THE NATURE, OCCURRENCE, AND ORIGIN OF ALUNOGEN AT VANDYKE, NEAR SPRINGSURE, CENTRAL QUEENSLAND.

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(With two Text-figures).

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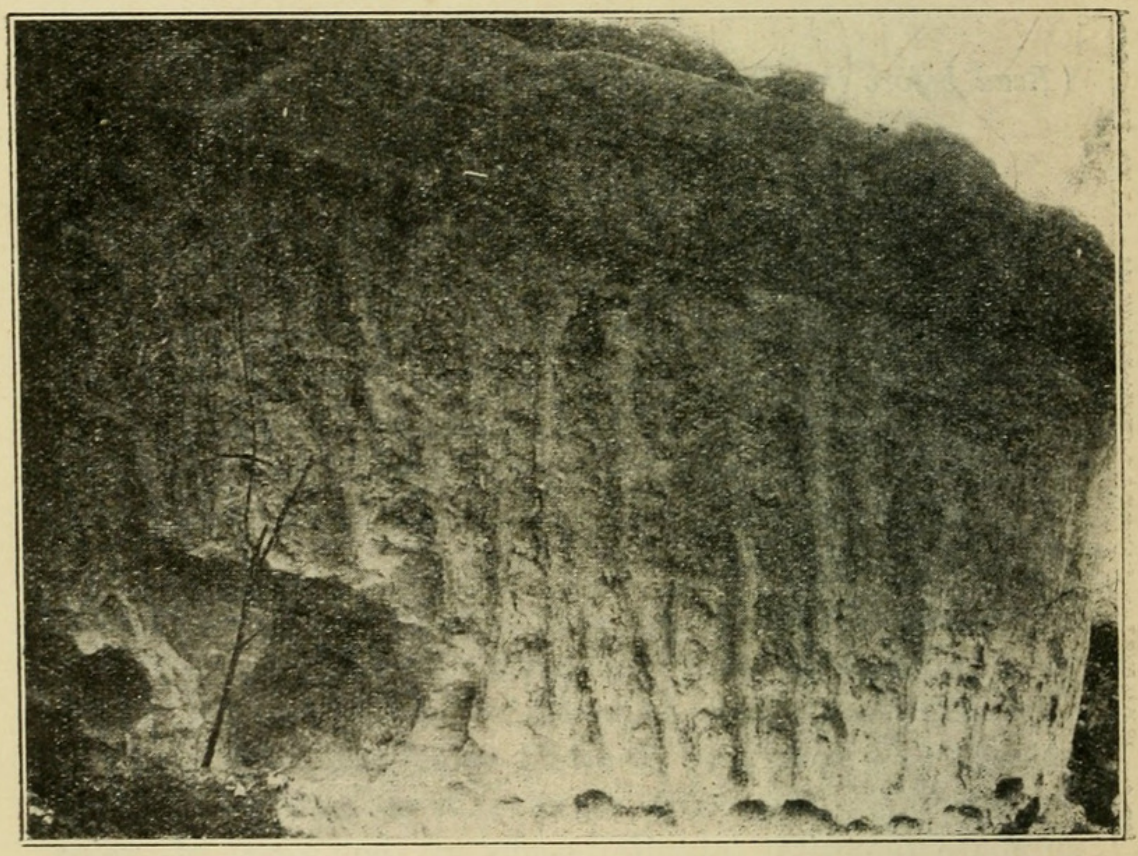
In the October number of the Queensland Government Mining Journal for 1916, Mr. B. Dunstan, F.G.S., while dealing with aluminium referred to a deposit of alunogen or basic aluminium sulphate which occurs at Vandyke, some 16 miles south-east of Springsure. A brief account of the nature and occurrence of the deposit was given, also an analysis which had been carried out in the Agricultural Chemist's Laboratory.

It has been known for some time that in the neighbourhood of Springsure there are alkaline trachytic rocks rich in potash-felspar. While potash-felspar rocks are not usually utilised as a source of potash it sometimes happens, as at Bulladelah, in New South Wales, that potassium aluminium sulphate deposits (alunite) occur in the form of veins through the rock owing, it is believed, to the attack of vapours such as sulphurous acid.

Queensland like many other places has, since the advent of the war, suffered a potash famine and the fruit-growing industry in particular has been much affected. Consequently the writer felt that with potash-rich volcanic rocks in the Springsure district and also an aluminium sulphate deposit the conditions for the occurrence of alunite might be favourable. As alunite by the simple process of

roasting under certain conditions is converted into a valuable potash fertiliser the importance of finding a reasonably high grade and extensive deposit is obvious.

As the Vandyke alunogen deposit had not been geologically examined and the origin of the aluminium sulphate was not known, the opportunity afforded the writer in August, 1917, of visiting and examining the deposit was gladly availed of. The deposit is in portion 9, parish of Osmondthorpe, at Vandyke holding, the property of Kavanagh Bros. Mr. Michael Kavanagh guided me to the deposit which is about 16 miles south-east of Springsure.



Text-Fig. 30—View of the sandstone cliff, showing the incrustation of alunogen. The top layer, from two to three feet thick, is formed of conglomerate and is free from any alunogen incrustation.

The alunogen is known to occur at three distinct hillocks in the same locality and each one is about one half-mile distant from the other two. The deposit visited was the main one and the occurrence of all three deposits is similar according to Mr. M. Kavanagh. The alunogen

occurs as an incrustation on the surface of a fine-grained white sandstone which is horizontally bedded and which outcrops all round a hill about 100 feet above the surrounding country. The sandstone is capped by a bed of conglomerate containing abundant quartz pebbles about the size of a walnut. The conglomerate is quite free from any alunogen incrustation while the sandstone immediately below it is thickly coated (*see* text-figure 30).

In the most recent geological map* the sandstones are mapped as belonging to the Star Series (Carboniferous). The sandstone bed is not exposed for any great depth but the main incrustation occurs on a cliff face about 16 feet high and in a cave in the sandstone. The cave, which is some 30 feet long and 10 feet wide, has its walls and roof thickly coated with the incrustation. In some cases this is four inches thick and shows a crusted banding, while here and there through the material there are small specks of limonite. The incrustation is much thicker on the walls and roof of the cave than anywhere else. The beds have a slight downward warp in the neighbourhood of the cave and this may result in an increased percolation of water through the sandstone here and consequently a thicker incrustation.

The forms taken on by the incrustation are varied, and where it is thin the usual one is distinctly crenulate. In the cave, however, where the deposit is thick one gets blanket-like forms as in limestone caves, also structures resembling giant rose blooms (*see* text-figure 31).

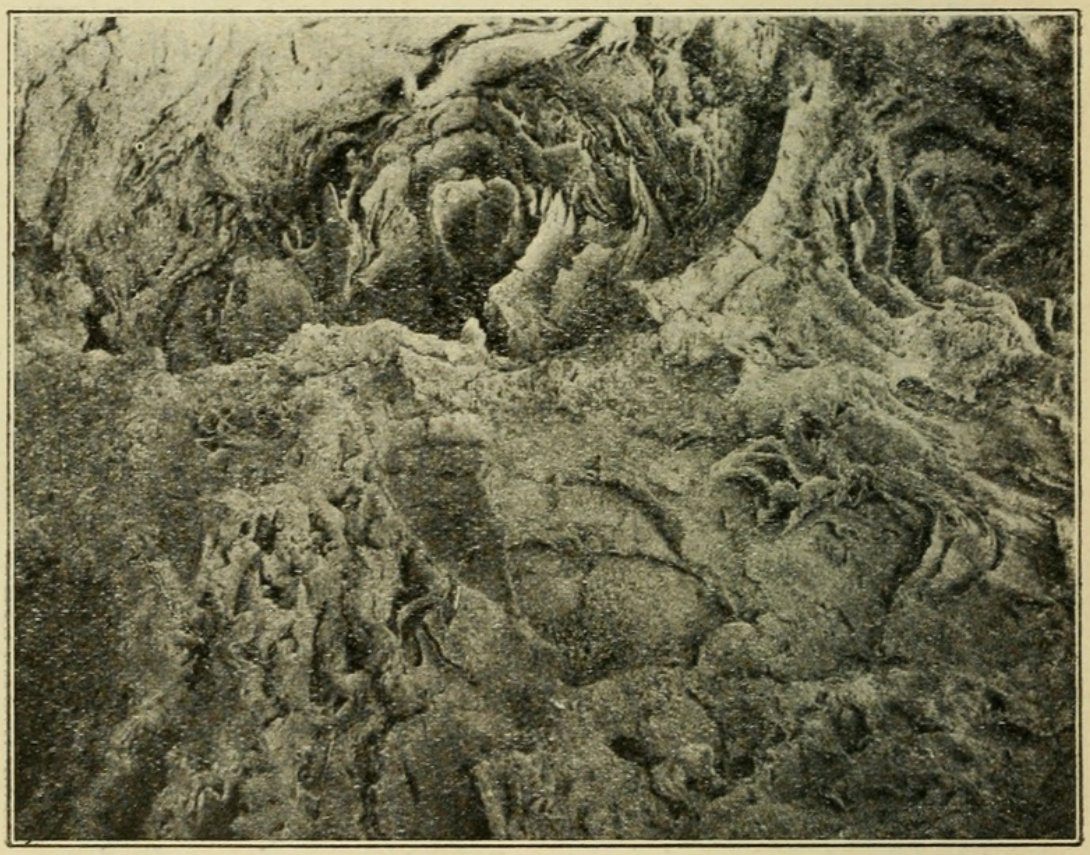
All round the hill the sandstone which is rather soft has been scalloped out and small amphitheatres formed by the action of wind and solution. Wherever there is a protective covering by means of a ledge over these small amphitheatres, a deposit of the alum incrustation is invariably found. Iu the cave, hornet nests built on the walls have become coated with the incrustation.

As the surface of the sandstone wherever slightly protected from the weather invariably shows traces of alunogen and the conglomerate bed above is quite free from it, the source of the material seems to be within the sandstone. Some of the sandstone in the cliff face had been scraped to remove the incrustation six weeks previous to my visit,

*Queensland Mineral Index, Plate 11.

and there were very evident signs of recoating in the form of wart-like incrustations, some of which were a half inch in length and rounded. About nine months previous to my visit some sandstone five feet in from the incrustation had been picked out and thrown in a heap at the foot of the cliff and exposed to the weather. The lumps of sandstone were coated with a spongy coat of the alum material 1½ inches thick in places and the lumps were firmly held together by the incrustation.

It is quite clear from the above that exposure to the weather of the freshly-broken sandstone results in the formation of the incrustation and that the sulphate is present in the sandstone.



Text-Fig.31—View of the incrustation of alunogen on the roof of the cave, showing the concentric arrangement of the layers.

Scattered through the sandstone there are small rounded nodules of limonite-stained material which resist weathering much better than the normal sandstone. These range in size from quite small pellets up to some which are nearly one inch in diameter. Also throughout the sandstone there are small specks of limonite.

The sandstone is believed by the writer to have originally contained iron pyrites which in decomposing has caused ferric sulphate and sulphuric acid to be formed and through subsequent attack on the aluminous cementing material, basic aluminium sulphate has resulted while the ferric sulphate has been reduced to ferric oxide and hydrated to form limonite.

The sandstone is a friable, white sedimentary rock with quartz grains rounded to subangular and averaging about .2 mm. in diameter. The cementing medium is very abundant and clayey in nature and when the stone is moistened the characteristic clay odour is given off.

The occurrence of alunogen as a decomposition product from iron pyrites in the presence of aluminous shales is recorded by G. P. Merrill* so that its development under the above conditions can be readily understood. The aluminium sulphate would be gradually leached out to the surface of the stone and deposited there as an incrustation while the iron sesquioxide would stain the sandstone in the immediate vicinity of its point of origin. In those places where the pyrites crystals were large we may have the nodules formed and where only small grains of pyrites existed we have the specks of brown limonite. The aluminium sulphate, being soluble, would be washed off the surface of the stone by the rain unless protected from the weather, so that one can understand the occurrence of the material in the cave on the cliff face and in the back of the small amphitheatres scooped out of the sandstone.

In the cave the best protection has been afforded, also probably the leaching effect has been more pronounced there owing to the downward warp of the bed above it giving more drainage in that direction, so that the greatest thickness of the incrustation therein is not unexpected.

In order to ascertain the extent to which the sandstone some distance from the surface was impregnated with sulphate material, a specimen of sandstone was obtained two feet in from the surface for analysis. This sandstone was analysed in duplicate by Mr. R. Graff, B.Sc., and the folowing results were obtained:

*Non Metallic Minerals. New York, 1910 Ed., pp. 352, 358.

ANALYSIS OF SANDSTONE, TWO FEET IN FROM THE CLIFF FACE.

	I.	II.
Moisture and combined water	3.22	3.21
Insoluble	95.10	95.24
Alumina (Al_2O_3) and Iron sesquioxide (Fe_2O_3) ..	1.60	1.40
Sulphuric anhydride (SO_3)	0.68	0.69
	100.60	100.54

It will be noted that the SO_3 content percentage averages 0.685, which corresponds to approximately 2 per cent. of $Al_2(SO_4)_3.18H_2O$ in the sandstone.

The solid incrustation was also analysed in duplicate by Mr. Graff. His results are set out below under I. and II. along with those obtained in the Agricultural Chemist's Laboratory under III, and recorded in the Queensland Government Mining Journal, 1916, p. 427.

ANALYSIS OF THE SOLID INCRUSTATION.

	I.	II.	Mean of I & II.	III.
Moisture and combined water	32.40	33.10	32.75	17.3
Insoluble..	26.35	26.53	26.44	36.5
Al_2O_3 and Fe_2O_3	13.37	13.78	13.57	16.1
SO_3	28.00	27.30	27.65	29.9
K_2O	—	—	—	tr.
	100.12	100.71	100.41	99.8

The sample whose analysis is shown under III. was dried at 100°C. before analysis.

Taking the mean of I and II and assuming that the insoluble material is made up of sand grains and recalculating to 100 per cent. we get the following results (A) which can be compared with the theoretical alunogen analysis (B).

	A.	B.
Water (H_2O)	44.30	48.7
Sulphuric acid anhydride (SO_3)	37.33	36.0
Alumina (Al_2O_3)	18.37	15.3
	100.00	100.0

The similarity is thus seen to be very close and, although in water percentage it is lower, chemically the material may be regarded as alunogen. The incrustation is soluble in water and has an alum taste in accordance with the properties of alunogen so that there is very little doubt about the nature of the material.

The alunogen deposit considered above is distant about 16 miles from the nearest potash-rich volcanic rocks, and this, coupled with the mode of origin put forward by the writer, renders the possibility of finding alunite in the area quite unfavourable. If the alunogen had occurred as a product of sublimation in a volcanic vent, as does sometimes happen, then the conditions might have been favourable.

The alkali-rich trachytes in the immediate vicinity of Springsure were examined by the author but nothing at all suggestive of an alunite deposit was noted.

There are undoubtedly many tons of the incrustation available but it is difficult to form any reliable estimate as to the quantity owing to the varying thickness of the deposit and the uneven surface of the cave and cliff. The formation of the material is still going on as evidenced by the recoating of scraped sandstone surfaces and the coating of the hornet nests in the cave.

The fact, that the broken up sandstone forms a coating of this material comparatively rapidly on exposure, suggests that after the main incrustation has been removed the sandstone could be broken down, crushed, and spread out evenly on trays. If the rain were kept off by some light covering and the crushed sandstone sprayed from time to time with a dilute solution of sulphuric acid no doubt the development of the incrustation would be accelerated. If the surface of the sandstone were smooth the coating might be scraped off, the sandstone raked up thoroughly and treated again until exhausted sufficiently when the sandstone could be renewed.

The question of whether it would pay to treat the sandstone in some such manner depends of course on the amount of aluminium sulphate in the sandstone and the cost of treatment, which would be mainly that of labour. The quantity of sandstone available is very large and, if necessary, sufficient material is available to be worked on a large scale. The sandstone would probably become less and less rich as one receded from the face in a horizontal direction, and what would happen on descending vertically is very difficult to conjecture.

The incrustation which has formed at present is easily removed and as the large flakes are broken away shrinkage cracks are very evident indicating that the deposit gradually becomes less hydrated ; this is borne out by the analysis in comparison with the theoretical alunogen analysis.

The amount of impurity in the incrustation is something over twenty-six per cent. and in order to remove as much as possible of this the syndicate which has been experimenting with the material adopted the following method. The incrustation is crushed and treated with water. Owing to hydrolysis, a flocculent gelatinous mass of aluminium hydrate is formed and the clay and sand impurities are thrown out on the bottom of the containing vessel. The whole is treated with hot water and the aluminium sulphate leached out as completely as possible ; the solution is then evaporated down in a large boiler and the crystalline aluminium sulphate obtained.

For such purposes as paper-making, water-clarification, tanning and dyeing, this material has a good commercial value, so that it is of economic importance.

Owing to its soluble nature, alunogen does not usually occur except in arid areas and as these generally have poor means of communication the material is not a regular commercial article.

Other Queensland Alum Occurrences.

Three occurrences are noted in the Mineral Index* ; in the old workings of the Golden Gate mine, four miles N.W. of Croydon ; on clay at the Blair Athol Coal Mines, near Clermont, and in caves of sandstone at Glen Haughton, 35 miles N.W. of Taroom. Another record of considerable interest is found in the evidence tendered by the Hon. A. C. Gregory to the Parliamentary Select Committee to report on the Sandstone Quarries of the Southern District 1888†. Speaking of the Highfields sandstone which was used in the first wing of the Treasury Building, Brisbane, the witness said :—" One peculiarity of this stone at this place is that it stands better if it is thoroughly washed by rain than when it is practically covered. The fact is that

*Q'ld Geol. Surv. Pub. 241, p.9.

†Votes and Proc., 1888, iii, p. 1037.

the pyrites and felspar in admixture form a description of alum which by its crystallisation causes the face of the stone to slip off, just as frost does. When the rain can wash over the face this alum is carried away rapidly and does not do the same amount of mischief."

In all the above occurrences the material seems to be associated with sedimentary rocks.

The occurrence of " alum " in association with trachytic breccia has been noted by Dr. Jensen at Mt. Flinders, near Ipswich*

He writes :—" On the south side of the mountain, fibrous Alum fills the joint cracks, and occurs as an excrescence on the rock. This is probably because the rock (breccia) is rich in sulphur, which by some process is being oxidised, and is reacting with the products of decomposition of the felspar."

Through the courtesy of the Minister for Mines (Hon. A. Jones, M.L.C.) and the Chief Government Geologist (Mr. B. Dunstan) I have been enabled to examine this deposit and to make use of the accompanying analysis.

The deposit occurs on portions of the floors of fairly extensive caves in the trachyte breccia and in cracks and joints on the rock forming the walls of the caves. The deposit is very limited in size and some of the more coarsely crystalline and pure material yielded on analysis by the Agricultural Chemist the following results :—

	Percentage
Loss at 100°C.	13.04
Loss on ignition	22.63†
Alumina	13.95
Ferric oxide	tr
Lime	1.70
Magnesia	nil
Soda	4.07
Potash	3.44
Sulphur trioxide	41.45
	100.28

†The sulphur trioxide lost here was deducted.

This analysis gives a composition corresponding to $(Na_2,K_2)O.\ Al_2O_3.\ 5SO_3.\ 12H_2O$. This does not correspond with the analysis of any of the common alums recorded by Dana. Some of the material is exceedingly fibrous and

*Proc. Linn. Soc., N.S.W., xxxiv, p. 76.

portions of it on being viewed in a certain position by reflected light show a decided pink tinge. Most of the material is columnar, but some of it is mealy in character.

The alum probably originated from the attack of sulphur dioxide on the felspathic material in the trachyte breccia which plugged up the vent through which the magma was effused. Sulphur dioxide is a very common mineraliser gas associated with acid magmas. As the plug of the material has been weathered down, the sulphate has become more concentrated and where protected from the weather in the floor of the caves and along cracks it has crystallised out in the forms found to-day.

Quite recently Mr. E. C. Saint Smith* has reported on an occurrence of natural alum at Boonmoo Pinnacle, about 80 miles south-west from Cairns. The material occurs through the altered acid lava forming the upper portion of the pinnacle. Mr. Saint Smith states that the lava is composed essentially of quartz and felspar with fairly abundant iron pyrites, and that the felspars have been very largely kaolinised. It is distinctly probable therefore, that the alum results from the attack of the products of alteration of the pyrites upon the kaolin.

New South Wales Alum Occurrences.

In New South Wales† it is found as a deposit from a volcanic vent at Mt. Wingen, and as an efflorescence in caves and under sheltered ledges of the Coal Measure sandstone, usually with epsomite, at Dabee, Wallerawang and Mudgee Road, the mouth of the Shoalhaven River, and other places. It is also found in crevices in blue slate at Alum Creek and at Gibraltar Rock.

To Mr. R. Graff, B.Sc., my best thanks are due for carrying out the very useful analyses of the alunogen incrustation and the sandstone behind it.

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*Q'land Govt. Min. Journal, xix, p. 56.

†Merrill, Non Metallic Minerals, 1910 Ed., p. 354.