Mitridatite: a remarkable octahedral sheet structure

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MITRIDATITE has a 17·53, b 19·35, c 11·25 Å, β 95·92°, space group $A2/a$ (Moore, 1974) and is closely related to robertsite and arseniosiderite. Its structure (the atomic co-ordinates of which are given) is based on a compact sheet, $Fe_9^{3+}O_6(PO_4)_9^{12-}$, with pseudotrigonal symmetry (fig. 1), formed from a ring of nine FeO_6 octahedra with a PO_4 tetrahedron at the centre, linked by two further PO_4 tetrahedra in the plane of the sheet and by six more PO_4 tetrahedra above and below the plane of the sheet (not shown on fig. 1); Ca ions and H_2O molecules lie between these sheets, the Ca in a $CaO_5(H_2O)_2$ polyhedron, and three water molecules not linked to any metal complete the asymmetric unit $Ca_6(H_2O)_6Fe_9^{3+}O_6(PO_4)_9 \cdot 3H_2O$.
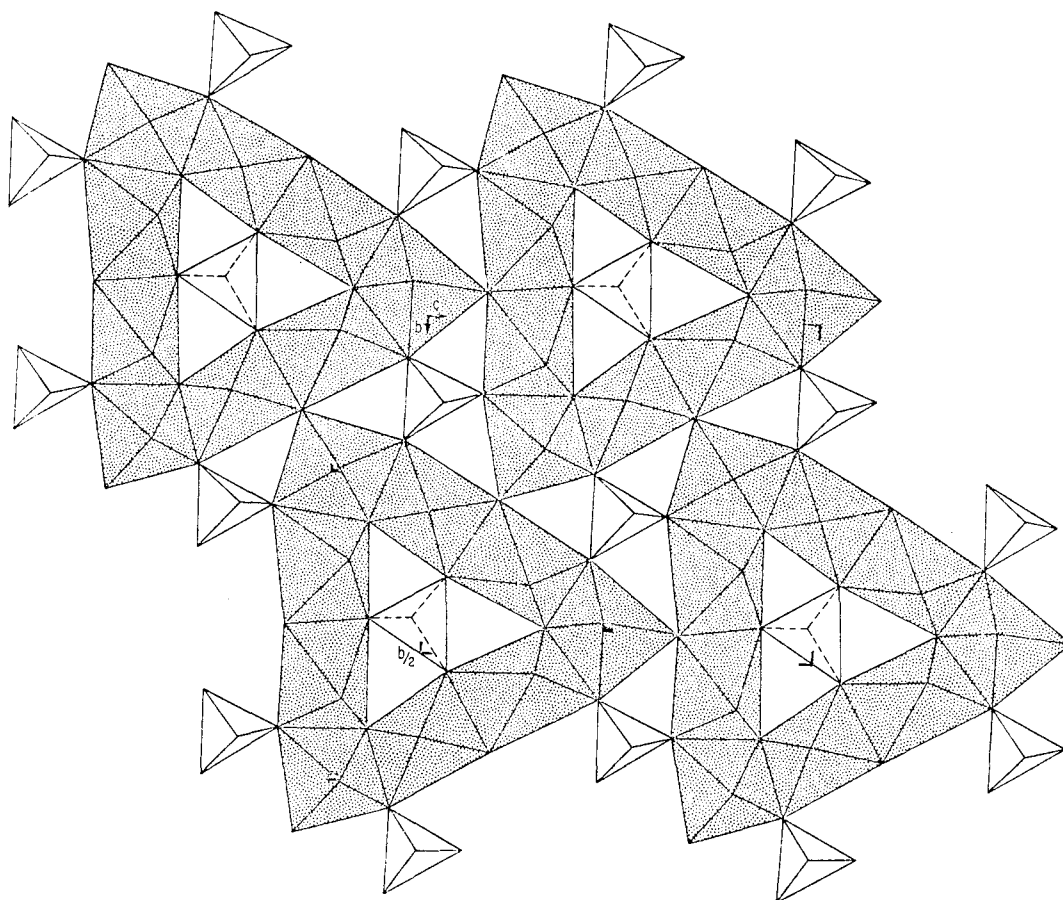
FIG. 1. The basic unit of the mitridatite structure.

Betpakdalite and melkovite, which have unit cells dimensionally similar to that of mitridatite, may be related structurally. Other structures, known or hypothetical, based on the Fe_9O_6 ring are shortly discussed.

REFERENCE

Moore (P. B.), 1974. *Am. Mineral.* **59**, 48.

The full text appears in the 'miniprint' section of this volume, pp. M8-M.

Metamorphism in a Himalayan thrust zone

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METAMORPHIC assemblages from the vicinity of a thrust in the Sikkim to Darjeeling area of the Himalayas contain some of the following minerals: quartz, plagioclase, epidote, sericite, lawsonite, chlorite, stilpnomelane, aragonite, phengite, and pumpellyite. Textural relationships suggest that stilpnomelane replaces pumpellyite and that both of these minerals are replaced by epidote. The assemblage lawsonite–quartz–aragonite appears to have been stable and indicates that a moderate- to high-pressure metamorphism developed coevally with the thrusting. The rocks involved are Proterozoic but it seems likely that the thrusting was Tertiary. The metamorphism associated with the thrusting may have outlasted a more general Tertiary metamorphism or may have been superimposed on a Precambrian event. Either way this is unusual for in general the stratigraphic age of rocks involved in such tectonic zones is not much greater than the age of the metamorphism.

The full text in the 'miniprint' section of this volume, p. M18.

Zoned amphibole in the Yirri intrusive complex, Manus Island, Papua, New Guinea

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FIVE representative probe analyses of zoned hornblendes in a dioritic suite and two rock analyses are tabulated and about sixty analysed hornblendes plotted to reveal petrogenetic relationships that are interpreted as showing that the brown amphibole cores are from a partially melted mafic source (base of the crust?) while the green margins have crystallized from the magma produced by partial melting.

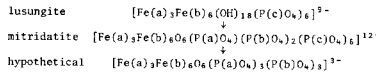The full text in the 'miniprint' section of this volume, p. M19.

Mitridatite: A remarkable octahedral sheet structure. Paul Brian Moore
and Takaharu Araki, Department of the Geophysical Sciences, The Univer-
sity of Chicago, Chicago, Illinois 60637, U.S.A. Mitridatite, a natural
phase, is a common product of weathering and oxidation of pre-existing
ferrous phosphate minerals. This basic ferric phosphate occurs as dull
green stains on granitic rocks, as colloidal to cryptocrystalline cement
and nodules in marls, sandstones and other ferruginous sediments, and as
a replacement of fossiliferous remains. It may be one of the more impor-
tant inorganic phases in phosphatic soils (Moore, 1974). Rarity of suit-
able single crystal material has inhibited more detailed study of this
phase.

Eventually a single crystal was found from the White Elephant pegmatite,
near Custer, South Dakota. Another three years' work was devoted to
unravelling its detailed crystal structure. We now report preliminary
results on this study. R(hkℓ) = 0.11 for 1271 medium to strong reflections
and 0.16 for 5449 reflections above background error. The essential cor-
rectness of the structure is attested by sharp contours on the Fourier
synthesis and reasonable bond distances (Fe–O 1.88-2.10, P–O 1.49-1.60Å).
Since 75 non-equivalent atoms occur in the asymmetric unit and since a sub-
structure occurs, further refinement proceeds slowly. Structure cell data
for mitridatite and related compounds appear in Table I. The atomic coor-
dinate parameters are given in Table II.

Mitridatite possesses a remarkable structure, the knowledge of which,
permits us to relate it directly with other important oxysalt structure
types. The underlying principle is a compact sheet of composition $[Fe_9^{3+}O_6$
$(PO_4)_9]^{12-}$ (fig. 1). This sheet possesses trigonal pseudosymmetry, two-
sided plane group p31m, a = 11.25Å (= c of mitridatite). It is based on
octahedral edge-sharing nonamers of general composition $M_9\phi_{36}$ where M is
an octahedral center and ϕ is an octahedral vertex. These nonamers link
at their extreme trigonal corners to form the octahedral sheet $M_9\phi_{33}$. At
the center of each nonamer is a PO_4 tetrahedron (call it P(a)) which
shares three of its corners with the octahedra. Removal of the three octa-
hedra at the extreme trigonal corners (call them Fe(a)) leads to an octa-
hedral cluster of composition $M_6\phi_{27}$. Including the central tetrahedron,
the composition is PFe_6O_{28} (call these Fe atoms Fe(b)). This cluster
(fig. 2) is topologically identical to the central girdle of the recently
reported (D'Amour, 1976) $[PMo_9O_{31}(H_2O)_3]$ polyanion which was shown to be
related to the well-known Keggin molecule. This polyanion can be parti-
tioned to better show the relationship with mitridatite, that is $[PMo_6O_{28}$]
$Mo_3O_3(H_2O)_3]$.

To create the full mitridatite sheet based on the Fe₉ stoichiometry, two
additional PO_4 tetrahedra (call them P(b)) link in the plane of the sheet
and six additional tetrahedra (call them P(c)) above and below this plane,
the latter each linking three of their corners to terminal oxygens above
and below the sheet. Remaining are six oxo-anions which bridge three Fe
atoms together. The fully assembled unit can be written $Fe(a)_3Fe(b)_6O_6$
$(P(a)O_4)(P(b)O_4)_2(P(c)O_4)_6$. The Ca atoms and H₂O molecules form a broken
sheet above and below the sheet already mentioned. Each Ca atom bonds to
five oxygen atoms and two H₂O molecules, the latter defining a shared edge
between the $CaO_5(H_2O)_2$ polyhedra. The polyhedron is made by adding a
seventh vertex above a face of an octahedron. Finally, three water mole-
cules occur which do not bond to any metals but participate in hydrogen
bonding only. Thus, the asymmetric unit has the composition $Ca_6(H_2O)_6Fe_9^{3+}$
$O_6(PO_4)_9\cdot3H_2O$.

A progressive sequence of sheets of increasing density (fig. 3) can now
be conceived, starting with the iron phosphate derivative (= lusungite) of
the familiar and important alunite structure (Wang et al., 1965; Blount,
1974):

  lusungite $[Fe(a)_3Fe(b)_6(OH)_{18}(P(c)O_4)_6]^{9-}$
                              ↓
  mitridatite $[Fe(a)_3Fe(b)_6O_6(P(a)O_4)(P(b)O_4)_2(P(c)O_4)_6]^{12-}$
                              ↓
  hypothetical $[Fe(a)_3Fe(b)_6O_6(P(a)O_4)_3(P(b)O_4)_3]^{3-}$

The hypothetical sheet is based on local oxygen cubic close-packing and can
be condensed to the general formula $[M_3O_2(TO_4)_2]$, where T is a tetrahedron.
It is known as a stable moiety in the crystal structure of chloritoid
(Wedepohl, 1972), $Fe_2Aℓ(OH)_4[Aℓ_3O_2(SiO_4)_2]$. Among phosphates, a related
sheet structure occurs in bermanite (Kampf and Moore, 1976), $Mn^{2+}(H_2O)_4$
$[\square Mn_2^{3+}(OH)_2(PO_4)_2]$, where □ is an ordered vacancy.

These relationships are of considerable interest since they point to
structures which are highly stable and which transform according to rear-
rangements of oxygens in the sheets. These rearrangements admit a variety
of tetrahedral decorations above, below and within such sheets. It is
noted that in all these structures the octahedral centres, M, reside at
the vertices of the familiar Kagomé net, a design of fundamental importance
in inorganic structures, from alloys to the important spinel, $Aℓ_2MgO_4$,
structure type.

Knowledge of the mitridatite structure may shed light on the crystal
chemistry of the curious phases betpakdalite and melkovite. These com-
pounds occur as oxidation zone minerals associated with molybdenum sulfide
deposits and their crystal chemistry was recently discussed (Skvortsova,
1972). Morphological and structure cell characters suggest a relationship
with mitridatite. Although the formula $CaFe_2^{3+}(H_2O)_{14}[As_2Mo_5O_{24}]$ was pro-
posed for betpakdalite, it can be rearranged isomorphically into a mitri-
datite-like formula, that is $Ca(H_2O)_8[\square_3Mo_5^{6+}Fe^{3+}O_6(FeO_4)(AsO_4)_2(OH)_{12}]$.
Such an arrangement conserves local electrostatic neutrality since the
three Fe(a) atoms in mitridatite are voided (= □) and since the $P(c)O_4$
tetrahedra above and below the sheet are voided, and the free octahedral
apices are bonded to (OH)⁻ groups only. Table I summarizes the relation-
ship; the agreement in the crystal cell data among the compounds is note-
worthy. Confirmation of this relationship must await discovery of suitable
single crystals for study.

References

Blount (A. M.), 1974. Am. Mineral. 59, 41-47.

D'Amour (H.), 1976. Acta Crystallogr. B32, 729-740.

Kampf (A. R.), and Moore (P.B.), 1976. Am. Mineral. 61, in the press.

Moore (P.B.), 1974. Am. Mineral. 59, 48-59.

Skvortsova (K. V.), Sidorenko (G. A.), Nesterova (Yu. S.), Arapova (G. A.),
    Dara (A. D.), and Rybakova (L. I.), 1972. Internat. Geol. Rev. 14,
    473-480.

Wang (R.), Bradley (W. F.), and Steinfink (H.), 1965. Acta Crystallogr.
    18, 249-252.

Wedepohl (K. H.)(ed.), 1972. Handbook of Geochemistry, II/3, Springer-
    Verlag (Berlin), 13-A-1 -13-A-24.

Table II. Mitridatite. Atomic coordinate parameters

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Fe(1)	0.253	0.460	0.489	O(1)	0.024	0.282	0.140	O(25)	0.378	0.116	0.046
Fe(2)	.247	.037	.246	O(2)	.136	.232	.229	O(26)	.250	.068	.946
Fe(3)	.248	.055	.745	O(3)	.137	.347	.235	O(27)	.262	.194	.953
Fe(4)	.250	.200	.268	O(4)	.136	.285	.047	O(28)	.253	.123	.147
Fe(5)	.249	.221	.768								
Fe(6)	.251	.373	.250	O(5)	.020	.455	.627	O(29)	.379	.287	.543
Fe(7)	.255	.382	.754	O(6)	.141	.467	.506	O(30)	.262	.360	.438
Fe(8)	.254	.295	.021	O(7)	.137	.395	.693	O(31)	.254	.232	.444
Fe(9)	.244	.131	.523	O(8)	.140	.030	.198	O(32)	.256	.296	.630
				O(9)	.013	.140	.640	O(33)	.131	.448	.975
Ca(1)	.084	.466	.299	O(10)	.136	.205	.733	O(34)	.250	.462	.876
Ca(2)	.084	.312	.842	O(11)	.153	.080	.730	O(35)	.238	.032	.563
Ca(3)	.080	.138	.343	O(12)	.131	.149	.545	O(36)	.262	.398	.074
Ca(4)	.419	.288	.208								
Ca(5)	.418	.496	.664	O(13)	.486	.472	.351	O(37)	.217	.118	.360
Ca(6)	.415	.156	.679	O(14)	.364	.393	.260	O(38)	.276	.143	.686
				O(15)	.359	.458	.477	O(39)	.282	.283	.184
P(1)	.108	.283	.160	O(16)	.358	.035	.767	O(40)	.221	.314	.860
P(2)	.106	.458	.634					O(41)	.222	.468	.311
P(3)	.104	.144	.667	O(17)	.486	.128	.401	O(42)	.280	.459	.666
P(4)	.396	.462	.337	O(18)	.354	.058	.301				
P(5)	.391	.121	.382	O(19)	.355	.118	.496	OW(1)	.493	.261	.405
P(6)	.396	.303	.880	O(20)	.364	.181	.310	OW(2)	.493	.388	.656
								OW(3)	.497	.064	.643
P(7)	.214	.457	.999	O(21)	.484	.302	.900	OW(4)	.497	.194	.182
P(8)	.289	.126	.017	O(22)	.366	.373	.810	OW(5)	.506	.474	.868
P(9)	.290	.292	.519	O(23)	.363	.236	.794	OW(6)	.486	.127	.894
				O(24)	.367	.301	.022				
								OW(7)	.426	.455	.055
								OW(8)	.574	.373	.483
								OW(9)	.572	.217	.018

Table I. Crystal-chemical relationships between mitridatite and related phases[*]

Species	a(Å)	b(Å)	c(Å)	Degrees	Formula unit
Mitridatite	17.52	19.35	11.25	95.92°	$Ca_6(H_2O)_6[Fe_3^{3+}Fe_6^{3+}O_6(PO_4)(PO_4)_2(PO_4)_6]\cdot3H_2O$
Robertsite	17.36	19.53	11.30	96.0	$Ca_6(H_2O)_6[Mn_3^{3+}Mn_6^{3+}O_6(PO_4)(PO_4)_2(PO_4)_6]\cdot3H_2O$
Arseniosiderite	17.76	19.53	11.30	96.0	$Ca_6(H_2O)_6[Fe_3^{3+}Fe_6^{3+}O_6(AsO_4)(AsO_4)_2(AsO_4)_6]\cdot3H_2O$
Betpakdalite	17.73	19.25	11.22	92.5°	$Ca(H_2O)_2[\square_3Mo_5^{6+}Fe^{3+}O_6(FeO_4)(AsO_4)_2(OH)_{12}]\cdot6H_2O$
Melkovite	17.46	18.48	10.93	94.5°	$Ca(H_2O)_2[\square_3Mo_5^{6+}Fe^{3+}O_6(FeO_4)(PO_4)_2(OH)_{12}]\cdot6H_2O$

[*]The cell parameters for the first three compounds are quoted from Moore, 1974 and the
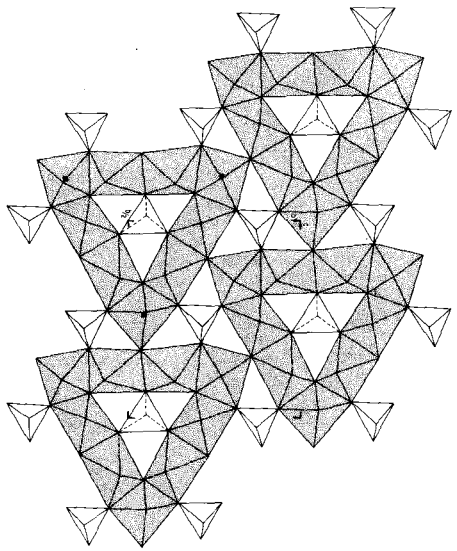last two from Skvortsova et al., 1972.

Fig. 1. Octahedral sheet (stippled) and intrasheet tetrahedra in mitridatite (unshaded) down the a^*-direction. The corner-linking tetrahedra above and below the sheet are not shown. Note the pseudo-trigonal symmetry of the structure.
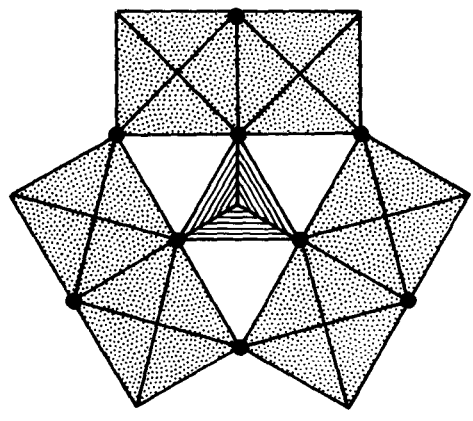

Fig. 2. The $[PFe_6O_{28}]$ cluster common to the crystal structure of mitridatite and the $[PMo_9O_{11}(H_2O)_3]$ polyanion.
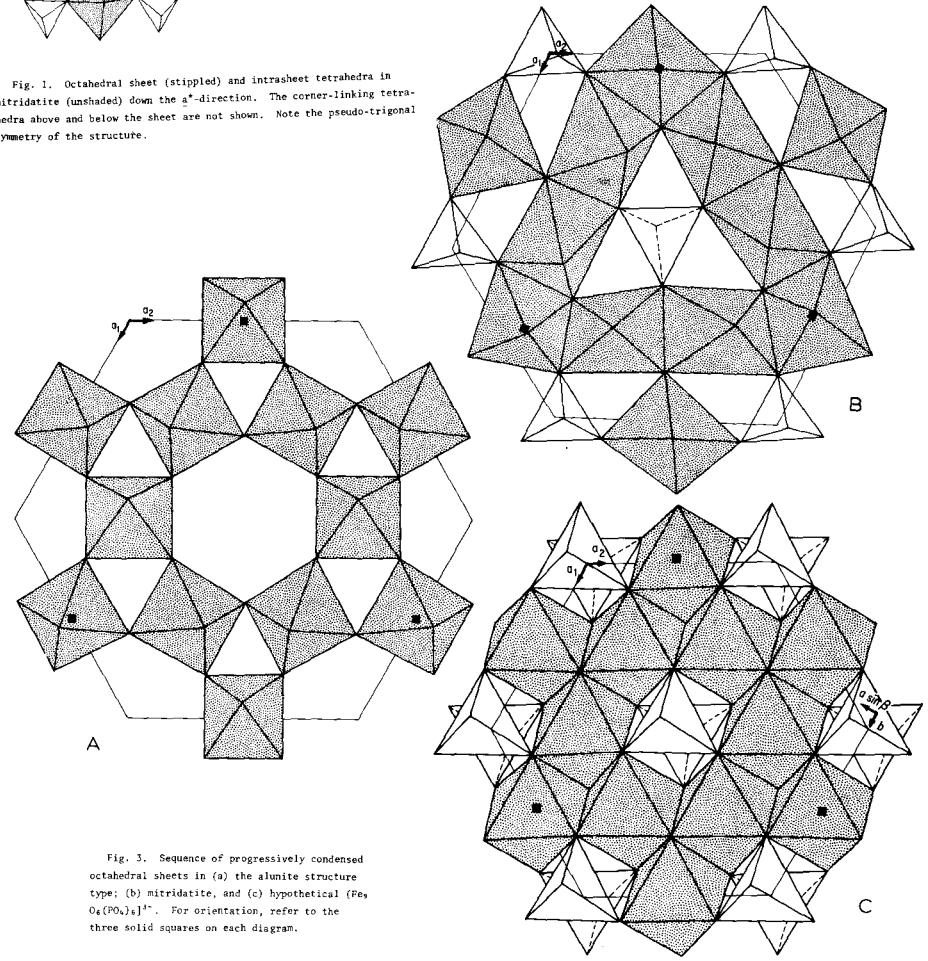

Fig. 3. Sequence of progressively condensed octahedral sheets in (a) the alunite structure type; (b) mitridatite, and (c) hypothetical $[Fe_9O_6(PO_4)_6]^{3-}$. For orientation, refer to the three solid squares on each diagram.