289. *Pickeringite and the System* $MgSO_4$–$Al_2(SO_4)_3$–H_2O.

By Henry Bassett and William Watt.

It has been shown that one double salt, $MgAl_2(SO_4)_4,22H_2O$, exists in the system $MgSO_4$–$Al_2(SO_4)_3$–H_2O at 25°. This is the essential constituent of pickeringite although all specimens of this mineral which we have examined contained excess of $MgSO_4,7H_2O$. Full analyses have been made of specimens of the mineral from widely differing localities and all disclosed a small excess of base which is probably caused by the presence of a small proportion of the soluble basic salt $Al_2O_3,2SO_3,11H_2O$. The general slight basic character of the conditions under which the mineral had been formed is further shown by the fact that all specimens contained, in intimate admixture, small amounts of insoluble alunite.

There is a group of minerals which are hydrated double sulphates of magnesium and aluminium, often containing appreciable amounts of zinc, manganese, or nickel. The molar proportions of magnesium and aluminium sulphates in these minerals range between about 1 : 1 and 6 : 1, and various names have been given to different members of the series (see Mellor, "Comprehensive Treatise of Inorganic Chemistry," 1924, Vol. 5, p. 354; Hintze, "Handbuch der Mineralogie," 1930, Vol. 1, section 3, ii, pp. 4503—4507). Pickeringite was first found at Iquique by Hayes (*Amer. J. Sci.*, 1848, **47**, 360) who named it and gave it the correct formula. It has been gradually realised by mineralogists that probably only one definite compound, $MgSO_4,Al_2(SO_4)_3,22H_2O$, was involved, mixed with varying amounts of additional $MgSO_4,7H_2O$ (epsomite). This double salt is "pickeringite" but the whole series is often classed under this name. No real proof has hitherto been put forward of the correctness of the above view but this has now been provided by means of a phase-rule study of the system $MgSO_4$–$Al_2(SO_4)_3$–H_2O at 25°. The double salt has often been credited with $24H_2O$ and called "magnesia alum" from a false analogy with the true alums. The experimental results, when plotted in a triangular diagram, appear to decide definitely in favour of the $22H_2O$ formula in spite of the relatively unfavourable geometrical conditions.

Only the one double salt, $MgSO_4,Al_2(SO_4)_3,22H_2O$ [which should be written $MgAl_2(SO_4)_4,22H_2O$] exists at 25°. It is the stable solid phase in equilibrium with solutions covering the small range of concentrations (*a*) $MgSO_4$ 10%, $Al_2(SO_4)_3$ 21%, and (*b*) $MgSO_4$ 15·5%, $Al_2(SO_4)_3$ 16% by weight. As the double salt separates in fragile needle-like monoclinic prisms and as it does not form a congruent solution at 25° it is almost impossible to obtain it as a pure dry solid. It seems that specimens of pickeringite with almost the correct composition do occur sometimes but, as a rule, the mineral contains excess of magnesium sulphate.

Native $Al_2(SO_4)_3,16H_2O$, because of the more tabular habit of its crystals, occurs in a more massive form than the fibrous pickeringite with which it is not very likely to be confused. Intimate mixtures of the two compounds might be expected but do not appear to be frequent. The six specimens of pickeringite from different localities which we have analysed all contained excess of magnesium sulphate and *X*-ray photographs showed that this was present as the heptahydrate, epsomite. In the massive state the fibrous mineral seems to retain its water very well although the surface often has a slightly effloresced appearance. Loss of water occurs more readily from the powdered mineral at ordinary temperatures in air of low humidity. One sample of the powdered mineral which had been kept for 6 months gave on analysis figures which corresponded to a mixture of the double salt with excess of $MgSO_4,6H_2O$ though the *X*-ray diagram taken before the grinding showed that the excess of magnesium sulphate was then present as heptahydrate. It is well known that $MgSO_4,7H_2O$ loses one molecule of water in a dry atmosphere at ordinary temperatures, so it is probable that excess of magnesium sulphate may be present in pickeringite as either hepta- or hexa-hydrate according to circumstances. Our specimens suggest that it is normally present as heptahydrate. All of them contained small or considerable proportions of one or more of the sulphates of Mn, $Fe^{\cdot\cdot}$, Co, Ni, Zn, K, and Na, and all appeared to be slightly basic. In several cases a small proportion of water-insoluble soda alunite was present.

Caven and Mitchell (*J.*, 1925, **127**, 527) determined the 30° isotherm of the system $MnSO_4$–$Al_2(SO_4)_3$–H_2O and showed that one double salt, $MnSO_4,Al_2(SO_4)_3,22H_2O$, existed, known as a mineral called apjohnite. They found no double salt in the system $NiSO_4$–$Al_2(SO_4)_3$–H_2O at 30° (*ibid.*, p. 2549). Wirth (*Z. angew. Chem.*, 1913, **26**, 81) gave the formula $FeSO_4,Al_2(SO_4)_3,24H_2O$ to the double salt which he found in the analogous $FeSO_4$ system, and which is identical with the mineral halotrichite, and Kane (*Trans. Irish Acad.*, 1837, **17**, 423; *Phil. Mag.*, 1836, [ii], **8**, 495; *Ann. Chim. Phys.*, 1839, [ii], **72**, 368) considered the corresponding zinc salt to be $ZnSO_4,Al_2(SO_4)_3,24H_2O$ (recorded as a mineral under the very unsuitable name zinc aluminite). There can be little doubt that both the ferrous and the zinc double salts are isomorphous with pickeringite and contain only $22H_2O$.

EXPERIMENTAL.

Suitable mixtures were prepared from distilled water and specially recrystallised and analysed $Al_2(SO_4)_3,16H_2O$ and $MgSO_4,7H_2O$. These were contained in glass tubes closed with waxed corks and rotated in a bath at 25° (thermostat) until equilibrium was reached, about 6 weeks being needed. The mixtures were filtered in a jacketed filter-tube, and the solution and the moist solid were analysed. Sulphate, alumina, and magnesia were determined. The solution was made 2N. with respect to ammonium chloride, a few drops of methyl-red were added, and then ammonia until the indicator just changed colour. The solution was then boiled for a few minutes, another drop or two of ammonia being added if necessary. The precipitated alumina was washed with 0·2N-ammonium nitrate till free from chloride, ignited to at least 1000° for an hour, and rapidly weighed.* One precipitation under these conditions gave a perfect separation from magnesium. Double precipitation of the magnesium as ammonium magnesium phosphate was necessary owing to the high concentration of ammonium salts. A single precipitation often gave high results, though not always.

The results obtained for the system $MgSO_4$–$Al_2(SO_4)_3$–H_2O are given in Table I and the figure; SO_3 found directly and the values calculated from the Al_2O_3 and MgO determinations are shown in Table I to give an idea of the correspondence achieved. The aluminium sulphate crystals obtained from the mixed sulphate solutions were like all other specimens of the normal hydrated salt. The tie lines show clearly that they consisted of $Al_2(SO_4)_3,16H_2O$ and thus confirm Bassett and Goodwin's conclusions (*J.*, 1949, 2244) as to the degree of hydration.

TABLE I.

System $MgSO_4$–$Al_2(SO_4)_3$–H_2O *at* 25°.

		Solution.				Moist solid.						
SO_3 found, wt.-%.	SO_3 calc., wt.-%.	$MgSO_4$,		$Al_2(SO_4)_3$,		$MgSO_4$,		$Al_2(SO_4)_3$,		SO_3 found, wt.-%.	SO_3 calc., wt.-%.	Solid phase.*
		wt.-%.	mol.-%.	wt.-%.	mol.-%.	wt.-%.	mol.%.	wt.-%.	mol.-%.			
—	—	27·60	5·40	nil	nil	—	—	—	—	—	—	A
18·78	18·88	22·69	4·49	5·40	0·37	43·03	10·34	1·18	0·10	29·65	29·44	A
19·82	19·98	19·30	3·91	10·18	0·725	46·43	11·66	1·00	0·088	31·58	31·72	A
21·21	21·43	15·24	3·18	16·09	1·18	16·45	3·85	23·25	1·91	26·88	27·26	A, B
21·24	21·23	14·63	3·04	16·38	1·20	14·44	3·43	26·01	2·17	27·95	27·88	B
21·38	21·22	12·71	2·64	18·19	1·33	13·28	3·15	27·15	2·27	27·85	27·89	B
21·14	21·20	11·72	2·44	19·12	1·40	12·60	2·99	27·55	2·30	27·77	27·74	B
20·99	21·12	10·29	2·14	20·50	1·50	8·92	2·04	28·57	2·30	25·71	25·98	B, C
21·13	21·27	10·18	2·12	20·66	1·52	—	—	—	—	—	—	C †
20·71	20·97	8·39	1·74	21·92	1·60	6·62	1·47	28·19	2·20	23·92	24·18	C
19·99	20·17	3·45	0·71	25·48	1·84	2·32	0·536	34·87	2·83	25·77	26·02	C
—	—	nil	nil	28·20	2·03	—	—	—	—	—	—	C

Calc. for $MgAl_2(SO_4)_4,22H_2O$: $MgSO_4$, 14·01; $Al_2(SO_4)_3$, 39·84 wt.-% by wt. (both 4·17 mol.-%).
Calc. for $MgAl_2(SO_4)_4,24H_2O$: $MgSO_4$ 13·46; $Al_2(SO_4)_3$, 38·25 wt.-% (both 3·84 mol.-%).
* Solid phases : A, $MgSO_4,7H_2O$; B, $MgAl_2(SO_4)_4,22H_2O$; C, $Al_2(SO_4)_3,16H_2O$.
† Only phase C, but not analysed.

Analysis of Specimens of Pickeringite.—Several good clean specimens of this mineral were available and it was of interest to make full analyses of these and to consider the results in the light of the findings of the phase-rule investigation.

Specimens Nos. 1—4 consisted of white silky-looking masses of long, brittle, needle-like crystals. The Tucumcari mineral (No. 6) was in the form of separate large nodular aggregates of similar but shorter white needles which appeared to have formed in a sandy matrix. Specimen No. 5 was a white mass which looked as if it might have resulted from a thick paste of small crystals formed as a small pool dried up. It had not the fibrous nature of the other specimens.

The material used for analysis was in each case selected so as to exclude any portion which was obviously not pickeringite. All the specimens were found to contain small proportions of some of the following : Na, K, Cu, Zn, Mn, $Fe^{\cdot\cdot}$, Co, and Ni; and it was important to determine these with resonable accuracy, often with only limited amounts of the mineral. The following method was satisfactory.

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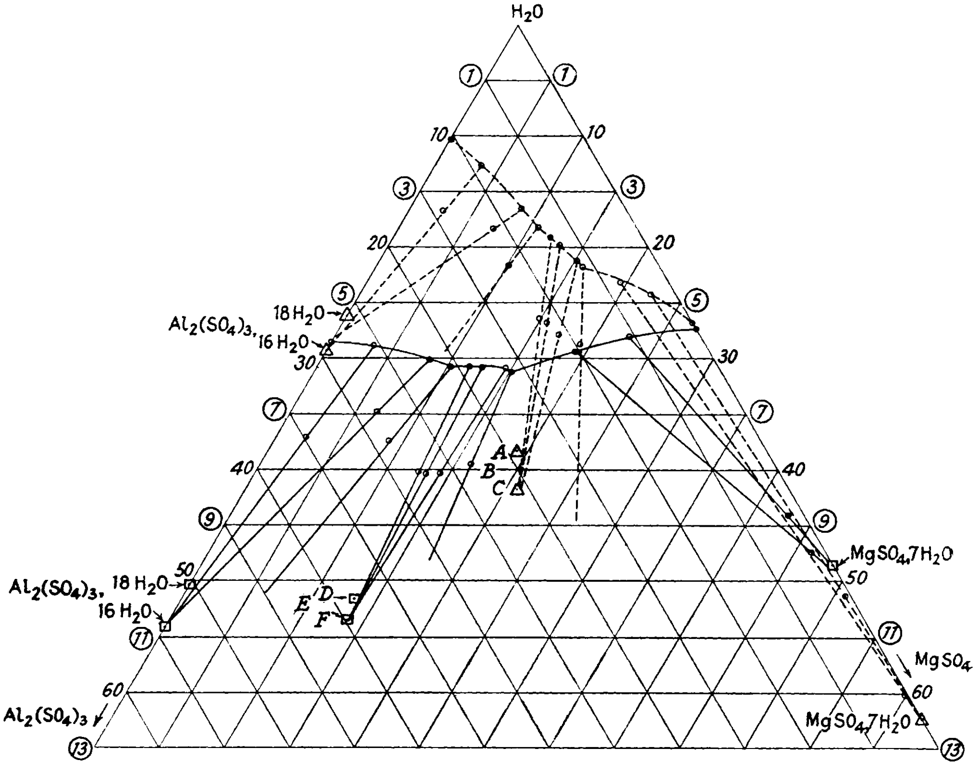
* It is the authors' experience that alumina ignited under these conditions, though not quite non-hygroscopic, absorbs moisture slowly enough for perfectly satisfactory results to be obtained, probably with an error considerably smaller than the 0·4—0·8% of the amount present which is suggested by Hillebrand and Lundell ("Applied Inorganic Analysis," p. 386). Our practice was to allow the crucible to cool for 12 minutes in a desiccator containing activated alumina and then weigh on an air-damped balance with the weights already in position. The furnace temperature was often 1100° rather than 1000°. Though a temperature of 1200° will make the alumina quite non-hygroscopic it shortens very considerably the life of the expensive heating elements. This was the main reason for using the lower temperature.

The powdered mineral (2 g.) was treated with cold water and the solution filtered from any insoluble matter through a sintered-glass Gooch crucible. The insoluble matter was weighed after being washed with cold water and dried to constant weight at room temperature. It was kept for subsequent examination. The solution was made up to 100 c.c. 50 C.c. were used for the determination of aluminium, magnesium, and other metals, and separate 10-c.c. portions were used for that of sulphate, iron, manganese, and sodium.

In determinations of aluminium and sulphate the precautions mentioned by Bassett and Goodwin (*loc. cit.*, p. 2241) were taken.

25° *Isothermal of system* $MgSO_4$–$Al_2(SO_4)_3$–H_2O *plotted both in wt.-% and mol.-%.*



KEY TO FIGURE.

A = $24H_2O$.
B = $MgAl_2(SO_4)_4$.
C = $22H_2O$.

D = $24H_2O$.
E = $MgAl_2(SO_4)_4$.
F = $22H_2O$.

Full curves and tie lines and squares relate to wt.-%. Broken curves and tie lines, and triangles relate to mol.-%. The figures within circles at the sides of the diagram are mol.-%, the other figures are wt.-%.

Ferrous iron was determined by titration with 0·01N-permanganate. Total iron was then determined in the titrated solution colorimetrically with thiocyanate. It was found in all cases that the traces of iron in the water-soluble portions of the pickeringite were present entirely in the ferrous state.

Manganese was determined colorimetrically after conversion into permanganate by oxidation with persulphate in presence of silver nitrate. Addition of the latter showed whether any chloride was present. If so, the silver chloride could either be estimated nephelometrically, filtered off and weighed, or determined on a separate, larger amount of the mineral. If more than about 0·25% of manganous oxide is present in the mineral, only 1 c.c. of the solution should be used for the colorimetric determination.

Sodium was precipitated and weighed as sodium zinc uranyl acetate. Determination of aluminium, magnesium, etc., was carried out as follows: 5 G. of ammonium chloride were added to the 50-c.c. solution, which was then heated to boiling and saturated with hydrogen sulphide until cold. If an appreciable amount of zinc was present it was precipitated and next morning could be filtered off and washed with cold hydrogen sulphide water. It was ignited carefully, weighed as ZnO, dissolved in sulphuric acid, and precipitated as ammonium zinc phosphate which was weighed as $Zn_2P_2O_7$. (If only traces of zinc are present they are only precipitated with the analytical Group-IV metals, which may contain some even when larger amounts are present in the mineral.) Hydrogen sulphide was expelled from the zinc sulphide filtrate by boiling before precipitation of the alumina. Special analysis showed that when the amount of ammonium chloride stated was present a single precipitation of aluminium with ammonia gave satisfactory separations from magnesium and the other metals present, and that double precipitation made no difference to the results. Separation from manganese was also proved to be complete in another way, as is shown later. It was found, however, that cobalt was always carried down in traces by the aluminium hydroxide and betrayed its presence by a slight blue colour of the ignited alumina. This was the case even when only very minute amounts of cobalt were present in the mineral.

Experiments were made in which known amounts of cobalt nitrate in very dilute solution were added to known weights of white alumina which, after being warmed to drive off the water, was ignited. These showed that the amounts of cobaltous oxide present in the alumina obtained in the pickeringite analyses were of the order of 0·00001—0·00005 g. and represented about 0·01—0·05% of the weight of alumina. This would correspond to 0·001—0·005% of cobaltous oxide in the original mineral. If the alumina obtained during the analysis was perfectly white it was evidence that the mineral being analysed contained much less cobalt than the amounts stated above. This carrying down of traces of cobalt by the alumina may be connected with the readiness with which cobalt is oxidised to the tervalent condition in alkaline solutions, but it may be that similar traces of all the other metals are also carried down but that their presence is not so easily detected. In any case the amounts would be too small to affect appreciably the general accuracy of the results.

2N-Ammonia (10 c.c.) was added to the filtrate from the aluminium hydroxide and the hot solution saturated with hydrogen sulphide. Next morning any precipitate was filtered off, washed with dilute colourless ammonium sulphide solution, and then extracted on the filter with hot 2N-hydrochloric acid which dissolved any manganous sulphide (and possibly a little zinc sulphide) and left any nickel and cobalt sulphide. The hydrochloric acid extract was evaporated to a very small volume, and the manganese precipitated as NH_4MnPO_4,H_2O and weighed after ignition as pyrophosphate. For the further examination of the pyrophosphate see below.

The filtrate from the Group-IV sulphide precipitate was evaporated to drive off hydrogen sulphide and decompose polysulphides. The small precipitate of sulphur, with traces of nickel and cobalt sulphides, was filtered off and ignited along with these sulphides left on the filter paper after removing the manganous sulphide with 2N-hydrochloric acid. After being weighed, the mixed oxides were dissolved by heating them with a few drops of concentrated hydrochloric acid. The solution was evaporated to dryness, the chlorides were dissolved in a little water, and any nickel was precipitated with a suitable small amount of dimethylglyoxime. The red nickel–dimethylglyoxime was filtered off and weighed on a sintered-glass Gooch crucible, and the filtrate was evaporated to dryness in a porcelain crucible. The residue was ignited to drive off organic matter, and any cobalt oxide weighed, converted into sulphate, and again weighed. The presence of cobalt was confirmed by treatment with a very small amount of 1-nitroso-2-naphthol. The cobalt precipitate was ignited and weighed as Co_3O_4. The filtrate from any cobalt precipitate was evaporated to dryness and sometimes left after ignition a small residue of cupric oxide.

Magnesium was precipitated as NH_4MgPO_4,xH_2O from the nickel–cobalt sulphide filtrate, filtered off, redissolved in hydrochloric acid, and reprecipitated as NH_4MgPO_4,xH_2O. After being weighed as pyrophosphate it was dissolved by warming it in the crucible with a few drops of 2N-sulphuric acid. Any flocks of carbon from the filter paper on which the NH_4MgPO_4,xH_2O had been filtered off were removed and weighed. The filtrate was made up to 100 c.c., and 5 c.c. were used for a colorimetric estimation of any manganese present.

By deducting the corresponding weight of manganous pyrophosphate from the original "$Mg_2P_2O_7$" the true weight of the latter was obtained. The manganous pyrophosphate obtained from the solution of manganous sulphide in hydrochloric acid should also be dissolved in sulphuric acid and estimated colorimetrically, to confirm that it consisted entirely of manganous pyrophosphate and contained no zinc pyrophosphate, as was sometimes the case.

A proportion of the manganese was usually found in the magnesium precipitate. The sum of the manganese obtained as phosphate *via* manganous sulphide and that found in the magnesium precipitate was always equal to the total manganese determined colorimetrically in the original solution of the mineral. This is good evidence that single precipitation of the aluminium under the conditions stated gives a practically complete separation from manganese. As this has also been found to hold for magnesium it may be taken as applying fairly generally. The case of cobalt has been dealt with already.

Three specimens of pickeringite were available in sufficient quantity to allow determination of the trace of potassium present. The solution in water of 4 g. of the mineral, after being made 0·2N. with hydrochloric acid, was treated with a small excess of barium chloride. The filtrate from the barium sulphate was treated with 70% perchloric acid in excess of that equivalent to all the bases present. The solution was evaporated to the stage at which it just solidified on cooling. 20 C.c. of 97% alcohol were added to the crystallised mixture and after some time the trace of potassium perchlorate was filtered off on a sintered-glass Gooch crucible and weighed. It was then dissolved off the crucible (which was reweighed afterwards) with a little hot water, and the solution was concentrated and, after addition of a suitable amount of 5% chloroplatinic acid, evaporated to dryness at about 80°. The residue was treated with a small amount of 95% alcohol, and the minute amount of characteristic cubes and octahedra of potassium platinichloride filtered off and weighed on a sintered-glass Gooch crucible. The SO_3 required to form normal sulphates with the bases found was in all cases greater than the SO_3 found by analysis. The deficit of SO_3 ranged from 0·18 to 0·79% calculated on the mineral. The deficits are not large, but it is thought that they are genuine in view of the care taken with the analyses. Determinations of the excess of base in the water-soluble portion of the specimens were made by Craig's potassium fluoride method (*J. Soc. Chem. Ind.*, 1911, **30**, 184), using 2 g., or in one case (the Tucumcari specimen) 4 g., of the mineral. The proportion of free base shown was of the same order as that indicated by the sulphate determinations. Unfortunately, the end-point in Craig's method is somewhat indefinite so that the accuracy of the determinations is in doubt. The slight basicity is probably caused by a small amount of the water-soluble basic salt $Al_2O_3,2SO_3,11H_2O$ (Bassett and Goodwin, *loc. cit.*, p. 2246), which is of some interest since this compound has never been found as a mineral and is not likely to occur as a separate relatively pure mineral because of its ready solubility and because it cannot form a congruent solution.

The basic sulphate is much more likely to be present as such than as a solid solution in the excess of $MgSO_4,7H_2O$ {$[AlOH(H_2O)_5]^{\cdot\cdot}$ replacing $[Mg(H_2O)_6]^{\cdot\cdot}$}, since if the latter were the case it would imply the possible existence of $[AlOH(H_2O)_5]SO_4,H_2O = Al_2O_3,2SO_3,13H_2O$. We have seen no evidence for the occurrence of any hydrate of this basic salt other than $Al_2O_3,2SO_3,11H_2O$. $Al_2O_3,2SO_3,11H_2O$ is the only basic aluminium sulphate which dissolves rapidly in cold water and is thus the only one which could account for the behaviour observed with the pickeringites. It is slowly hydrolysed by pure water but can remain permanently stable in presence of solutions containing sufficient $Al_2(SO_4)_3$.

Our analyses of the pickeringite specimens are recorded in Table II. The case for a genuine small basicity of the water-soluble portion of the pickeringite specimens is greatly strengthened by the observation that, in several cases, the portion of the minerals insoluble in water consisted entirely or partly of soda alunite. At ordinary temperatures alunite always separates from solutions which are somewhat basic. In these pickeringites it occurs partly as a crystalline film between the crystal fibres of the pickeringite, but mainly as minute well-formed crystals, which shows that it does not represent fine alunite dust blown in from outside but that it had actually crystallised from the solutions which by evaporation had given rise to the pickeringite. Some separation of $Al_2O_3,2SO_3,11H_2O$ crystals during the drying up of such solutions is quite probable. It was considered necessary to show that this association of pickeringite with alunite is apparently quite general by making a full examination of the water-insoluble matter from as many specimens of pickeringite as were available. This was also desirable because of the interest attached to the deviations from the conventional alunite formula which are often shown by specimens formed at low temperatures, as those associated with pickeringite must have been.

The Alunitic Material Associated with Pickeringite.

(The numbers refer to the specimen numbers in Table II.)

1. The matter insoluble in water was very unevenly distributed and contained little alunite, as judged from its appearance. It was only weighed after ignition and consisted of dark and colourless isotropic glassy fragments.

2. The water-insoluble matter was extracted with hot concentrated hydrogen chloride, and the residue of angular quartz grains weighed. Only Al_2O_3 and SO_3 were determined in the acid extract. The amounts found would correspond to the presence in the mineral of 0·97% of an alunite of composition $Na[Al_3(OH)_6][SO_4]_2 + 0{\cdot}2\{Na[Al_2(OH)_3(H_2O)_3][SO_4]_2\}$.

3(*a*). The insoluble matter consisted of minute square rhombs and aggregates of these. They were strongly doubly-refracting and extinguished parallel to the diagonals of the rhombs. They had all the appearance of being crystals of alunite and gave an excellent *X*-ray diagram of that mineral. The loss on ignition (*i.e.*, $H_2O + SO_3$ not associated with Na_2O) was 53·1% and the Na_2O content 2·7%. This corresponds closely to the figures required by an alunitic mixture $Na[Al_3(OH)_6][SO_4]_2 + 1{\cdot}9\{H_2O[Al_3(OH)_5H_2O][SO_4]_2\}$.

3(*b*). The 4 g. of pickeringite used for the analysis contained 1·434% of air-dry water-insoluble matter though this was quite invisible in the mineral before treatment with water. It had a pale buff colour and consisted almost entirely of well-formed, though minute, doubly-refracting square rhombs of alunite. They were considerably larger than any obtained from other specimens of pickeringite. The distribution of the insoluble alunite in this specimen of pickeringite is somewhat erratic. Another 4 g. of the mineral adjacent to that used for the analysis and identical in appearance yielded only 0·208% of insoluble residue. As the pickeringite dissolved in the water it could be seen that some of the alunite was present in little pockets. Dissolution was allowed to proceed as quietly as possible and a little of the insoluble matter was taken out by means of a glass tube for microscopic examination. Some of the characteristic small rhombs could be seen, but also a considerable proportion of long thin flakes which showed uniform faint but quite distinct double refraction. Each flake polarized as a whole, suggesting that the flakes represented thin films of alunite intergrown with the pickeringite crystals and deposited from solution at the same time. The larger well-formed crystals seem to have been deposited in pockets among the crystals of pickeringite rather than on the actual faces of the growing crystals. Specimen No. 3(*b*) showed a number of brown inclusions just at places where groups of pickeringite prisms started off in different directions. It seemed likely that the brown material might consist of larger alunite crystals formed at about the same time as the pickeringite rather than just inclusions of clay or other foreign bodies. A quantity of the brownish material was accordingly separated and weighed 1·0541 g. It was washed with water to remove pickeringite, etc., and after being dried at 100° weighed 0·6220 g. (alunite does not lose water when heated at 100°). Microscopic examination showed it to consist mainly of undoubted small crystals of alunite with some particles which were probably quartz. It was hard to say whether any ferric oxide was present as such or whether much of the alunite was coloured. The 0·622 g. of alunitic material was digested with concentrated hydrochloric

TABLE II.

Pickeringite analyses.

Origin, etc., of specimens: (1) San Juan, Argentine (purchased as alunogen). (2) Iquique, Chile. (3*a*) South Africa (Imperial Institute 1735/28). (3*b*) South Africa, probably from Vioolsdrift, Namaqualand (Imp. Inst. 176344). (4) South America (labelled "Alumbre Sodico"). (5) South America (labelled "Alumbre Sodico"). (6) Tucumcari, New Mexico.

Number of specimen :	1	2	3*a*	3*b*	4	5	6
Insol. in acid, %	—	0·135	—	—	0·09	0·032	10·75
Sol. in acid but insol. in cold water, %	(1·69 after ignition)	0·97	0·81	1·434	0·04 after ignition	0·68	1·45
SO_3, %	35·60	36·93	36·00	34·58	36·10	35·42	32·42
Cl, %	0	0	0	0	trace	0·09	0
As $M^{II}Al_2(SO_4)_4,22H_2O$, %	9·40	10·62	5·78	5·87	8·44	8·23	8·53
Al_2O_3 (figure found), %	(10·03)	(10·97)	6·64	(6·53)	(9·13)	(9·25)	(8·74)
As $Al_2O_3,2SO_3,11H_2O$, %	0·63	0·35	0·86	0·66	0·69	1·02	0·21
MgO, %	5·45	5·06	10·08	9·76	7·19	6·66	5·55
MnO, %	Not determined (only trace)	0·05	0·23	0·23	0·23	0·18	0·76
FeO, %	,,	0·007	<0·002	< 0·001	<0·001	0·17	0·01
CoO, %	0·002	trace	0·03	0·016	trace	—	absent
NiO, %	0·71	0·01	0·12	0·018	0·21	0·14	0·08
CuO, %	—	0·01	—	0·018	—	—	0·018
ZnO, %	0·94	—	0·01	—	0·37	0·76	absent
Na_2O, %	Not determined	0·98	0·476	0·042	0·03	0·036	0·034
K_2O, %	—	—	—	0·0056	—	0·0078	0·003
H_2O (by diff.), %	45·578	44·868	45·604	47·366	46·65	46·574	40·185
SO_3, calc. from bases as normal salts, %	36·092	37·204	36·68	35·10	36·64	36·22	32·60
SO_3, deficit by KF method, %	—	0·20	0·24	—	0·21	0·72	0·18
H_2O calc. $M^{II}SO_4,7H_2O$, %	45·81	44·75	49·15	47·83	47·43	46·61	41·74
H_2O calc. $M^{II}SO_4,6H_2O$, %	44·57	44·34	45·58	44·44	45·52	44·80	40·51
Approx. $M^{II}Al_2(SO_4)_4,22H_2O$, %	78·3	89·4	48·7	49·4	71·0	69·3	71·8
Approx. $M^{II}SO_4,7H_2O$, %	15·9	5·6	48·9	46·2	26·2	23·7	16·3

Notes to Table II.—Nitrate was shown to be absent in Specimen No. 2, and absence of calcium was shown in Specimen No. 3(*b*). These ions were not looked for in the other specimens but were probably absent. The SO_3 percentage required to form normal salts with all the bases found was calculated for each specimen and was in all cases more than the amount actually found by analysis. On the assumption that the deficit was due to a portion of the alumina being present as $Al_2O_3,2SO_3,11H_2O$ instead of as pickeringite $MgAl_2(SO_4)_4,22H_2O$, distribution of the Al_2O_3 between these two salts was calculated and is shown in the table. The amount of MgO in the minerals was in all cases greater than that required to form pickeringite with the whole of the $Al_2(SO_4)_3$ present. It was assumed that the small amounts of other bivalent metals present were replacing magnesium isomorphously. The percentage of water which should be present in each specimen was then calculated on the assumption that the mineral was a mixture of $M^{II}Al_2(SO_4)_4,22H_2O$ and either $M^{II}SO_4,7H_2O$ or $M^{II}SO_4,6H_2O$. The sulphates of sodium and potassium were assumed to be present as such, in the anhydrous state. The values so calculated are shown in Table II. In four cases the water content found by difference in the analysis agrees very closely with that calculated for the presence of $M^{II}SO_4,7H_2O$. In two cases the experimental values agree with those calculated for the presence of $M^{II}SO_4,6H_2O$, and in one case the experimental result is about midway between the values calculated for hepta- and hexa-hydrate. The *X*-ray diagrams of Specimens 1, 3(*a*), 3(*b*), and 6 showed the same lines, but the diagrams of specimens 3(*a*) and 3(*b*) were different in that certain of the lines were relatively stronger. These lines were all present in the *X*-ray diagram of $MgSO_4,7H_2O$ as well as being present in the diagrams of all the pickeringite specimens. The approximate percentages of $M^{II}Al_2(SO_4)_4,22H_2O$ and $M^{II}SO_4,7H_2O$ present in each specimen calculated from the analyses are shown in Table II and explain the prominence of the $M^{II}SO_4,7H_2O$ lines in the *X*-ray diagrams of specimens 3(*a*) and 3(*b*). Owing to the complexity of the diagrams and the presence of the $M^{II}SO_4,7H_2O$ lines and probably of some due to $Al_2O_3,2SO_3,11H_2O$, it is uncertain what lines would be present in the *X*-ray diagram of a pure preparation of $MgAl_2(SO_4)_4,22H_2O$. The *X*-ray diagrams had been taken about five years before the full chemical analyses were made and show the presence of $M^{II}SO_4,7H_2O$ in all cases. Where the mineral had been kept in the massive state, little if any loss of water had occurred. The mineral 3(*a*) analysed was in small fragments of very thin fibres, while 3(*b*) was broken off a large lump. Specimen 6 had been ground and kept in a cardboard box for 6 months before analysis. The heptahydrate seems to have changed completely to the hexahydrate under these conditions. The presence of epsomite, $MgSO_4,7H_2O$, as an impurity in pickeringite has been recorded by Meixner and Pillewizer (*Zentr. Min. Geol.*, 1937, A, No. 9, 263). All the pickeringite specimens contained small amounts of material insoluble in water. Much of this, sometimes practically all, was soluble in acid and consisted of alunite. Methods for examining the small amounts of this material which were available were developed during the course of the investigation. Alunite is rhombohedral, crystallising in rhombs looking like cubes with angles of 90° 50′.

acid. The ferruginous matter quickly dissolved suggesting that it was Fe_2O_3,H_2O rather than Fe_2O_3 or jarosite. As the iron went into solution the remaining mineral became practically colourless and on microscopic examination the square rhombs showed up well. Measured with a micrometer eyepiece, the largest crystals were found to have sides about 0·0125 mm. long. Complete dissolution of the crystals took a long time because of their relatively large size, but after 50 hours' digestion with acid, crystals of alunite could no longer be found among the portion still remaining undissolved, which seemed to be angular fragments of quartz. This was filtered off and washed; after air-drying it weighed 0·2276 g. and after ignition 0·2199 g. This small loss on ignition almost certainly means that a small proportion of alunite had still remained undissolved by the hydrochloric acid. The solution containing the 0·3944 g. of dissolved alunite was made up to 250 c.c. and analysed with the following results : Fe_2O_3, 23·46; Mn_2O_3, 0·21; Al_2O_3, 28·51; Na_2O, 4·67; K_2O, 1·55; SO_3, 29·64; H_2O (difference), 11·96%. These figures agree closely with those required by a mixture of Fe_2O_3,H_2O 26·11% and Mn_2O_3,H_2O 0·23%, with the alunite percentages, $Na[Al_3(OH)_6][SO_4]_2$ 60·22, $K[Al_3(OH)_6][SO_4)_2$ 13·63, and $H_2O[Al_3(OH)_5H_2O][SO_4]_2$ 0·42. Since this gives a total of 100·75% it is likely that some of the Fe_2O_3 is present as such.

4. The trace of insoluble matter in this specimen had only been weighed after ignition and not further examined. If its composition had been similar to that of the insoluble of Specimen No. 5 the percentage of air-dried insoluble matter would have been 0·09.

5. The portion of this specimen insoluble in water was flocculent and no crystals could be detected. Most of it dissolved fairly easily in hydrochloric acid. The material from 6·28 g. of the pickeringite was found to contain Na_2O 2·81, K_2O 1·67, Al_2O_3 35·30, Fe_2O_3 1·41, SO_3 31·97, and H_2O (difference) 26·84%. These figures agree exactly with those calculated for an alunitic complex which can be represented by the following mixture, given in wt.-% : $Na[Fe_2(OH)_3(H_2O)_3][SO_4]_2$, 3·81; $Na[Al_2(OH)_3(H_2O)_3][SO_4]_2$, 30·65; $K[Al_2(OH)_3(H_2O)_3][SO_4]_2$, 13·83; $H_2O[Al_3(OH)_5H_2O][SO_4]_2$, 22·81; $H_2O[Al_2(OH)_2(H_2O)_4]SO_4]_2$, 5·83; $H_2O[Al_2(OH)_4(H_2O)_2][Al(OH)_4]_2$, 23·07.

An interesting feature of this sample of alunitic material is that approximately 77% of the structure appears to have only two-thirds of the aluminium positions occupied.

6. The Tucumcari mineral contained a very variable and sometimes considerable amount of quartz sand in addition to alunite, the amount of which varied little and was of the order of 1·5%. The alunite was visible under the microscope as minute square crystals which were much smaller than those obtained from specimen 3(*b*) and so dissolved much more readily in acid. They contained Na_2O 4·32, K_2O 0·70, Al_2O_3 38·12, Fe_2O_3 1·43, SO_3 29·24, and H_2O (difference), 26·19%. The Fe_2O_3 may be present either as Fe_2O_3,H_2O or as a constituent of the alunitic complex, and on either basis the figures correspond to a true alunitic complex. The figures are given for the case of the Fe_2O_3 being present as 1·59% of Fe_2O_3,H_2O. The remaining 98·41% of alunitic complex can be regarded as containing in wt.-% : $Na[Al_3(OH)_6][SO_4]_2$, 11·55; $Na[Al_2(OH)_3(H_2O)_3][SO_4]_2$, 41·30; $K[Al_3(OH)_6][SO_4]_2$, 6·15; $H_2O[Al_3(OH)_5H_2O][SO_4]_2$, 11·24; $H_2O[Al_2(OH)_4(H_2O)_2][Al(OH)_4]_2$, 28·16. It is to be noted that, while the alunite present in the South African pickeringite has the conventional formula, that in the American specimens has compositions much more like that of the synthetic alunites prepared by Bassett and Goodwin (*loc. cit.*, p. 2255). The calculated compositions of the alunitic complexes have been given in order to show that in spite of their variability all the analyses of the alunitic material were in fact consistent with a true alunitic composition.

It is, however, necessary to point out that the alunitic material from any one specimen of pickeringite is essentially a homogeneous isomorphous mixture. The types of replacement which are possible in the alunite structure are somewhat complex and, though such replacement occurs no doubt in a random manner, the method here used for showing the variation in composition of the alunites appears to be more convenient than that generally employed for indicating isomorphous replacement in silicate structures.

A number of *X*-ray spectrograms of pickeringite and other specimens were taken by Dr. T. H. Goodwin, Dr. G. H. Cheesman, and Dr. G. B. Greenough in connection with this investigation, and Dr. W. Cule Davies was instrumental in obtaining some of the pickeringite specimens. It is a pleasure to thank them for the valuable help thus given.

The phase-rule work described in this paper was done at Reading, the examination of the pickeringite mineral specimens at Widnes.

THE UNIVERSITY, READING.
RESEARCH DEPT., MESSRS. PETER SPENCE & SONS, LTD.,
WIDNES.

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