

Fluid inclusions in quartz crystals from South-West Africa*

KEITH A. KVENVOLDEN

Exobiology Division, Ames Research Center, NASA,
Moffett Field, California 94035

and

EDWIN ROEDDER

U.S. Geological Survey, Washington, D.C. 20242

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Abstract—Quartz crystals from calcite veins of unknown age in Precambrian metasedimentary rocks at Geiaus No. 6 and Aukam farms in South-West Africa contain both primary and secondary inclusions filled with one or a variable combination of: organic liquid, moderately saline aqueous liquid, dark-colored solid, and vapor. Analysis of these materials by microscopy and by gas chromatography and mass spectrometry shows the presence of constituents of both low and high molecular weights. The former include CH_4 , C_2H_6 , C_3H_8 and possibly C_4H_{10} as well as CO , CO_2 , H_2O , N_2 and H_2 . High molecular weight components are dominantly n-alkanes and isoprenoid hydrocarbons. The n-alkanes range from at least n- C_{10} to n- C_{33} . Concentrations of n-alkanes larger than n- C_{17} decrease regularly with increasing carbon number. An homologous series of isoprenoid hydrocarbons ranging from at least C_{14} to C_{20} is present in unusually high concentrations. Pristane (C_{19}) is most abundant, and C_{17} isoprenoid is least abundant. The molecular composition and distribution of hydrocarbons suggest biological precursors for these components.

Consideration of data provided by freezing, crushing and heating experiments suggests that the pressures at the time these in part supercritical fluids were trapped probably exceeded 30–40 atm, and the minimum trapping temperature was about 120–160°C. Both primary and secondary inclusions apparently containing only organic materials were trapped by the growth of the host quartz from aqueous solution. The data obtained neither prove nor preclude Precambrian, Paleozoic or younger sources for the organic materials.

INTRODUCTION

FLUID inclusions in euhedral and anhedral quartz crystals from two South-West African localities—the Aukam farm, Bethanie District and the Geiaus No. 6 farm, Warmbad District, were found to contain both organic and inorganic substances. Although there is little information published on the two localities, which are separated by about 100 km, they are apparently quite similar geologically. MARTIN (1965, p. 133) briefly described the locality at Geiaus No. 6 farm. The quartz crystals are contained in calcite-filled gash veins in a pre-Nama (about 700×10^6 yr or earlier) diabase dike emplaced in metasedimentary rocks of the Kheis System which is at least 1.0×10^9 and probably is older than 2.6×10^9 yr. The area was formerly overlain by beds of both the Nama (upper Precambrian and Cambrian) and Karroo (Carboniferous and Jurassic) Systems and remnants of these beds are still preserved in the general area. Martin suggests that the veins are “probably the result of post-Nama and/or post-Karroo faulting which has taken place along some of the north-south striking diabase dikes.” A description of the locality at Aukam could not be found, but examination of the geological map of South-West Africa (SOUTH AFRICA GEOLOGICAL SURVEY, 1963) suggested that the geological

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situation at Aukam is similar to that at Geiaus. Because of the sketchy knowledge concerning the geology of these localities, it has not been possible to ascertain the age of the source of the organic materials in the fluids of the inclusions in these quartz crystals.

There have been many studies of organic fluid inclusions in sedimentary, metamorphic and igneous rocks (TOURAY, 1969; ROEDDER, 1971). In particular, Russian investigators have reported finding organic gases as well as bituminous substances in a number of igneous samples (KUDRIATSEV, 1958; VDOVKIN, 1963; PETERSIL'E, 1964; KROPOTKIN *et al.*, 1966; MOGAROVSKY and MARKOV, 1966; IKORSKII, 1967; ZEZIN and SOKOLOVA, 1967; PETERSIL'E and SORENSSEN, 1970). Detailed description of the composition of the bituminous substances, however, is generally lacking. GROGAN and SHRODE (1952) noted the presence of a yellow petroleum, which fluoresced under ultraviolet light, in fluid inclusions of fluorite from Illinois. Later MUELLER (1969) also reported oily phases in fluorite crystals from the same region. In neither of these studies was the composition of the oil in the fluorite examined in detail. ROEDDER (1967, 1970) has shown that there apparently has been a degradation of the originally homogeneous organic fluids in these inclusions to form dark bitumens and more volatile constituents, and that they now contain much methane under pressure. Fluid inclusions in quartz studied by MURRAY (1957, p. 951) contained hydrocarbon molecules having from one to eight carbon atoms and produced the "light blue fluorescence of a hydrocarbon condensate."

MUELLER (1970, p. 464) studied quartz crystals from South-West Africa and reported inclusions containing a "vaselinous oil, which produces crystals with paraffinic optical properties when frozen, some dark resinous flakes (possibly olefinic differentiates), and black globules, which appear to be aromatic differentiates." The quartz crystals originated from veins which traverse granite, and MUELLER concluded that the bitumens of the inclusions probably are abiogenic magmatic condensates.

Hydrocarbon inclusions in quartz crystals from one of the localities studied here have been mentioned by MARTIN (1965, p. 133). He describes quartz crystals from the Geiaus No. 6 farm that contain numerous bubble cavities filled with water and oil. He thought that the oil was "derived from substances rich in chlorophyll," based on an internal report from Artnell Exploration Company. The Artnell report in turn was based on an internal report from the Mobil Oil Corporation.

The unpublished data on which the Mobil Oil Corporation report was based showed that a highly paraffinic oil was present which contained unusually high concentrations of compounds tentatively identified as acyclic isoprenoid hydrocarbons. Mass spectrometric analysis of a composite of hydrocarbons extracted with carbon disulfide from several cavities showed an approximate composition of 92% saturated hydrocarbons and 8% aromatic hydrocarbons. A portion of the hydrocarbon extract was treated with 5 Å molecular sieves in order to remove n-alkanes from branched-cyclic alkanes. The original sample extract and the branched-cyclic fraction were examined by gas chromatography, infrared spectrometry and mass spectrometry. The evidence provided by these techniques

indicated that n-alkanes from about n-C₁₃ to n-C₂₅ were present and that from n-C₁₉ to n-C₂₅ the relative abundance of odd- and even-carbon numbered molecules was equal. More interesting, however, was the observation that acyclic isoprenoid hydrocarbons were present. Phytane, pristane and 2,6,10-trimethylpentadecane were tentatively identified and 2,6,10-trimethyltridecane, 2,6,10-trimethyldodecane, and 2,6,10-trimethylundecane were suggested. The present study, in part an extension of unpublished work originally done by the Mobil Oil Corporation, was undertaken in order to determine the composition of the hydrocarbon fluids. The data on hydrocarbons along with observations made by freezing, heating and crushing studies provide a basis for speculation concerning the origin of the fluids of these inclusions.

PROCEDURES

From the Aukam farm locality came six, doubly terminated, 1-cm quartz crystals (designated 68-B) and one crystal 1.7 cm long (68-A; Fig. 1). The six smaller crystals were pulverized to less than 1 mm, as described later, to obtain organic extracts of the fluids in the larger inclusions. A detailed optical examination was made of the large crystal (68-A) and of a portion of the pulverized residue (68-B). The former was subjected to nondestructive tests only. Material from Geiaus No. 6 farm consisted of anhedral and euhedral quartz crystals 1–2 cm long. After five of these crystals, 68-1 through 68-5, were examined in liquid of matching index of refraction, doubly polished plates were cut from them in directions chosen to preserve the best inclusions. The remaining crystals from Geiaus were designated 68-6.

Previous experience had shown that when individual inclusions were opened there was a sudden release of pressure and loss of volatile constituents. Because of this experience the samples were processed for organic analyses in two different ways: (1) to obtain high molecular weight constituents, the quartz was crushed under n-hexane with a mortar and pestle, and the resulting hexane solution was analyzed. In another experiment the quartz was crushed without solvent present, and the crushed material was extracted with a mixture of benzene–methanol (9:1), and this solution was examined. Solvents were evaluated prior to use, for all this work, and in every case the background was acceptable relative to the concentrations of individual components identified in the samples. (2) For low molecular weight components, the samples were crushed under vacuum in a glass ball mill, in a bakeable crushing chamber, and on a microscope crushing stage.

Besides these analyses, the fluids of the inclusions were studied by means of microscope stages designed for freezing and heating. For this work doubly polished plates of samples 68-1 through 68-5 and the single crystal 68-A were used.

Crushing with mortar and pestle

Six crystals, constituting sample 68-B (about 3.3 g) were rinsed with water, 6 N HCl, water and methanol. After drying, the crystals were placed in an all glass Soxhlet extraction apparatus and cleaned with a mixture of benzene–methanol (9:1) for four hours. Each crystal was crushed in an alumina mortar with a pestle while n-hexane was added to maintain a slurry. The slurry was transferred to a centrifuge tube, n-hexane was added, and the mixture was agitated, sonicated and centrifuged. The resulting extract was decanted and the residue rinsed twice with n-hexane. The rinses were added to the extract. The extract was reduced in volume to about 50 μ l and portions of this extract were examined for hydrocarbons by gas chromatography.

A portion of sample 68-6 (about 31.5 g) was processed in the same manner. The final extract was reduced in volume to about 70 μ l; gas chromatography and gas chromatography–mass spectrometry were used to analyze the extract.

Gas chromatography was carried out on three different chromatographic columns: 100 ft \times 0.02 in. support coated open tubular column with OV-1; 6 ft \times 0.25 in. glass column with 3% OV-17 on 60–80 mesh Gas Chrom Q; and 12 ft \times 0.125 in. stainless steel column with 3% Polysev on 80–100 mesh AW, DCMS Chromasorb W. Of the three columns, the one

containing OV-1 gave the best resolution of n-alkanes and isoprenoid hydrocarbons. This column was used for gas chromatography-mass spectrometry which was carried out on a Perkin-Elmer 270 gas chromatograph-mass spectrometer and on a combination of a Loenco 160 X gas chromatograph attached by means of a membrane separator to a CEC 21-491 mass spectrometer.

Identification of compounds was based on equivalence of gas chromatographic retention times and mass spectra of unknowns and standards of n-alkanes and isoprenoid hydrocarbons. Isoprenoid hydrocarbon standards used were farnesane (C_{15}); 2,6,10-trimethyltetradecane (C_{17}); 2,6,10-trimethylpentadecane (C_{18}); pristane (C_{19}); and phytane (C_{20}). The first two standards were synthesized by Dr. E. D. McCarthy, University of California. The third and fifth standards were synthesized from phytol by J. E. Cooper, Mobil Oil Corporation and pristane was obtained from Eastman Organic Chemicals, Rochester, N.Y. Standard n-alkanes were supplied by Lachat Chemicals Incorporated, Chicago, Ill.

A second portion of sample 68-6 (about 30 g) was cleaned as described previously, crushed in the mortar with a pestle, and 25.5 g was extracted with a mixture of benzene-methanol (9:1) by agitation and sonication. The extract was handled in the same manner as the n-hexane extract described previously. The final extract was reduced just to dryness. This extract was divided so that 30 per cent was examined for porphyrins and 70 per cent was removed for carbon isotopic determinations which also were made on portions of the pulverized quartz before extraction and on portions of the quartz remaining after extraction.

The amount of extract examined for porphyrins was equivalent to about 8 g of sample 68-6. This extract was subjected to spectrophotometric and spectrofluorometric techniques following procedures outlined by HODGSON *et al.* (1970).

For carbon isotopic determinations, samples were heated in oxygen at 1100°C to form CO_2 which was analyzed on a dual collecting Nuclide Corporation mass spectrometer. Results are reported in ‰ relative to the PDB standard.

Crushing under vacuum and with microscope stage

For one experiment, 7 g of sample 68-6 were placed in a Pyrex ball mill equipped with three Lucalox balls. The mill was evacuated to about 10^{-4} torr for two hours. The quartz was crushed by rotating the ball mill for 20 hr. The mill was heated to 150°C and the gases evolved during crushing were expanded into the inlet system of a CEC 21-110 mass spectrometer. Part of the evolved gases was also analyzed by gas chromatography (Varian Aerograph 1520) on a 6 ft \times 0.125 in. aluminum column packed with 80-100 mesh Poropak Q. The column was maintained at room temperature for 2 min and then the temperature was increased at $10^{\circ}/\text{min}$ to 140°C .

A mass spectrometric study was made of the composition of the gases emitted on vacuum crushing of individual inclusions. For this work a bakeable crushing chamber, with bellows to permit transmission of the crushing force into the vacuum system, was connected directly to an AeroVac model 610 mass spectrometer. All interior surfaces of the crusher, tubing, valves and gaskets were gold plated to avoid loss of any sulfur compounds which might be present. The system was baked under vacuum without sample and cooled; the crusher was opened and the clean sample inserted and again baked under vacuum to temperatures below the homogenization temperatures of the inclusions. The sample was cooled still under vacuum, and crushed at room temperature. Mass spectra were recorded of the evolved gases.

The microscope crushing stage (ROEDDER, 1970) was used for detection of noncondensable gases. The method is only qualitative, but is highly sensitive (as low as 10^{-14} g).

Freezing and heating studies

The behavior of the inclusion fluids was observed by means of a freezing stage on a microscope (ROEDDER, 1962b). For studies of aqueous solutions, samples 68-1 through 68-5 were frozen at -78.5°C and allowed to warm gradually. First and final melting temperatures were observed. Organic liquids were examined at -196°C and at -78.5°C . These substances were then gradually warmed to $+35^{\circ}\text{C}$.

Inclusions in three of the doubly polished plates (samples 68-1, 68-3 and 68-5) were

examined on a Leitz 350 heating stage. The individual runs were of 3–6 hr duration and used incremental heating, with adequate time to achieve approximate thermal equilibrium after each temperature change. The thermometers were calibrated with organic melting point standards, in tiny sealed capillaries, directly on the stage itself. Although the relative temperature differences between some of the sequential photographs taken of the inclusions are probably accurate to 0.1°C, the actual temperature may be accurate to only $\pm 5^\circ\text{C}$.

RESULTS

Optical studies

All samples examined contain fluid inclusions of several types and origins (Table 1 and Figs. 2a–f). There was little difference in the appearance of the inclusions from any given sample from either of the two localities except, of course, the obvious lack of large primary inclusions in crushed sample 68-B. The primary inclusions are large, up to several millimeters long, and are randomly distributed through the crystals. Most are faceted negative crystal cavities. The secondary inclusions occur in groups of several hundred individuals outlining slightly curving healed fracture planes. These inclusions also are generally faceted to some degree and elongate parallel to one of the crystallographic axes of the enclosing quartz.

Several features not listed in Table 1 may have compositional significance. Organic liquids in inclusions of types I and IV fluoresce blue under irradiation with either short- or long-wave length ultraviolet light. This fluorescence is readily seen even in very small inclusions as long as the organic layer is more than a few micrometers thick (Fig. 2d), and is useful in distinguishing colorless organic liquids from the much less abundant aqueous solutions (Figs. 2c, d and f). The fluorescence likely results from the presence of aromatic hydrocarbons noted earlier. There is no recognizable phosphorescence.

Most of the organic liquid is completely colorless except for some large globules

Table 1. Inclusion types

Type	Contents	Origin	Sample occurrence
I	Organic liquid, generally colorless but occasionally yellowish, plus a vapor bubble comprising approximately 15–45 per cent by vol. Large inclusions contain one or more blebs of a nearly opaque phase (possibly bitumen) and occasionally other phases (see text).	Primary	All
II	Organic gas, sometimes with a visible film of liquid up to 15 per cent by vol.	Secondary	68-1 68-2 68-B
III	Aqueous solution plus vapor bubble comprising less than 5 per cent by vol.	Primary and Secondary	All
IV	Composite; aqueous solution, organic liquid and gas bubble.	Primary and Secondary	68-2 68-4 68-5 68-A

such as in 68-A (Fig. 2a), which are yellowish brown in transmitted light and exhibit a yellowish fluorescence. The color difference cannot be merely a matter of differences in path length, however, because many of the colorless inclusions from samples 68-1 through 68-5 have organic liquid path lengths almost as long. The color of the organic liquid in sample 68-A is not uniform from inclusion to inclusion, but this variation may be related to the presence of various amounts of aqueous solution. Those inclusions that contain yellow organic liquid have up to several volumes of aqueous solution per volume of organic liquid.

The dark blebs (bitumen?) in the organic liquid apparently formed after the fluid was trapped because they occur in each of the large inclusions and in almost all small inclusions (Fig. 2d). If the blebs formed before trapping, they probably would not be found in almost all inclusions unless the bleb material had been finely dispersed. Similar blebs have been found in many other inclusions of organic liquids (ROEDDER, 1962a; ROEDDER, 1965, Fig. 8). In the present study, a single bleb generally occurs adhering to the quartz wall. Under intense illumination the smaller blebs are dark-red brown and strongly birefringent, with undulatory extinction, as though made of feathery or fibrous crystals. In sample 68-A, some of the large inclusions have numerous separate birefringent dark blebs, although the largest blebs are opaque (Fig. 2a). Some of the small blebs apparently are spherical with sectorial extinction indicating internal structure. A few, small, isolated, colorless, strongly birefringent crystals of unknown composition are also present in many of the organic inclusions.

High molecular weight components

Results of our analyses confirm and extend what was first discovered at the Mobil Oil Corporation and provide a sound basis for the identification of n-alkanes from n-C₁₀ to n-C₃₀ and for isoprenoid hydrocarbons from C₁₁ to C₂₀. Figure 3 is a typical chromatogram showing the principal constituents in the hexane extract from quartz crystals of the Geiaus farm locality.

Gas chromatography on three columns having different liquid phases increased the confidence of peak assignments. Co-chromatography of standards along with the sample was also used to support the identity of the major constituents in this extract. An example of the co-chromatographic technique is illustrated in the insert in Fig. 3 where the peak assigned to 2,6,10-trimethyltetradecane is enhanced by the presence of the standard. Similar co-chromatography supported identifications of phytane, pristane, 2,6,10-trimethylpentadecane and farnesane.

Mass spectra of the compounds in sample 68-6, assigned to n-alkanes by gas chromatography, have fragmentation patterns typical of these molecules (BURLINGAME and SCHNOES, 1969). Mass spectra for seven isoprenoid hydrocarbons, C₁₄ through C₂₀, obtained from the fluids of inclusions of the same sample closely match mass spectra of standards available here and also published spectra (see EGLINGTON *et al.* (1966) for phytane, pristane and farnesane, and MCCARTHY and CALVIN (1967) for 2,6,10-trimethyltetradecane). Published mass spectra of standard, regular isoprenoids C₁₁, C₁₂, C₁₃, C₁₄ and C₁₆, apparently are not available. For the C₁₁, C₁₄ and C₁₆ isoprenoids, the mass spectra of the compounds from the sample match spectra obtained from various geological samples and assigned

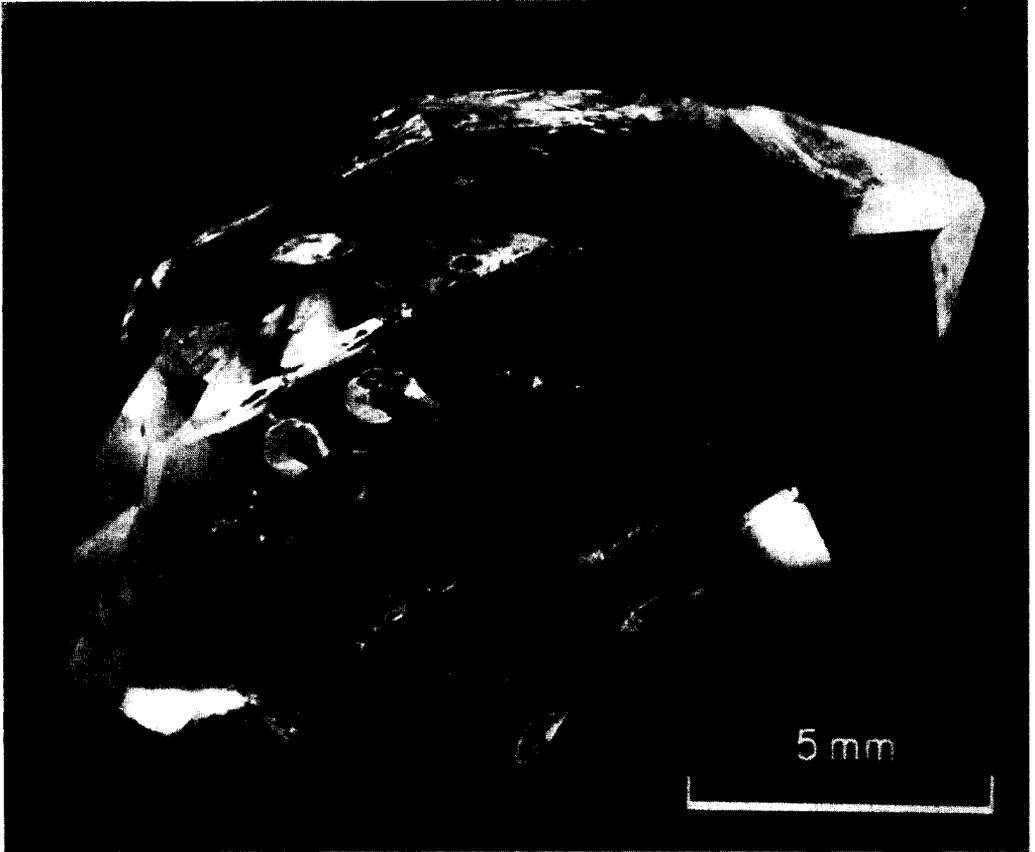


Fig. 1. Photograph of sample 68-A showing faceted primary inclusions.

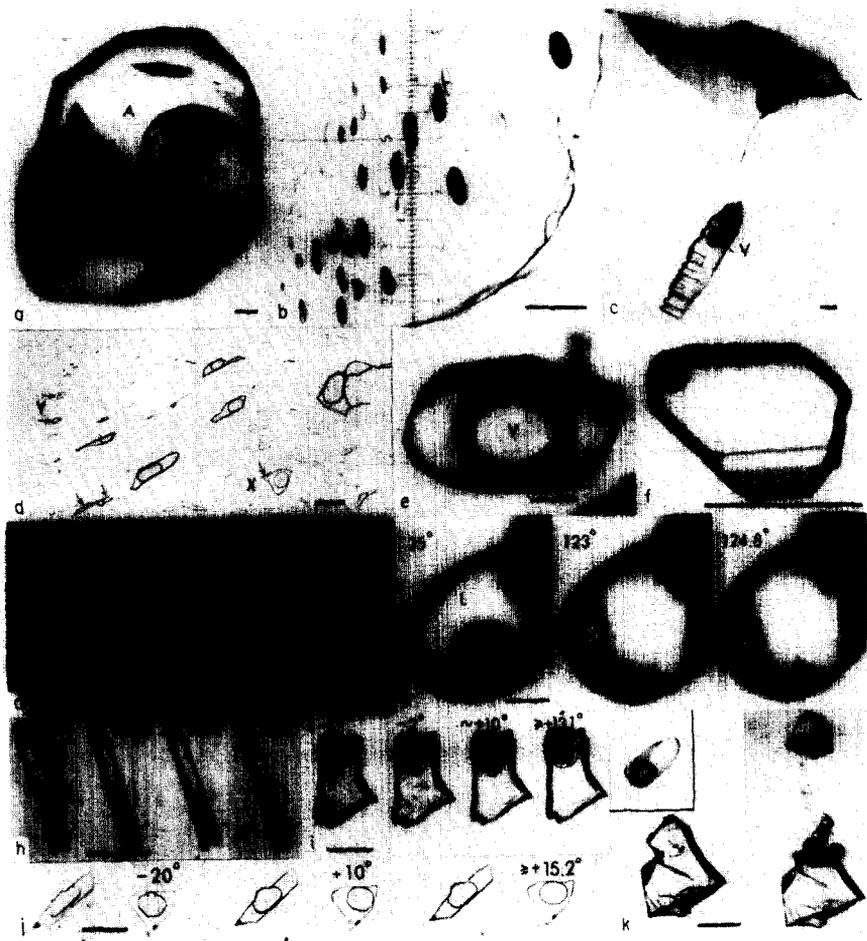


Fig. 2

Fig. 2. In each photograph, the black bar represents 100 μm . All photographs were taken in ordinary transmitted light except 2d.

(a) Large composite (type IV) primary inclusion in sample 68-A. Organic liquid globule (O) is yellow in transmitted light, and contains many blebs of dark-red to opaque bitumen (?). The aqueous solution (A) is colorless. Note the relatively small size of the vapor bubble (V), discussed in the text.

(b) Organic gas inclusions (type II) in a fragment of sample 68-B. The transparent inclusions are open to the surface and hence filled with the mounting oil, but in this lighting, the unopened ones exhibit total reflection and are black.

(c) Large primary aqueous inclusions (type III) in sample 68-5, each with a vapor bubble (V) and a mass of opaque black material, presumably bitumen (?). This bitumen (?) may have precipitated from a coexisting organic liquid phase that has since been eliminated through recrystallization and necking down of the inclusions.

(d) Plane of flat secondary organic liquid inclusions in sample 68-5, in transmitted white light (above) and incident short-wave ultraviolet light (below). The water solution (arrows) in composite type IV inclusions (as at X) and in simple type III aqueous inclusions (as at Y) does not fluoresce.

(e) Primary organic liquid inclusion, showing some negative crystal facets and containing opaque bleb of bitumen (?) and large vapor bubble (V). Sample 68-3.

(f) Faceted primary aqueous inclusion, with small vapor bubble, in sample 68-A.

(g) Sequential photomicrographs of faceted, negative crystal, primary inclusion in sample 68-5, containing large vapor bubble (V) taken at the temperatures indicated, showing the large thermal coefficient of expansion of the included organic liquid (L). Homogenization of the tiny bubble (arrow) occurred after an immeasurable rise above 124.8°C.

(h) Sequential photomicrographs of faceted, negative crystal, secondary inclusion in sample 68-3, containing large vapor bubble (V) in organic liquid (L) taken at the temperatures (°C) indicated. The average (filling) density is about the critical density, resulting in homogenization by fading of the meniscus at the critical temperature of 150.3°C, and subsequent violent "boiling" to form two phases on cooling to 150.2°.

(i) Sequential photomicrographs of composite type IV inclusion in sample 68-5, taken at approximately the temperatures indicated. At $< -23^\circ\text{C}$ the vapor bubble (V) is small and misshapen, and the aqueous solution (A) is a fine-grained, dark, solid mass. At about -2°C only a few ice crystals remain in the aqueous solution (arrows), but the organic material is still largely solid, causing distortion of the bubble. At $\sim +10^\circ\text{C}$ the organic material has started to melt and coalesce, and by $> +13.1^\circ\text{C}$ it is all melted.

(j) Photomicrographs of area X from Fig. 2d viewed from opposite side of plate, on the freezing stage, showing the distortion of the vapor bubble by invisible crystals formed in the organic liquid at low temperatures. This distortion disappears suddenly on heating to $+15.2^\circ\text{C}$.

(k) Fragment of quartz from sample 68-B, mounted in oil on the crushing stage, before squeezing (left) and after (right). On crushing, the contents of the tiny organic liquid inclusion (see arrow and enlarged inset photograph) has expanded several hundred fold in volume to form the two vapor bubbles.

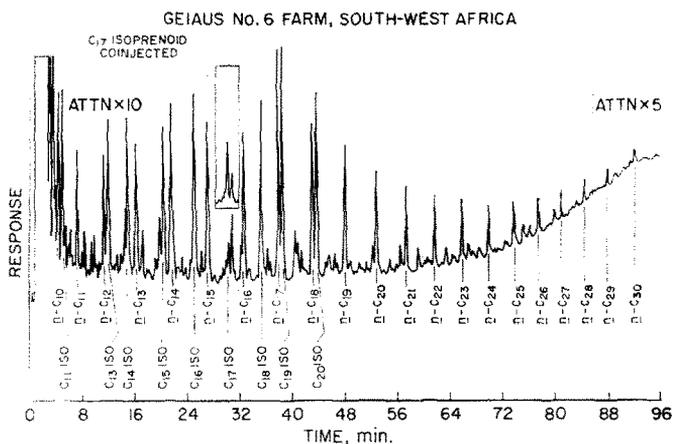


Fig. 3. Gas chromatogram of hydrocarbons extracted from inclusions in sample 68-6. Chromatography: Perkin-Elmer 881; OV-1 support coated open tubular column 100 ft \times 0.02 in.; temperature program 80°–250°C at 2°C/min.

isoprenoid structures based on predicted fragmentation patterns and not on mass spectra of standards. (See GOHRING *et al.* (1967) for C_{11} ; HAN and CALVIN (1969) for C_{14} and EGLINTON *et al.* (1966) and JOHNS *et al.* (1966) for C_{16} .) Table 2 compares partial mass spectra for isoprenoid hydrocarbons from the quartz crystals with spectra from synthetic standards and with published spectra. A C_{13} isoprenoid hydrocarbon is present in the quartz sample (Fig. 3), but its mass spectrum does not show the predicted fragmentation pattern for the regular isoprenoid 2,6-dimethylundecane nor does the spectrum match that published for 2,6-dimethylundecane reported in an oil shale by GOHRING *et al.* (1967). The principal difference lies in the fact that the published spectrum lacks a prominent m/e 141 peak. There is no prominent C_{12} isoprenoid (Fig. 3). Some mass spectra obtained for compounds

Table 2. Partial mass spectra for isoprenoid hydrocarbons—Relative peak intensity*

m/e	C_{20} S	C_{20} F	C_{19} S	C_{19} F	C_{18} S	C_{18} F	C_{17} S	C_{17} F	C_{16} P†	C_{16} F	C_{15} S	C_{15} F	C_{14} P†	C_{14} F	C_{13} P‡	C_{13} F	C_{11} P‡	C_{11} F
99	70	90	80	84	100	>100	>100	>100	67	76	78	70	47	24	50	<100	10	9
113	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
127	90	90	60	50	40	40	41	47	30	35	100	100	25	14	25	12	10	4
141	34	32	22	23	22	28	25	28	80	94	32	20	10	4	15	40	10	8
155	24	20	18	22	14	20	53	65	16	16	27	10	12	10	15	11	—	—
169	16	16	10	8	50	50	11	12	9	10	12	8	8	3	25	16	—	—
183	38	40	60	50	31	25	34	39	33	34	35	30	16	7	—	—	—	—
197	32	28	2	4	3	5	7	7	8	8	14	10	—	—	—	—	—	—
211	2	2	2	2	4	10	5	6	8	12	—	—	—	—	—	—	—	—
225	3	4	3	2	5	5	9	9	—	—	—	—	—	—	—	—	—	—
239	2	2	2	2	6	10	—	—	—	—	—	—	—	—	—	—	—	—
253	6	6	3	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—
267	5	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
281	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

* For series C_nH_{2n+1} peaks relative to m/e 113.

S = synthetic; P = published, F = found in quartz crystal sample 68-6.

† (JOHNS *et al.*, 1966, p. 1208) approximate values.

‡ (HAN and CALVIN, 1969, p. 736) approximate values.

§ (GOHRING *et al.*, 1967, p. 504) very approximate values based on measurements of published spectra of extremely reduced size.

producing chromatographic peaks between the C_{11} and C_{13} isoprenoids suggest that C_{12} isoprenoid structures are present, but they are in low concentration, and none of the spectra resemble that published for 2,6-dimethyldecane from oil shale (GOHRING *et al.*, 1967).

Because of agreement of mass spectra and the results from co-chromatography of standards with the sample extract the C_{20} , C_{19} , C_{18} , C_{17} and C_{15} isoprenoid hydrocarbons from the quartz crystals are assigned the following structures, respectively: phytane (2,6,10,14-tetramethylhexadecane); pristane (2,6,10,14-tetramethylpentadecane); 2,6,10-trimethylpentadecane; 2,6,10-trimethyltetradecane; and farnesane (2,6,10-trimethyldodecane). Because standards were not available for the C_{16} , C_{14} and C_{11} isoprenoid hydrocarbons, these compounds are

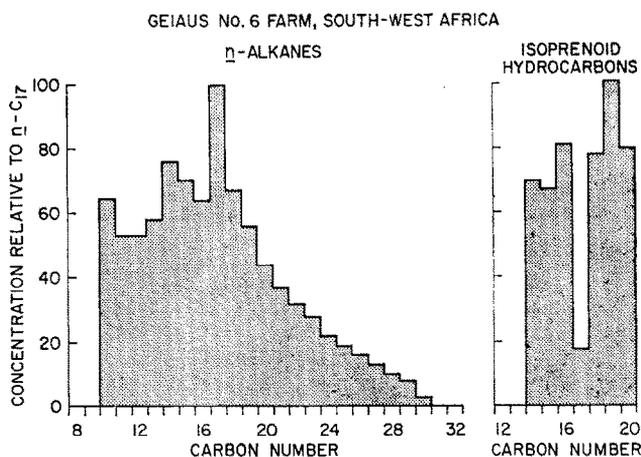


Fig. 4. Distribution of n-alkanes and isoprenoid hydrocarbons from inclusions in sample 68-6.

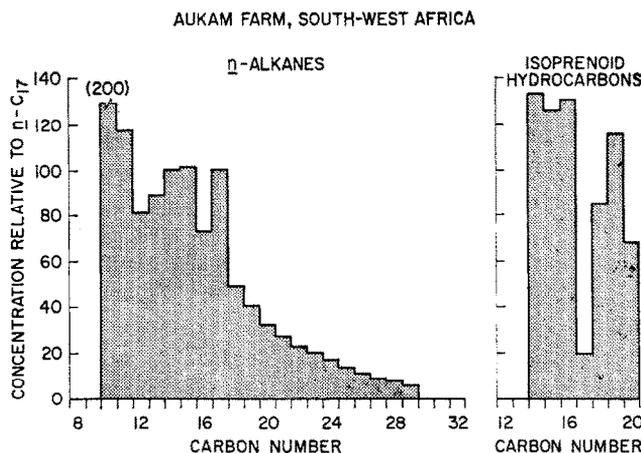


Fig. 5. Distribution of n-alkanes and isoprenoid hydrocarbons from inclusions in sample 68-B.

tentatively identified as 2,6,10-trimethyltridecane, 2,6,10-trimethylundecane and 2,6-dimethylnonane.

The distribution of n-alkanes and isoprenoid hydrocarbons in quartz crystals from each locality can be approximated from the gas chromatograms of the extracts. Figures 4 and 5 were constructed by measuring chromatographic peak heights and normalizing the distribution to n-C₁₇ alkane. Such a procedure, however, is qualitative at best. The mixtures of hydrocarbons from Aukam (68-B) and Geiaus (68-6) are remarkably similar in distributional pattern. Notable for both samples is that the isoprenoid hydrocarbons, except C₁₇, are very abundant. The occurrence of the C₁₇ isoprenoid is not common and has been reported before in Antrim shale (McCARTHY and CALVIN, 1967) and in Bell Creek crude oil (HAN and CALVIN, 1969). In both of these reports the C₁₇ isoprenoid is much less abundant than the other isoprenoid hydrocarbons.

The concentration of hydrocarbons can only be roughly estimated. In preparing the extracts, the hexane solutions were never evaporated to dryness in order to conserve constituents of low volatility. Consequently, no gravimetric measurements were made. The concentration of n-C₁₇, as determined from the chromatograms of samples and from chromatograms of standards at known concentrations, is about 1.5 µg per g of crushed quartz for both samples 68-6 and 68-B.

Table 3. Carbon isotopic composition of organic material from sample 68-6

Description	$\delta C_{PDB}^{13} (\text{‰})$
Total carbon—in pulverized quartz before extraction	-20.0
Total carbon—in pulverized quartz remaining after extraction	-21.7
Carbon—in benzene-methanol extract (two determinations)	-19.8 -20.1

In these chromatographic studies the smallest n-alkane identified was n-C₁₀ and the smallest isoprenoid C₁₁. That smaller compounds were not found can be attributed to the method and not to the samples. In fact, examination of the chromatogram (Fig. 3) indicates that lower molecular weight compounds are present. One attempt to determine these compounds failed and analysis of the molecular weight range from C₅ to C₁₀ is being deferred until additional samples of quartz crystals can be obtained.

Absorption spectrometry (Cary Model 14, 0-0.1 absorbance) of the extract prepared for porphyrin analysis showed no distinct features which could be related to porphyrins in the region from 380 to 700 nm. Spectrofluorometry (Turner Model 210), in which fluorescence is detected on incremental demetallation of the sample with methanesulfonic acid (HODGSON *et al.*, 1969), also failed to indicate the presence of porphyrins. Based on these results, the concentration of porphyrins, if present in the sample, must be less than 2×10^{-5} µg/g.

The results of carbon isotopic determinations are summarized in Table 3. Here δC^{13} values of total carbon and extractable carbon are remarkably similar, with an average value of about -20‰.

Low molecular weight components

The compounds removed from the quartz by crushing in a glass ball mill under vacuum were examined by high resolution mass spectrometry and by gas chromatography. Of the 7 g of sample 68-6 placed in the mill only about 5 g were pulverized to less than 1 mm during the 20-hr milling period. The pressure of the evolved gases as measured in the 250 ml inlet system of the mass spectrometer was about 0.5 mm. By high resolution mass spectrometry, CO was resolved from N₂ and CO₂ from C₃H₈. Also identified in the spectra were H₂O, CH₄ and C₂H₆. Gas chromatography (flame ionization detection) confirmed the presence of CH₄, C₂H₆, C₃H₈ and possibly C₄H₁₀. Table 4 lists the minimum concentrations of low molecular weight components evolved with this technique.

In an independent experiment using a bakeable crushing chamber attached to a mass spectrometer several gases were evolved from another portion of sample 68-6. The absence of adequate calibration spectra made identification of constituents qualitative at best, but CH₄, CO, N₂, CO₂ and H₂ appeared to be the major gaseous products. C₂H₆, C₃H₈ and C₄H₁₀ were not evident and only traces of heavier hydrocarbons were detected.

Table 4. Minimum concentration ($\mu\text{g/g}$ of quartz)
low mol. wt. components from sample 68-6

Hydrocarbons		
Methane	CH ₄	8 $\mu\text{g/g}$
Ethane	C ₂ H ₆	2
Propane	C ₃ H ₈	1.5
Butane	C ₄ H ₁₀	?
Others		
Carbon dioxide	CO ₂	4.1
Carbon monoxide	CO	3.6
Water	H ₂ O	?

When quartz grains from several samples were crushed on the microscope crushing stage, large quantities of gases were evolved indicating a several hundred fold volume expansion (Fig. 2k). This experiment suggested that a considerable portion of the organic liquid was composed of volatile compounds that were liquefied by the pressure within the inclusion. The evolved gases were readily soluble in kerosene, a result that would be expected for a mixture composed dominantly of alkanes. Several grains from crushed sample 68-B that still contained small inclusions of organic liquids behaved similarly. One grain was found in this sample that contained dozens of oval inclusions seemingly filled only with gas (Fig. 2b). When this grain was crushed, the pressure in the inclusions was found to be near atmospheric.

Freezing studies

Aqueous solutions. Freezing studies permitted the determination of salt concentrations in the aqueous solutions. When samples 68-1 through 68-5 were frozen at -78.5°C (to avoid problems from supercooling), the aqueous fluids in inclusions of types III and IV froze to a brownish mass and the vapor bubbles became smaller (type IV) or were eliminated completely by expansion on formation

of ice (type III). On gradual warming, the first melting temperature (that at which enough liquid phase forms to wet the ice and salt crystal interfaces, making the mass translucent) was found to range from -28.5 to -20.8°C (Fig. 2i). The freezing temperature (that at which the last ice crystal melts on warming, and at which ice should form on cooling, if equilibrium could be maintained) for five small secondary inclusions in 68-5 was found to be -2.1 , -1.9 , -1.9 , -1.9 and -1.5°C . This corresponds to concentrations of salts in solution of 23,000–35,000 ppm (0.4–0.6 M NaCl equivalent). Five very large primary inclusions in this same sample (Fig. 2c) yielded freezing temperatures of $-0.2(1)$, $-0.1(2)$ and $0.0^{\circ}\text{C}(2)$, corresponding to 0–4000 ppm of salts in solution.

Organic liquids. Organic liquid inclusions exhibited a different behavior from aqueous solutions on freezing. After the temperature was held at -196°C for 30 min, the "liquid" appeared clear and transparent, but the vapor bubbles were deformed, as though invisible crystals were present (Fig. 2j). Additional small and large immobile, deformed vapor bubbles were present in the "liquid," presumably from shrinkage on crystallization, and many inclusions contained small, indistinct, apparently isotropic crystals, visible by their slightly greenish tint (presumably from slight differences in index of refraction). Freezing at -78.5°C for 1/2–2 hr produced similar results, but more greenish crystals and very few extra bubbles. On slow warming no visible changes occurred to about -36°C , at which temperature some of the new, extra bubbles in one inclusion disappeared. Little else changed to about -15°C , above which the greenish crystals seemed to grow in size (as evidenced by greater bubble deformation) but became even fainter in outline, presumably from a closer match in index of refraction between the crystals and the liquid. At about -9°C , the bulk of the mass began to melt visibly, as evidenced by the shrinking, rounding and coalescence of most of the bubbles, and by $+13$ to $+16^{\circ}\text{C}$, most of the crystals had melted. Small amounts of very faint crystals seem to persist to room temperature in those larger inclusions that permitted good viewing. The last of these melted on heating to about $+35^{\circ}\text{C}$. Many of the inclusions contained two bubbles at room temperature after freezing, but maintained the same apparent total gas/liquid ratio. Freezing had no visible effect on the dark blebs of bitumen(?).

Composite inclusions (type IV) exhibited the same phenomena as described above, for the organic and the aqueous phases, and in addition, plainly visible globules of organic liquid seemed to form spontaneously from faintly visible masses in the water phase and coalesce with the main mass of organic liquid, on warming to about $+9^{\circ}\text{C}$. From this behavior, it is presumed that clathrate compounds such as $\text{C}_2\text{H}_6 \cdot 5\frac{3}{4}\text{H}_2\text{O}$ (PAULING, 1961; JEFFREY and MAK, 1965) may have formed during freezing, and were melting to two immiscible fluids on warming.

Heating studies

Aqueous inclusions. Relatively few aqueous inclusions (type III and IV) were examined, all from samples 68-3 and 68-5. One plane of 10 small, flat secondary aqueous inclusions in sample 68-3, with very tiny bubbles, homogenized (lost the vapor phase) at about 70°C , and one other aqueous inclusion in this sample homogenized at 124°C . One group of six type III inclusions in sample 68-5

homogenized at 104°, 109°(2), 121°, 129° and 131°C, and another group of 73, in the plane shown in Fig. 2d, all homogenized in the range 155°–160°C. Two composite (type IV) inclusions in 68-5 homogenized partially at 124° and 147°C. All of these homogenized in the liquid phase, i.e. by elimination of the vapor bubbles. The distribution of inclusions was inadequate to detect variation in temperature with growth zoning of the quartz, if such variation occurred.

Organic inclusions. The plane of secondary inclusions shown in Fig. 2d contained approximately 300 type I organic inclusions interspersed with the 73 aqueous inclusions mentioned above. Although the aqueous inclusions homogenized in the range 155°–160°C, the organic inclusions, including some with small amounts of water (type IV), all lost their vapor phase in the narrow range 124°–133°C, with most at about 127°C. There was no visible change in the "bitumen" blebs on heating, and they were still strongly birefringent at 157°C. Two large primary organic inclusions in this same sample homogenized at 124·8° (Fig. 2g) and 130·5°C. A single large primary inclusion in sample 68-1 homogenized at 142°C and a plane of about 11 secondary organic inclusions in 68-3 (Fig. 2h) all homogenized within a few degrees of 150°C.

Most of the organic inclusions homogenized in the liquid phase (i.e. expansion of the liquid phase eliminated the vapor bubble, see Fig. 2g). However, the coefficient of expansion of this liquid (assuming a vapor density of zero) was rather large, approximately four times that of water in this range, and became increasingly larger as the temperature of homogenization was approached, as indicated by the rapid decrease in the bubble size. This behavior is characteristic of inclusions filled with fluid of a density not much greater than its critical density. It is thus not surprising that some inclusions happened to have the critical density of filling, and hence homogenized by a fading of the meniscus at the critical point. A plane of about 100 secondary inclusions in sample 68-3 homogenized uniformly in this manner, as shown in serial photographs of one of them (Fig. 2h). This section was heated slowly to 195°C, cooled and the homogenization temperature redetermined. There was no recognizable change.

The large coefficient of expansion of the organic fluid resulted in an interesting and useful change in the relative indices of refraction of the organic liquid and the aqueous solution. If the salt present was NaCl, the index of the aqueous solution in the inclusion shown in Fig. 2i could be estimated to be 1·3366 at 18°C. At this temperature, the organic liquid had an index well above that of the water, yielding the contrast that is obvious in Fig. 2i obtained at room temperature ("> +13·1°"). On heating this inclusion, however, the interface between the two liquids became fainter and finally disappeared at 107°C, and reappeared at 109°C, with the organic liquid now lower in index than the water solution. Similar organic/water interfaces in other inclusions also disappeared at specific but different temperatures, indicating differences in compositions of the phases involved. Thus another secondary type IV inclusion (X in Fig. 2d), which lay in the same plane with that shown in Fig. 2i, had this crossover point at 65°C. The aqueous solution in these inclusions seemed to be uniform in freezing temperature, so the variation in composition was probably in the organic liquid. This test for compositional uniformity is sensitive. Some small beads of organic liquid in the inclusion shown

in Fig. 2i had become embedded in the aqueous solution during a freezing run and hence were separated from the main mass. These matched the surrounding aqueous solution in index of refraction about 2°C lower than the main mass. The compositional difference here was probably caused by the presence of the vapor bubble in the main mass of organic liquid, permitting continuous reequilibration of liquid with vapor during temperature change, whereas the little droplets could only reequilibrate by diffusion through the surrounding water.

It is probable that primary inclusions from the Aukam locality would have lower homogenization temperatures than those from Geiaus. This is suggested by the apparent low ratio of vapor/organic liquid plus water in sample 68A. Thus the inclusion shown in Fig. 2a had a lower vapor/organic liquid ratio than those shown in Figs. 2e and 2g, yet this vapor bubble represents shrinkage, on cooling, of both the organic liquid and a much larger volume of water solution.

ORIGIN OF THE ORGANIC FLUIDS

Two opposite opinions have been offered already for the origin of the organic substances in these quartz crystals. MARTIN (1965) suggested that some of the components may be derived from chlorophyll and thus implied a biological origin. MUELLER (1970), on the other hand, thought there was a strong probability that the organic fluids in the quartz crystals he examined are abiogenic magmatic condensates. Our detailed analyses of the composition of the hydrocarbons present in quartz from Geiaus and Aukam farms have shown that the fluid is composed mainly of two classes of compounds, n-alkanes and isoprenoid hydrocarbons, and is very similar to alkane fractions of crude oils. [For examples of gas chromatograms of alkane fractions see JOHNS *et al.* (1966); VAN HOEVEN *et al.* (1966); HAN and CALVIN (1969).] Not only are the kinds of molecules present in the quartz reminiscent of petroleum but also the distribution of molecules is like that in crude oil. The regular decrease in concentrations of n-alkanes with increasing carbon number is commonly found in petroleums. Where a series of isoprenoids has been reported in petroleum and other geochemical samples [BENDORAITIS *et al.*, 1963; CUMMINS and ROBINSON, 1964; JOHNS *et al.*, 1966; VAN HOEVEN *et al.*, 1966; HAN and CALVIN, 1969] the C₁₇ isoprenoid is either absent or in much lower concentration than C₁₆ and C₁₈ isoprenoids. Again the same type of distribution is found for the isoprenoids of the quartz crystals. It should be emphasized that comparisons being made here are between a fraction of petroleum in which alkanes have been concentrated by removing other kinds of molecules and the total extract from the quartz crystals. Indeed, the mixture in the quartz crystals, although complex, is more simple than the mixtures generally called petroleum. The alkane constituents of petroleum, particularly the isoprenoid hydrocarbons, are generally considered to be of biological origin. If these are of biological origin, it follows that the quartz crystal alkanes which are similar in kind and distribution to those in petroleum, are very likely also of biological origin. A mixture formed by abiological processes would be expected to have a distributional pattern different from what was found. If, for example, the isoprenoids resulted from polymerization and hydrogenation of isoprene, the dominant products likely would be the C₁₀, C₁₅

and C₂₀ isoprenoids as suggested by the work of MUNDAY *et al.* (1969). Polymerization-hydrogenation reactions also would likely produce a complex association of multibranched and cyclic saturated molecules possibly in thermodynamic equilibrium.

If the isoprenoids were ultimately derived from biological precursors, then a number of precursors can be suggested such as carotenoid pigments, lycopene, squalene or phytol (BENDORAITIS *et al.*, 1963). Assuming phytol as a precursor, all the isoprenoids found in the quartz crystals can be accounted for by the application of the scheme of MCCARTHY and CALVIN (1967). In this scheme phytol is reduced to phytane. The subsequent formation of all isoprenoids requires one cleavage except for C₁₇ and C₁₂ both of which require two cleavage points. This is considered inherently less probable. The low concentration of C₁₇ and apparently missing C₁₂ could be accounted for in this manner. In this scheme cleavage takes place relative to the end of the phytane molecule which originally possessed the hydroxyl group of phytol. Although this scheme generally satisfies the observed distribution of isoprenoids in geological samples, it has a weakness in that cleavage could equally likely take place relative to the other end of individual C₂₀ molecules producing a second series of isoprenoids having structures different from the ones found. Unless some reason is found which explains cleavage from only one end of the phytol (phytane) molecule, this scheme does not provide a sufficient explanation for what is observed in nature.

Another scheme is suggested based on the hypothesis proposed by COOPER (1962) and COOPER and BRAY (1963). In order to account for the distribution of n-alkanes and n-alkanoic acids in sediments, a free-radical, decarboxylation scheme was proposed. These same ideas can be extended to the isoprenoid hydrocarbons. Consider that a portion of the phytol is reduced to account for phytane (C₂₀). The remaining phytol is oxidized to phytanic acid which undergoes decarboxylation to form a highly reactive free-radical intermediate, usually a primary free-radical. This free radical can react by hydrogen abstraction to form an alkane or it can react with an oxidizing agent ultimately forming the carboxylic acid with one less carbon atom than the original acid. When decarboxylation yields a secondary free radical, a ketone rather than an acid is produced by oxidation. The ketone can cleave to form either of two acids with two or three fewer carbon atoms than the original acid. The newly formed acid or acids undergo the same reactions as the original one. Consequently, a series of alkanes and alkanolic acids result from the single precursor. The sources of energy for this postulated free-radical decarboxylation are not known, however. The scheme accounts for all isoprenoid hydrocarbons except C₁₇ and C₁₂. The C₁₇ isoprenoid was found, however in the quartz crystals, but in low concentration relative to the other isoprenoids and C₁₂ isoprenoid could not be identified with certainty.

Neither of the two schemes is totally satisfying, but it appears that, if phytol is the precursor for isoprenoid hydrocarbons, the degradation of this molecule must take place through reactions at the hydroxyl end of the molecule. Whether or not phytol came from chlorophyll is not answered by this work. Although no evidence was found for porphyrins, which would be likely degradation products of the porphyrin ring structure of chlorophyll, they may have been removed or destroyed.

Carbon isotopic studies have not helped to resolve the problem of the origin of the hydrocarbons in these crystals. The isotopic composition of the carbon in the fluids is $\delta C^{13} = -20.0\text{‰}$. This composition falls between the values generally found for organic deposits (values more negative than about -25‰) and the values of inorganic materials (values more positive than about -15‰). The value of -20‰ is in the range usually associated with the organic carbon of living organisms (DEGENS 1969).

The time at which the hydrocarbon fluids were entrapped in the quartz crystals cannot be ascertained. The host rock is Precambrian and probably more than 2.6×10^9 yr old. If the hydrocarbons were transported from below by hydrothermal activity the precursors of the present hydrocarbons may be Precambrian in age, but the trapping could have occurred any time from late Precambrian to at least Jurassic if the veins containing the quartz indeed formed during post-Nama and/or post-Karoo faulting. The hydrocarbon-bearing fluids may have come, via deep circulation, from rocks younger than the Kheis system host rocks. Mixing with other hydrothermal waters in the vein is also not precluded.

MECHANISM OF TRAPPING OF THE INCLUSIONS

The mechanism by which either primary or secondary inclusions of organic liquids could become trapped in minerals such as quartz has always been a problem. If the quartz grew (or recrystallized) from the organic fluid, there would be no difficulty in such trapping, but the solubility of quartz in such fluids is presumably too low. It is generally assumed that the organic fluids found in primary inclusions occurred as immiscible droplets in a water solution, from which the quartz actually grew, and were trapped by accidental enclosure within a water inclusion. This process is most evident in large composite inclusions, such as Fig. 2a. There are many large primary inclusions in these samples, however, that appear to contain only organic fluids (Fig. 2e). Apparently these formed when a droplet of the organic fluid came in contact with the surface of the growing quartz crystal, precluding further growth at that point. Further growth of the rest of the crystal continued, surrounding and finally enclosing it without enclosing any water. There are numerous examples of similar trapping of globules of an inert, extraneous fluid, without any of the nutrient fluid, during the growth of crystals, e.g. exsolved air bubbles in sucrose crystals growing from a water solution (ROEDDER, 1965, Fig. 20).

This process, however, seems unlikely for groups of hundreds of secondary inclusions of organic fluid, as are common in these samples (Fig. 2d), because it is difficult to visualize a process whereby the healing of a deep, thin fracture via an aqueous fluid could trap only the associated organic globules. Careful examination of such planes of secondary inclusions with both ultraviolet fluorescence (Fig. 2d) and the freezing stage revealed, however, that many of them do indeed contain some water, lining the walls of the cavities, that is not always visible with ordinary microscopy. Presumably on opening the fracture filled with water containing globules of an immiscible organic phase, and healing via the water phase took place sufficiently slowly, and from the bottom of the crack outwards, so that very little water was trapped. The organic inclusions were sealed in wherever the organic fluid contacted the quartz walls and prevented further growth. Further evidence

for this mechanism was found in the healed fracture shown in Fig. 2d. The thin, wedged-out end of this crack, at the left side (Y), is marked by a series of tiny inclusions, all of which contain only water (note small bubbles and lack of fluorescence in Fig. 2d).

TEMPERATURE AND PRESSURE OF FORMATION (TRAPPING) OF THE INCLUSIONS

In ordinary inclusions, the temperature of homogenization represents a minimum temperature of trapping, and the difference between the temperatures of homogenization and trapping (the "pressure correction") is a function of the pressure on the system at the time of trapping. If that pressure is about equal to the vapor pressure of the fluid (i.e. the system was near to "boiling") the pressure correction is zero, and the homogenization temperature is the trapping temperature. This holds true regardless of the compositions of the fluid and vapor involved. If the pressure on the system is higher than the vapor pressure, the fluid is compressed to some degree, and hence when it is sealed into the crystal with this higher density, the inclusion must be cooled the amount of the pressure correction before a vapor bubble can form. The more compressible the hot fluid, the larger the pressure correction for a given pressure in excess of the vapor pressure. The compressibility of most organic fluids is about twice that of pure water, and most salts in solution decrease the compressibility of an aqueous phase still further. It should be noted, however, that in organic inclusions some molecular species may have changed since trapping. The magnitude and even the direction of the effects of such changes on homogenization temperatures are unknown.

In addition to differences stemming from the composition of the two fluids, the compressibility of any fluid increases rapidly with decrease in its density. This compressibility increase becomes particularly rapid in the vicinity of the critical density, and as the homogenization determinations show that the organic inclusions have degrees of filling near to or at the critical density for such fluids, the compressibility of these fluids, after homogenization, can be assumed to be very high. The resultant large difference in pressure correction is believed to be the main cause for the systematic and very appreciable (30°C) difference between the homogenization temperatures for aqueous and organic inclusions in the same healed fracture. The aqueous inclusions have relatively small pressure corrections, and hence homogenize at higher temperatures, nearer to the trapping temperature.

In theory it should be possible to calculate both pressure and temperature from these homogenization temperatures, but this calculation requires also a knowledge of the density, thermal expansion, and compressibility of both phases. Such data are available for the aqueous phase, but as the organic fluid is a mixture of many components, on most of which such data are unavailable, all that can be stated is that the pressure of trapping was in excess of the vapor pressure of either phase. The vapor pressure of pure water at 150°C is only 3.5 atm (the small amounts of salts would have little effect), but there are several indications that the vapor pressure of the organic fluid was probably much greater. First, the explosive and large volume expansion to form gas bubbles on crushing the inclusions at one atmosphere and room temperature indicates considerable pressure in the

inclusions, which must necessarily have been much higher at the temperature of trapping. The magnitude of pressure changes from internal degradation since trapping (ROEDDER, 1967, 1970), resulting in the formation of bitumen(?) blebs, is unknown but presumably small.

The evidence of near-critical to critical behavior for this organic fluid also permits a very rough estimate of the minimum pressure. Data are available on the critical constants for various pure n-alkane compounds (ROSSINI *et al.*, 1953). Pure n-butane (C_4H_{10}) has a critical temperature (C_T) of $152.01^\circ C$, at a critical pressure (C_p) of 37.47 atm, and the higher paraffins have much higher critical temperatures. Thus n-decane, the lightest alkane actually identified in the mixture by gas chromatography, has a critical temperature of $346^\circ C$. Mixtures of several alkanes probably exert little interaction and hence have critical constants intermediate between those of the pure components. Thus methane ($C_T - 82.5^\circ C$; C_p 45.8 atm) and ethane ($C_T + 32.27^\circ C$; C_p 48.20 atm) added to the n- C_{10} and higher alkanes could yield mixtures with critical constants similar to n-butane and to the inclusion fluids. Such mixtures have been proposed for similar inclusions in quartz crystals in dolomite from the Herkimer, N.Y., area, which exhibited critical behavior at -5.55° and $-7.85^\circ C$ (ROEDDER, 1963, p. 201). As the organic inclusions in the present samples were trapped as an homogeneous fluid (all inclusions now have the same gas/liquid ratio) the pressure at the time must have been $\geq C_p$ for the mixture, and hence ≥ 30 –40 atm. If the pressure were hydrostatic, this requires trapping at a minimum depth of 300–400 m to satisfy the data on the organic fluid inclusions alone. The actual depth must have been greater than this, to account for the 30° difference in homogenization temperatures of organic and aqueous inclusions, and the unknown but probably small additional pressure correction to be applied to the aqueous inclusions. The secondary, low-density gas inclusions (type II) presumably formed at a later stage, at near-surface conditions.

The large differences between the homogenization temperatures for different planes or groups of inclusions in the same or different samples is attributed to real differences in conditions at the various times of trapping. These differences are most apparent in the occurrence of some planes of secondary aqueous inclusions with homogenization temperatures as low as $70^\circ C$, and are also evident from the obvious variations in the compositions of both the organic and aqueous fluids which were trapped.

SUMMARY

1. Primary and secondary inclusions in quartz crystals from two localities in South-West Africa (Geiaus No. 6 and Aukam farms) are filled with one or a variable combination of organic liquid, moderately saline aqueous liquid, dark-colored solid, and vapor.

2. High molecular weight components present consist of n-alkanes from at least n- C_{10} to n- C_{33} and a series of isoprenoid hydrocarbons. The following isoprenoid compounds were identified by gas chromatographic and mass spectral techniques: phytane, pristane, 2,6,10-trimethylpentadecane, 2,6,10-trimethyltetradecane and farnesane. Isoprenoid compounds tentatively identified were 2,6,10-trimethyltridecane, 2,6,10-trimethylundecane and 2,6-dimethylnonane. The distribution of

n-alkanes and isoprenoid hydrocarbons in quartz crystals from both localities were quite similar and resemble alkane fractions from some petroleum. If petroleum alkanes are biological in origin, quartz crystal alkanes which are similar in kind and distribution to them, are also probably of biological origin. Isotopic abundances of carbon in the quartz crystals of $\delta^{13}\text{C} \cong -20\text{‰}$ do not deny a biological origin for the carbon.

3. The precursor for the isoprenoid hydrocarbons may have been phytol. Whether phytol came from chlorophyll could not be ascertained because porphyrins, thought to be likely degradation products from chlorophyll, could not be detected. The isoprenoid hydrocarbons may also be primary biological products.

4. Low molecular weight components in the inclusions include: CH_4 , C_2H_6 , C_3H_8 and possibly C_4H_{10} ; CO , CO_2 , N_2 , H_2 and H_2O were also present. Hydrocarbons containing five to ten carbon atoms are likely present but were not characterized. Fluids in these inclusions are generally maintained at high pressures.

5. The concentration of salts in the aqueous solution in these inclusions is variable and ranges from 0 to 35,000 ppm (NaCl equivalent).

6. In the same healed fracture aqueous inclusions homogenized in the range 155–160°C and organic inclusions homogenized at about 127°C. The 30°C difference in homogenization temperatures is due to the high compressibility of the organic fluids. The temperature of trapping was probably not far above 160°C.

7. The pressure at the time of trapping some organic fluids is estimated to be equal to or greater than 30–40 atm. If this pressure were hydrostatic, the minimum depth of trapping must have been 300–400 m, and probably was greater than these estimates.

8. The time at which the fluids were entrapped in the quartz crystals cannot be ascertained at present. Trapping may have occurred any time from late Precambrian to at least Jurassic.

9. The primary inclusions containing only organic fluids probably formed when a droplet of the fluid came in contact with the surface of the growing quartz crystal, precluding further growth at that point. Secondary inclusions containing organic fluids were probably trapped by healing of fractures in the presence of aqueous and hydrocarbon fluids.

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