

POLLUCITE FROM KARIBIB, SOUTH WEST AFRICA*

H. J. NEL, *Geological Survey of the Union of South Africa,
Pretoria, South Africa.*

ABSTRACT

Pollucite, the only caesium silicate mineral known, is recorded from a new locality. It has a refractive index of 1.5173 (Na light) and the dispersion $n_F - n_C = .0083$. A chemical analysis of the mineral is given and from a consideration of this and other available analyses, it appears that an isomorphous series exists between pollucite and analcite. This series results from the isomorphous replacement of Cs^+ by Na^+ with the concomitant introduction of a water molecule into the unit cell. The variation of the refractive index within this series is shown graphically. Some dehydration results obtained on the pollucite from Karibib are briefly discussed.

INTRODUCTION

The first known occurrence of pollucite in Southern Africa came to light recently when a specimen submitted to the Geological Survey by Mr. F. J. Jooste† was found to consist mainly of this mineral. According to Mr. Jooste the pollucite, of which he considered some twenty-five tons to be available, was discovered on the farm Okongava Ost No. 72, approximately seven miles S.S.E. of the town of Karibib in South West Africa. Subsequently further prospecting work was done, though it is not known whether additional tonnages have been proved.

The pollucite is associated with lithium minerals in pegmatites, thus once again illustrating its characteristic paragenesis. De Kock (1), who described the lepidolite deposits of the Karibib area in 1932, found the more important of them to be grouped on and around the farm Okongava Ost No. 72. In addition to lepidolite, petalite and amblygonite are found here in exploitable quantities.

Because of pressure of work it has not been found possible to visit these deposits, so that the present paper will necessarily be confined to a description of the mineralogical and chemical properties of the pollucite.

MINERALOGY

The massive pollucite from Karibib is traversed by numerous thin white veins up to a millimetre in thickness. These veins are composed mainly of an extremely fine-grained clay-like mineral which is anisotropic with $n = 1.55-1.56$. Veins of lepidolite of the order of 4 millimetres thick and some quartz are also present in the pollucite available for study.

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† Managing Director, Jooste Lithium Mines (Pty.) Ltd., Karibib, South West Africa.

Physical Properties

The pollucite is perfectly colorless, glassy clear and fully isotropic. The refractive index, determined by measuring the angle of minimum deviation on a small prism specially prepared for the purpose, is $1.5173 \pm .0002$ (Na light). The dispersion, similarly obtained, is given graphically in Fig. 1. The specific gravity, determined by suspension of pure fragments of pollucite in a solution of bromoform and alcohol, was found to be $2.865 \pm .005$.

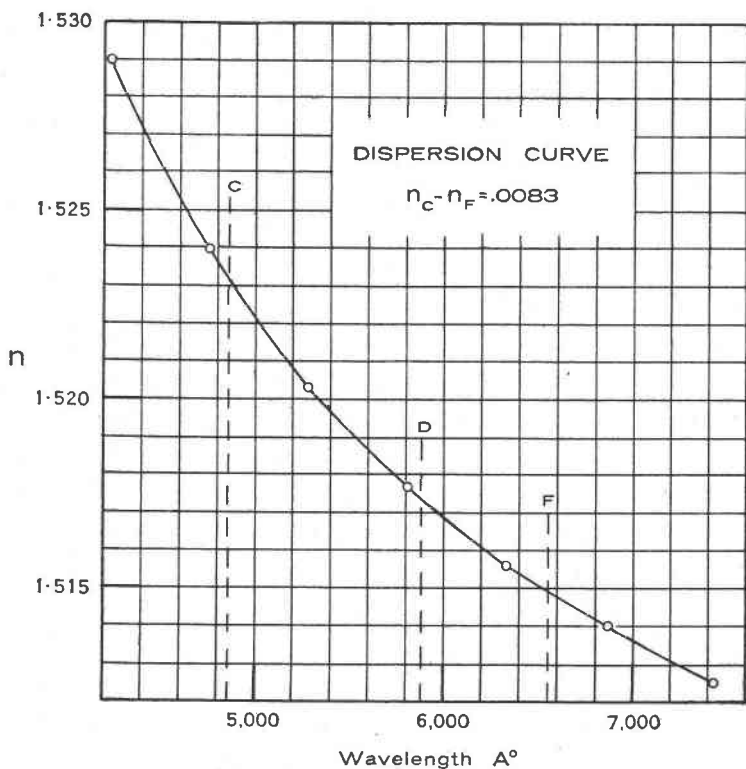


FIG. 1. Dispersion curve of pollucite from Karibib, S. W. A.

Chemical Composition

For analytical purposes pure fragments of pollucite were selected from crushed material under a binocular microscope. In this way pollucite of ideal purity was obtained.

A qualitative spectrographic analysis of the pollucite by Dr. B. Wasserstein of the Geological Survey yielded the following results:—

Present: Cs, Na, Al, Si, Rb, Tl, K

Trace: Li, Ga.

Absent: Sr, Ca, Mg, Mn, Fe, F, B, Ti, V, Cr, Pb.

The chemical analysis given in Table 1 was done by Dr. C. F. J. van der Walt of the Division of Chemical Services, Pretoria. The micro-method employed by him to determine Cs₂O and Rb₂O + K₂O is based on a method described in "The Analysis of Minerals and Ores of the Rarer Elements" (2nd Ed.) by W. R. Schoeller and A. R. Powell (Griffin and Co. Ltd., London, 1940).

TABLE 1

a		b	c		d	e	
SiO ₂	45.7	.7608	Si	.7608	33.39	SiO ₂	46.4
Al ₂ O ₃	17.2	.1688	Al	.3376	14.81	Al ₂ O ₃	16.3
Cs ₂ O	30.2	.1073	Cs+Rb+K	.2286	10.03	Cs ₂ O	32.0
Rb ₂ O+K ₂ O*	1.3	.0070	Na	.0904	3.97	Na ₂ O	2.8
Na ₂ O	2.8	.0452	O	2.1875	96.00	H ₂ O	2.5
H ₂ O	2.66	.1477	H	.2954	11.69		
							100.0
Total	99.86						

* Calculated as Rb₂O

a. Chemical analysis by C. F. J. van der Walt.

b. Molecular proportions.

c. Atomic proportions.

d. Calculation of formula on a water-free basis of O=96.

e. Theoretical composition for pollucite with the unit cell Cs₁₀Na₄Al₁₄Si₃₄O₉₆ · 6H₂O.

The crystal structure of pollucite has been investigated by Strunz (2) and Náráy-Szabó (3), and it appears to be accepted that the unit cell contains 96 atoms of O (water-free basis) and that Si+Al=48. In the ideal case 2Al=Si, though to what extent the actual formulae may depart from the theoretical as far as this consideration is concerned, will be shown later. The unit cell formula for the pollucite from Karibib, calculated from the analysis on the basis of O=96, is as follows:



THE RELATIONSHIP OF ANALCITE AND POLLUCITE

Various authors have commented on the similarity of pollucite and analcite. The unit cell of analcite has the symmetry of the space group O_h¹⁰(7, 15), and that of pollucite O_h¹⁰—Ia3d or D_{4h}²⁰—I4/acd(2, 3). The respective sizes of the unit cells are to all intents and purposes similar, viz. pollucite a₀ = 13.64—13.74 Å (2, 3, 4, 5, 6) and analcite a₀ = 13.68 Å (7).

The unit cell formula for analcite is $\text{Na}_{16}\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot 16\text{H}_2\text{O}$ and that of "ideal" pollucite has been given by Strunz (2) as $\text{Cs}_{16}\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot 8\text{H}_2\text{O}$. It will be shown in the following pages however, that the unit cell of sodium-free pollucite should not contain any water.

The crystal structure of pollucite has been investigated by Strunz (2) and Náray—Szabó (3, 12) and that of analcite notably by Taylor (7, 11). Both minerals are built up of alumina and silica tetrahedra conforming to the silica type, though there is some difference of opinion regarding the positions occupied by the alkali ions. According to Náray-Szabó (3) pollucite and analcite have the same Al-Si-O frameworks: in pollucite the caesium and in analcite the sodium ions occupy the 16-fold positions ($\frac{1}{8}\frac{1}{8}\frac{1}{8}$) etc., while the water molecules partially occupy the 24-fold positions ($0\frac{1}{4}\frac{1}{8}$) etc. Taylor, however, maintains that in analcite the 16 sodium ions are distributed at random over the 24-fold positions ($0\frac{1}{4}\frac{1}{8}$) etc., and the water molecules occupy the 16-fold positions ($\frac{1}{8}\frac{1}{8}\frac{1}{8}$) etc.

In the past investigations have not indicated Cs and Na separately in the formulae for pollucite, thereby missing a rather interesting relationship. The pollucite analyses which were available in 1938 are quoted by Quensel (8). Three later analyses are given by Richmond and Gonyer (5). These analyses may be consulted by referring to the two above mentioned publications.

The unit cell formulae given below were calculated from some of these analyses on the water-free basis of $\text{O} = 96$ and adjusted slightly in some instances to satisfy the condition $\text{Al} + \text{Si} = 48$. In this case it may readily be seen that $\text{Cs} + \text{Na}$ must be equal to the number of Al atoms given in the unit cell formula, so as to satisfy the valencies. Here $\text{Cs} + \text{Ca} + \text{K} + \text{Mg} + \text{Rb}$ is given as Cs, $\text{Na} + \text{Li}$ as Na and in a few instances $\text{Al} + \text{Fe}$ as Al. It may be as well to mention that in these chemical analyses CaO , MgO , K_2O , Fe_2O_3 and Li_2O are occasionally present only in very small amounts, usually well below 0.5% each. The presence of these elements in some cases may probably be ascribed to impurities present in the pollucite analyzed.

For the unit cell formulae given below only analyses were used where the original references could be consulted:

Localities

- | | |
|---|--|
| A. $\text{Cs}_{12}\text{Na}_3\text{Al}_{15}\text{Si}_{33}\text{O}_{96} \cdot 4\text{H}_2\text{O}$. | i. Tamminen Quarry, Greenwood, Maine (5). |
| | ii. Rumford, Maine (13). |
| | iii. Hebron, Maine (14). |
| B. $\text{Cs}_{11}\text{Na}_4\text{Al}_{15}\text{Si}_{33}\text{O}_{96} \cdot 5\text{H}_2\text{O}$ | i. Leominster, Massachusetts. (5) |
| C. $\text{Cs}_{11}\text{Na}_3\text{Al}_{14}\text{Si}_{34}\text{O}_{96} \cdot 5\text{H}_2\text{O}$ | ii. Varutråsk, Sweden (8). |
| D. $\text{Cs}_{10}\text{Na}_4\text{Al}_{14}\text{Si}_{34}\text{O}_{96} \cdot 6\text{H}_2\text{O}$ | i. Karibib, South West Africa. |
| | ii. Elba (6). |
| E. $\text{Cs}_7\text{Na}_7\text{Al}_{14}\text{Si}_{34}\text{O}_{96} \cdot 9\text{H}_2\text{O}$ | i. Oxford Milling and Mining Co. Quarry, Greenwood, Maine (5). |

In some instances a formula slightly modified from that given above would also satisfy the relevant analyses sufficiently well to be accepted. This is, however, of secondary importance as these alternative formulae would do equally well to illustrate the relationship between analcite and pollucite.

From these formulae the following relationships may be deduced:

1. The number of Cs ions is inversely proportional to the number of Na ions in the unit cell.
2. $Cs^+ + H_2O = 16$.

In view of the importance of the second relationship, it may be as well to give the actual values obtained (Table 2) in calculating the unit cell formulae. The total of $Cs^+ + H_2O$ is considered to be constant at 16 within the range of experimental error.

TABLE 2

	A			B	C	D		E
	i	ii	iii	i	i	i	ii	i
Cs	11.66	11.99	12.41	11.00	10.81	10.03	10.90	7.38
H ₂ O	4.09	3.98	3.82	5.03	4.31	5.85	6.54	8.69
Total	15.75	15.97	16.23	16.03	15.12	15.88	17.44	16.07

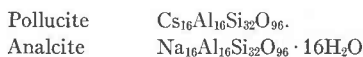
(In the case of formula D ii, the analysis shows 0.72% CaO and 0.77% Fe₂O₃. This total shows the greatest deviation from the average total of 16.)

From the formulae it will be seen that when one sodium ion replaces one caesium ion, there is a concomitant introduction of a molecule of water into the unit cell. It is interesting to note that the replacement suggested here involves two ions whose ionic radii are by no means comparable: that of Cs⁺ is 1.65 Å, while that of Na⁺ is 0.98 Å (Goldschmidt). The most obvious explanation for this unique type of replacement would be that when Na⁺ is substituted for Cs⁺, "free" space would be left by the latter which would facilitate or permit the introduction of a water molecule into the unit cell. In this case the structure for pollucite and analcite as proposed by Náray-Szabó would appear to be more acceptable than that advanced by Taylor.

Thus an isomorphous series, at least of limited miscibility, exists between analcite and pollucite, and is effected by the isomorphous replacement of Cs⁺ by Na⁺, with the accompanying introduction of a water molecule. The miscibility of pollucite and analcite is thought to depend more on the composition of the mineralizing solutions at the time of

formation, rather than on any inherent characteristics of the respective unit cells.

Omitting for the purpose any replacement affecting the Al and Si ions, theoretical end members of the series, with idealized unit cell formulae as follows, are obtained.



Thus it will be seen that the unit cell of sodium-free pollucite should not contain any water, and that it is therefore not a zeolitic mineral. With analcrite which is a typical zeolite, it forms a series which becomes progressively more zeolitic as the analcrite end of the series is approached. The series may be represented by the following generalized theoretical formula where $x=0$ in pollucite and $x=16$ in analcrite



The Replacement Affecting the Al and Si ions

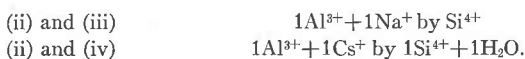
In the determination of the replacement affecting the Al and Si ions, formula *A* may be taken as an example:



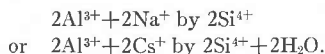
and compared with the nearest theoretical formulae (see i)



The following replacements may therefore be considered to have taken place:



Similarly in formulae *C*, *D* and *E*



It is interesting to note that the reverse replacements to those indicated above do not take place. This is in agreement with the conception of ionic replacement according to comparable ionic radii.

A generalized formula for the analcrite-pollucite series, taking these replacements into consideration, may be written as follows:



where $x=0$ and $y=0$ for the theoretical end-member pollucite.

When $x=16$ and $y=0$ the ideal analcrite formula is obtained. As can be

seen from the formulae, y is either 1 or 2, and in ideal analcite and pollucite equal to zero.

Richmond and Gonyer (5) proposed the formula $Cs_{14+x}Al_{14}(Al_xSi)_{34}O_{96} \cdot 4-9H_2O$ for pollucite. Here $x=0, 1$ or 2 . As this formula fails to express the relationship of Cs^+ to Na^+ and H_2O , formula (v) should be more acceptable.

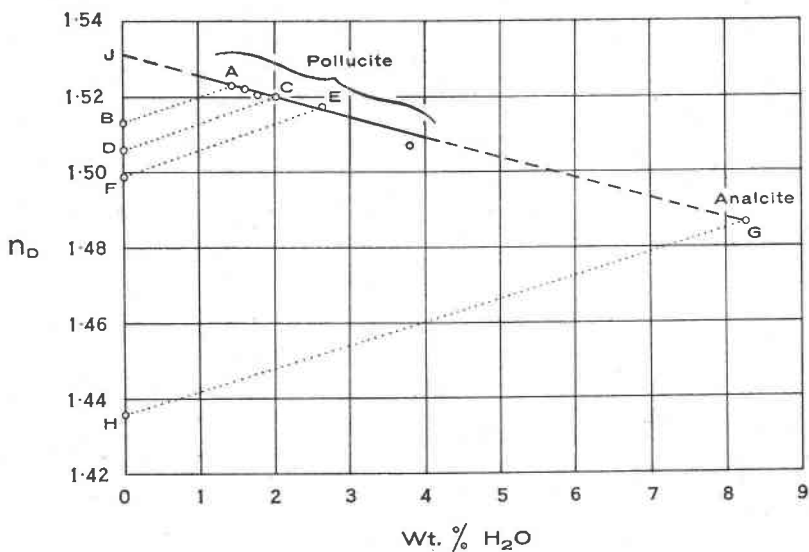


FIG. 2. Variation of the refractive index in the pollucite-analcite series.

In Fig. 2 the variation of the refractive index with the water content of the pollucite-analcite series is shown by means of the graph JG , where J represents the interpolated refractive index (1.532) of water-free and sodium-free pollucite. The point G represents pure analcite. Fleischer and Ksanda (9) and Strunz (2) have shown that the refractive index of pollucite is lowered on dehydration. The dotted lines AB , CD , EF and GH represent the changes undergone by the refractive indices of pollucite from Hebron (9), Elba (9) and South West Africa and that of analcite (Fassathal, Tyrol) on dehydration. For the loss of every 1.46% H_2O in pollucite and 1.66% H_2O in analcite, n_D is lowered by 0.01.

THE DEHYDRATION OF POLLUCITE

This subject was studied carefully by Fleischer and Ksanda (9) who came to the conclusion that "the shape of the dehydration curve is not, in this case at least, a reliable means of deciding the role of water in a mineral." From other considerations, such as the similarity of the rota-

tion powder spectrum photographs of natural and dehydrated pollucite, the difficulty of dehydration and rehydration, the latter even under high temperatures and pressures, led these authors to the conclusion that the water present in the mineral is not an essential part of the crystal lattice.

Náray-Szabó (3) is of the opinion that the effect of dehydration is so slight, due to the low water content, that no difference will be observed on the x -ray photographs of the natural and dehydrated material and that consequently this argument cannot be advanced in the discussion of the role of water in pollucite. Fleischer and Ksanda (9) have sought to explain the difficulties of dehydration and rehydration by virtue of the fact that "the very large caesium ion occupies much of the 'free' space in the pollucite structure. This steric effect would also account for the low water content and for the difficulty of dehydration."

Kenny, Jenny and Brown (10) have shown that particle size is an important factor determining variations in dehydration properties. In view of their results the dehydration properties in the present investigation were determined on two sieved grades of coarseness of pollucite from South West Africa. These curves are given in Fig. 3. Approximately 1.5 grams were used in each case and simultaneously heated in weighed platinum crucibles in an electric furnace for periods of 24 hours at a time, until the loss of weight, as compared with the previous weighing, did not exceed 0.03%, after which the temperature was raised another step. The crucibles were allowed to cool in a desiccator and weighed.

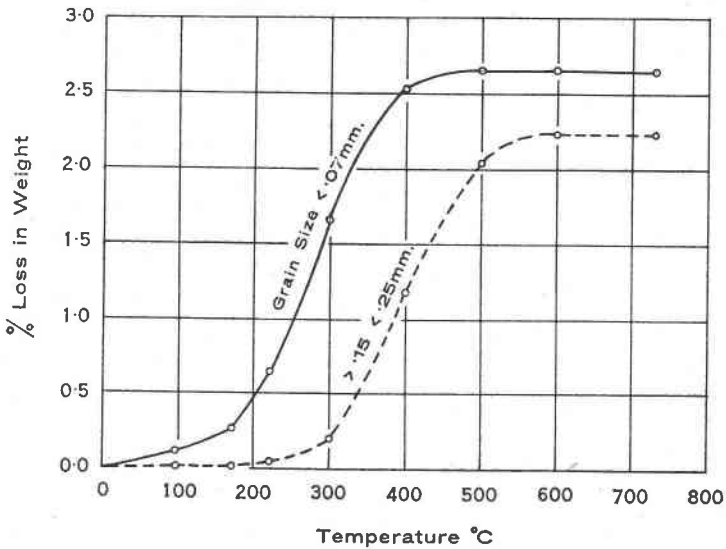


FIG. 3. Dehydration curves for pollucite from Karibib, S. W. A.

As is to be expected the pollucite of grain-size $<.07$ mm. was much more readily dehydrated than the coarser material, losing most of its water in the temperature range $200-400^{\circ}\text{C}.$, while the coarser material lost most of its water between 300° and $500^{\circ}\text{C}.$ It is interesting to note that whereas the pollucite of finer grain lost 2.66% the coarser material lost only 2.23% $\text{H}_2\text{O}.$ It is thought that the thermal agitation in the latter instance is not sufficient to allow the water molecules to escape from the interior of these comparatively large grains. It would therefore seem as if grain size, among others, was an important factor which led to the different dehydration curves obtained by Strunz (2) and Fleischer and Ksanda (9). In this connection it may be of interest to mention that the dehydration curve of the Karibib pollucite of $<.07$ mm. corresponds closely to that obtained by Strunz (2) on pollucite (2.58% $\text{H}_2\text{O}.$) from Elba.

The dehydrated pollucite of $>.15<.25$ mm. grain size shows decided though faint signs of anisotropism under the microscope. While this feature is well known in the case of dehydrated analcite, it has not yet been mentioned in connection with pollucite. The pollucite used in the past in dehydration experiments was probably too finely powdered to show any signs of anisotropism.

In both cases the dehydration curves of the pollucite from Karibib seem to indicate that the water is "bound," while the discussion in the previous section would certainly lead one to the conclusion that the water is an essential part of the crystal lattice, by virtue of the isomorphous replacement of Cs^+ by Na^+ and the concomitant introduction of a water molecule into the unit cell. This replacement results in the pollucite-analcite series which this investigation has shown to exist.

ACKNOWLEDGMENTS

In conclusion I wish to express my gratitude to my colleague, Dr. J. E. de Villiers who originally identified the pollucite, for his interest and numerous helpful suggestions; to Dr. B. Wasserstein for the qualitative spectrographic analysis and to Dr. C. F. J. van der Walt for the chemical analysis. I am indebted to the Drawing Office staff of the Geological Survey for the preparation of the text-figures.

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PROCEEDINGS OF SOCIETIES

ABSTRACTS OF MINUTES OF THE NEW YORK MINERALOGICAL CLUB

Meeting of April 19, 1944

The president, Mr. Taylor, announced the death of John A. Grenz, an active member of the club since 1894. The officers for the following year were elected, as follows:

James A. Taylor, President
 Frederick H. Pough, First Vice-President
 Robert B. Sosman, Second Vice-President
 Cecil H. Kindle, Treasurer
 Gilman S. Stanton and John N. Trainer, Directors
 Elizabeth Armstrong, Secretary

Dr. Michael Fleischer of the United States Geological Survey spoke on "The Mineralogy of the Manganese Oxides," reviewing the various oxides and the identification techniques necessary for distinguishing them.

Meeting of May 17, 1944

The officers gave their annual reports and a club trip to the William Boyce Thompson collection was planned. The president, Mr. Taylor, announced the death of William H. McClelland. The speaker of the evening, Dr. Frederick H. Pough, reported on some of the mineralogical highlights of his recent trip to South America.

ELIZABETH ARMSTRONG, *Secretary.*