



GEOLOGICAL  
SURVEY  
OF  
CANADA

DEPARTMENT OF MINES  
AND TECHNICAL SURVEYS

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**BULLETIN 104**

**GEOCHEMICAL STUDY OF  
SOME CHERT AND RELATED DEPOSITS**

**John A. Maxwell**

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AND RELATED DEPOSITS





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*BULLETIN 104*

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By  
John A. Maxwell

DEPARTMENT OF  
MINES AND TECHNICAL SURVEYS  
CANADA

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## PREFACE

Chert and other related high-silica deposits are widely distributed in the crust of the earth. Relatively few detailed studies have been made of them, although their origin has been a controversial subject for many years.

This report contains the results of chemical, spectrographic, and petrographic work on twenty-four chert and related high-silica deposits, carried out by the author at the University of Minnesota in 1952 and 1953, as part of a doctorate thesis. It adds materially to the available geochemical knowledge of these deposits.

J. M. HARRISON,

*Director, Geological Survey of Canada*

OTTAWA, November 27, 1962

Bulletin 104—Geochemische Untersuchung einiger  
Hornsteine und verwandter  
Ablagerungen.  
Bulletin, zwei Bilder, drei Tafeln.  
Von J. A. Maxwell

Eine geochemische und petrographische Untersuchung von vierundzwanzig Proben von quarzreichen Naturstoffen, einschliesslich Chert, Novaculit, Flint, Jaspilit und Chalzedon hat ergeben, dass die geringfügigen und Supren-Elemente in diesen Proben auf die Nichtsilikat-Mineralien zurueckzufuehren sind.

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Бюллетень 104 — Геохимическое изучение некоторых роговиков и связанных с ними отложений. Д. А. Максвелл.

Бюллетень, две страницы фотографий, три таблицы.

Геохимическое и петрографическое изучение двадцати четырех образцов высококремнистых природных материалов, включая роговик, новакулит, кремь, джеспилит и халцедон, показывает, что второстепенные и рассеянные элементы в этих образцах генетически связаны с некремниевыми минералами образцов.

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## GEOCHEMICAL STUDY OF SOME CHERT AND RELATED DEPOSITS

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### *Abstract*

A geochemical and petrographical study of twenty-four specimens of high-silica natural materials, including chert, novaculite, flint, melikaria, oolite, algal (?) core, jaspilite, chalcedony, breccia cement and petrified wood, shows that the minor and trace elements in these samples are attributable to the non-silica minerals in the specimens. These include clay minerals, limonite or secondary iron oxides, calcite, dolomite, sericite, pyrite, biotite, magnetite, hematite, aragonite, and carbonaceous matter. Water and aluminium can be correlated directly with the clay minerals, iron with the iron oxides, calcium, magnesium, and carbon dioxide with calcite and dolomite, potassium and sodium with clay and sericite. Only in germanium is there some indication that diadochic substitution of the silicon may have occurred, and this only to a very minor degree. Although the minor and trace element composition of some specimens reflects the composition of the sediments in which they occur, other specimens exhibit a remarkable freedom from such a relationship.

### *Résumé*

Il ressort d'une étude géochimique et pétrographique de vingt-quatre échantillons de matériaux riches en silice, à savoir du chert, de la novaculite, du silex, du mélíkaria, de l'oolithe, des noyaux d'algue (?) silicifiés, de la jaspilite, de la calcédoine, du ciment de brèche et du bois pétrifié, que les éléments accessoires et de trace y sont attribuables aux minéraux non siliceux au sein des échantillons. Parmi ces derniers, mentionnons les minéraux argileux, la limonite ou les oxydes de fer secondaires, la calcite, la dolomite, la séricite, la pyrite, le biotite, la magnétite, l'oligiste, l'aragonite et la matière carbonée. L'eau et l'aluminium peuvent être reliés directement aux minéraux argileux, le fer aux oxydes de fer, le calcium, le magnésium et l'anhydride carbonique à la calcite et à la dolomite, le potassium et le sodium à l'argile et à la séricite. C'est seulement dans le cas du germanium qu'il y a certains indices qu'il pourrait y avoir eu un remplacement diadochique du silicium, et encore dans une très faible mesure. Même si la nature des éléments accessoires et de trace de certains échantillons reflète la composition des sédiments au sein desquels ils existent, d'autres échantillons sont remarquablement dépourvus d'une telle relation.



## INTRODUCTION

An important aspect of geochemistry is the investigation of the elements in the lithosphere and the determination of their relative abundances. Such basic data as the latter are necessary to the better understanding of the laws that govern the distribution of elements in the crust of the earth and of the processes that effect this distribution. Extensive studies have been made of the geochemistry of the igneous and, to a lesser extent, the metamorphic rocks, but much remains to be done for the sedimentary rocks. There have been many studies of high-silica deposits, but chemical and spectrographic data are few, incomplete, and often unreliable.

This study was made to lessen the gap in our knowledge of the chemical composition of chert, novaculite, and related high-silica materials, and to investigate possible relationships between the chemical and mineralogical composition of the analyzed samples.

### Previous Work

The numerous published analyses of chert, flint, novaculite and similar materials vary greatly in quality and completeness. Brief mention is made here of only a few of these, but a more complete list of references, to 1953, is available (Maxwell, 1953)<sup>1</sup>.

Most of the published analyses list only  $\text{SiO}_2$  (usually obtained by difference),  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{H}_2\text{O}$  and/or loss on ignition. Values are sometimes given for  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{FeO}$ , and  $\text{CO}_2$ , and powder density determinations are occasionally cited. The most complete analyses are those of Stout and Schoenlaub (1945), who include  $\text{FeS}_2$ ,  $\text{SO}_3$ ,  $\text{ZnO}$ , and  $\text{ZrO}_2$  among the constituents determined. Additional elements for which data are cited include  $\text{Pb}$ ,  $\text{Cu}$ ,  $\text{Zn}$ , and  $\text{Ni}$  in jasperoid (Cox, Dean, and Gottschalk, 1916),  $\text{Ni}$  in chert (Dietrich, 1953),  $\text{C}$  and  $\text{As}$  in flint (Lankester, 1917),  $\text{Mn}$  in jasper (Sampson, 1923) and in chert (Burchard and Rankin, 1943; Pieruccini, 1951),  $\text{V}$  and  $\text{Fe}$  in chert (Shoup, 1947), and  $\text{Ge}$  in opals (Kimura, 1952). The determination of 'soluble'  $\text{SiO}_2$  has received attention over the years (Hovey, 1894; Jukes-Brown and Hill, 1889; Foster, 1953); however, early determinations are likely of dubious value.

A number of physicochemical studies have been made of the silica minerals and much of the earlier work is summarized by Sosman (1927), in his monograph on the properties of silica. Studies by Washburn and Navias (1922) and Midgley (1951) of chalcedony and flint, and by Weymouth and Williamson (1951) of flint alone, suggest that they consist almost entirely of quartz; their low density is believed to be due to the presence of submicroscopic pores. Folk and Weaver (1952) investigated the composition and texture of chert with the

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<sup>1</sup>Names and dates in parentheses refer to publications given in the Selected Bibliography.

electron microscope and concluded that chalcedony is quartz, the optical properties of which are modified by swarms of minute, water-filled cavities. Infrared absorption spectrography has shown that the absorption spectrum for chert is also characteristic of quartz, and that for chalcedony differs only slightly (Keller and Pickett, 1949; Hunt, Wisherd, and Bonham, 1950). Both Kokta (1930) and Lovering (1952) found that a linear relationship exists between the water content and the refractive index and density of opal; a similar relationship was found by the writer among the various materials used in this study. Taliaferro (1935) regarded natural opals and cherts as hardened, greatly dehydrated silica gels in which dehydration was accompanied by a steady and constant loss of volume and structural modification, which caused a progressive increase in refractive index and density. Some X-ray photographs have revealed a weak cristobalite pattern for the opal structure.

Petrographic studies of chert, novaculite, flint, and related materials are abundant in the literature, although little effort has been made to correlate petrographic and chemical data. Hull and Hardman (1878) give petrographic descriptions of fifteen analyzed specimens, and good petrographic studies are offered by Laney (1917), Sargent (1929), Taliaferro (1934), Laird (1935), Ruedemann and Wilson (1936), Keller (1941), and Frye and Swineford (1946) among others.

### Acknowledgments

This report is condensed from a thesis submitted in partial fulfilment of the requirements for the Ph.D. degree at the University of Minnesota, 1953. The problem of the geochemistry of chert and related materials was suggested by S. S. Goldich, to whom the writer is indebted for advice and guidance both during the course of the work and in the preparation of this manuscript. The chemical analyses were done in the Rock Analysis Laboratory at the University of Minnesota and the advice of E. B. Sandell of the School of Chemistry is gratefully acknowledged, as is the help received from Hiroshi Onishi, P. K. Kuroda, and E. L. Horstman with some aspects of the chemical work. The spectrographic analyses were made in the School of Mines and Metallurgy with the guidance and generous help of S. R. B. Cooke. Special thanks are owing to those who supplied the writer with specimens, and to E. M. Cameron for his critical reading of the manuscript.

### Terminology

The definition of chert accepted in this report is that of Keller (1941, p. 1292), who described chert as being "composed chiefly of microcrystalline quartz, a fine to very fine-grained silica which commonly shows undulatory extinction but otherwise possesses the optical properties of ordinary coarse-grained quartz". Because of the widely varying chemical composition of chert, no compositional restrictions can be added to the above definition.

The terminology of Folk (1949) is followed in describing the three types of quartz that occur in chert nodules. Microcrystalline quartz, which constitutes most chert, is an aggregate of minute grains producing pin-point extinction; chalcedonic quartz, which forms radiating bundles of fibres, and normal, drusy quartz are the other two types.

Chalcedony is used for coarsely fibrous quartz in the form of large bundles and sheaves. Flint closely resembles chert but has distinctive chemical and microscopic characteristics. Novaculite has a porcelaneous and gritty appearance and is regarded as a deposit of silica allied with, but not a variety of, chert.

### Choice of Samples

Twenty-four specimens were selected for detailed study because of their apparent high degree of freshness and homogeneity and differing modes of occurrence. The decision to limit the study to this material was made in order to provide a basis of comparison for the experimental data and because it was felt that it would be of greater value to explore one corner of the field more fully than to attempt a reconnaissance of the whole. The other basis for selection was that of variety in nature and occurrence and, although the possibilities in this respect have only been touched upon here, the samples selected have a wide range in time and space. Macroscopic and petrographic descriptions of the samples, together with a tabulation of their physical properties and other pertinent data (Table III), are given in the Appendix.

## METHODS OF INVESTIGATION

### Preparation of Samples for Analysis

The relatively high degree of purity of most of the samples made it imperative that contamination from outside sources during the crushing and grinding operations be kept to a minimum. Opposed to this was the extreme hardness of the material, which necessitated crushing it to about 20-mesh in a steel mortar before it could be ground in an agate mortar. The procedure, which proved generally satisfactory, was as follows: the carefully cleaned sample, varying in quantity from one to several hand specimens, was broken into small pieces with a steel hammer and those pieces showing adhering particles or smears of metal were rejected; the rest were then crushed to about 20-mesh in a hardened steel mortar, with frequent screening of the material through a silk cloth (about 100-mesh), followed by final grinding of the approximately 20-mesh material in an agate mortar until all the material passed through the silk cloth. A magnetized spatula was used to remove 'tramp' iron<sup>1</sup>, and the sample was then thoroughly mixed by hand on glazed paper and transferred to a sample bottle.

### Chemical Methods

Silica was determined gravimetrically after fusion of the sample with  $\text{Na}_2\text{CO}_3$  and a double dehydration with hydrochloric acid in a platinum dish. The residue remaining after the treatment of the impure silica with HF had an average weight of about 0.0005 grams and the loss in weight of the platinum crucible during fusion and ignition was slight, about 0.0002 grams. The average weight of  $\text{SiO}_2$  recovered from the pyrosulphate fusion of the ignited  $\text{R}_2\text{O}_3$  group was 0.0002 grams.

The  $\text{R}_2\text{O}_3$  group was precipitated with ammonium hydroxide, ignited, and fused with potassium pyrosulphate. A recovery of  $\text{SiO}_2$  was made from the sulphuric acid solution of the cake and then the solution was used for the colorimetric determinations of aluminium, titanium, and total iron. Titanium was determined as the yellow peroxy complex, total iron by the mercaptoacetate (thioglycolate) method (Sandell, 1950, pp. 378-80), and aluminium by the aurintricarboxylic acid (aluminon) method of Sandell (1950, pp. 146-9, Procedure B).

Ferrous iron was determined titrimetrically on a separate sample, after decomposition of the sample in the absence of oxygen.

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<sup>1</sup>The average weight of 'tramp' iron removed from each sample was approximately 0.6 mg per gram of sample; in four samples it was found that this iron contamination increased the  $\text{FeO}$  content by 0.07 per cent if not removed.

Calcium and magnesium were determined gravimetrically by precipitation with ammonium oxalate and diammonium phosphate respectively. The modified periodate method of Richards (op. cit., p. 431) was used to measure the manganese content of the samples, and phosphorus was determined by the colorimetric procedure of Baadsgaard and Sandell (1954), utilizing the yellow phosphovanadomolybdate complex.

A modification of the Penfield method, with lead oxide as flux, was used to determine the total water in the samples. Carbon dioxide was determined by the acid-evolution method, and by taking a large sample as little as 0.0001 gram of  $\text{CO}_2$  could be determined satisfactorily. A simplified version of the combustion method, as described by Hillebrand, *et al.* (1953, p. 770), was used to obtain a measure of the carbon in these samples.

Sodium, potassium, and lithium were determined by a flame photometric procedure using a Beckman DU spectrophotometer with flame attachment and a mixture of air and natural gas as fuel. The equipment has been described in detail by Ellestad and Horstman (1955).

The arsenic determinations were made by Hiroshi Onishi, using the molybdenum blue method (Onishi and Sandell, 1953); molybdenum was determined by the thiocyanate-stannous chloride procedure<sup>1</sup> of Sandell and Kuroda (1952), germanium by the phenylfluorone method described by Schneider and Sandell (1954).

Frequent tests were made on the reagents, and negligible blanks were usually obtained; however, corrections were applied when necessary.

## Spectrographic Method

The instrument used for this work was a large Littrow quartz spectrograph manufactured by the Gaertner Scientific Company. The samples were placed directly into the cups of one-quarter-inch graphite electrodes and arced in air, using anode excitation at 150 volts DC, with volatilization at 9 to 10 amperes. The samples were completely burned, and their spectra were recorded on Eastman No. 33 photographic plates in both the visible and ultraviolet wavelength regions. Iron arc spectra were photographed in juxtaposition for use in line identification.

A preliminary examination of samples of the relatively impure Helderberg chert (10)<sup>2</sup> indicated that a preconcentration of the non-silica portion of the samples was necessary before an estimate could be made of the concentration of the trace elements. Five grams of each sample were decomposed in a 50-ml platinum dish with 30-50 ml HF and 0.5 ml  $\text{H}_2\text{SO}_4$  (1:1); when decomposition was complete, the excess acid was removed by evaporation and the residue heated

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<sup>1</sup> It was found necessary to add  $\text{CaCO}_3$  to the mixture of  $\text{Na}_2\text{CO}_3$  and sample before fusion in order to have the bulk of the silica in the residue after extraction of the fused cake with water; failure to remove most of the silica will result in a turbidity in the isopropyl ether extract, which makes transmittance measurements impossible.

<sup>2</sup> Italicized numbers in parentheses refer to the sample numbers in the Appendix.



over a flame until no further expulsion of  $\text{SO}_3$  was observed. The cooled residue was transferred to a small agate mortar and thoroughly mixed by light grinding.

Spectrographic analysis of a 3 mg residue obtained from the evaporation of 200 ml of hydrofluoric acid revealed Fe, Al, Ti, Mn, Pb, Cu, Ni, Co, Sn, and B in trace quantities. Only boron was found in a sufficiently high concentration to make purification of the acid necessary and, as boron was known to be present in the graphite electrodes also, it was omitted from the list of elements to be sought and the hydrofluoric acid was used for both the chemical and spectrographic work without purification.

A synthetic reference standard was prepared by adding aliquots of solutions of Ba, Be, Bi, Co, Cr, Cu, Ga, Ni, Pb, Sc, Sn, Sr, V, and Zr to pure, 200-mesh quartz in a platinum dish, such that the final concentration of each element was 100 ppm. One ml  $\text{H}_2\text{SO}_4$  (1:1) was added and the whole evaporated to dryness and then to the expulsion of  $\text{SO}_3$ . The residue was mixed by prolonged grinding in an agate mortar.

Ten mg samples of the synthetic reference standard and of each sample were arced as described. Semiquantitative estimates of the concentration of the elements present in the spectra were made by visual comparison of element lines with similar lines in the synthetic reference standard powder. The choice of spectrum lines used for each element was made by reference to Brode (1939) and Ahrens (1950).

### Grain Density and Refractive Index

Determinations of the grain densities of the samples were made with a fused-silica pycnometer of the type designed and described by Ellsworth (1928). Measurement of the mean refractive index of the aggregate particles of each sample was made with a calibrated series of refractive index oils, using light from a sodium-vapour lamp.

## CHEMICAL AND SPECTROGRAPHIC ANALYSES

Chemical and spectrographic analyses of the twenty-four samples are given in Table I.

Because the presence of abundant carbonaceous material rendered meaningless the determination of FeO, only the value for total Fe, as  $\text{Fe}_2\text{O}_3$ , is given for the Maravillas chert (14), although from other evidence it is inferred that the Fe is present chiefly in the  $\text{Fe}^{++}$  state. Carbon was determined in eight samples only and is shown as 'not determined' (n.d.) in the other analyses.

The semiquantitative spectrographic values for eleven trace constituents are expressed as ranges of ppm. The average preconcentration ratio of residue to sample is 100:1 and on the basis of this it is calculated that the lower limits of detection for the elements sought are:

0.1 ppm—Bi, Ga, Pb, Sc, Sn, Zr

0.05-0.02 ppm—Co, Ni, V

0.01 ppm—Ba, Be, Cr, Cu, Sr

The symbol 'P' in Tables I and II means that an element is present but near the lower limit of detection; 'n.f.' means that it is below this limit.

Geochemical Study of Some Chert and Related Deposits

Table I  
*Chemical and Spectrographic Analyses*

(J. A. Maxwell, analyst)

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12
Nature	chert	novaculite	novaculite	chert	novaculite	chert	melikaria	chert	chert	chert	oolite	chert
SiO <sub>2</sub>	99.11	99.66	99.33	99.44	99.26	97.80	99.66	97.99	98.63	95.72	99.47	99.30
Al <sub>2</sub> O <sub>3</sub>	.18	.03	.01	.06	.12	.60	.15	.07	.12	.32	.06	.08
Fe <sub>2</sub> O <sub>3</sub>	.00	.00	.08	.00	.02	.06	.00 <sup>d</sup>	.05	.00	.09	.00 <sup>d</sup>	.05
FeO	.13	.15	.23	.16	.17	.23	.11 <sup>d</sup>	.12	.09	.12	.17 <sup>d</sup>	.07
MgO	.01	.00	.01	.01	.01	.03	.01	.03	.00	.21	.00	.00
CaO	.00	.00	.00	.02	.02	.18	.01	.80	.45	1.25	.06	.07
Na <sub>2</sub> O	.06	.01	.01	.01	.01	.03	.02	.01	.01	.04	.01	.01
K <sub>2</sub> O	.04	.01	.03	.02	.02	.15	.03	.01	.02	.10	.03	.02
H <sub>2</sub> O+	.29	.11	.17	.14	.12	.50	.08	.31	.13	.55	.19	.36
H <sub>2</sub> O-	.04	.02	.05	.01	.04	.14	.02	.03	.08	.11	.02	.07
CO <sub>2</sub>	.00	.00	.00	.01	.01	.00	.00	.57	.25	1.17	.00	.02
C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	.00	.03	.04	.03	n.d.
	99.86	99.99	99.92	99.88	99.80	99.82 <sup>a</sup>	100.09	99.99	99.81	99.72	100.04	100.05
Trace elements (ppm)												
Ti	35	28	205	38	32	35	38	25	14	168	13	22
P	14	9	9	7	63	458	14	19	14	39	14	13
Mn	10	3	5	6	5	18	4	8	3	15	9	6
Li	2	0	2	0	2	13	9	15	28	36	11	21
As <sup>b</sup>	0.7	0.9	0.9	0.9	0.9	0.9	0.2	1.0	.05	0.9	0.9	0.9
Mo	0.3 <sup>c</sup>	0.0 <sup>c</sup>	0.1 <sup>c</sup>	0.3 <sup>c</sup>	0.0 <sup>c</sup>	0.9 <sup>c</sup>	0.0	3.2	3.2	2.2	3.4	1.8
Ge	0.6	1.5	0.2	0.0	0.2	0.4	0.0	0.0	0.0	2.0	0.0	0.0
Co	P	n.f.	n.f.	n.f.	n.f.	P	n.f.	n.f.	n.f.	n.f.	P	P
Cu	0.1-1	P	0.1-1	0.1-1	0.1-1	1-10	0.1-1	0.1-1	0.1-1	0.1-1	1-10	0.1-1
Cr	0.1-1	0.1-1	0.1-1	0.1-1	0.1-1	1-10	1-10	1-10	1-10	1-10	1-10	0.1-1
Ni	P	P	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.
Sn	0.1-1	P	0.1-1	0.1-1	P	P	P	n.f.	0.1-1	n.f.	n.f.	P
V	n.f.	n.f.	n.f.	n.f.	P	P	n.f.	n.f.	0.1-1	0.1-1	n.f.	P
Ba	1-10	0.1-1	0.1-1	1-10	1-10	10-100	10-100	10-100	10-100	1-10	1-10	1-10
Sr	0.1-1	P	0.1-1	0.1-1	0.1-1	1-10	0.1-1	10-100	1-10	10-100	1-10	0.1-1
Be	P	P	P	P	P	0.1-1	P	P	P	P	P	P
Ga	P	P	P	P	P	n.f.	n.f.	n.f.	P	n.f.	P	0.1-1
Sc	P	P	P	P	P	1-10	P	P	n.f.	P	n.f.	n.f.

<sup>a</sup> Includes 0.10 P<sub>2</sub>O<sub>5</sub>

<sup>b</sup> Determinations by Hiroshi Onishi

<sup>c</sup> Determinations by P. K. Kuroda

<sup>d</sup> Failure to remove steel filings introduced from mortar during crushing gives high results for FeO and low results for Fe<sub>2</sub>O<sub>3</sub>

<sup>e</sup> Includes 0.05 TiO<sub>2</sub>, 0.07 P<sub>2</sub>O<sub>5</sub>, 0.01 MnO, 0.07 S, 0.01 SO<sub>3</sub>, less 0.03 for O equivalent to S

<sup>f</sup> Includes 0.08 TiO<sub>2</sub>, 0.20 P<sub>2</sub>O<sub>5</sub>, 0.18 MnO, and 0.01 Li<sub>2</sub>O

<sup>g</sup> Includes 0.04 Cl and 0.01 S, less 0.01 for O equivalent to S and Cl

Table I

*Chemical and Spectrographic Analyses—(conc.)*

13	14	15	16	17	18	19	20	21	22	23	24	Sample No.
algal (?) core	chert	novaculite	novaculite	chert	flint	jasplite	chalcedony	chert	breccia cement	chert	petrified wood	Nature
98.76	96.39	99.47	99.82	95.89	98.36	99.43	99.95	95.00	99.86	96.45	96.84	SiO <sub>2</sub>
.00	.78	.23	.11	1.95	.12	.01	.00	1.70	.00	.07	.02	Al <sub>2</sub> O <sub>3</sub>
.03 <sup>d</sup>	.43 <sup>d</sup>	.00	.00	.24	.00	.03	.00	.78	.00	.07	.00	Fe <sub>2</sub> O <sub>3</sub>
.13 <sup>d</sup>		.09	.07	.13	.08	.16	.06	.11	.06	.06	.05	FeO
.01	.05	.00	.00	.05	.01	.01	.00	.23	.00	.49	.11	MgO
.06	.23	.00	.00	.04	.16	.08	.00	.41	.03	1.25	1.54	CaO
.04	.04	.01	.00	.04	.04	.00	.00	.09	.01	.01	.01	Na <sub>2</sub> O
.02	.18	.05	.03	.30	.04	.00	.01	.33	.01	.04	.01	K <sub>2</sub> O
.64	.96	.07	.03	1.03	.84	.16	.01	.71	.07	.35	.26	H <sub>2</sub> O+
.22	.16	.01	.00	.15	.11	.01	.00	.08	.00	.03	.03	H <sub>2</sub> O-
.02	.01	.01	.00	.00	.07	.06	.00	.06	.00	1.20	.64	CO <sub>2</sub>
n.d.	.31	n.d.	n.d.	.15	.02	n.d.	n.d.	n.d.	n.d.	n.d.	.06	C
99.93	99.72 <sup>e</sup>	99.94	100.06	99.97	99.85	99.95	100.03	99.97 <sup>f</sup>	100.04	100.02	99.57 <sup>g</sup>	
Trace elements (ppm)												
0	306	88	82	544	23	8	0	456	23	107	13	Ti
18	308	84	37	207	101	18	15	884	22	145	13	P
6	41	8	6	6	3	32	3	1394	7	8	63	Mn
4	9	2	2	32	13	8	0	26	0	15	11	Li
1.1	10.1	0.6	1.0	2.0	1.1	0.6	0.7	0.5	0.4	1.6	0.8	As <sup>b</sup>
3.6	11.4	3.0	2.6	1.0	1.8	3.2	1.6	4.4	1.8	1.0	0.4	Mo
0.2	0.0	0.2	0.2	0.2	0.2	0.7	3.0	0.9	0.4	0.2	0.2	Ge
P	0.1-1	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	0.1-1	n.f.	n.f.	n.f.	Co
0.1-1	10-100	0.1-1	0.1-1	0.1-1	0.1-1	0.1-1	0.1-1	1-10	P	0.1-1	0.1-1	Cu
0.1-1	1-10	1-10	0.1-1	1-10	0.1-1	1-10	0.1-1	10-100	0.1-1	1-10	1-10	Cr
n.f.	1-10	n.f.	n.f.	n.f.	0.1-1	n.f.	P	10-100	n.f.	n.f.	n.f.	Ni
P	n.f.	0.1-1	n.f.	n.f.	0.1-1	n.f.	0.1-1	n.f.	n.f.	n.f.	n.f.	Sn
P	10-100	0.1-1	0.1-1	0.1-1	0.1-1	n.f.	n.f.	P	n.f.	0.1-1	P	V
1-10	10-100	10-100	1-10	10-100	1-10	0.1-1	0.1-1	10-100	0.1-1	1-10	10-100	Ba
0.1-1	10-100	1-10	0.1-1	1-10	0.1-1	P	P	10-100	P	1-10	10-100	Sr
0.1-1	0.1-1	P	P	0.1-1	P	P	P	0.1-1	P	P	P	Be
0.1-1	n.f.	P	n.f.	0.1-1	0.1-1	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	Ga
n.f.	P	1-10	0.1-1	1-10	n.f.	n.f.	n.f.	10-100	n.f.	n.f.	n.f.	Sc

## DISCUSSION OF RESULTS

### Distribution of the Elements

The following minerals occur in small amounts in the samples: clay minerals, as fine-grained aggregates; limonite or secondary iron oxides that could not be specifically identified; calcite, dolomite, sericite, pyrite, and detrital quartz; biotite, magnetite, hematite, and aragonite, tentatively identified and present only in very small amounts; carbonaceous matter. These account for most of the minor and trace elements reported in the chemical analyses.

*Water* (average of twenty-four samples=0.40 per cent) is the most important of the minor constituents and makes up about 30 per cent of the non-silica portion of each sample. In general, those samples having a high water content also contain relatively large amounts of clay minerals, such as the upper Caballos (6), Helderberg (10), Maravillas (14), Huntersville (17) and radiolarian (21) cherts, and to a lesser degree, the sample of flint (18). The algal (?) core (13), with 0.86 per cent total  $H_2O$ , contains no visible clay minerals; in this instance the water probably occurs in the chalcedony, filling swarms of minute cavities as suggested by Folk and Weaver (1952). The specimen of Caballos chert (6) also contains the greatest amount of sericite.

*Aluminium* (average=0.28 per cent as  $Al_2O_3$ ) also can be correlated directly with the clay mineral content, as shown by the upper Caballos (6), Maravillas (14), Huntersville (17) and radiolarian (21) cherts. The Helderberg chert (10) also contains more than the average  $Al_2O_3$  content, but the flint (18) is low in  $Al_2O_3$ , suggesting also that the high water content may owe more to the chalcedony present than to the clay minerals.

*Iron* (average=0.21 per cent total Fe as  $Fe_2O_3$ ) does not vary much between samples, with the exception of the reddish radiolarian chert (21), and can be attributed to the presence of secondary iron oxides (limonite). Because of the possible introduction of metallic iron during the preparation of the sample, no definite statement can be made about the distribution of  $Fe^{++}$  and  $Fe^{+++}$  in the samples. Some  $Fe^{++}$  is certainly indicated, of course, by the presence of pyrite, but most of the iron is probably in the secondary iron oxides.

*Calcium* (average=0.28 per cent CaO) is supplied by finely divided calcite, as shown by the Staendebach (8,9), Helderberg (10) and Bird Spring (23) cherts, and the sample of petrified wood (24).

*Magnesium* (average=0.05 per cent MgO) can be correlated directly with the presence of dolomite, as in the Helderberg (10) and Bird Spring (23) cherts, and the petrified wood (24). The lack of correlation between relatively high MgO

content and dolomite in the radiolarian chert (21) is probably due to the red iron oxide dust that made mineral identification very difficult; mention has been made of numerous unidentified grains seen in the thin section of this specimen.

*Carbon dioxide* (average=0.17 per cent CO<sub>2</sub>) correlates directly with the calcite and dolomite in the specimens.

*Potassium* (average=0.06 per cent K<sub>2</sub>O) and *sodium* (0.02 per cent Na<sub>2</sub>O) can be attributed to the clay and sericite in the specimen, as for example in the upper Caballos (6), Maravillas (14), Huntersville (17), and radiolarian (21) cherts. Potassium exceeds sodium in all specimens except the lower Caballos chert (1), algal (?) core (13) and flint (18).

*Lithium* (average=11 ppm Li) is very variable in concentration, but generally varies directly with the Mg content of the specimens.

*Barium* and *strontium* vary directly with each other, with Ba exceeding Sr except in the Helderberg chert (10) and the petrified wood (24); the increase of Sr over Ba may be related to the increased calcite content of these two specimens.

*Phosphorus* (average=105 ppm P) and *titanium* (96 ppm Ti) are present in about equal average amounts, but there is no evident relationship between their concentrations in individual specimens, other than that an increase in both generally accompanies an increase in the total impurities present. The high phosphorus content of the radiolarian chert (21) and the flint (18) may have originated in organic phosphate. In other specimens the phosphorus may occur as collophane, although certain identification could not be made.

The generally low content of *manganese* (average=70 ppm Mn) in all specimens except the radiolarian chert (1394 ppm) is surprising but a similarly low content was found by Pieruccini (1951). The Mn may be in the calcite and dolomite, iron minerals, and clay aggregates. The very high Mn content of the radiolarian chert is characteristic of the Franciscan deposits; Taliaferro (1943, pp. 150-53) stated that the manganese is present in these rocks in part as neotocite, a light to dark brown manganiferous opal that is converted, under slight pressure, to manganiferous chalcedony.

It is difficult to evaluate the significance of *tin*, *chromium*, *nickel*, *copper*, *cobalt*, *molybdenum*, and *vanadium* in these samples because of the known presence of some of them (Sn, Cu, Co, and Ni) in the hydrofluoric acid used to prepare concentrates of the non-silica portions of the samples, and also because of their probable presence in the steel of the mortar used to crush the samples. Support for a valid relationship between these elements and the amount of impurity naturally present in the samples is derived from the fact that the two very pure samples, the algal (?) core (13) and the chalcedony nodule (20), contain none, or only a trace of them. Significant amounts of one or more of these elements occur in only three samples, the Maravillas (14), Huntersville (17), and radiolarian (21) cherts. In the Maravillas chert, Cu, Ni, Co, Mo, and V are probably

present in pyrite; Cr, Ni, Co, and Cu in the radiolarian chert may have been accumulated by the radiolaria. The trace of V in the algal (?) core (13) and flint (18) may also have been derived from organisms.

*Scandium* occurs in amounts greater than a trace in only five specimens, the upper Caballos (6), Huntersville (17), and radiolarian (21) cherts, and the Arkansas novaculites (15, 16). It is probably in the limonite and clay of the first three specimens, but its presence in the very pure Arkansas novaculites and as a trace in all of the Caballos specimens may be a characteristic feature of these formations.

*Arsenic* is present in very low concentrations in all specimens except the Maravillas chert (14). It may be concealed in the pyrite in most samples, although sponges and freshwater algae may have contributed the As found in the flint (18) and the algal (?) core (13). In the black, carbonaceous Maravillas chert (14) it is likely that the pyrite was formed by precipitation from a metal sulphide sol.

Particular interest was taken in the *germanium* concentration of the specimens, for  $\text{Ge}^{4+}$  (0.44 Å) may diadochically replace  $\text{Si}^{4+}$  (0.39 Å) to form  $\text{GeO}_4$  tetrahedra. During weathering and sedimentation Ge may be precipitated and enriched in hydrolyzate and oxidate sediments. Ge is present in very low concentration in all samples, but only the Caballos lower novaculite (2), the Helderberg chert (10) and the chalcedony nodule (20) contain significantly greater amounts; the 3 ppm of the chalcedony nodule is conspicuously high. Clay and limonite may be the source of the germanium in the Helderberg chert and other specimens, but the very pure Caballos novaculite and chalcedony nodule suggest that diadochic substitution of Ge for Si may have occurred in these instances.

## Comparison of Chert and Novaculite

Novaculite is considered by some to be only a variety of chert possessing slightly different physical properties, whereas others regard it as similar to chert but not a variety of it. An examination of the chemical and physical data accumulated in this study suggests that the latter view is probably more correct.

Average values for the major, minor, and trace constituents in twelve cherts and five novaculites are given in Table II. Although individual samples of chert approach the average composition of the novaculites, it is seen that chert is less pure than novaculite (the average non-silica portion of chert is 2.23 per cent compared to 0.43 per cent for novaculite). These differences are the result of the larger amounts of clay, calcite, and other minerals in the cherts, a reflection in turn of the differing environments of the specimens.

These chemical differences between chert and novaculite are in part emphasized by physical differences between the specimens. The larger amounts of clay and other impurities that characterize cherts commonly result in cherts being dark coloured. The average density for the chert specimens is 2.631 gm/cc

**Table II**  
*Comparison of the Average Values for Constituents of Chert and  
 Novaculite with those for all Samples*

	Chert (12)	Novaculite (5)	All samples (24)
	%	%	%
SiO <sub>2</sub> .....	97.59	99.51	98.40
Al <sub>2</sub> O <sub>3</sub> .....	0.50	0.10	0.28
Total Fe as Fe <sub>2</sub> O <sub>3</sub> .....	0.29	0.17	0.21
MgO.....	0.09	0.00 <sub>4</sub>	0.05
CaO.....	0.40	0.00 <sub>4</sub>	0.28
Na <sub>2</sub> O.....	0.03	0.00 <sub>8</sub>	0.02
K <sub>2</sub> O.....	0.10	0.02 <sub>8</sub>	0.06
Total H <sub>2</sub> O.....	0.54	0.12	0.40
CO <sub>2</sub> .....	0.28	0.00 <sub>4</sub>	0.17
	ppm	ppm	ppm
Ti.....	147	87	96
P.....	177	40	105
Mn.....	129	5	70
Li.....	17	2	11
As.....	1.7	0.9	1
Mo.....	2.7	1.1	2.1
Ge.....	0.4	0.5	0.2
Ba.....	10-100	1-10	1-10
Sr.....	1-10	0.1-1	1-10
Cr.....	1-10	0.1-1	1-10
Ni.....	n.f.-P	n.f.-P	n.f.-P
Co.....	n.f.-P	n.f.	n.f.-P
Cu.....	0.1-1	0.1-1	0.1-1
V.....	P	P	P
Sn.....	n.f.-P	P	n.f.-P
Be.....	P	P	P
Ga.....	n.f.-P	P	n.f.-P
Sc.....	n.f.-P	0.1-1	n.f.-P

with a range of 2.600 - 2.649, appreciably lower than that of quartz ( $2.649 \pm 0.002$ ); the average density of the novaculite specimens is 2.650 gm/cc, with a range of 2.646 - 2.660. Although there is no significant difference between the average index of refraction for chert (1.544 - 1.545) and for novaculite (1.546), the range for chert (1.538 - 1.550) is considerably greater than that for novaculite (1.544 - 1.549).

The above data, together with the coarser texture and high proportion of normal quartz characteristic of novaculite, as opposed to the smooth texture and high proportion of cryptocrystalline and even optically isotropic material of chert, support Griswold's conclusion (1892) that novaculite is a deposit of silica allied with chert, but not a variety of it.

### Problem of Origin

The theories of the origin of chert have been reviewed in detail by Pettijohn (1949, pp. 328-33) among others, and it will suffice here to recapitulate briefly. The contemporaneous or syngenetic theories involve the deposition of silica during



sedimentation by normal clastic, biochemical, magmatic, or direct chemical processes. The subsequent or epigenetic theories assume that the silica was introduced after sedimentation and was precipitated either in the zone of cementation or in the zone of weathering. These differing explanations have been commonly referred to as the primary versus secondary theories of origin of chert. A compromise between these views is a theory of penecontemporaneous precipitation wherein it is suggested that the silica is deposited after sedimentation but before consolidation of the enclosing rock.

This study was made primarily to obtain compositional and mineralogical data for these twenty-four samples, but it was hoped that compositional differences, particularly among the minor and trace elements, would supply information about the mode of origin of the specimens.

Consideration of the chemical data suggests that deposits of remarkable purity are found in very different environments. For example, the flint nodule from Dover Chalk, a replacement chert, compares closely in composition with the remarkably pure samples of novaculite. The chalcedony nodule (20) from a clay pit and the core of the siliceous algal (?) deposit (13) were formed in very different geologic environments and they are among the least impure of the twenty-four samples. Similarly the melikaria (7), believed by Burt (1928) to have been deposited directly from aqueous solution, has a non-silica portion of only 0.34 per cent and yet it formed in an alluvial deposit of clay and silt. Jaspilite (19) from the Precambrian Soudan Formation has generally been referred to as a chemical precipitate, but its chemical analysis is in no way distinctive from that of the other samples.

The chemical analyses of a number of the samples, however, clearly reflect the geological environment. The Helderberg (10) and Bird Spring (23) cherts are relatively impure samples, the impurities being chiefly calcium, magnesium, and carbon dioxide in the form of calcite and dolomite. The Huntersville chert (17) contains appreciable amounts of aluminium and water supplied by clay minerals. The first two samples are interbedded with, and enclosed by, limestone; the Huntersville chert is interbedded with shale. The chemical and petrographic data support the generally accepted replacement origin of these deposits.

The common close association of petrified wood with deposits of volcanic ash has suggested (Murata, 1940) that altered volcanic ash is a common source of silica for silicified wood. The analysis of the single sample (24) of petrified wood from the Chinle Formation shows no unusual chemical characters, although additional samples might yield different results.

Thus, although the minor and trace element composition of some specimens reflects the composition of the sediments in which they occur, other specimens exhibit a remarkable freedom from such a relationship. On the basis of the relatively small number of samples studied, it would appear that chemical composition is not a reliable criterion of the mode of origin.

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1943: Devonian system of West Virginia; *West Virginia Geol. Surv.*, vol. 15, pp. 256-278.

## APPENDIX

### Macroscopic and Petrographic Description of Samples

Table III

*Physical Properties of the Samples, Grouped According to Type of  
Material and Decreasing Geologic Age*

Material	Location	Sample No.	Colour and Diaphaneity	Texture	Fracture	Density <sup>a</sup>	N <sub>d</sub> <sup>b</sup>	Geological Age	Other Minerals
Chert (jasplite)	Soudan, Minnesota	19	pinkish to greyish white	granular	irregular	2.649	1.549	Precambrian	hematite, magnetite, limonite, calcite
Chert	Near San Saba, Texas	8	grey to bluish grey with milky patches	semi-chalcedonic	semi-conchoidal	2.642	1.544	Lower Ordovician	calcite, clay, limonite, sericite
Chert	Same as above	9	white to light-buff	porcellaneous	irregular	2.639	1.544	Lower Ordovician	same as above
Chert	Llano County, Texas	12	grey to bluish grey with light-brown and yellow patches	semi-chalcedonic	irregular	2.641	1.542	Lower Ordovician	clay, limonite
Chert	Solitario, Texas	14	black to brownish black	subgranular	sub-conchoidal	2.600	1.550	Upper Ordovician	limonite, pyrite, clay, carbonaceous material, detrital quartz
Chert	Near Keyser, West Virginia	10	dark-grey to bluish grey	subgranular	irregular	2.620	1.538	Lower Devonian	calcite, dolomite, clay, pyrite, detrital quartz, carbonaceous material
Chert	Huntersville, West Virginia	17	grey to buff, with yellow, purple and dark-grey patches	granular	irregular	2.606	1.544	Middle Devonian	limonite, clay, hematite detrital quartz
Chert	Near Marathon, Texas	1	dark-grey, with buff to brown mottling	chalcedonic	sub-conchoidal	2.632	1.542	Devonian	pyrite, clay, limonite, sericite
Chert	Same as above	4	white to light-grey	semi-chalcedonic	irregular	2.638	1.546	Devonian	limonite, clay
Chert	Same as above	6	greyish white, brownish yellow, reddish brown and black bands	chalcedonic	sub-conchoidal	2.620	1.541	Devonian	limonite, clay, pyrite, sericite, detrital quartz
Chert	Clark County, Nevada	23	light reddish brown	semi-chalcedonic	irregular	2.633	1.541	Pennsylvanian	calcite, dolomite, hematite, limonite, detrital quartz, clay

Chert	Near Oakland, California	21	reddish brown with white and yellow patches	semi-chalcedonic	irregular	2.646	1.549	Jurassic	hematite, magnetite, clay (?), much amorphous material
Novaculite	Near Marathon, Texas	2	white	semi-porcelaneous	irregular	2.660	1.544	Devonian	clay
Novaculite	Same as above	3	white to buff with pink and brown tinges	subgranular to semi-porcelaneous	irregular	2.646	1.544	Devonian	limonite
Novaculite	Same as above	5	white, with a tinge of pink	subgranular	irregular	2.647	1.544	Devonian	limonite, sericite, clay?
Novaculite	Near Butterfield, Arkansas	15	grey to greyish white	porcelaneous	semi-conchoidal	2.650	1.549	Devonian-Mississippian	limonite, clay, dolomite, detrital quartz
Novaculite	Same as above	16	white to light-grey	semi-porcelaneous	irregular	2.648	1.546	Devonian-Mississippian	clay, limonite, biotite?, detrital quartz
Flint	Dover Chalk, England	18	black, with white to yellowish white patina	chalcedonic	conchoidal	2.599	1.541	Cretaceous	pyrite, sericite, carbonaceous material
Cement from chert breccia	Burnt Creek, Labrador	22	translucent	subgranular	irregular	2.646	1.546	Precambrian	none
Siliceous oolite	Center County, Pennsylvania	11	black-centred oolites in a grey matrix	oolitic	irregular	2.647	1.546	Upper Cambrian	limonite, sericite, calcite, clay
Petrified wood	Petrified Forest, Arizona	24	light-grey to greyish white with waxy buff patches	semi-chalcedonic	smooth	2.633	1.544	Triassic	calcite, dolomite
Chalcedony nodule	Augusta County, Virginia	20	translucent	chalcedonic	irregular	2.650	1.549	Tertiary	clay
Silicified algal (?) deposit core	Moffat County, Colorado	13	translucent	chalcedonic	conchoidal to irregular	2.610	1.539	Tertiary	limonite, aragonite?, carbonaceous material
Melikaria	Brazos County, Texas	7	light-buff to white	porcelaneous	irregular	2.656	1.539	Quaternary	

<sup>a</sup>grain density, gm/cc, at room temperature.

<sup>b</sup>mean refractive index of aggregate, sodium light.



## Chert

*Sample No. 1.* Lower chert member, Caballos Formation, Three-Mile Hill, near Marathon, Texas.

Dark grey chert, with greyish brown to buff mottling and some larger buff-coloured patches. Fractured appearance because of a network of parallel and intersecting cracks. Specimen is from the lower chert member, Caballos Formation (Devonian), 3 to 6 feet above the base of the section at Three-Mile Hill, near Marathon, Texas, and was collected by R. W. Graves, Jr. The Caballos Formation, a five-membered sequence of bedded chert and novaculite, with intercalations of shale and limestone, varies in thickness from 200 to 600 feet. A detailed description of the stratigraphic section at Three-Mile Hill, from which samples Nos. 1-6 were taken, is given by Graves (1954).

The specimen consists chiefly of microcrystalline quartz with irregularly scattered cryptocrystalline spots and larger patches of possibly chalcedonic quartz. Many roughly circular spots are thought to be radiolarian skeletons. The thin section is cut by a fissure (shrinkage crack?) filled with radiating bundles of chalcedonic quartz growing from both walls. Scattered detrital quartz grains occur and in reflected light a rough, irregular banding is visible.

A few pyrite grains, some reddish orange and yellow clots of secondary iron oxides, and yellowish white patches and tiny grains of clay-like material<sup>1</sup> are present. Some of the larger grains of pyrite and limonite have tails of clear fibrous quartz. The tail part is clear in ordinary light, fibrous and with undulatory extinction between crossed nicols, and generally is developed perpendicular to the surface of the pyrite grain.

*Sample No. 4.* Upper novaculite member, Caballos Formation, Three-Mile Hill.

White to light grey chert, marked by a number of thin cracks. Upper novaculite member, 120 feet below the top of chert in member, Caballos Formation, at same locality as No. 1. Collected by R. W. Graves, Jr.

Microcrystalline quartz of particularly fine grain, with irregular cryptocrystalline spots and short desiccation or tension cracks. Very few foreign mineral grains.

*Sample No. 6.* Upper chert member, Caballos Formation, Three-Mile Hill.

Banded chert, with thin greyish white, brownish yellow, reddish brown and black bands, and a number of thin vertical black lines. Upper chert member, at top of member, Caballos Formation, at same locality as No. 1. Collected by R. W. Graves, Jr.

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<sup>1</sup> For ease of reference these minerals will hereafter be referred to as 'limonite' and 'clay' respectively.

Variations in the grain size and colour of the microcrystalline quartz impart a banded appearance to the specimen. Yellow and reddish orange limonite appear to be concentrated in some layers, and thin bands of this material are parallel to the layers and also cut the section at all angles. Shrinkage cracks having the shape of a holly-leaf are present, with a core of coarse quartz rimmed with radiating bundles of chalcedonic quartz. Scattered detrital quartz grains are abundant, as are minerals such as fresh pyrite grains, limonite, and sericite.

The most interesting feature is the presence of the thin bands that cut the thin section. They are layers in which impurities appear to have collected (minute clay and limonite particles, and tiny quartz clusters), and microstylolites, outlined by an admixture of black carbonaceous material and clay (*see* Pl. I).

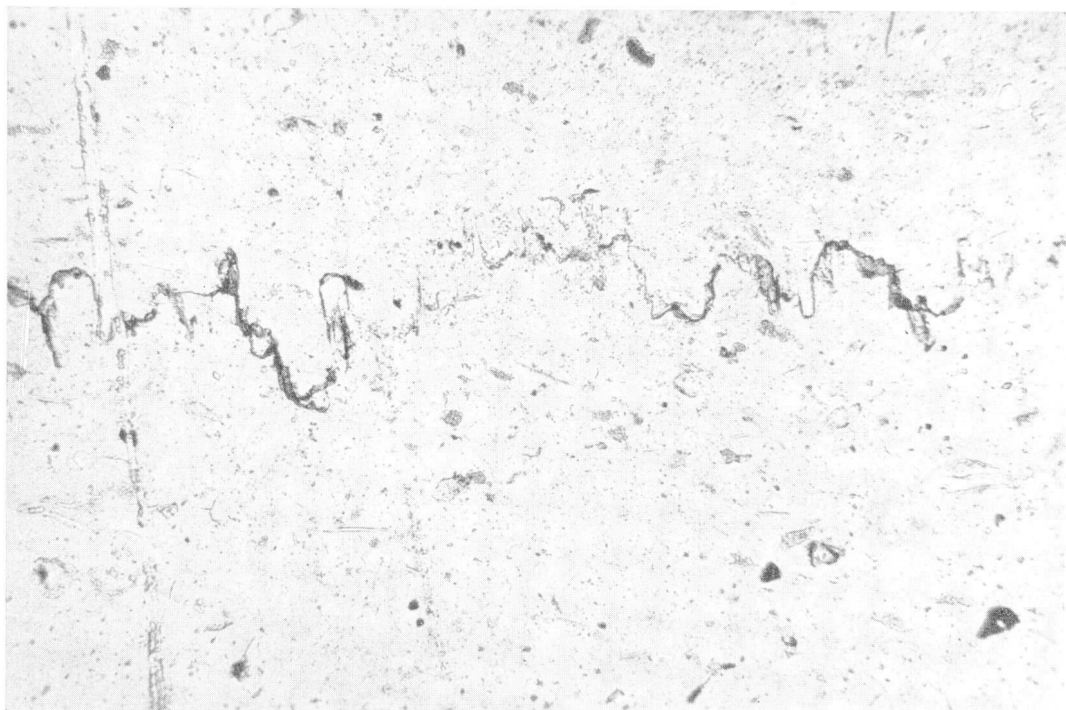


PLATE I. *Photomicrograph of microstylolite in chert. The microstylolite is outlined by an admixture of clay and carbonaceous matter. Sample No. 6, upper chert member, Caballos Formation, West Texas. Plane polarized light. x150. (J.A.M.)*

*Samples Nos. 8 and 9.* Staendebach Member, Tanyard Formation, near San Saba, Texas.

Sample No. 8 is grey to slightly bluish grey chert, with milky white patches that occasionally show agate-like banding, and a few clusters of quartz. Sample No. 9 is white to faintly buff chert, which encloses the darker chert of No. 8, partly dolomoldic, with small cavities lined with quartz and colloform silica. From

## Geochemical Study of Some Chert and Related Deposits

Staendebach Member, Tanyard Formation, Ellenburger Group (Lower Ordovician) in upper calcitic facies, from quarry 8 miles south of San Saba and a quarter of a mile east of Texas Highway 16. Collected by V. E. Barnes. The Tanyard Formation consists predominantly of irregularly bedded dolomites and limestones; the Staendebach, or upper, member is characterized by the presence of abundant chert (Cloud and Barnes, 1948).

In thin section the microcrystalline quartz contains many narrow veins of coarse quartz rimmed with chalcedonic quartz, and irregular patches of cryptocrystalline, almost amorphous quartz; holly-leaf shrinkage cracks are present, chiefly in No. 8.

Calcite occurs in opaque dusty layers, and in irregular patches; a few shreds and specks of sericite and limonite are present also. More calcite dust is present in No. 9, which probably explains its lighter colour than sample No. 8 and is the only visible difference between the two types.

*Sample No. 10.* Nodules and beds in Helderberg Limestone, West Virginia.

Uniformly dark grey chert with numerous black specks disseminated throughout, which give it a slightly layered appearance. From a horizon near the middle of the Helderberg Limestone (Lower Devonian) at the eastern end of the road-cut on route 46, just east of Limestone Run, east of Keyser, West Virginia. Collected by M. T. Heald, who has described the occurrence of this chert in nodules and as distinct beds in the limestone (Heald, 1952).

The microcrystalline quartz encloses clusters of chalcedonic quartz, and scattered grains of detrital quartz. Many irregularly shaped structures (sponge spicules?) are visible in reflected light, and give an impression of banding to the section.

Calcite is present in irregular dusty patches, together with scattered dolomite rhombs (both unaltered and fragmentary). Small black patches and shreds, which appear to be carbonaceous material, are often associated with the dolomite. A few grains of pyrite and clay are also present.

*Sample No. 12.* Staendebach Member, Tanyard Formation.

Light grey to bluish grey chert, interspersed with white to light yellow and brown patches, some of which have a nodular appearance. Locally dolomoldic and with a brecciated appearance because of numerous cracks. From the calcitic facies of the Staendebach Member, Tanyard Formation, Ellenburger Group (Lower Ordovician), approximately 40 feet from the top of the formation, at Moore Hollow section, Riley Mountain, Llano County, Texas. Collected by E. B. Parmelee. This stratigraphic section is described by Goldich and Parmelee (1947) and by Cloud and Barnes (1948).

The microcrystalline quartz is marked by many irregular curved fissures filled with chalcedonic quartz and small grains of normal quartz, and with areas of dense cryptocrystalline quartz, which may be related to the nodules in the hand specimen. Radiolaria skeletons (?) are present also.

Foreign minerals are abundant, including many tiny apparently amorphous grains, which may be silicified and clay-coated dolomite rhombs. Other dolomite rhombs are altered to clay and quartz, or appear to be partial cavities. Clumps of yellowish white clay are scattered through the section, as are a few specks of limonite. No calcite was observed.

*Sample No. 14.* Upper part of Maravillas Formation, Solitario, Texas.

Black to dark brown chert, resembling anthracite coal in appearance, with numerous cracks. From the upper part of the Maravillas Formation (Upper Ordovician), at Water Gap, east of East Tank, Solitario, Texas. Collected by S. S. Goldich. This formation consists of interbedded limestone and black bedded chert, varying in thickness from 100 to 400 feet, with chert predominant towards the top of the formation (King, 1937).

In thin section this black chert appears as microcrystalline quartz with much disseminated black and brown organic material. Large clear grains of detrital quartz are present, and small veins of microcrystalline quartz, some with black carbonaceous material in them, cut the specimen. Some oval patches may represent fossils, and the remains of sponge spicules are probably also represented.

Abundant foreign minerals include limonite, pyrite in various stages of alteration, and amorphous clumps of material, but identification is difficult because of the disseminated carbonaceous matter.

*Sample No. 17.* Huntersville Chert, type section at Huntersville, West Virginia.

Grey to buff chert, with brownish yellow, purple and dark grey patches, of shaly appearance because of suggestion of layering and with numerous small cavities and black specks visible beneath the hand lens. Huntersville Chert (Middle Devonian) from the type section at Huntersville, West Virginia. The formation is about 80 feet thick; the exact stratigraphic position of the sample, collected by M. T. Heald, is not known. The type section, described by Woodward (1943), consists of black cherty shale and rusty chert, with interbedded glauconitic sandstone and a top layer of grey clay.

The microcrystalline quartz is marked by abundant light brown clay with scattered black stringers and clumps of carbonaceous material, and is cut by a narrow vein of reddish brown limonite.

The clayey material appears yellowish white in reflected light, as do abundant small scattered rhomb-shaped grains, which may be silicified or clay-coated dolomite rhombs. Grains of reddish black iron oxide in various stages of alteration to limonite, and a few fragments that resemble biotite, are present.

*Sample No. 21.* Franciscan bedded radiolarian cherts, near Oakland, California.

Reddish brown siliceous radiolarian chert, with greyish white to yellowish white patches. From the Franciscan Group of bedded cherts (Jurassic?) near Oakland, California, in a quarry along the north side of Mountain View Cemetery property, about 1,500 feet northwest of the most northerly corner of the city of Piedmont. Collected by R. W. Graves, Jr. The Franciscan Group consists of

arkosic sandstones, radiolarian cherts, shales, conglomerates, limestones, pillow lavas, basalts, andesites, dacites, and volcanic ash, breccias and agglomerates; the maximum development of radiolarian cherts coincided with, and immediately followed, maximum volcanism (Taliaferro, 1943).

This red chert in thin section is seen to consist of microcrystalline to cryptocrystalline quartz with much disseminated red iron oxide dust (hematite?). Small circular areas, transparent in ordinary and reflected light, and filled with cryptocrystalline and chalcedonic quartz, are probably skeletons of radiolaria. Numerous small curving shrinkage cracks and narrow veins cut the section. Identification of the numerous tiny grains of foreign minerals present was not possible because of the red dust.

*Sample No. 23.* Bird Spring Formation, Clark county, Nevada.

Light reddish brown chert, with disseminated reddish brown specks visible beneath a hand lens, and numerous small cavities. From the Bird Spring Formation (Pennsylvanian) in beds up to 6 inches thick, interbedded with medium-bedded, sandy limestone, and making up less than 10 per cent of the formation. From Section 29, T23S, R59E, Clark county, Nevada. Collected by R. W. Graves, Jr.

Much cryptocrystalline quartz, as irregular small areas, occurs in interstitial microcrystalline quartz, with clusters of coarse quartz grains (shrinkage cracks?), spherulitic chalcedony and chalcedonic quartz, holly-leaf areas of chalcedonic quartz and detrital quartz grains. A reddish brown dust, dotted with tiny dark grains surrounded by dark brown haloes, outlines some of the irregular cryptocrystalline areas, as does yellowish white clay.

Calcite occurs as stringers and as dust, and dolomite rhombs are scattered throughout the section, with the reddish brown iron oxide dust and clay material. Limonite also occurs, some particles having tails of chalcedonic quartz.

## Novaculite

*Sample No. 2.* Lower novaculite member, Caballos Formation, Three-Mile Hill.

Milky-white novaculite, mottled with translucent quartz and with small cavities lined with small quartz crystals. Specimen from near middle of lower novaculite member, Caballos Formation, at same locality as No. 1. Collected by R. W. Graves, Jr.

Microcrystalline quartz is spotted with scattered clusters of coarse quartz and fissure-fillings of quartz, but lacks the chalcedonic quartz found in chert. Small circular spots (radiolarian skeletons?) are present with a network of short anastomosing lines, which may be desiccation cracks. Foreign minerals are almost absent from this specimen.

*Sample No. 3.* Upper novaculite member, Caballos Formation, Three-Mile Hill.

White to light buff novaculite, with tinges of pink and brown. Two stylolite seams, one a band  $\frac{3}{8}$  to  $\frac{1}{4}$  inch wide, the other a thin, wavy line. Stylolites are

striated and coated with red-brown iron oxide, and terminal stylolites are inclined towards the centre at a small angle. Upper novaculite member, 20 feet above the base of member, Caballos Formation, at same locality as No. 1. Collected by R. W. Graves, Jr.

In thin section the specimen closely resembles No. 2 but with a number of fine wavy lines that extend for varying distances across the section and which may be microstylolites. These consist of irregular narrow bands of fine-grained clay particles.

*Sample No. 5.* Upper novaculite member, Caballos Formation, Three-Mile Hill.

White novaculite, with a slightly pink tinge, and marked by a number of cracks with red-brown stains at the surface. Upper novaculite member, 10 feet from top of member, Caballos Formation, at same locality as No. 1. Collected by R. W. Graves, Jr.

The texture of the microcrystalline quartz in this specimen, as viewed in thin section, is coarser than that of the previous two specimens, with more clear quartz grains. Numerous geodal cavities (shrinkage cracks?) of the holly-leaf type are present; in reflected light these cavities appear as milky outlines and in ordinary light the cavities are rimmed with a brown colour typical of chalcedonic quartz.

Foreign minerals are scarce, but limonite and sericite are present; a grain was found that suggests a dolomite rhomb replaced by very fine-grained quartz.

*Samples No. 15 and No. 16.* Grey and white Arkansas Novaculite, Butterfield, Arkansas.

Sample No. 15 is grey to greyish white novaculite, with a network of thin black lines and a few tiny cavities and yellow specks. Sample No. 16 is white to light grey novaculite, with slabby appearance; a few oval spots are present on surface, filled with slightly coarser quartz, and weathered parts are covered with a fine white dust. Arkansas Novaculite (Devonian-Mississippian) from a quarry half a mile west of Butterfield, Arkansas. Collected by R. L. Erickson. This formation contains a wide variety of lithologic types, including novaculite, spiculite chert, calcareous chert, radiolarian chert, sapropelic chert, siliceous shale, and sapropelic paper shale (Goldstein and Hendricks, 1953).

In thin section these specimens are seen to consist of dense, cryptocrystalline, almost amorphous quartz, with scattered grains of detrital quartz; there is a notable absence of chalcedonic quartz.

Sample No. 15 contains a few clusters of tiny dolomite rhombs whereas No. 16 has abundant rhomb-shaped pits, generally empty but some containing residual patches of clay.

Foreign minerals are scarce, but limonite, clay, and biotite (?) occur as scattered particles.

## Flint

*Sample No. 18.* Black nodular flint, Dover Chalk, England.

Black nodular flint, brown in thin splinters, with a thin (1 mm) white to slightly yellow patina. From Dover Chalk (Cretaceous), England; specimen No. 5922 in the University of Minnesota Collection.

In reflected light the translucent greyish blue groundmass is crowded with vague outlines and cloudy structures that are pale-brown in ordinary light.

The cryptocrystalline quartz contains a few clusters of chalcedonic quartz and numerous tiny curved fractures that may be tension or desiccation cracks. Curved, oval, and circular structures, filled with chalcedonic quartz, may be fossil outlines but only one trident-shaped spicule was found.

Specks and stringers of black carbonaceous material, pyrite, sericite, and abundant brown organic material are scattered throughout.

## Chalcedony

*Sample No. 13.* Siliceous core of silicified algal (?) deposit, Uinta Formation, Moffat county, Colorado.

The translucent siliceous core of a biscuit-shaped deposit of silicified algae (?). From a weathered exposure of the Uinta (Eocene) Formation (Bridger equivalent in age and stratigraphic position) in Section 20, T9N, R99W, Moffat county, Colorado. Collected by R. L. Manly.

The specimen was cut from translucent silica core so as to include part of a brownish black mammillary deposit, which may be silicified algae; only the siliceous core was sampled for analysis. There is an irregular fissure in the core, lined with colloform silica.

In reflected light the thin section appears uniformly cloudy, with pale brown areas adjacent to dark brown layered masses (algae?). The specimen consists of fibrous chalcedony varying from short radiating fibers (colourless in ordinary light), which adjoin the algal (?) structures, to long sheaves (pale brown in ordinary light) that grow towards the centre of the core and intersect other similar sheaves. Between the short fibers and the long sheaves is a thin cryptocrystalline band that is in optical continuity with the inner and outer layers and which, under high magnification, is seen to consist of very minute fibers.

Only a few specks of limonite and some shreds of black carbonaceous material are present also. The brown colour of the algal (?) layers is due to admixed calcite and clay.

*Sample No. 20.* Nodule in clay pit, Augusta county, Virginia (Allen, 1952).

Translucent, roughly spherical nodule of chalcedony believed to be of Early Tertiary age, with a thin white coating of clay. Collected by Josiah Bridge, from whose notes the following description of the occurrence is taken:

Pit of the Cold Springs Mining Company, of Elizabeth, New Jersey, a subsidiary of the Georgia Kaolin Company. The Cold Spring Mine in Augusta County, Virginia, near Cold Spring station, on the Norfolk and Western, locally known as

the 'Chalk Mine'. It is visible from the Lee Highway and consists of a series of pits along the west face of the Blue Ridge. The east wall of the pit is in the Erwin (Lower Cambrian) quartzite which dips 60-75 degrees west. A 10-15 foot bed of soft, rather arkosic limonite lies on top of the Erwin and this in turn is overlain by the Shady dolomite, now completely weathered to clay. The fireclays are of various colours, mostly white and more or less sandy, containing balls of chalcedony. North pit is now abandoned about 40 feet deep. There is said to be clay to the bottom and bauxite in the centre, about a car load was taken out. This is all gone now except for a few pieces on the dump . . . These fireclays are totally different from the residual clays of the Shady dolomite and appear to have been deposited in sinks in that formation.

The specimen resembles the cryptocrystalline appearance of flint in thin section but lacks any suggestion of a fibrous nature. Some marginal areas consist of slightly coarser, chalcedonic quartz and a few clumps of clay are also present.

### Flamboyant Quartz

*Sample No. 22.* Siliceous cement from chert breccia, Burnt Creek area, Labrador.

Translucent to greyish white banded cement from the Precambrian Fleming chert breccia, showing colloform banding. From the Burnt Creek area, near the triangulation point of the Geodetic Survey of Canada, Labrador, Canada. Collected by G. M. Schwartz.

The thin section is composed of large blades and sheaves of flamboyant quartz, which have formed in successive layers that are visible in both reflected and ordinary light. The boundaries of the successive growth stages, visible as saw-toothed lines, are marked by thin bands of tiny quartz grains, but the whole maintains optical continuity throughout the length of the blade. Microcrystalline and chalcedonic quartz forms the core of a sheaf of quartz blades; the core exhibits beautiful anomalous blue and yellow colours between crossed nicols. No other minerals were found.

### Miscellaneous

*Sample No. 11.* Siliceous oolite (Wielandite), Mines Formation, Centre county, Pennsylvania.

Dark grey siliceous oolite, with black-centred oolites about 1 mm in diameter, in a greyish white matrix, stained yellow in places. The specimen, probably from the Mines Formation (Upper Cambrian), is from Centre county, Pennsylvania and is in the University of Minnesota Collection (No. P-107G). Numerous descriptions have been given of this oolite (Pettijohn, 1949, pp. 75, 328).

In reflected light the appearance of the oolites varies from well formed to vague in outline. Some have milky centres, while others have translucent centres surrounded by concentric cloudy, milky or brown rings in places showing possible tension cracks. Some oolites are deformed. The nuclei range from very small to large, and some oolites have small grains of limonite at their centres.

Between crossed nicols the oolites show all varieties of coarse- to fine-grained quartz, with possibly some opal as well. The nuclei consist of large rounded



grains of clear quartz and of cryptocrystalline and microcrystalline quartz. The matrix enclosing the oolites is made up of generally microcrystalline quartz containing small incipient oolites, and some chalcedonic quartz, but few foreign mineral grains.

Fine-grained calcite and clay occur as narrow bands in some oolites, together with grains of limonite and shreds of sericite. The limonite grains often have tails of chalcedonic quartz.

*Sample No. 19.* Jaspilite from drill-core, Soudan Formation, Soudan, Minnesota.

Pinkish white to white jaspilite, present as bands about three quarters of an inch thick, in a  $\frac{7}{8}$  drill-core. From the Precambrian Soudan Formation, hole No. 842, at 83 feet, in 1,900-foot level of the Soudan Mine, Soudan, Minnesota. Collected by G. M. Schwartz.

The Soudan iron formation, consisting of a great thickness of several varieties of contorted and banded jasper and associated slaty beds, with zones of hematite, is interbedded with greenstone of the Precambrian Ely greenstone formation, and originated as a chemical precipitate (Schwartz and Thiel, 1954).

The specimen consists entirely of a uniform mosaic of interlocking quartz of varying grain size, cut by a single vein filled with coarser grains. In reflected light the section is translucent and colourless, with a network of fine red lines that outline many of the grains of the mosaic and impart the pink colour to the specimen.

Specks of limonite, bluish black grains (probably magnetite) surrounded by red masses of limonite, and an unidentified green mineral, also surrounded by limonite, are present together with a few small patches of calcite.

*Sample No. 7.* Melikaria from Quaternary alluvial deposit, Brazos county, Texas.

Light buff to white melikaria, of flattened oval shape, with dimensions  $8\frac{1}{2}$  by 5 by  $1\frac{1}{4}$  inches, and cell walls varying from  $\frac{1}{16}$  to  $\frac{1}{2}$  inch thick. From Quaternary alluvial deposit on top of Yegua Formation (Eocene) at Lake Cimeno, 4 miles east of Bryan, Brazos county, Texas. Collected by F. A. Burt (1928) and given the name melikaria (from the Greek for 'honeycomb'). The specimen (see Pl. II) was generously donated by Clay Seward, Agricultural and Mechanical College of Texas.

The flattened honeycomb structure, although appearing fragile, is of surprising toughness. The specimen is brownish white and translucent on thin edges, with a smooth hard surface reminiscent of unglazed porcelain; the luster is dull and earthy, the surface pitted, and the specimen breaks irregularly, revealing masses of quartz grains (2 to 3 mm) on the fracture surface. There is a gradation of quartz grains, from larger grains at the centre of the break to smaller grains at the outside of the wall. No thin section could be made of this material.

The specimen was found in a bed about 10 feet below the surface and about 5 feet above the contact of the Quaternary alluvial deposits with the Yegua (Eocene) Formation, in the upper part of which are many dense, impervious beds

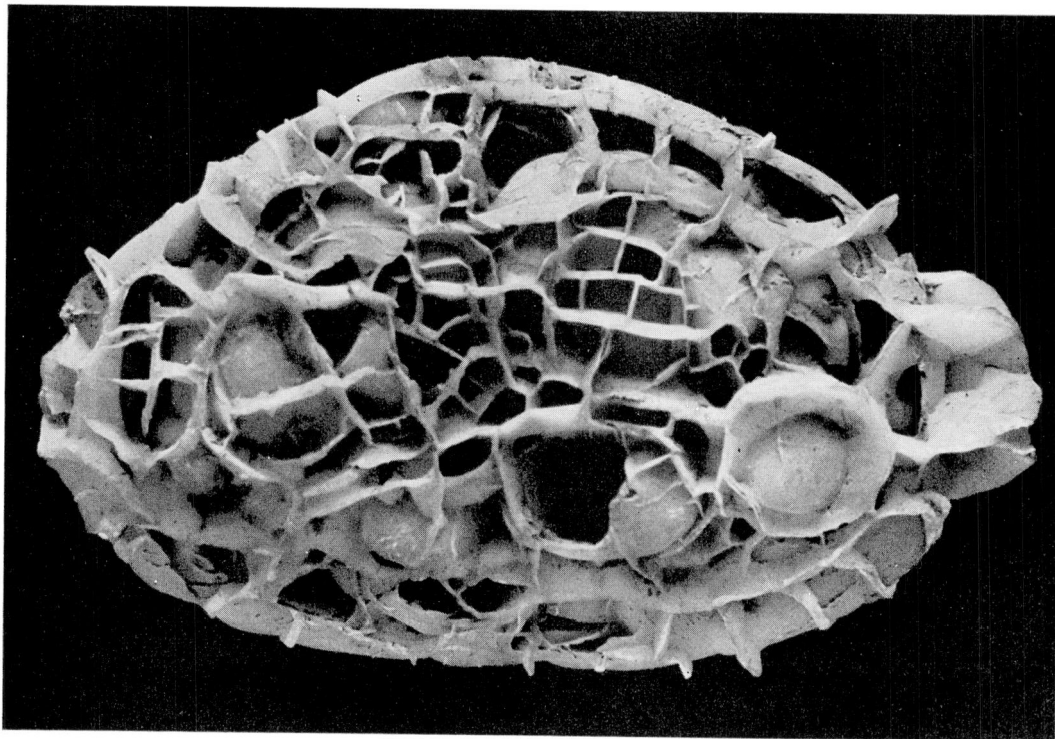


PLATE II. *Melikaria* from an alluvial deposit, freed from interstitial sand and clay. Sample No. 7, Bryan, Brazos county, Texas. Specimen about half size. (Photograph by R. B. Taylor)

of clay. Associated with the melikaria are petrified wood, selenite, limonite, and traces of halite.

Burt (1928) concluded that this is an epigenetic structure that formed in place in the bottom of deep desiccation cracks by acidification of silica-bearing waters rising from below through fractures in the wet season, and by precipitation through evaporation above the water table, from rising waters during the dry season.

*Sample No. 24.* Petrified wood, Chinle Formation, Arizona.

Light grey to greyish white petrified wood, with buff waxy patches. From the Triassic Chinle Formation in sand and clay, near Petrified Forest, Arizona. Collected by C. E. Evensen.

In ordinary light, the thin section of the specimen is seen to consist of a greyish brown matrix containing numerous tiny circular outlines, some of which are transparent. Viewed between crossed nicols, the section consists of cryptocrystalline quartz with numerous irregular amorphous patches. A large, irregular and discontinuous crack is filled with chalcedonic and coarse quartz. The patchy greyish brown material is very fine-grained calcite. Apart from a few scattered dolomite rhombs, no other minerals could be found.