The iron-rich blueschist-facies minerals: 3. Zussmanite and related minerals

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SUMMARY. Zussmanite has been found at only one locality: the Laytonville Quarry, Mendocino County, California. There are, however, present at this locality, two separate, but apparently inter-related minerals that from the evidence of chemistry, and limited diffraction information, appear to be zussmanite-type species. Their relative structural similarities are demonstrated within two rocks from the quarry in which a manganese concentration gradient has allowed ferrous-iron-rich zussmanites to develop partly contiguous overgrowths of one or other of these two minerals, one of which is a new form that has a provisionally determined ideal formula of $KAIMn_{3-5}Fe_{10-8}^{2+}Si_{17}O_{42}(OH)_{14}$ and that is separated from ideal zussmanite compositions (of the form $KAlFe_{13}^{2+}Si_{17}O_{42}(OH)_{14}$) by an immiscibility gap. The other 'zussmanite-type' mineral has a composition that closely resembles a manganese-rich form of minnesotaite.

The first zussmanite-type species (ZU2) has been separated and not unambiguous diffraction information obtained of its cell dimensions and powder lines, which are similar to those of zussmanite but appear to have an 8% smaller cell-base and only a two-layer repeat (as in some of the zussmanite polytypes, and as in the talc structure). It is therefore considered possible that ZU2 has an altered compatibility between the tetrahedral and octahedral sheet overlap, perhaps from t3 (as in zussmanite) to 12. Whilst zussmanite appears to be a blueschisteclogite mineral, ZU2 occurs under conditions at the lowpressure side of the blueschist facies.

An intermediate between zussmanite and the manganoan 'minnesotaite' is found in one rock in which the rims of zussmanite have been leached of potassium. As minnesotaite is more of a range of compositions than a structure (there is mounting evidence that it is not a simple talcanalogue) a consideration of the Laytonville manganoan minnesotaite as a zussmanite mineral is not unreasonable.

AT high pressures conventional mineral structures are unable to cope with continued substitution of large ionic species such as iron and manganese and new structures become stable to take their place. Within any simple sheet-silicate structure trioctahedral (full) occupancy of the octahedral layer cannot cope with the size differentials between the layers as easily as the dioctahedral form. This

disparity of layer sizes is a controlling influence on both structure and chemistry throughout layer silicates; once the incompatibility between octahedral and tetrahedral layers becomes critical the silicate layer cannot expand and the octahedral layer cannot contract without disruption. A sharp substitution maximum therefore marks the entry of alternative structures that contain adaptations to the problems of compatibility. Such adaptations include the regular reversals of structural polarity, as in antigorite, or, as within the alkali-hydroxyl sheet-silicates, the regular replacement of roughly half the alkali ion positions with a silicate 'bridge'. The two parallel silicate layers become conjoined but lose their own continuity to become crossconnected rafts, which through the articulation are very flexible, and capable of fitting with a wide range of octahedral layer sizes. Such problems of compatibility are exacerbated with pressure; within the blueschist-facies trioctahedral micas are unstable and dioctahedral sheet silicates are restricted to aluminous assemblages in which Al can also substitute into the tetrahedral site, permitting layer compatibility, as in chlorite. In place of the trioctahedral micas, particularly for the more iron-rich rocks, lie the double-sheet-silicates (see Liebau, 1972).

The changed dimensions of the double-sheet layer have to match with the octahedral layer; in general the tetrahedral ionic lattice forms a hexagonal mesh that overlies the smaller-sized hexagonal grid of the octahedrals. As a result the possible overlap of the new large silicate hexagonal cell on the old octahedral hexagonal grid is restricted to certain specific 'overlap vectors' that themselves form a series as roots of the integer functions representing the number of octahedral ions within the base of the new unit cell. The possible number of ions increases according to the formula $(3n^2 + m^2)$ where both n and m are integers (0, 1, 2, 3 etc.); the first twenty of the overlap vectors are illustrated in fig. 1. (The area series is 1, 3, 4, 7, 9, 12, 13, 16, 19, 21, 25, 27, 28, 31, 36, 37, 39, 43, 48, 49. . . .) The mica/chlorite/talc sheetsilicate series all have 12 octahedral cations in the hexagonal overlap. If 11 were permissible then expansion of the octahedral sheet would result in the shift of the cell vector without change in the tetrahedral layer. As it is not, the adaptation structures become important: zussmanite with 13, pyrosmalite with 16, and stilpnomelane with 48.



FIG. I. Hexagonal mesh overlaps of a hexagonal grid.

Some of these have stability ranges that are restricted to the blueschist-facies alone though within the manganous sheet-silicates the divergence between octahedral and tetrahedral sheet sizes becomes too great even at low pressures and manganpyrosmalite takes the place of any hypothetical manganese chlorite or talc.

The double-sheet silicate group of minerals includes the simplest articulation of gillespite through the single ring of six tetrahedra, as in the 'raft unit' of zussmanite or pyrosmalite, to the twenty-four tetrahedra 'raft unit' of the stilpnomelane structure. Several rare mineral species possess affinities to this group, either as chemical variants (ekmanite or parsettensite from stilpnomelane, Eggleton, 1972) or as structural adaptations of an unidentified nature (for example, ganophyllite and bannisterite are considered to be stilpnomelane 'form' minerals, Smith and Frondel, 1968).

Zussmanite structure. The zussmanite as originally defined by Agrell *et al.* (1965) is now, within this study, considered to be the model for a series of three minerals probably sharing a common, or at least closely related, structure. The structure of the original zussmanite is similar to that of stilpnomelane but simpler in form; this simplicity imposes constraints on ionic substitution, and ultimately stability ranges, making zussmanite a much rarer and much more compositionally constant mineral than stilpnomelane. The rarity is most odd; zussmanite has been found only from its type locality where it is, however, both well crystallized and abundant. The Laytonville Quarry exotic block must thus represent some kind of extreme.

A brief account of the optical properties, unitcell dimensions and composition of zussmanite was presented in the original announcement of Agrell et al. (1965) and an ideal formula of $KFe_{13}^{2+}Si_{17}$ $Al_1O_{42}(OH)_{14}$ established. The structure was refined by Lopes-Vieira (1967) and Lopes-Vieira and Zussman (1969). The silicate sheet framework contains six-fold rings or 'rafts' that alternate to face the adjacent octahedral layer and that are interconnected by three-fold silicate rings linking three six-fold rings above and three below. This articulation enables the silicate layer to enjoy a limited flexibility. As the three-fold rings lie in the plane that would within a mica structure be restricted to the alkali ions, the alkali ion site remains only between the centres of the overlying six-fold rings; in all, three-quarters of the alkali ions have been lost. The cross-bonding of the silicate structure through the alkali layer makes the mineral more compact and the (0001) cleavage less pronounced.

The cross-bonded double-sheet matches the octahedral cation (and hydroxyl) layer for a '13' overlap with a hexagonal cell edge of $\sqrt{13}$ (multiplied by the octahedral ion repeat). The actual structure varies a little from the ideal: the octahedral layer is slightly too large and there is a consequent distortion of the six-fold rings (a uniform outward tilt) and an undulation in the octahedral layer to bend it nearer to the three-fold ring than to the potassium-ion site. With the increased substitution of manganese for iron the incompatibility will magnify until outfolding of the octahedral layer can no longer accommodate the size imbalance. It might be predicted that the hexagonal mesh of the silicate layer would then swing over to match with a 12 (or even for two-unit cells a 25) octahedral ion unit cell. The possibility of the real existence of such structural variants is considered below.

Polytypism within the zussmanite structure is very prolific for certain compositions, as shown by Jefferson (1973 and 1976). Polytypism reflects the degeneracy of permissible stacking vectors and increases with a reduction of the restrictions on superimposition controls. Jefferson found that polytypes were more abundant (along with the degree of disorder) in the potassium-poor zussmanite that is found at the rims of the crystals in A2138. The compositions that he obtained have been recalculated here to show the restriction on cell-contents and the relationship between these disordered forms and the more ideal zussmanite (see Appendix 3 and figs. 2 and 3). Jefferson noted that polytypes involving a 180° rotation of successive octahedra are missing and found it impossible to account for this absence in the K-poor zussmanite if such polytypism and disordering had appeared during crystal growth. Two suggestions are presented in Jefferson (1976): that the zussmanite formed from an earlier sheet silicate topotactically, or that the faults are a result of a secondary deformation mechanism. These are both likely to be partially correct, for the rare zussmanites that do show the development of these disordered rims have evidently suffered minor leaching (apparently without appreciable mass wasting). Potassium has been depleted through the formation of adjacent and subsequent stilpnomelanes leaving remnant, disordered (probably metastable) zussmanite. The 'earlier sheet silicate' is thus the normal zussmanite, in which such rotations are not permitted. The disruption that has formed polytypes within this outer band of depleted zussmanite took place during or even after the leaching when the exotic block suffered considerable strain, and the impositions forcing regimentation on the original layer stacking had been removed. The accessible polytypes are, however, only those that can be arrived at through translation, not rotation.

The growth and resorption zonings present within the zussmanites of A2138 can be seen to be



FIGS. 2 and 3. FIG. 2 (above). Aluminium vs. manganese cell content of the zussmanite minerals. FIG. 3 (below). Potassium vs. manganese cell content.

discrete. Most zussmanites show some growth (probably depletion) zoning from Al-rich, Mn-poor centres to Al-poor, Mn-rich rims that can be seen to provide a continuous series of compositions of A2138 zussmanites in fig. 2 (a Mn vs Al plot for the zussmanite cell contents). In contrast the variation in potassium content is discontinuous, and extends to these depleted compositions only in those from A2138, as may be seen in fig. 3 (K vs Mn plot). The potassium ion diffuses out of the zussmanite without causing structural disruption. It might be thought, therefore, that such a 'subpotassic' zussmanite could grow independently (see below).

The zussmanite originally identified by Agrell, occurs as moderate-size tabular crystals, pale-green in thin section, in a restricted series of Fe^{2+} -rich metacherts, metalimestones, and metashales. During the course of a meticulous examination of the Laytonville Quarry exotic block assemblages, two other mineral species have come to light, in more manganese-rich rocks, which appear to be related to the original zussmanite. In contrast to the well-crystallized zussmanite that appears to have grown during the culmination of metamorphism, the two 'zussmanite-analogues' form fine-grained aggregates as part of late-stage replacement assemblages.

The first of these occurs as small colourless rosettes in the iron- and manganese-rich assemblages as a late-stage attack on carbonates. It has a birefringence of 0.045 (higher than zussmanite) and although the crystal platelets within the rosettes are too small to allow a complete optical determination, they appear biaxial (or possibly strained uniaxial) with 2V approximately 15°. The rosettes, when seen in thin section, consist of blades set around an axis, with a tangential c direction. After several unsuccessful attempts it proved possible to isolate a small quantity of this material and to obtain both X-ray diffraction powder photographs and electron diffraction photographs that together confirm the mineral's status as an analogue of zussmanite. As yet, however, it has proved impossible to be certain that some of the lines on the powder photograph and some of the images found from electron diffraction are not from contaminant mineral species. The powder diffraction lines are listed in Table I, alongside those of zussmanite, minnesotaite, and talc (see below). The electron diffraction photographs suggest that this mineral has a two layer orthorhombic repeat unit cell, of dimensions c c.19.46 Å, b c.9.38 Å, a c.11.37 Å, with the partly confirmed assumption that it possesses a near-hexagonal base. Until the cell dimension data can be more definitely ratified the mineral is known as ZU₂. (It has previously appeared in footnotes and within the author's thesis as 'streichelite' after Theodor Streicher, 1874-1940.)

The composition of this mineral recalculated on the 49 oxygen basis, through analogy with zussmanite, is $KAIMn_{3-5}Fe_{10-8}^{2+}Si_{17}O_{42}(OH)_{14}$. In section B733 from the Laytonville Quarry the rock composition becomes progressively more manganous from one end to the other; at the Fe²⁺-rich end zussmanite crystals sit within quartzite whilst at the manganiferous end the rock is enriched with small rosettes of ZU₂. Towards the boundary from the Fe²⁺-rich end the zussmanite becomes progressively smaller and compositionally zoned towards higher manganese contents but without any decrease in potassium. At the limit of manganese substitution in the zussmanite the zussmanites are very small, though still tabular, but also rimmed by the ZU₂, which lies in both optical and crystallographic continuity, but with a chemical discontinuity between 2 and 3 manganese ions in the structural formula. The existence of this immiscibility gap ensures that ZU₂ is a distinct mineral species. It has a more restricted compositional range than zussmanite with regard to aluminium and magnesium ion substitution, and maintains a very constant potassic ion content, see figs. 2 and 3.

The second mineral variant that appears to be related to zussmanite forms more irregular minute colourless to pale yellow clusters of crystals that form ragged corn-sheaf, or partial rosette clusters, but never with the simple radial symmetry shown by ZU₂. The birefringence is a little lower than ZU2 though still higher than zussmanite and the crystals are uniaxial, or pseudo-uniaxial negative. It is even rarer than ZU2 and is only found occurring as a late-stage replacement mineral in a very limited number of Fe²⁺- and manganese-rich assemblages from Laytonville Quarry. The composition and properties of the mineral are, as far as can be ascertained, identical with those of minnesotaite, but a more manganese-rich minnesotaite than has ever previously been reported. As it has so far proved impossible to separate this material for the purposes of X-ray or electron diffraction, evidence for its structural affinities comes from its similarity to the potassium-depleted zussmanite rims investigated by Jefferson and found within specimen A2138. It is however both chemically and physically distinct from these; again as with B733 and mineral ZU2 there is a single rock specimen that demonstrates more effectively the interrelation.

In specimen 102459 (from Laytonville Quarry) there is another manganese concentration gradient from one side to the other of the rock though the over-all composition is more pelitic than B733. At the Fe^{2+} -rich end there are medium-size zuss-

manites that pass into a zone that contains a rich concentration of stilpnomelane that has replaced an earlier garnet-carbonate assemblage. The stilpnomelane is itself attacked by the colourless 'minnesotaite' (that is therefore part of the final stage of hydrous replacement reactions) but at the boundary between the zussmanite-rich and stilpnomelane-rich assemblages the zussmanites are mantled by the 'minnesotaite', which again maintains a limited degree of optical and crystallographic, but not chemical, continuity. The zussmanites are themselves zoned, but not towards the potassium-depleted forms of A2138; instead to only moderate Mn-enrichment, which evidently defines some limit of solid solution existing before the overgrowths of the 'minnesotaite'. In A2138 the low-K species only exists in the rims of zussmanite crystals and apart from being depleted in potassium has a chemistry identical to that of ordinary zussmanite. In 102459 the low-K form has grown independent of the zussmanite and has both a low potassium and a low aluminium content. Thus it is not the metastable adaptation product of the potassium depletion process that was active in A2138. It is instead a mineral in its own right. But how can its parallels with zussmanite be made compatible with its similarities to minnesotaite?

The structure of minnesotaite has never been determined. Minnesotaite was, however, considered to be the iron-rich analogue of talc by Gruner (1944) who discovered that the cell dimensions of the mineral were $d_{0001} = 19.10$ Å, b = 9.2A, and a = 5.4 Å, which are closely equivalent to those of talc and anyway fit with a 12-octahedra hexagonal cell-base. Blake (1965) found that powder diffraction photographs of minnesotaite from Cuyuna approximated those of talc (see Table I) although the DTA curves were surprisingly different and the chemical analysis revealed that the mineral contained a small amount of both potassium (0.44 wt % K₂O) and aluminium (1.46 wt % Al_2O_3). A number of the chemical and physical properties of this material suggest a minor resemblance to zussmanite. A more recent attempt at a structure determination of this material failed because of the presence of pervasive sub-microscopic twinning (Papike, pers. comm.). Minnesotaite can be recalculated as a sub-potassic zussmanite in the following manner: the talc form $Fe_6^{2+}Si_8O_{20}(OH)_4$ becomes 'zussmanite' $Fe_{13.5}$ $Si_{18}O_{45}(OH)_9$, a close approximation to true subpotassic zussmanite, Fe13Si18O42(OH)14, and one that is too close to be capable of accurate resolution from electron-probe-determined analyses. If the ambiguity is genuine there is no reason why 'minnesotaite' from different localities need be identical.

This last possibility must be taken seriously because of the particular evidence of the Laytonville Quarry assemblages.

Minnesotaite is common as fine-grained rosettes and sheaves in many of the low-grade metamorphosed iron formations (greenschist facies) in which it is accompanied by greenalite and stilpnomelane (Klein, 1974; French, 1973). With the knowledge that is available of the talc structure the existence of a Fe²⁺-rich analogue is somewhat unexpected; the smaller magnesium ion octahedral layer is already too large to match with the simple Si₂O₅ sheet unit. The substitution of ferrous iron would be expected to compound this mis-match to the point of structural disruption; attempts to substitute iron into talc have only succeeded in introducing it into the octahedral layer when it is trivalent and therefore smaller than the magnesium ions. Whilst natural tales do not show considerable solid-solution towards minnesotaite, minnesotaite can contain up to 50% talc component. If the Laytonville Quarry 'minnesotaite' possesses a talc structure then it could enlarge its stability range by containing less manganese, but instead it is only found in more manganese-rich assemblages. If such an iron-rich talc-structure minnesotaite were stable it would take the place of zussmanite, for even if it is only at the end stages of metamorphism that the exotic block re-enters the stability field of such a manganese-free minnesotaite, the zussmanite could decompose to the iron-rich talc quasi-isochemically, with loss of water. Talc is found in the Laytonville Quarry assemblages but only as a late-stage replacement mineral in certain of the accompanying metabasites, in which it shows very little solid solution towards any theoretical minnesotaite, instead preferring to be the mineral with the highest Mg/Fe^{2+} ratio of any in the rock.

It is thus concluded that minnesotaite is not a simple talc analogue. It is only left to enquire what alternative structures the mineral could adopt.

All the compositions of the Laytonville zussmanites, 'minnesotaites', and ZU2 mineral analyses have been plotted after recalculation to the 49 oxygen unit cell, in figs. 2, 3, and 4. The changes in colour, birefringence, and crystal morphology are all composition-related and are plotted in fig. 5.

The extent of the zussmanite solid-solution towards more manganese-rich compositions is most likely controlled by layer matching. The separation of zussmanite from ZU₂ compositions, as well as the chemical linearity demonstrated by the latter (see fig. 4) suggest a structural distinction. The failure to form good crystals of either ZU₂ or 'minnesotaite' suggests that there is poor layermatching within the structures. For both these

TABLE I. X-ray powder diffraction lines

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Talc			Minneso	aite**	ZU2		Zussmanite		
hkl	d	I	d	1	d	I	hkl	d	I
002	9.35 Å	vvs	9.6 Å	vs	9.71 Å	5	003	9.60 Å	vs
		_	_	_	(9.17)* (8.52)*	-			
			_		(6.52)		_	_	_
					(0.07) ₄		104. 110	5.82	_
		_		_			105, 113	4.98	_
004	4.67	_	4.78	s	4.85	\$	006	4.78	vs
020	4-59	vs	4.58	m	—		_	—	_
ΙIΪ	4.56	s	-	—	-				
110	4-53	m	_	_	(4.50)§		-	_	_
112	4.33		_	_				_	_
022	4.12		_				-	_	_
112	3.87	_		—			107 205	2 78	 m
112	3.09		_	_	(2.66)		107, 205	2.60	m
	3.34		2 22	5	(3.00)		108 214	3.38	
006.113	3.12	vs	3.17	vs	3.22	s	009. 207	3.10	s
					3.01	_	208, 220	2.92	_
			_	_	2.91		119, 217	2.79	_
141 461	2642				{ 2.77)	206 212	2.74	-
131, 201	2.043		2.75	s	2.76	·}	300, 312	2./4	111
130	2.635	s	2.65	\$	2.64		314, 218	2.61	
202	2.627				. (-				
200	2.010	m	_	_	2.01			_	_
132	2.597	5		_					_
	2.309		2 5 2	vs	2 5 5		215.401	2.51	_
133	2.496	s							_
132	2.479	s	_		_		-	-	_
117	2.464	m	_					_	
204	2.457	m	-					—	_
		—	2.40	s	—		0.0.12	2.39	_
133	2.360	_	_		_			_	_
008	2.337	—	_	—					
221, 040	2.289	_	2.310	_	2.29		309, 317	2.31	-
222, 041	2.278		-		_				
220 223	2.205	_	2.24	_	{ 2.26		-		_
042	2 2 2 7		_	_	(2.25			_	_
124	2.227	_	2 204		_		410. 324	2.20	m
118, 221	2.208	_		_	_				
206	2.188	_		_	_			_	_
224	2.164	_	_	_	_				_
204	2.130	_	-	—				_	
136	2.104	—	2.105	m	—		413	2.14	_
028	2.086	_		_	—		- ,		_
135	2.071	. —	2.003		_		3.1.10, 416	2.00	_
	1.967	_	1.952		_		ni	1.938	
_	1.921	_	1.907	ш			3.1.11, 2.1.13	1.908	ш
208	1.870	_	1.818	m			2.1.14	1.806	
	1.731	m	-				3.1.13, 3.2.11	1.731	_
_	-	—	1.692	—					
—	~	—	1.651	m	1.671		3.1.14	1.653	m
—		-	-	_	1.037			1.616	m
_		_	1.606	•	1.021		434, 320		
_		_	1.502	m	1.500		0.0.18. 345	1.594	_
_		_	1.563	s	1.563			_	—
_		_	1.541	m			526, 612	1.531	

* howieite? $d_{100} = 9.18$ Å. † riebeckite? $d_{110} = 8.40$.

 \ddagger ??. § riebeckite??? $d_{040} = 4.51$.

|| riebeckite??? $d_{221} = 3.66.$ ** Blake (1965).

forms the higher manganese content of the octahedral layer, given the limitation of manganese substitution within zussmanite, cannot be accommodated without a revised scheme of layer matching. The ratio of the base area of the known zussmanite cell to that of the provisional ZU2 cell is approximately 13/12. It is thus tentatively proposed that ZU2 contains a zussmanite silicate unit that matches with a 12 octahedra iron-manganese sheet. This would require a revised formula of KAl(Fe,Mn)₁₂Si₁₇O₄₂(OH)₁₂, with the unverified



FIGS. 4 and 5. FIG. 4 (above). Zussmanite and rival minerals from Laytonville Quarry, plotted in the Fe-Mg-Mn ternary system. FIG. 5 (below). Morphology related to composition of the zussmanite minerals: potassium vs. manganese, cell contents.

assumption that two loose hydroxyls formerly bonded to the octahedral layer are also lost. This would give an anion charge of 96. A less radical adaptation can be proposed if the overlap of silicate on octahedral layer changed from 13 to 25, requiring a revision of the formula to $K_2Al_2(Fe,$ $Mn)_{25}Si_{34}O_{84}(OH)_{26}$. It is also, however, possible that the adaptations involved entail changes in the cross-bonded double silicate raft layer. These proposals are further discussed below.

Within the Laytonville Quarry assemblages zussmanite occurs with quartz as medium-sized tabular crystals up to $500 \ \mu m$ in length and $200 \ \mu m$ in thickness, which may make up to $90 \ \%$ of the

rock. These crystals are commonly foliated, though where their distribution appears more random there is often a suggestion of rational orientation towards one another, either from earlier mineral control or interconnected nucleation and growth. Thin horizons of small deerite needles cross-cut a number of the zussmanite quartzites and medium to large garnets may also coexist, although in most assemblages these have been partially or totally replaced by stilpnomelanes of intermediate oxidation state. Zussmanite compositions at their most aluminium-rich become quasi-isochemical with stilpnomelane and in many rocks a back-reaction can be seen with a fine-grained stilpnomelane fuzz (brown in colour) developing along cracks in the Crocidolite is a less common zussmanite. secondary replacement mineral. In some rocks in which there has been no late-stage hydrous incursion, the garnet still shows partial resorption and is now skeletal, evidently from the process of ionic transfer caused by zussmanite growth. In the metalimestones the zussmanites are surrounded by aragonite; the presence of zussmanite-aragonite horizons in some quartzites indicates the earlier existence of iron-rich carbonate layers. Iron-rich oligonite carbonates may, in the general absence of quartz, coexist with zussmanite, as may apatite and graphite.

Growth zoning is common in zussmanite and can be detected optically from changes in absorption colours and birefringence, but not always together. The paling of the green accompanies manganese substitution while increased birefringence follows from potassium deficiency. Zussmanites that have been subjected to the greatest degree of secondary attack have the greatest marginal potassium deficiency, but zoning towards low (but not completely depleted) potassium contents may be a result of fractionation of the available potassium supply on growth. It is not, however, a feature of increased manganese contents that concomitant potassium deficiency is required to compensate, as suggested by Jefferson (1973).

One rock, C644, has scarce zussmanites that zone to higher magnesium compositions, evidently again as a result of fractionation, but in this instance from a more magnesic, ferrous-iron-rich quartzite. In general the magnesium content of all the zussmanites is very constant. Magnesium rich manganoan minnesotaite is found in one assemblage, C58, as a fuzz around stilpnomelane bow-tie clusters, and in association with ekmanite (as defined by Nagy, 1954), which consumes pseudomorphed iron-manganese carbonates. The assemblage is too magnesic for deerite but not, apparently for the minnesotaite, which coincidentally lies on the extended trend of zussmanite compositions found in C644, see fig. 4.

New mineral ZU₂ occurs in most of the manganese-rich assemblages that contained original oligonitic carbonates. At the most Fe³⁺rich extremes of such assemblages, it is only present where it has had a direct carbonate precursor; thus only where P_{CO_2} during metamorphism has remained high. That it is colourless is taken as confirmation of the low oxidation state of the included iron: that it replaces carbonate confirms this. In assemblages in which there is abundant late-stage ZU2 replacement it replaces other manganese and Fe²⁺-rich minerals, particularly deerite. In C130 it selectively and effectively replaces chalcopyrite leaving adjacent pyrite completely unattacked (see illustration in fig. 6: a series of zussmanite, ZU2 and 'minnesotaite' associations). This can only be from a low activity of sulphur rather than actual 'attack';



Zussmanite with included garnets that have become altered to stilpnomelane intergrowths.



<u>Streichelite consuming the edge of a large</u> chalcopyrite aggregate.Cl30.



FIG. 6. Zussmanite textures.

i.e. the site for new mineral growth was provided by the potential for resorption. In some assemblages that have suffered oxidation, probably on weathering, ZU2 has undergone partial alteration to an orange-brown hydrated mineral that appears to be a decomposition product rather than an adaptation to changing oxidation potentials (as in the case of chlorite, stilpnomelane, or howieite).

The major input for information needed for the estimation of the stability range of the zussmanite

group of minerals must come from the mineral's exclusivity. As zussmanite itself has only been found at the Laytonville Quarry, and as its composition and phase relations do not allow its rarity to have arisen from rock composition alone (zussmanite is quasi-isochemical with ferrostilpnomelane, which is common in low-grade assemblages, though a scarcity of potassium could on occasion be a restriction), it is necessary to consider its stability with regard to the physical environment of metamorphism. Zussmanite at Laytonville Quarry coexists with relatively few other FeMgAl silicates; namely stilpnomelane, grunerite, garnet, and the Fe³⁺-containing species deerite and crossite. The simplest formation reactions are those between minnesotaite or grunerite and stilpnomelane, but within the Laytonville Quarry assemblages, extreme iron-rich ferrostilpnomelane itself is no longer stable; its place being taken by garnetzussmanite. In assemblages that contain stilpnomelane or sodic amphibole with zussmanite, the minerals show no sign of contemporaneity and the zussmanite is often suffering some resorption. It is thus unclear as to whether even the more magnesic ferrostilpnomelanes are compatible. Ferrous iron appears to have been in a carbonate rather than in a hydroxy silicate prior to zussmanite formation and so there is no detail on the possible minnesotaitezussmanite coexistence and hardly any on the grunerite-zussmanite; the grunerites are anyway manganese-rich, as are the garnets.

From the evidence of the compatibilities present at Laytonville Quarry a grid of zussmanite-forming reactions is produced in fig. 7. This is a simplified form of the Schreinemakers plot; the full topology of the system is not represented as all the minerals present show extensive solid-solutions that smear anything other than the simplest of representations. The influence of the fluid will be important in determining the hydration/dehydration reactions that mark zussmanite entry, also decarbonation for those zussmanites from Laytonville that have arrived through the decomposition of siderites. Because the only zussmanite locality is in material in which zussmanite formed as part of a hydration rather than a dehydration reaction the information on the lower limits and compatibilities of zussmanite is missing. Under restricted availabilities of water zussmanite-magnetite might be stable in place of deerite-zussmanite. The conditions of zussmanite stability must be around 8-10 kbars $P_{\rm H_2O}$ and 400 °C.

It is not, however, so simple to allot such extreme conditions to the range of stabilities of the two associated zussmanite-type minerals, both of which occur as late-stage replacement minerals, at conditions below those necessary for the stability of, for





FIGS. 7 and 8. FIG. 7 (above). Zussmanite formation reactions. FIG. 8 (below). Composition of ZU2 from Powers Quarry, Oregon. K vs. Mn unit cell formula for 49 oxygens.

example, deerite. After some meticulous examination the ZU₂ mineral was found at another locality, the Powers Quarry exotic block, Coos County, Oregon, that had already revealed itself to be a good locality for howieite (Muir Wood, 1979). It occurred within a quartzite vein cutting through the most manganese-rich of all the assemblages collected from the quarry, but only as tiny poorly formed crystal aggregates that resembled minnesotaite and that for a time evaded analysis. The successful composition determinations, are however, presented in fig. 8. As the Powers Ouarry assemblage failed, even at culmination, to produce deerite, the stability range of ZU2 was shown to include, at least, lowest grade blueschist conditions, perhaps 250 °C and 3-4 kbar. It is almost certain, however, that the mineral would not be noticed unless specifically searched for. Without the analysis for potassium it could actually be minnesotaite.

The manganoan minnesotaite from Laytonville Ouarry does not form until after the ZU₂, which is contemporaneous with the development of crocidolite/riebeckite, howieite, and stilpnomelane. This is in agreement with the evidence of other assemblages at the quarry concerning the final, lowest pressure, phase of recrystallization, which includes actinolite and talc (and possibly howieite and stilpnomelane). The conditions are now below those of the blueschist facies, in the greenschist facies, not so very different to those of the metamorphosed iron formations of Cuyuna or Minnesota, although the absence of greenalite requires that they remain too high-temperature (and perhaps high-pressure). The failure of more normal minnesotaites to form in manganese-poor assemblages also defines some P-T restriction on compositions; there is, as noted above, no apparent local restriction on water content. As to whether the manganoan minnesotaites contain a 12, a 25, or a 13 octahedra overlap of silicate unit upon octahedral, and/or a reconstructed silicate unit, remains to be discovered. Evidence from the electron diffraction photographs of ZU2 indicates considerable disorder as indicated by the in-layer arrangement of reflections, which may indicate a variety of alternating sheet-overlap vectors. It seems likely that a similar arrangement will eventually explain the curious compositional detachment of the one, or two (or more) minnesotaite structure(s).

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THE IRON RICH BLUESCHIST FACIES MINERALS: 3.ZUSSMANITE AND RELATED MINERALS - APPENDICES.

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APPENDIX 1. APPERDIX 1. The analyses listed in Appendix 3 are from two electron microprobes within the Department of Mineralogy and Petrology, Cambridge. These were: a Cambridge Instrument Geoscan system, using analytical methods described by Sweatman and Long (1969); and the energy dispersive microprobe, for which the analytical procedure and data processing are discussed in Statham (1975).

APPEN	NDIX 3.1	Zussm	anite	analy	ses,	weight	per	cent	oxides.	A11
iron	conside	ered	as FeC							
No.	Rock	\$10	TIO	N 1 O	FeO	MnO	Mao	C=0	K O N-	

		2	2		3	raio	1190	cuo	~20	na ₂ 0	Total
1.	A2138	51.39	- "	1.50	33.71	3.96	1.97	.10	.16	.16	92.96
з.		46.92	-	5.00	35.83	2.18	1.31	.03	34	1.79	93 40
4.		48.01	-	3.78	34.58	3.05	1.58	06	23	1 81	92 10
12.	*	46.45	.02	5.97	35.40	2.41	1.77	.04	. 20	1 66	93.10
21.	A2125	46.58	.02	3.89	35.89	1.23	1.97	13	16	2 06	54.11 01 02
22.	102480	46.28	-02	5.20	35.65	51	1 56	.13	.10	1 00	91.93
27.	A2138	47.61	.02	3.40	35.82	1 16	1 82	-04	10	1.00	91.40
47.	47	49.42		. 72	34 04	3 42	1 01	.00	.13	1.04	92-70
50.	B733	46.73	-	2.52	37 68	6 28	1 72	.07	.00	1 22	89.78
59.	B153	46.39	-	3.99	36 44	1 72	2 59	.08	12	1.09	92.17
60.	C644	46.46	_	3 75	36 75	1 20	2.20	.03	. 1.5	1.9/	93.25
65.	93724	46.86	04	4 14	37 01	1.25	2.32	.00	. 40	1.83	92.71
66.	B733	46.74	-	2 19	33 18	5 24	1 97	-	.01	2.04	94.09
68.		47 64	-	2 25	75 66	3.24	2.10	-	-	1.11	90.93
70.		44 40	-	2 23	21 25	2.7/	2.10	-	-	1.70	92.32
71.		43.97	-	2 21	30 71	10.70	.4/	-		1.92	87.25
76.	C21	49.23	-	3 41	37 72	1 51	1 90	2.1	. 31	1.89	90.00
82.	102459	50 98	-		21 61	11.00	1.05	. 21	-	1.20	92.71
83.		51 09	-	-	37.01	11.00	1.03	-	-		94.69
85.		48 42	_	2 79	27 07	0.23	1.50	-	-		94.04
86.		49 76	_	2 20	37.07	2.30	1.59	-	-	1.90	95.13
87.	C649	45 14	-	2.29	30.39	3.58	1.69		-	1.71	95.21
92	A 21 31	44 55	-	2.07	29.31	13.48	.42	.04	. 32	2.11	93,70
93	C130	44.35	-	2.39	20.04	15.23	. 72	.06	.43	1.92	91,92
100	102510	44.00	-	2.36	28.40	13.40	. 35	.06	. 34	1.95	91.62
100.	102519	47.00	-	2.74	22.65	15.89	- 90	-	-	1.86	93,70
101.		47.00	-	2.78	24.41	16.61	.44	-	-	2.08	93,32
100.	M2119	46.24	-	2.68	29.91	10.95	.56	-	-	1.88	92,22
111	CE0	46.00	-	2.52	26.68	14.66	.30	-	-	1.90	92.32
116		50.19	-		30.52	6.73	3.89	-	-	.16	91.81
		50.27	-	.41	30.31	8.58	3.25	.04	-	.26	93.12

<u>APPENDIX 2</u>. The problem with all electron probe determined compositions is the irresolution of the ferrous and ferric iron spectral lines. Thus a method is adopted to enable the abstraction of the ferrous/ferric ratio of the iron that involves the solution of the two simultaneous equations that are considered inherent within the nature of the crystal she ideal formula shalance and site occupancy. For zussmanite sites, the ferric iron contender or however, generally insignificant and have been ignored.

Reca	alculate	ed cell	co	ntent	for	49 ox	gen o	ell.		
No.	Rock	51	Ti	Al	Fe ²	+ Mn	Ma	Ca	Na	ĸ
1.	A2138	17.95	- "	. 62	9.85	1.17	1.03	.04	.11	.07
з.	**	16.64	-	2.09	10.63	.65	.69	.11	.23	.81
4.	-	16.97	-	1.58	10.22	.91	. 83	.02	.16	.82
12.		16.34	-	2.47	10.42	.72	. 93	.02	.27	. 74
21.	A2125	16.84	-	1.66	10.85	. 38	1.06	.02	.11	.95
22.	102480	16.69	-	2.21	10.95	.16	.84	.02	.21	.87
27.	A2138	17.03	-	1.43	11.01	.35	.97	.02	.13	.75
47.	*5	18.00	-	. 31	10.37	1.05	1.04	.03	.06	.06
50,	B733	17.01	-	1.08	9.94	1.97	.93	.02	.12	.87
59.	B153	16.59	-	1.68	10.89	.52	1.38	.01	.09	. 90
60.	C644	16.70	-	1.59	11.05	.39	1.24	.02	.17	.84
65.	93724	16.60	.02	.34	10.96	.46	1.32	-	.07	.92
66.	B733	17.16	-	.95	10.21	1.63	1.02	-	-	. 80
68.		17.19	-	.95	10.76	.91	1.13	-	-	.78
70.		16.58	-	1.05	10.47	3.04	.28	-	-	.98
71.		16.74	-	1.04	9.78	3.32	.26	-	-	. 92
76.	C 21	17.58	-	.59	11.15	- 46	.98	.08	-	.55
82,	102459	17.93	-	-	9.32	3.29	.54	-	-	-
83.		17.99	-	-	9.72	2.45	.82	-	-	.05
85.		16.93	-	1.56	10.86	. 70	.83	-	-	.85
86.		17.27	-	.94	10.72	1.06	.88	-	-	.76
87.	C649	16.55	-	1.04	8.98	4.19	,23	.02	.23	.99
92.	A2131	16.63	-	1.24	8.32	4.82	. 39	.02	.31	.92
93.	C130	16.56	-	1.13	9.08	4.27	.19	.02	.25	.93
100.	.102519	17.49	-	1.14	6.67	4.74	.47	-	-	.84
101.		17.01	-	1.18	7.39	5.09	.24	-	-	.96
105.	A2119	16.97	-	1.16	9.18	3.41	. 30	-	-	.88
108.	102519	16.90	-	1.09	8.20	4.56	.16	-	-	. 89
114.	C58	17.88	-		9.11	2.03	2.06	-	-	,07
115.		17.71	-	.17	8.91	2.56	1.70	.01	-	.11

1,3,4,12,27,47, (A2138) Ar,Z,S,Gr,R. (Jefferson,1973). 21,(A2125) (Jefferson,1973). 22 (102480) (Jefferson,1973). 50,65,66,70,71,(8733) Z,Q,S, + 01,Ga,St,Q,S,G. 50, 65,64,70,71,(8733) Z,Q,S, + 01,Ga,St,Q,S,G. 50, (5644) Q,Z,S,D. 61, (93724) (Wet chemical - Scoon). 75, (21) D,Z,Ar,S. 82,83,85,85,(102459) Z,Q,D + Ga,S,D,Q,Mi,O1,Py. 87,(C130) Q,A,Ga,D,Cu,PY,O1 - S,St,R. 100,101,108, (102519) A,Ga,O1-WC,D,Gr-R,Q - St,S,Ho. 105, (A2119) Q,D,O1,Xu,Gr-R,Ga - Ho,S,St. 114,115 (C58) Ga,S,Mi,O1-Ca.

<u>XEY</u> A = aegirine, Ar = aragonite, Ca = calcite, Cu = chalcopyrite, D = decrite, G = graphite, Ga = garnet, Gr = gruperite, Ho = howisite, Xu = kuthahorite, MC = mangano-calcite, Mi = minnesotaite (Gamma-russman-is) richeckite, S = stipnomelane, St = "streichelite (Beta-sussmanite)", Z = zussmanite.

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[Note added in proof. New X-ray diffraction cell dimensions obtained by Guggenheim (S.), Wilkes (P.), and Bailey (S. W.), 1977. (Eos 58, 525) for minnesotaite are a 25.4, b 9.4, and c 57.2 Å, α 90°, β ?, and γ 90°. The cell base matches with 26 (= 2×13) or 27 octahedral ions.]