs in magmatic steam." It can be formed by the reaction:

$$CO + 3H_2 = CH_4 + H_2O$$

Marx (1964) has reviewed the results of reactions between graphite and hydrogen. Previously methane was recorded as the sole petroleum-like product, but now there is evidence of the formation of an increasing proportion of the higher paraffins in the reaction products below 650° C. At pressures of 1–2 atm., ethane, propane and butane were formed down to a limiting temperature of about 360° C.

It can be concluded that the hydrocarbon-fluorine gases of the Colorado carbonatites and their related rocks are, like those of the Kola alkalic rocks, of magmatic origin, a conclusion not at odds with experimental results. The presence of these gases seems to be a property peculiar to alkalic subsilic rocks and their derivatives and increases the diverse and numerous forms in which carbon is represented in such rocks:

1. Carbonate minerals: calcite, dolomite, ankerite, etc.
2. Silicate minerals: cancrinite
3. Native elements:
   a. Graphite
   b. Diamonds (kimberlites)
4. Moissanite
5. CO_2 gas in vacuoles of calcite and apatite
6. Hydrocarbon gases
7. Bitumens

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