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On Gearksutite at Gingin, Western Australia.<sup>1</sup>

By EDWARD S. SIMPSON, D.Sc., B.E., F.C.S.

Government Mineralogist and Chemist, Geological Survey of Western Australia.

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G EARKSUTITE, a hydrous fluoride of aluminium and calcium, is one of the rarest of minerals, having been found hitherto in but three localities, and in those only in quite small quantities. The previously known localities are in Greenland, Colorado, and the Urals, in all of which the mode of occurrence is essentially identical. The discovery of such a rare species in an entirely new region appears well worth recording, the more so as the genesis and mode of occurrence in this new instance are entirely different to those previously described.

#### Historical.

The history of the species may be briefly summarized thus:

1862. J. Thomsen observed an earthy white mineral, consisting of fluorides of aluminium and calcium, to be associated with cryolite from Ivigtut (Evigtok) on Arksut-Fiord, Greenland. Tidsskr. Phys. og Chem., 1862, p. 828.

1866. G. Hagemann's detailed description of cryolite and associated minerals from Greenland contained no reference to any mineral resembling gearksutite. Amer. Journ. Sci., ser. 2, vol. 42, p. 268.

<sup>1</sup> Published by permission of A. Gibb Maitland, Government Geologist.

1867. G. Hagemann recognized the presence of this mineral in Ivigtut cryolite ore, and made an imperfect analysis of it. He did not publish these results, however, but communicated them to J. D. Dana.

1868. Hagemann's analysis with a very imperfect mineralogical description published by J. D. Dana, who recognized the mineral as a new species under the name gearksutite. System of Mineralogy, 5th edit., p. 180.

1888. W. Flight published an imperfect analysis of the mineral from the type locality, and, under the impression that it was hitherto undescribed, gave it the name evigtokite. Journ. Chem. Soc., vol. 43, p. 140.

1883. P. Groth gave a more detailed description of the Greenland mineral, including its microscopic appearance and most obvious optical properties (qualitative only). He also first suggested that hydroxyl replaced part of the fluorine. Zeits. Kryst. Min., vol. 7, pp. 460, 481.

1883. W. Cross and W. F. Hillebrand described a second occurrence of gearksutite, viz. at St. Peter's Dome. Colorado, with a complete analysis and partial physical, chemical, and paragenetical description. They pointed out the identity of Flight's evigtokite with this species. Amer. Journ. Sci., 'ser. 3, vol. 26, p. 284; Bull. U.S. Geol. Survey, 1885, no. 20, p. 58.

1885. The first perfect analysis of Greenland gearksutite made by G. Lindström and published by A. E. Nordenskiöld, who discussed the origin of the mineral. Geol. För. Förh. Stockholm, vol. 7, p. 684.

1886. A. E. Nordenskiöld observed in specimens from a third locality, viz. Missk in the Ilmen Mountains, Russia, a mineral which he considered to be gearksutite, because of its structure and blowpipe reactions. Geol. För. Förh. Stockholm, vol. 8, p. 175.

1896. The sixth edition of Dana's System (p. 181) gives a very brief account of the physical and chemical properties of the mineral with Hillebrand's and Lindström's analyses, and reference to the first two localities only.

1905. O. B. Bøggild gave a general account of the Greenland mineral. Mineralogia Greenlandica, Meddel. om Grønland, vol. 32, pp. 126-128.

1912. O. B. Bøggild published a very full account of the 'minerals of the cryolite group' which included a fairly complete description of some specimens from Miask containing gearksutite. He gave its refractive index for the first time. Meddel. om Grønland, vol. 50, p. 125; translation in Zeits. Kryst. Min., 1913, vol. 51, p. 610.

1918. C. Hintze gave a summary of the available physical and chemical data with a brief account of its occurrence in all three localities. Handbuch der Mineralogie, vol. 1, p. 2546.

#### Localities and Matrix.

Ivigtut, Frederikshaab district, Greenland.—At this locality gearksutite is a minor constituent of the famous cryolite deposit. The latter has been described as a pneumatolytic or hydrothermal pipe in granite, which in turn is surrounded by a biotite-gneiss. The central core of the pipe,  $500 \times 100$  ft. in cross-section, consists mainly of cryolite with quartz, siderite, galena, blende, pyrite, chalcopyrite, and wolframite. Surrounding this central core is a pegmatitic shell 100 ft. wide consisting mainly of quartz, microcline, and ivigitie (a variety of mica), but carrying also in smaller proportions all the minerals found in the central core as well as fluorite, cryolithionite, cassiterite, molybdenite, arsenopyrite, and columbite. Fissures in the main cryolite mass contain crystallized cryolite as well as many later formed or derived minerals, including pachnolite, thomsenolite, chiolite, ralstonite, and finally gearksutite. The gearksutite is said mostly to fill small cavities and fissures in cryolite and in its associates, particularly thomsenolite, being often accompanied in these cavities by quartz, ralstonite, pachnolite, and thomsenolite. Masses up to 2 dm. in diameter are recorded.

St. Peter's Dome, El Paso Co., Colorado.—The occurrence in this locality is essentially similar to that at Ivigtut. Considerable quantities of cryolite have been found in 'veins of secretion' in the Pike's Peak granite, a rock composed of orthoclase, albite, biotite, and quartz. The pegmatite-veins are composed chiefly of quartz and microcline, and in these are found small masses of cryolite, pachnolite, thomsenolite, ralstonite, elpasolite, gearksutite, and fluorite, as well as zircon, astrophyllite, and columbite. As at Ivigtut, gearksutite is the last-formed fluoride, filling cavities lined with pachnolite and other associated minerals.

Miask, Ilmen Mtns., Urals, Russia.—The available descriptions of this occurrence are very incomplete. It would appear, however, that geark-sutite occurs as the filling of minute fractures in a topaz- and cryolite-bearing pegmatite. Cryolite, fluorite, cryolithionite, chiolite, thomsenolite, lithia-mica (zinnwaldite r), topaz, microcline, phenacite, and quartz are recorded as associated minerals.

Gingin, Swan Co., Western Australia.—Gingin is a small farming town, situated forty miles north of Perth, on the banks of Gingin Brook at the point where it emerges from the Darling Plateau on to the Coastal Plain. This plain rises gradually from a few feet above sea-level immediately east of Perth, to an elevation of about 250 feet at Gingin, whilst the western edge of the Darling Plateau descends gradually from 1,000 ft. to about 650 ft. For twenty miles north of the latitude of Perth the scarp of the plateau is coincident with a fault marking the junction between the Archaean granite and gneiss of the plateau and the thick accumulation of almost horizontal sediments, ranging from Carboniferous to Recent, which forms the coastal plain. Twenty miles south of Gingin, however, the scarp and the faulted junction of granite and sediments diverge, so that at Gingin itself only sediments are seen in the spurs of the plateau as well as on the plain, and no granite is met with for eight miles to the east (see section, fig. 1).



Fre. 1.—Geological section, west to east, through Gingin, Western Australia, to illustrate the gearksutite occurrence.

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The Gingin sediments are practically horizontal and have been considerably dissected down to the level of the coastal plain by Gingin Brook and its tributaries. Faulting has possibly occurred at or close to the scarp immediately west of Gingin, but no definite evidence of this, other than the purely physiographical one, has been adduced. Immediately to the east of Gingin, where the gearksutite occurs, there is no indication of any dislocation, folding, vulcanism, or metamorphism, nor of any vein-forming action of any kind.

The Gingin beds have yielded a good suite of marine fossils which determine their age to be Cretaceous.<sup>1</sup> Owing to the soft nature of the beds and the somewhat thick accumulation of soil on the slopes of the spurs of the plateau, the exact sequence of beds has not been made out. In descending order it appears to be:

1.	Hard ferruginous sandstone (wea-	
	thered greens and 10	) feet.
2.	Glauconitic sand and sandy shale 140	),,
8.	Chalk with abundant fossils (In-	
	oceramus, Spirulaea, Ammo-	
	nites, &c.)	,,
4.	Greensand 100	,,
5.	Shale with little or no glauconite 150	"

At several horizons in the chalk and the two greensands there are phosphatic nodules in more or less abundance, and it is on one of these horizons, viz. in the lower portion of the upper greensand, a few feet above the chalk, that the gearksuite occurs.

<sup>1</sup> R. Etheridge, Jnr., The Cretaceous fossils of the Gingin chalk. Geol. Surv. West. Aust., 1913, Bull. 55. F. Chapman, Monograph of the foraminifera and ostracoda of the Gingin chalk. Geol Surv. West. Aust., 1917, Bull. 72.

So far, gearksutite has only been found in a single small shaft 10 ft. deep, sunk on Loc. 457, two miles due east of the railway station. The shaft, which was originally put down in search of phosphatic nodules, is situated on the northern slope of Molecap Ridge, about 120 ft. below the summit, and 250 above the level of Gingin Brook, which flows along the foot of the ridge. The gearksutite appears to be confined to a narrow (12 inch), rather clayey bed with abundant glauconite and small phosphatic nodules, lying horizontally six feet below the surface. Closer to the surface the glauconitic material carries brown laterite pebbles, which appear again in some abundance on a clayey outcrop about 50 ft. higher up the slope. The crest of the ridge is composed of a hard sandstone with abundant limonite, which a shallow shaft (about a mile distant) has proved to be merely a weathered greensand, probably to some extent laterized. Only the one shaft has been sunk through the gearksutite horizon, whose horizontal extent is therefore in doubt. A second shallow shaft sunk in highly glauconitic sand and clay about 30 ft. higher up the slope has disclosed numerous small phosphatic nodules, but no gearksutite. About 80 ft. farther down the slope is a small open cut in the chalk, which has yielded numerous large phosphatic nodules, but no gearksutite. Beside this open cut is a shaft penetrating the chalk and underlying greensand to a depth of over 30 ft. No gearksutite was encountered in this lower greensand.

Summarizing the evidence of these openings, it appears that the beds in the immediate vicinity have been exposed over a vertical distance (with many gaps) of nearly one hundred feet, encountering gearksutite at but one horizon over a thickness of about 12 in. near the base of the upper greensand. There are no other openings in the vicinity at the same level, so that evidence is lacking as to its horizontal extension.

Within the narrow band referred to gearksutite is so abundant that no hand-specimen of the bed was broken out which did not contain at least one nodule of the mineral. The matrix is a soft, rather plastic, sandy rock which is saturated with water for the greater part of the year. It contains abundant glauconite and many small phosphate nodules. The composition and plasticity of the material suggest the presence of some kaolinite. An analysis of this matrix, picked free from visible gearksutite and thoroughly air dried, gave the following composition :

SiO <sub>2</sub>	 59.79	$H_2O +$	 4.73
Al.0,	 8.15	TiO,	 0.09
Fe <sub>2</sub> O <sub>2</sub>	 10.47	CO,	 0.25
FeO	 0.38	$P_2 \overline{O_5}$	 1.72
MnO	 nil	F	 0.77
CaO	 2.96	Organic	 0.42
MgO	 2.82		 
Na,O	 0.17		 100-18
<b>K</b> .0	 2.84	Less $\mathbf{O} = \mathbf{F}_{\mathbf{o}}$	 0.82
H.0 -	 5.17		 
-			 99.86

#### Gearksutite Matrix, Gingin.

The proportion of fluorine, which was determined gravimetrically, is greatly in excess of that required to make fluorapatite with the phosphoric oxide. It appears probable, therefore, that gearksutite is present in finely divided form throughout the matrix or the associated phosphate nodules. I can find no other complete analyses of greensand from other parts of the world with which to compare this analysis, particularly in regard to fluorine contents.

The scarp of the plateau, two miles to the west, is possibly a fault-scarp, but there are no signs of other faults nearer. No consolidation of any of the strata has been observed except that due to lateritic action, (1) at the summit of the upper greensand and, to a minor extent, on its sloping sides; (2) at the surface of the chalk, where this forms the uppermost bed, as at Molecap Hill; (3) at the sloping surface of the shales below the lower greensand. No signs of metasomatic action, other than these surface ones, nor of any secondary vein formation is known anywhere in the district.

#### Associated Minerals at Gingin.

The immediate associates of the gearksutite are the granular quartz, glauconite, kaolinite, and probably halloysite, which in approximately equal amounts constitute the dull green matrix. Occasional grains of microcline are observed with the quartz. These, like the quartz, are derived from the granite massif of the Darling Plateau. The quartz grains at this horizon appear never to exceed 1 mm. in diameter, but in other beds close by reach to 5 or even 7 mm., quite coarse grits appearing at certain horizons of the greensand.

Small, hard, phosphatic nodules, from 5 to 30 mm. in diameter. are abundant at and near the gearksutite horizon. These are grey in colour and enclose visible grains of glauconite and quartz. Much larger nodules are associated with the chalk in the pit a few yards below the gearksutite shaft. These are rather dark grey in colour, and analysis and microscopic examination show them to consist of a mixture of fluorapatite and calcite with included glauconite, quartz, microcline, and organic matter. A typical specimen from the chalk pit was found to have the following composition :

Phosphatic Nodule : Gingin.	Apatized Wood : Dandarragan.	
17.83		1.26
. 2.24		trace
2.26		1.01
. <del></del>		0.78
40.60		53-88
1.00		1.17
0.66		<u> </u>
1.10		_
24.80		38-80
2.94		3.00
nil		0.01
5.02		1.81
0.04		0.22
2.11		0.80
0-48		0.18
101.08	•••	102.42
1.24		1.26
99.84	 	101.16
	Phosphatic Nodule : Gingin. 17.83 2.24 2.26 40.60 1.00 0.66 1.10 24.80 2.94 nil 5.02 0.04 2.11 0.48 101.08 1.24 99.84	Phosphatic Nodule : Gingin. 17.83 2.24 2.26 40.60 1.00 0.666 1.10 24.80 2.94 2.94 0.04 101.08 1.24 99.84

The analysis in the first column indicates the presence in the Gingin nodules of about 15 per cent. of granular quartz, 11.4 per cent. of calcite, and 57.7 per cent. of fluorapatite. These account for 84 per cent. of the nodules, after which there remains 0.73 per cent. of fluorine and 1.57 per cent. of lime, besides alumina, magnesia, &c. None of the other minerals recognized in the section is fluorine-bearing. There is a possibility, therefore, that the excess of fluorine is due to the presence of very finely divided gearksuite or some other fluoride. At least part of the calcite is present in the form of foraminifera shells, many of which were found on microscopic examination to be scattered through the nodule.

With two exceptions, none of the Gingin phosphate nodules examined so far has shown any indication of organic structure. The exceptions were (1) a rather small (5 cm.) angular nodule from Molecap Hill, which close examination proved to be a pseudomorph after a much worm-eaten fragment of wood, (2) a very perfect piece of fossil wood over 30 cm. long and about 8 cm. in diameter, with a clearly defined 'knot' on one side, the whole completely converted into fluorapatite. This came from a valley in the Cretaceous about 4 miles east of Gingin.

<sup>1</sup> By chromic acid oxidation.

Fifty miles farther north, at Dandarragan, coniferous wood petrified in fluorapatite is quite abundant in the upper and lower greensands of the Gingin series.<sup>1</sup> An analysis of a typical specimen of this fossil wood is given above for comparison. It is associated with nodules of structureless and impure apatite similar to the Gingin nodules. This apatized wood is of interest as indicating the solution and migration of the fluorapatite of the ncdules (coprolites?). At Dandarragan, where so far no gearksuite has been found, dufrenite is a common mineral in the beds immediately above and below the chalk. With it is associated a little vivianite and wavellite. None of these minerals has been found at Gingin.

In addition to the calcite present in all the phosphatic nodules, the same mineral exists in small proportions in the greensands and constitutes about 80 to 90 per cent. of the chalk bed lying a few feet below the gearksutite horizon.

Kaolinite and halloysite are minor constituents of the greensand and are abundant in the shales which lie 150 feet below the gearksutite, too far distant probably to affect the origin or distribution of the mineral under review. The outcrops of these shales, however, are crowded thickly with small round and subangular pebbles of ferruginous gibbsite, whose form is strongly reminiscent of that of the gearksutite. Some bands in the upper greensand are distinctly shaly, one such being seen about 20 feet above the gearksutite. Lateritic action has gone on in these upper greensands with the formation of a hard crust of brown ferruginous sandstone on the cap of the ridge and occasional dark brown, subangular nodules, mainly limonite, on the flanks of the hill near the workings described.

Not a single one of the fluorides elsewhere associated with gearksutite has been observed at Gingin. The small excess of fluorine, however, found in the analyses of the greensand matrix and the phosphate nodule, may be due to the presence of one of this series, though more probably to gearksutite itself.

To summarize, the minerals which have been found immediately associated with the gearksutite are:

Quartz, glauconite, kaolinite, halloysite, and fluorapatite, with small quantities of calcite, limonite, and organic matter. In the vicinity, limonite, calcite, and gibbsite become abundant, in addition to the first five above mentioned; whilst opal (sponge spicules) is comparatively common in the chalk. The gearksutite nodules themselves are remarkably

<sup>1</sup> E. S. Simpson, Unusual types of petrifaction from Dandarragan. Journ. Nat. Hist. Soc. W. Austr., 1912, vol. 4, p. 83. free from inclusions, the only impurities revealed by microscopic and chemical methods being traces of quartz, glauconite, and a phosphate.

#### Physical Properties of the Gingin Gearksutite.

In the thin bed of clayey greensand mentioned, the gearksutite is extremely abundantly developed in the form of well-rounded or subangular nodules ranging from about 3 mm. to nearly 30 mm. in their greatest dimension. The accompanying photograph (fig. 2) gives a very good idea



Fig. 2.—Gearksutite in Greensand matrix, from Gingin, Western Australia. (Natural size.)

of some typical nodules. Whilst most of them are sufficiently well rounded to be reminiscent in form of the gibbsite pebbles of the shale outcrops, not a few of them are of very irregular form. They are very conspicuous objects in the dark green matrix, being, even in the completely waterlogged condition in which they are taken out of the ground, almost pure white in colour, a slight creamy tinge only being noticeable. After air drying they become pure white in colour and extremely friable, and, having shrunk slightly in drying, are very readily detached from the matrix, usually in small broken fragments or even dust. With care it is sometimes possible to detach a nodule whole from its surroundings, as has been done with one of those photographed. This extreme friability of the mineral makes it a difficult matter to transport dry specimens either in the matrix or separate from it.

In external appearance, the mineral is 'earthy', resembling a pure white kaolin or fine-grained chalk. The same appearance is ascribed to the gearksutite from the previously known localities, but whereas in each of these instances the mineral under the microscope is found to be composed of minute prisms with oblique extinction (0° to 15°), the gearksutite from Gingin is found under the microscope to consist of minute angular particles, devoid of crystalline outline, but having the appearance of finely crushed quartz. The diameter of these particles ranges from one to at most ten microns, with an average of three microns.

Under a  $\frac{1}{4}$ -inch objective the mineral appears colourless and perfectly transparent. Bøggild gives the mean refractive index of the Ural gearksutite as 1.448. The Gingin mineral disappears from sight when immersed in kerosene with a refractive index of 1.445. Gingin gearksutite is birefringent, but owing to the very small diameter of the particles, the strength of the birefringence could not be determined.

The hardness of the mineral aggregates is less than that of talc, but this is not necessarily the hardness of an individual solid crystal.

The density of gearksutite has not previously been determined, but the author had no difficulty in determining it with great accuracy by immersion in methylene iodide. Taking clean fragments of the mineral about 2 mm. in diameter, these were immersed in liquid of density 2.65, which was alternately heated to about 80° and cooled to 20° until all interstitial air was removed and no further increase in density of the fragments took place. Then taking perfectly transparent quartz crystal (D, 2.65) and Elba rubellite (D, 3.04) as indicators the densities determined were:

One fragment	• • •	 sp. gr. = 2.710	
One fragment		 ., 2·715	I
Several fragments		 ,, 2.720	•

The melting-point was found to be approximately 1,000° C., fusion being accompanied by intumescence.

No phosphorescence was observed at temperatures below a bright red heat. At and above the melting-point the mineral emits a bright white light.

With the assistance of Professor A. D. Ross, the author was enabled to test the fluorescence of the Gingin mineral. Neither ultra-violet rays nor X-rays were found to cause any fluorescence whatever.

#### Chemical Properties.

A chemical investigation of Gingin gearksutite has shed some further light upon the constitution of the mineral and its susceptibility to various reagents.

The results of a careful duplicate analysis, made in vessels only of platinum and quartz, is given in the following table, together with the theoretical composition and the only reliable analyses previously made of the same mineral from other localities:

	Gingin. (Bowley & Simpson.)	Colorado. (Hillebrand.)	Greenland. (Lindström.)	Theory CaF <sub>2</sub> . AlF(OH) <sub>2</sub> . H <sub>2</sub> O.	Theory CaF <sub>2</sub> . AlF <sub>2</sub> OH . H <sub>2</sub> O.
Al	15.88	15-20	15.37	15.38	15.21
Ca	22.18	22.30	21.02	22.74	22.48
Na	0-06	0.10	1.06	<b>—</b>	
ĸ	0-06	0.04	0-23	—	
F	41.26	42.07	41-81	32.35	42.65
$H_{2}O -$	0.12				—
$H_{2}0 +$	15.88	15-46	15.03	20.44	15.17
0	[4.88]	[4.88]	[4.82]	9.09	4.49
Fe <sub>2</sub> O <sub>3</sub>	0.03 <sup>1</sup>		Fe 0.30		
K,O	0-01 1	_	Mg 0.16	—	
P205	trace		Cl 0.20	-	
Quartz	0.19			-	-
	100.00	100.00	100.00	100.00	100.00

#### Analyses of Gearksutite.

Direct determinations of the fluorine gave 39.96 and 40.16 per cent., but such determinations give figures which represent only 95 to 98 per cent. of the true fluorine content.<sup>2</sup> The figures 41.26 given above were calculated on the following basis. The water was first determined in duplicate with the greatest accuracy to be 15.88 per cent. Then assuming that hydroxyl and fluorine are mutually replaceable, calculation showed that this percentage of water was present in a co-crystallization of

The amount of 'free' water in such a mixture was calculated to be 10.12 per cent. The remaining water, viz. 5.76 per cent., was combined with the alumina to form  $Al(OH)_s$ , and a calculation was then made to

<sup>1</sup> Present as glauconite.

<sup>9</sup> W. F. Hillebrand, Bull. U.S. Geol. Survey, 1910, no. 422, p. 188.

determine the quantity of fluorine required to form  $CaF_2$  with all the calcium, and  $AlF_3$  with the remaining aluminium, thus satisfying the general formula  $CaF_2$ .  $Al(F,OH)_3$ .  $H_2O$ .

The constitution first assigned to gearksutite was  $CaF_2$ . AlF<sub>3</sub>. 2H<sub>5</sub>O. Groth in 1883, however, suggested that hydroxyl replaced part of the fluorine, his suggestion being based upon Hagemann's original imperfect analysis in which the fluorine content is insufficient to satisfy all the calcium and aluminium. Cross and Hillebrand, as the result of their complete analysis of the Colorado mineral, were able to definitely confirm Groth's suggestion. They stated:

It will be seen that by combining hydroxyl and fluorine the ratio  $Al: Ca: H_2O: (F, OH)$  is 1:1:1:5, and the formula for the mineral becomes  $CaF_2$ .  $Al(F, OH)_3$ .  $H_2O$ , in which the fluorine and hydroxyl combined with the aluminium stand nearly as 2:1. Were the latter proportion exactly fulfilled, the formula might be written  $8CaF_2$ .  $2AlF_3$ .  $Al(OH)_3$ .  $3H_2O...$ 

It is not clear from this statement whether they considered that there were any limits to the relative ratio of F:OH, but the general formula as written would lead to the assumption that in the case of gearksutite two isomorphous molecules were present, viz.  $CaF_2.AlF_3.H_2O$  and  $CaF_2.Al(OH)_3.H_2O$ , and that the mineral might be expected to range from one pure compound which is a normal salt to the other which is basic.

This the present writer does not consider to be the case. In the first place, a study of the three reliable analyses now available show that in no instance does the actual composition approach that of either endmember of the series, but, on the contrary, in every instance is very close to the formula CaF, AlF,OH. H,O; the slight variations from this formula being best explained as due to co-crystallization of small proportions of the isomorphous compound CaF<sub>2</sub>. AlF(OH)<sub>2</sub>. H<sub>2</sub>O. These two formulae confine the possible range of composition within much narrower limits than Hillebrand's formula, the general formula derived from them and now put forward as representing the true constitution of the mineral being CaF2. AlFOH(F,OH). H2O. This constitution is supported by consideration of the genesis of the mineral (as described below) which points to 'basic' water being a necessary component of all gearksutite. The analysis of the Gingin mineral indicates a co-crystallization of the two newly suggested end-members in the molecular proportion of 86.5:18.5.

Hillebrand and Cross have published the result of a dehydration experiment with the Colorado mineral, the results of which are tabulated

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below with those of a similar experiment made by the present writer with Gingin mineral: \_\_\_\_

	H <sub>3</sub> O lost per cent. <sup>1</sup>				
Temperature.		Colorado. (Hillebrand.)	Gingin. (Simpson.)		
140°			•••	nil	
145		0.35	•••		
160				0.05	
200		—		0.05	
220			•••	0.10	
280	•••	0.92	•••		
250		7.02		0.10	
260	•••		•••	0.18	
270		9-49	•••	_	
280			•••	1.65 (4 hours)	
295	•	13-92	•••		
300		18.92	•••	2.74 (9 hours)	
820		_	•••	14-00 (8 hours)	
Water remaining		1.76+	•••	1.88 +	
Total water	•••	15.68	•••	15.88	

As in both cases the heating was continued at each successive temperature until constant weight was attained, it seems impossible to reconcile these very conflicting figures obtained on material which a reference to the table of analyses shows to be identical in ultimate composition. In the case of the Gingin material, the desiccation was carried out in an air-oven up to 145°, and subsequently in a thin metallic container of high conductivity immersed in an oil-bath up to 270°, and beyond that in a bath of tin, the thermometer readings being checked against wellestablished melting-points.

It is to be noted that Hillebrand obtained an appreciable dissociation at as low a temperature as 230°, with a loss of almost one-half the water at 250°. The present writer obtained no appreciable dissociation at temperatures below 270°, and less than one-fifth of the water lost at 300°, with almost complete dissociation at a few degrees above 800°.

When heated rapidly to red heat in a closed tube Gingin gearksutite gives off both water and hydrofluoric acid, the latter of which etches the glass strongly close to the mineral. The reaction appears to be

 $CaF_2$ . AlF<sub>2</sub>OH. H<sub>2</sub>O  $\rightarrow$  CaF<sub>2</sub>. AlOF + HF + H<sub>2</sub>O.

The solubility of the Gingin mineral in water is inappreciable. It is, however, even in quite coarse powder, very readily soluble without effervescence in cold dilute (2E) hydrochloric, nitric, and sulphuric acids. The action of moderately dilute (5E) acetic acid, even on warming to

<sup>1</sup> Includes small amount of HF, in the Colorado mineral about 1.5 per cent. at conclusion of experiment.

90°, is extremely slow. The solution in mineral acids rapidly etches glass. Upon adding ammonia to an acid solution a gelatinous white precipitate is formed, which is probably very close, if not identical, in composition to the original mineral.

On heating the mineral with dilute caustic soda solution it is partly dissolved and partly converted into a light flocculent precipitate. The action appears to be

 $2(\text{CaF}_2, \text{AlF}_2\text{OH}, \text{H}_2\text{O}) + 6\text{NaOH} \rightarrow 2\text{CaF}_2 + \text{Na}_2\text{Al}_2\text{O}_4 + 4\text{NaF} + 6\text{H}_2\text{O}.$ 

#### Genesis.

In Greenland, Colorado, and the Urals gearksutite is found in pegmatites, where it is the last-formed mineral of a series of fluorides, the earliest of which appear to be anhydrous normal fluorides such as fluorite, cryolite ( $Na_sAlF_6$ ), elpasolite ( $K_sAlF_6$ ), and chiolite ( $Na_sAl_sF_{14}$ ) The intermediate ones are hydrous normal fluorides, such as pachnolite and thomsenolite (both  $NaCaAlF_6$ .  $H_2O$ ), whilst the latest are basic fluorides or fluosilicates, such as gearksutite, ralstonite, topaz, and fluorine-bearing micas. It appears evident from the nature of the matrix and of the above sequence of secondary minerals that we are dealing in all three instances with the results of a gradually cooling and weakening solution of hydrofluoric acid of magmatic origin which has acted upon pre-existing felspars and possibly other associated rock-forming minerals. Thus the reactions with microcline and albite are:

(1)  $3KAlSi_sO_e + 66HF \rightarrow K_sAlF_e + 2AlF_s + 9H_2SiF_e + 24H_2O$ .

(2)  $8N_{a}AlSi_{s}O_{s} + 66HF \rightarrow Na_{s}AlF_{s} + 2AlF_{s} + 9H_{2}SiF_{s} + 24H_{s}O.$ 

(3)  $5N_{a}AlSi_{s}O_{s} + 110HF \rightarrow Na_{s}Al_{s}F_{14} + 2AlF_{s} + 15H_{2}SiF_{6} + 40H_{2}O.$ 

Equation (1) yields elpasolite; (2) cryolite; and (3) chiolite.

The attack of oligoclase, a constant constituent of granite, yields pachnolite or thomsenolite by interaction with one molecule of each of the two components, albite and anorthite, thus

$$NaAlSi_{3}O_{8} + CaAl_{2}Si_{2}O_{8} + 42HF \rightarrow NaCaAlF_{6} \cdot H_{2}O + 2AlF_{6} + 5H_{3}SiF_{6} + 15H_{6}O_{6}$$

The three anhydrous fluorides may be expected to form at high temperatures, but the hydrous ones only at a greatly reduced temperature. At the same time decreasing acidity would influence the precipitation, and when all or almost all the free hydrofluoric acid had been exhausted, the same solution which had yielded thomsenolite would by hydrolysis yield gearksutite, or previously-precipitated thomsenolite might alter to gearksutite. In both cases the reaction is expressed by the equation :

 $NaCaAlF_{e}$ ,  $H_{2}O + H_{2}O \rightarrow CaF_{2}$ .  $AlF_{2}OH$ ,  $H_{2}O + NaF + HF$ .

The above explanation of the formation of these fluorides in granite country agrees both with the observed sequence of deposition and with chemical theory, the order of precipitation to be expected from a hot, acid solution which was cooling, and weakening in hydrogen ions, being (1) normal anhydrous salts, (2) normal hydrous salts, (8) basic salts.

From the description which has been given of the Gingin occurrence it is quite evident that the origin of gearksutite there must be of an entirely different kind. In this connexion the following points are to be observed:

(1) The only felspar at Gingin is the microcline which in small proportions is scattered through the greensands.

(2) No sign of any pneumatolytic or hydrothermal action has been observed anywhere in the vicinity, nor, in fact, is there any evidence of any local post-Cretaceous vulcanism known, with which such activities might be correlated.

(3) Any magmatic acid penetrating to the gearksutite bed would have to pass through a 15 feet bed of chalk before doing so.

The normal origin being excluded by these considerations, what possible explanations are available to account for the genesis of the Gingin gearksutite? They seem to be confined to three, viz.—

(a) Transportation to the present site, during sedimentation, of gearksutite previously generated within the granite massif to the east.

(b) Alteration in situ of thomsenolite or other similar fluoride, transported from the granite plateau during sedimentation.

(c) Formation in situ, by interaction between solutions of minerals, still to be found in the immediate vicinity.

The first alternative is completely discredited by the extreme fragility of the gearksutite masses, which would certainly not permit of rounded, subangular, and angular masses up to an inch in diameter being transported at least 8 miles and deposited in moderately deep ocean-water without complete disintegration. There are two strong objections to the second alternative. In the first place, there are no similar pebbles of common minerals such as quartz associated with the gearksutite. In the second place, even were there a comparatively large vein or a series of veins of thomsenolite or other related mineral exposed in the platean during Cretaceous times, it is inconceivable that hundreds of fair-sized pebbles of the mineral should be carried out to sea and during a very short period of sedimentation deposited in one restricted spot in deep water.

The third alternative appears to be the only one that will stand criticism, i.e. the formation in situ of the mineral from interaction between solutions of minerals in the near vicinity. The thick bed of chalk a few feet below the mineral and the distribution of small amounts of calcite throughout the greensands indicate that the solutions must have contained no stronger acid than carbonic. The constituents required in addition to water to build up the mineral are fluorine, calcium, and aluminium. The most uncommon of these, fluorine, is known only in the fluorapatite nodules, but these are in abundance in actual association with the gearksutite, as well as in the adjacent beds. They also contain a superabundance of the second constituent, calcium. It is known that fluorapatite is soluble in carbonic acid, and there is local evidence, in the shape of apatized wood, that there has been solution and migration of fluorapatite. At Dandarragan (50 miles distant) there is evidence of this migration having been on a large scale, and having led to the formation of much apatized wood and dufrenite, and some wavellite. Lateritic action accompanied by the deposition of limonite and gibbsite has gone on, on a small scale, quite close to the gearksutite, and on a considerable scale not many hundreds of yards away. In fluorapatite, gibbsite, and carbonated water we have all the necessary components for the formation of gearksutite according to the equation  $2(3Ca_{2}P_{2}O_{1}.CaF_{2}) + Al(OH)_{3} + H_{2}CO_{3} \rightarrow$ 

 $CaF_2$ . AlF<sub>2</sub>OH.  $H_2O + CaCO_3 + H_2O + 6Ca_3P_2O_3$ . In this equation the calcium phosphate has been shown as persisting throughout, but a portion of it at least might be expected to interact with iron or aluminium hydrates to form the basic phosphates dufrenite or wavellite. At Gingin we know that calcite is associated with the gearksutite, but no dufrenite or wavellite is known so far, nor has it been proved that any of the phosphatic material is devoid of fluorine or below normal in that constituent. In precisely similar beds at Dandarragan no gearksutite is known, but dufrenite is abundant and wavellite somewhat rare, whilst the one analysis of phosphatized wood shows a deficiency of 13 per cent. of fluorine.

It is highly probable that the above reactions are those which have yielded gearksutite, and the discovery of this mineral at Dandarragan, or of dufrenite, wavellite, or phosphorite deficient in fluorine at Gingin, would go far to establish this theory of its origin, thus giving another illustration of the formation of the same mineral in nature by widely different means.

In conclusion, I desire to express my thanks to my assistant, Mr. H. Bowley, for the very careful analyses made of the gearksutite and phosphatic nodule: and to Prof. A. D. Ross of the University of Western Australia for testing the fluorescence of this mineral.

#### Summary.

A description is given of the occurrence of gearksutite under novel conditions, viz. in Cretaceous greensand, at Gingin in Western Australia. Some additions are made to the previously known physical and chemical properties of the mineral and a new suggestion is put forward as to its constitution. Its genesis is discussed and theories put forward to account for its origin under the previously known and newly discovered conditions.