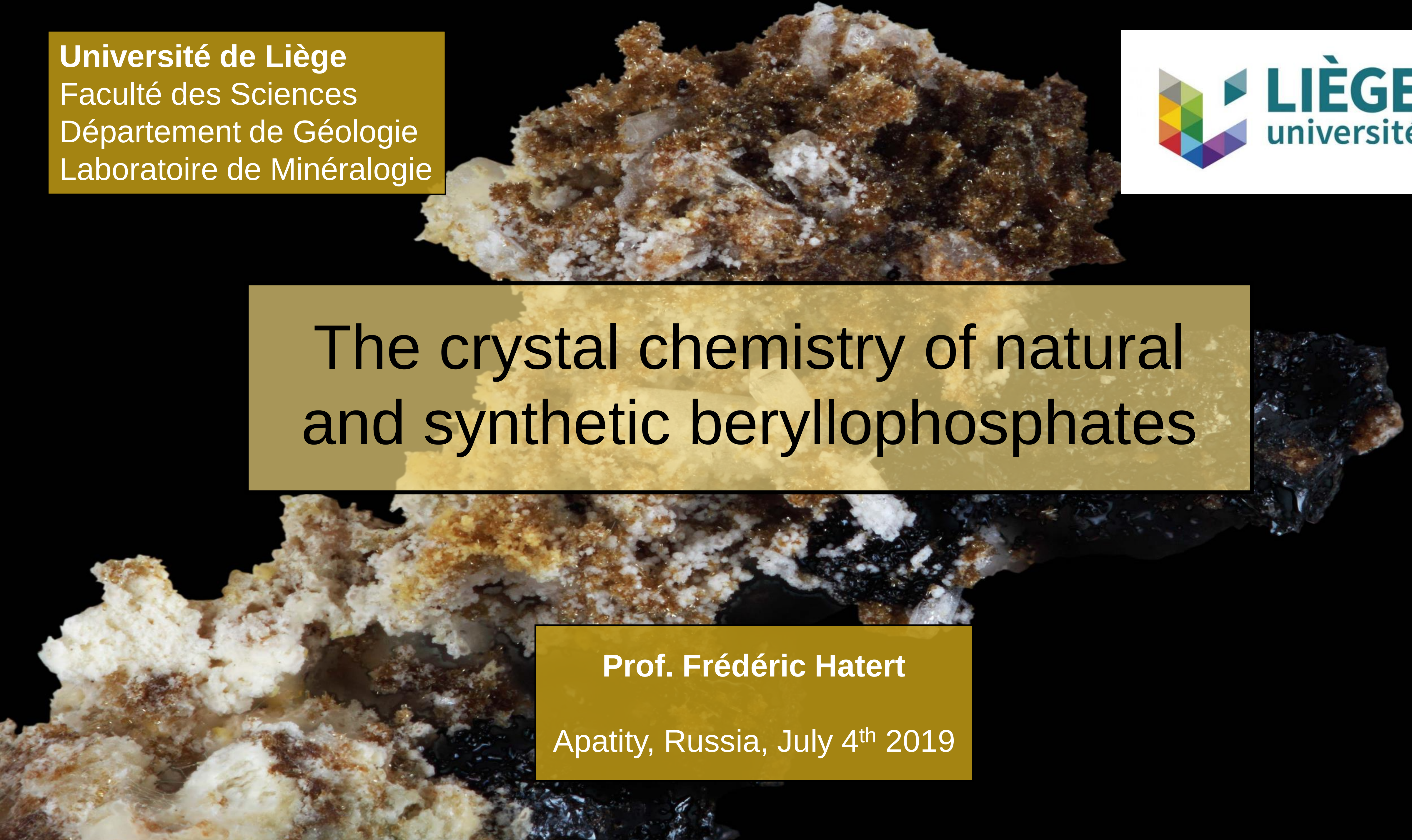


Université de Liège
Faculté des Sciences
Département de Géologie
Laboratoire de Minéralogie

The crystal chemistry of natural and synthetic beryllophosphates

Prof. Frédéric Hatert

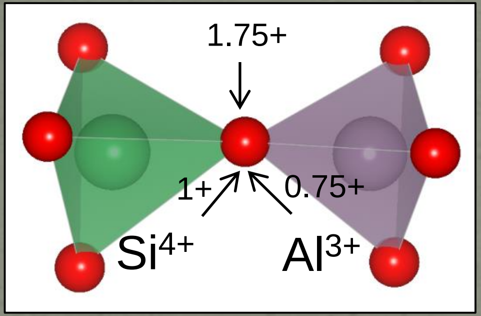
Apatity, Russia, July 4th 2019

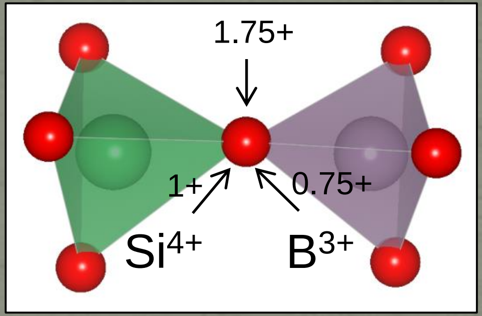
Table of contents

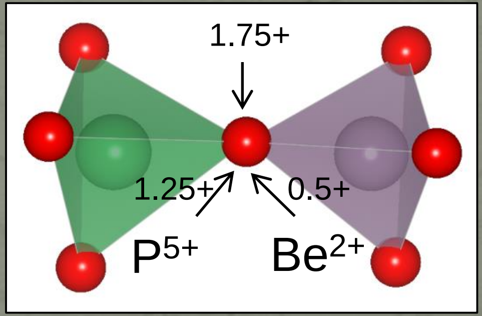
Natural beryllophosphates

- Approximately 35 mineral species
- Occurring in granitic pegmatites
- Reaction between beryl and P-bearing hydrothermal solutions

Crystal structures similar to those of aluminosilicates and borosilicates



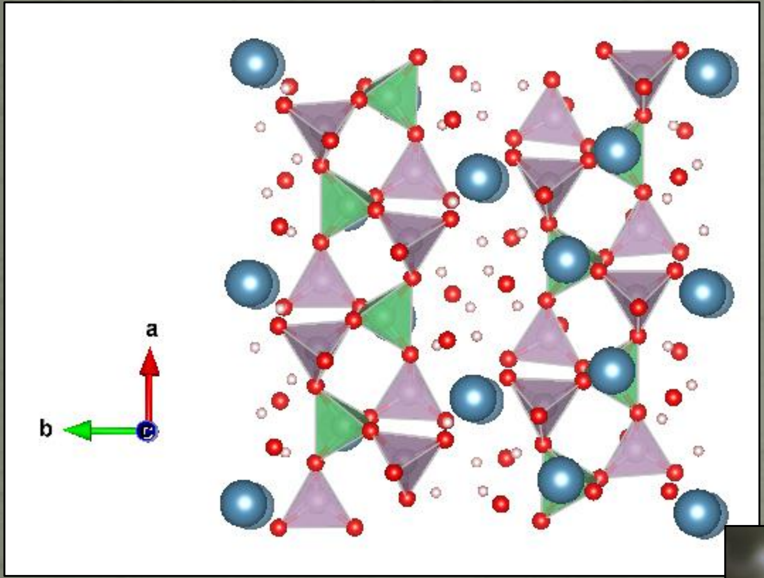




Pauling bond-valence sum on shared oxygen = 1.75

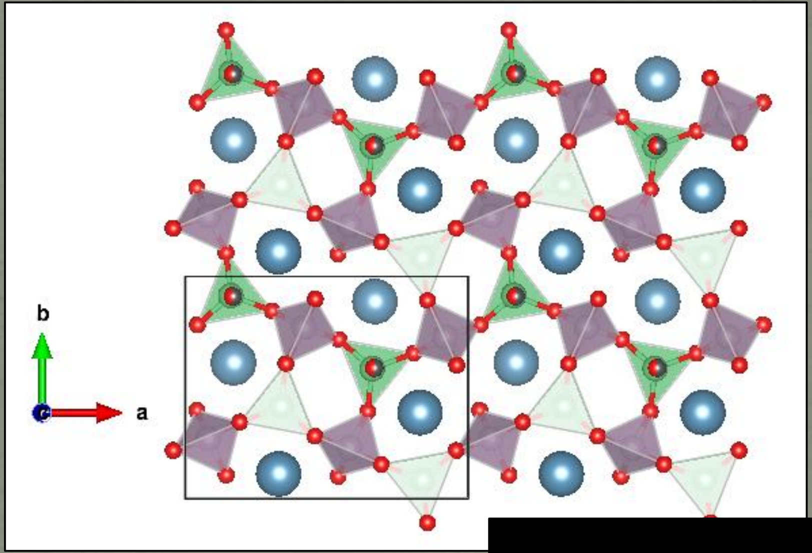
Crystal chemistry of beryllophosphates

Chain structures



Fransoletite
$Ca_3Be_2(PO_4)_2(PO_3OH)_2.4H_2O$

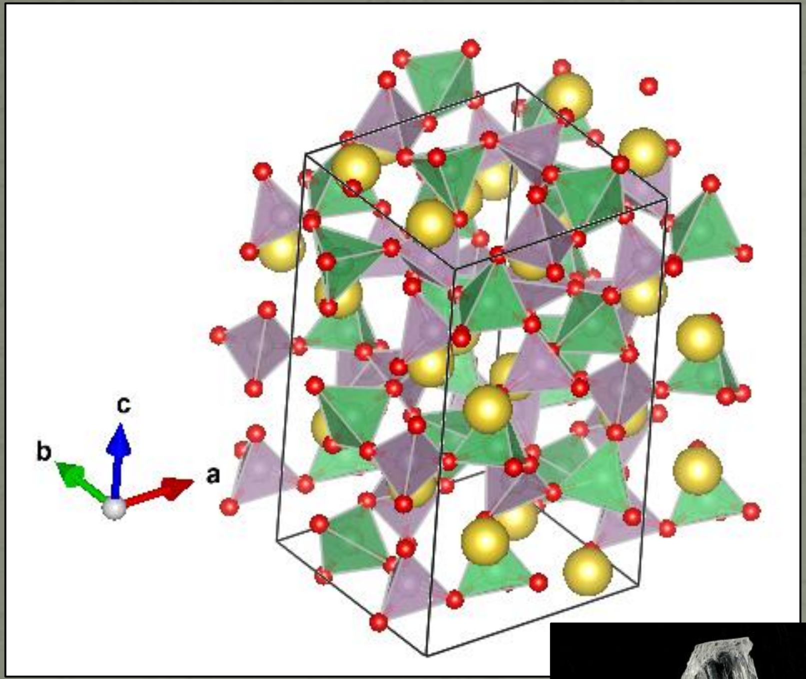
Sheet structures



Herderite
$CaBe(PO_4)(F,OH)$

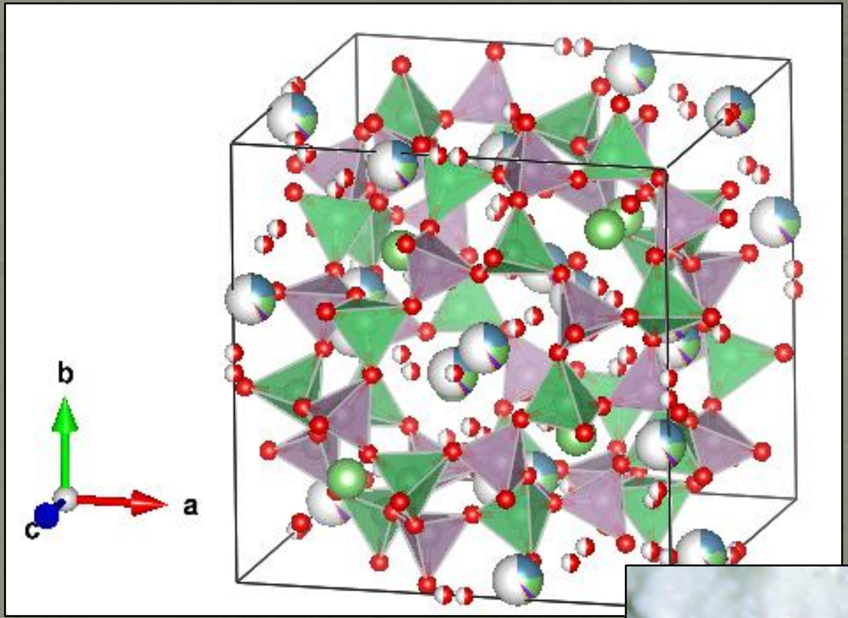
Crystal chemistry of beryllophosphates

Framework structures



Beryllonite
$NaBe(PO_4)$

Zeolite-type structures



Pahasapaite
$Li_8(Ca,Li,K)_{10}Be_{24}(PO_4)_{24}.38H_2O$

Hydrothermal experiments

$M^{2+}Be_2P_2O_8$ (M^{2+} = Ca, Sr, Pb, Ba)

The Canadian Mineralogist
Vol. 52, pp. 337-350 (2014)
DOI: 10.3749/canmin.52.2.337

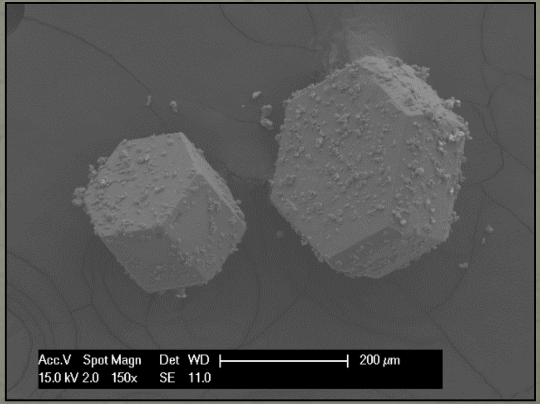
CRYSTAL CHEMISTRY OF SYNTHETIC $M^{2+}Be_2P_2O_8$ (M^{2+} = Ca, Sr, Pb, Ba) BERYLLOPHOSPHATES

FABRICE DAL BO, FRÉDÉRIC HATERT§, AND MAXIME BAIJOT
Laboratoire de Minéralogie, B18, Université de Liège, B-4000 Liège, Belgium

Dr. F. Dal Bo

- **Starting materials: BeO, H_3PO_4, $NH_4H_2PO_4$, $CaHPO_4$, $Sr(NO_3)_2$, $Pb(NO_3)_2$, $Ba(OH)_2.8H_2O$**
- **® Parr hydrothermal bomb: T = 200°C, 7 days, autogeneous pressure**
- **Cold-seal bombs, T = 400-600°C, P = 1 kbar**

- **Samples investigated by single-crystal X-ray diffraction techniques**



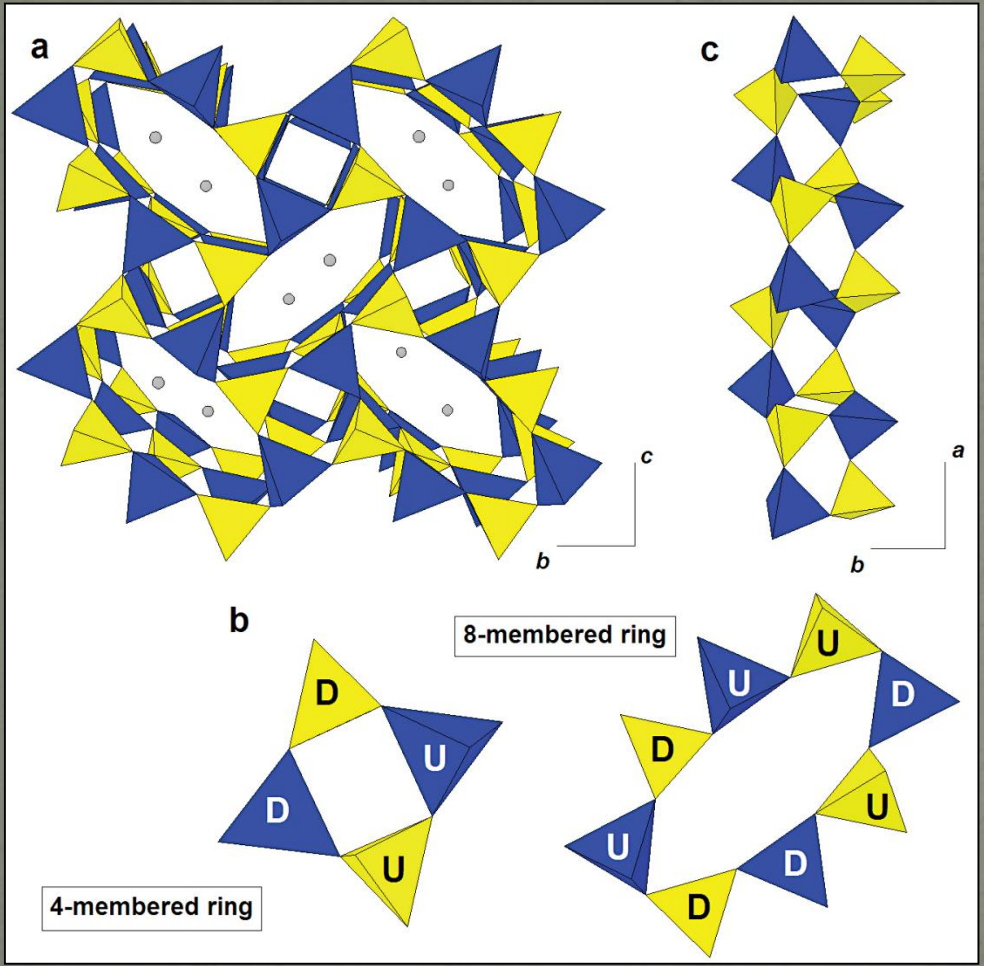
Hydrothermal experiments

TABLE 1. HYDROTHERMAL SYNTHESIS PERFORMED IN THE M^{2+}-BE-PO_4 SYSTEM

N° sample	BeO (mg)	$CaHPO_4$ (mg)	$Sr(NO_3)_2$ (mg)	$Pb(NO_3)_2$ (mg)	$Ba(OH)_2.8H_2O$ (mg)	$NH_4H_2PO_4$ (mg)	H_3PO_4 (mL)	T (°)	Time (days)	Synthesized compounds
CaBeP200-1	101	203	-	-	-	-	2	200	7	$CaBe_2P_2O_8$
CaBeP200-2	50	400	-	-	-	-	2	200	7	$CaBe_2P_2O_8$
CaBeP200-3	100	136	-	-	-	-	0.07	200	7	$CaBe_2P_2O_8$, BeO
CaBeP200-4	50	408	-	-	-	-	0.07	200	7	$CaBe_2P_2O_8$
CaBeP150-5	100	271	-	-	-	-	0.07	150	7	$CaBe_2P_2O_8$
CaBeP200-7	50	407	-	-	-	115	-	200	7	$CaBe_2P_2O_8$, $Ca_5(PO_4)_3(OH)$
CaBeP200-8	100	135	-	-	-	115	-	200	7	$CaBe_2P_2O_8$, $Ca_5(PO_4)_3(OH)$
SrBeP200-1	25	-	212	-	-	117	-	200	7	$SrBe_2P_2O_8$, $Sr(HPO_4)$, BeO
SrBeP200-2	100	-	211	-	-	230	-	200	7	$SrBe_2P_2O_8$, BeO
SrBeP200-3	100	-	212	-	-	-	2	200	7	$SrBe_2P_2O_8$
PbBeP200-1	162	-	-	331	-	-	2	200	7	$PbBe_2P_2O_8$
BaBeP200-1	150	-	-	-	315	-	2	200	7	$BaBe_2P_2O_8$
CaBeP400	Products of the CaBeP200-1 experiment used as starting materials							400	7	$CaBe_2P_2O_8$
CaBeP600								600	7	$CaBe_2P_2O_8$
SrBeP400	Products of the SrBeP200-3 experiment used as starting materials							400	7	$SrBe_2P_2O_8$
SrBeP600								600	7	$SrBe_2P_2O_8$
PbBeP400	Products of the PbBeP200-1 experiment used as starting materials							400	7	$PbBe_2P_2O_8$
PbBeP600								600	7	$PbBe_2P_2O_8$
BaBeP400	Products of the BaBeP200-1 experiment used as starting materials							400	7	$BaBe_2P_2O_8$
BaBeP600								600	7	$BaBe_2P_2O_8$

- **$CaBe_2P_2O_8$, $SrBe_2P_2O_8$, $PbBe_2P_2O_8$: *$P2_1/c$*, isostructural with hurlbutite**
- **$BaBe_2P_2O_8$: *P6/mmm*, new structure type**

$M^{2+}Be_2P_2O_8$ (M^{2+} = Ca, Sr, Pb)



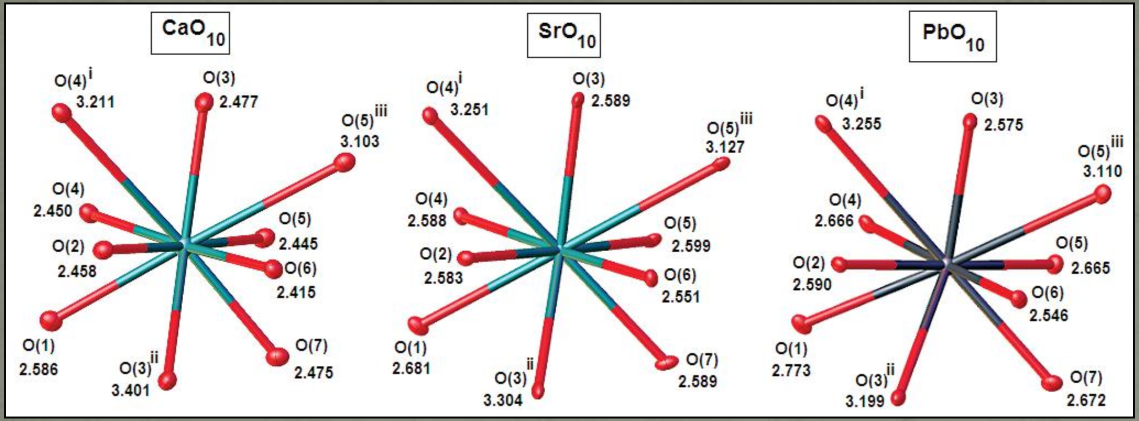
	$CaBe_2P_2O_8$	$SrBe_2P_2O_8$	$PbBe_2P_2O_8$
a (Å)	7.809(1)	8.000(1)	8.088(1)
b	8.799(1)	8.986(1)	9.019(1)
c	8.309(1)	8.418(1)	8.391(1)
β (°)	90.51(1)	90.22(1)	90.12(1)
V (Å³)	570.98(2)	605.10(6)	612.22(1)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$

- **Framework beryllophosphates**
- **Feldspar topology**

- **4-membered rings UUDD**
- **8-membered rings DDUDUUDU**
- **Double crankshaft chain parallel to *a***

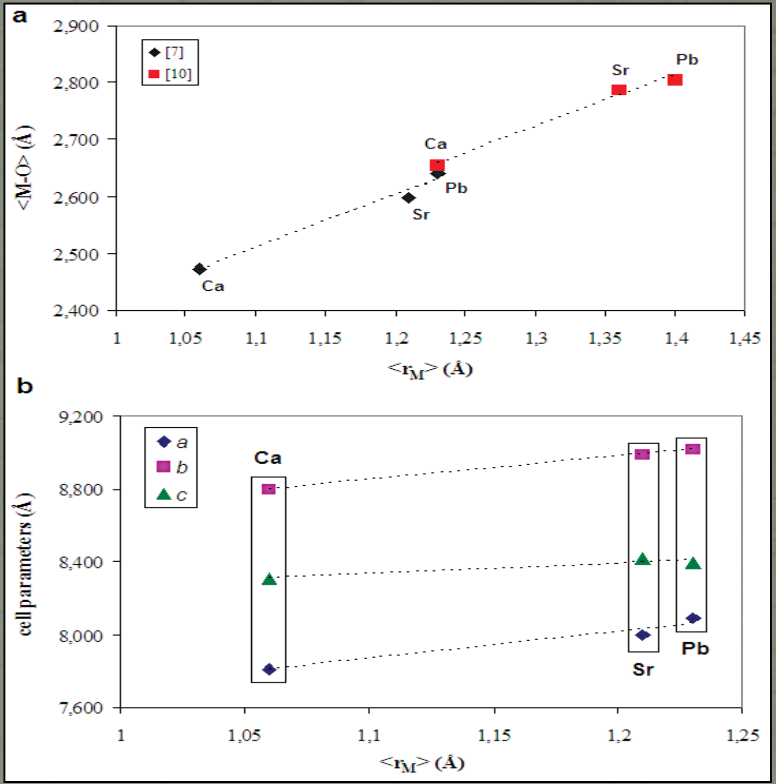
Hurlbutite
$CaBe_2P_2O_8$

$M^{2+}Be_2P_2O_8$ (M^{2+} = Ca, Sr, Pb)



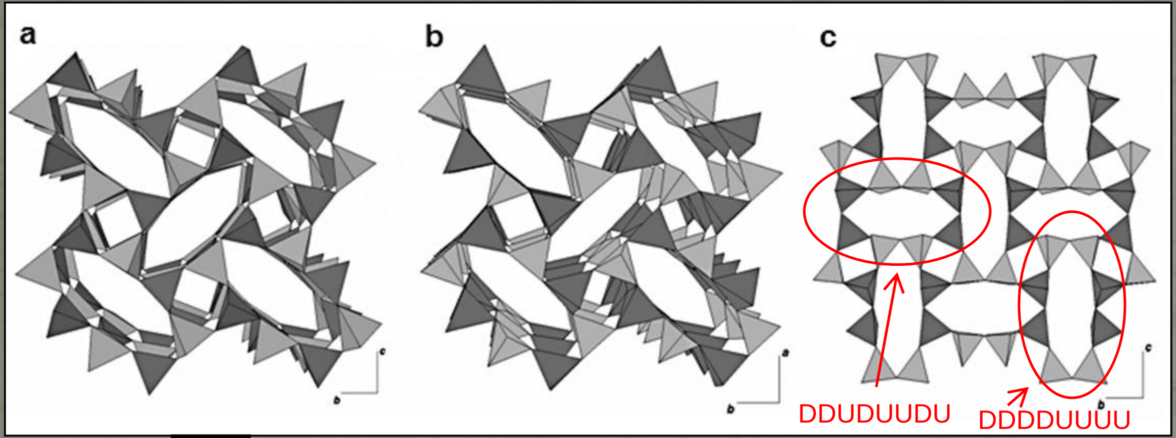
	CaBeP	SrBeP	PbBeP
M-O(1)	2.586(1)	2.681(4)	2.773(2)
M-O(2)	2.458(1)	2.583(4)	2.590(2)
M-O(3)	2.477(1)	2.589(4)	2.575(2)
M-O(4)	2.450(1)	2.588(3)	2.666(2)
M-O(5)	2.445(1)	2.599(4)	2.665(2)
M-O(6)	2.415(1)	2.551(3)	2.546(2)
M-O(7)	2.475(1)	2.589(4)	2.672(2)
<*M*-O> [7]	2.472(1)	2.597(4)	2.641(2)
M-O(3)	3.401(1)	3.304(4)	3.199(2)
M-O(4)	3.211(1)	3.251(4)	3.255(2)
M-O(5)	3.103(1)	3.127(4)	3.110(2)
<*M*-O> [10]	2.702(1)	2.786(4)	2.805(2)

- [7 + 3] coordination polyhedra for the M^{2+} cations
- Distortion of Pb site due to lone-pair electrons



- Correlation between unit-cell parameters and *M*-O bond lengths
- EIR Sr^{2+}[7] = 1.21 Å; EIR Pb^{2+}[7] = 1.23 Å

$M^{2+}Be_2P_2O_8$ (M^{2+} = Ca, Sr, Pb)



$CaBe_2P_2O_8$ Hurlbutite

$CaB_2Si_2O_8$ Danburite

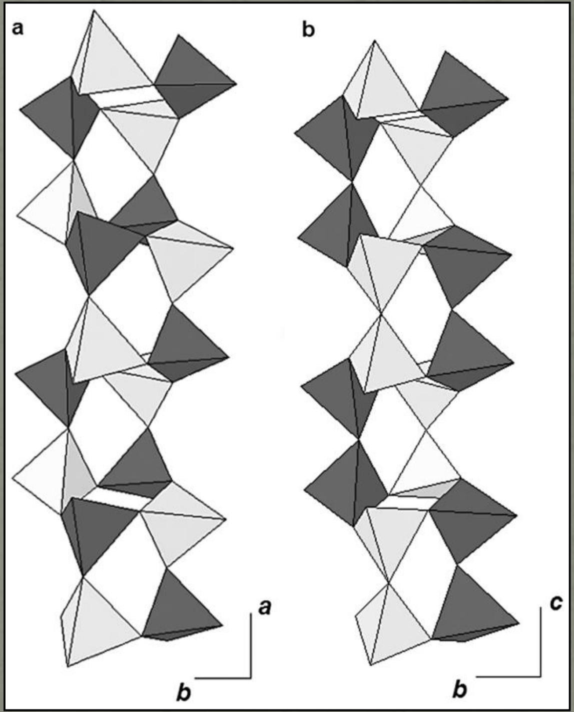
$KAlSi_3O_8$ Orthoclase

- DDUU 4-membered rings

- Hurlbutite and danburite: DDUDUUDU only
- Orthoclase: DDUDUUDU and DDDDUUUU

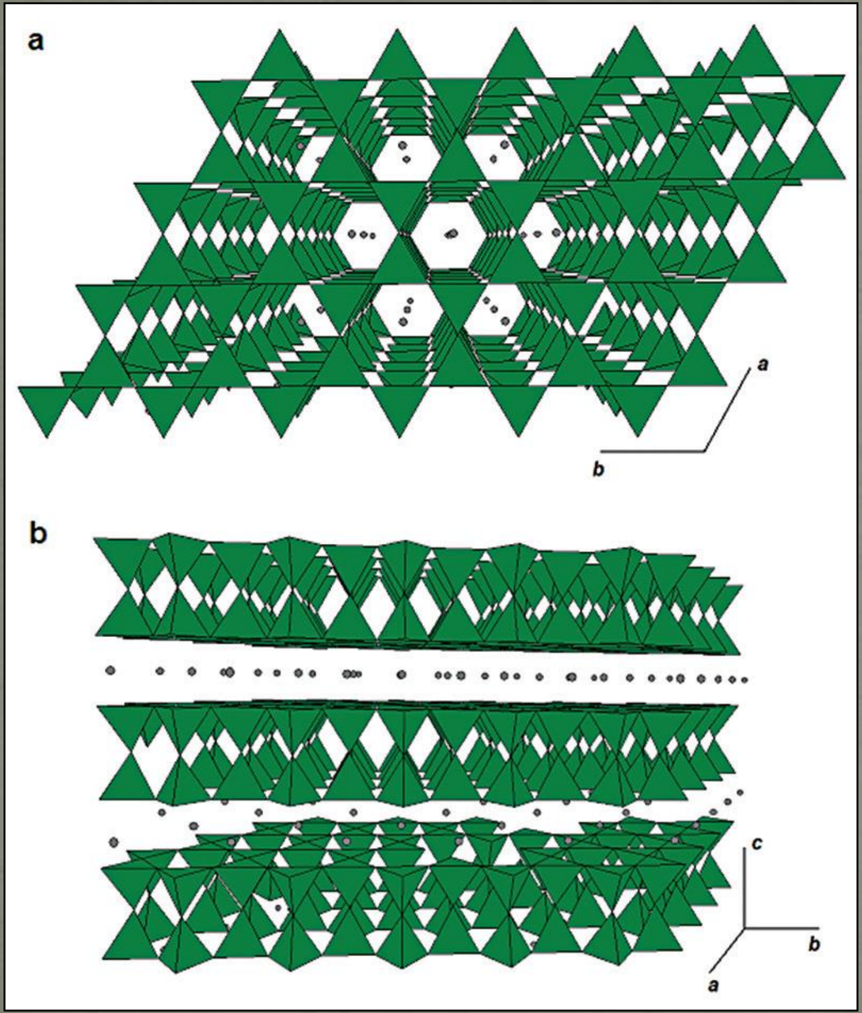
- No Be-O-Be or P-O-P connections in hurlbutite
- B-O-B and Si-O-Si connections in danburite

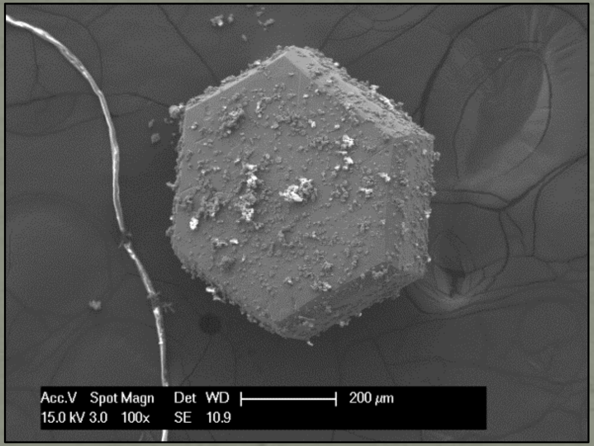
Danburite

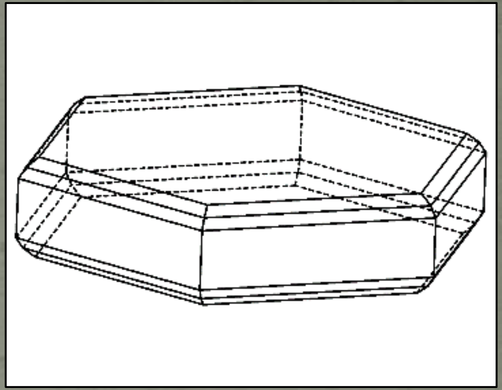


Hurlbutite

$BaBe_2P_2O_8$



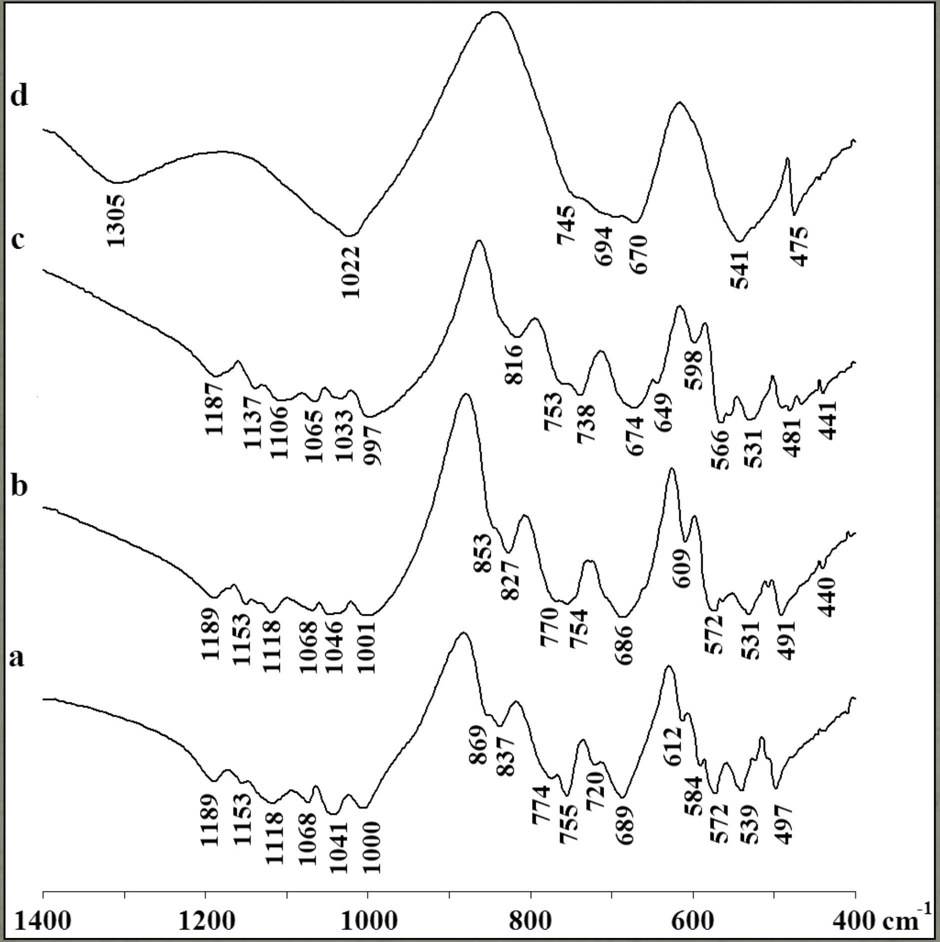




- *a* = 5.028(1), *c* = 7.466(1) Å
- SG *P6/mmm*

- Phyllophosphate structure
- Double layer of $(P_{0.5}Be_{0.5})O_4$ tetrahedra
- Six-membered rings
- 12-coordinated Ba atoms

Infrared spectroscopy



$BaBe_2P_2O_8$

$PbBe_2P_2O_8$

$SrBe_2P_2O_8$

$CaBe_2P_2O_8$

Large bands for
The Ba compound

Disordered distribution
of P and Be on the
tetrahedral sites

Four new mineral species

Dr. Rao Can
Hangzhou, China

Strontiohurlbutite
$SrBe_2P_2O_8$
Nanping No. 31, China

Minjiangite
$BaBe_2P_2O_8$
Nanping No. 31, China

Dr. Simon Philippo
Luxembourg

Wilancookite
$(Ba,K,Na)_8(Ba,Li,[])_6Be_{24}P_{24}O_{96}.32H_2O$
Lavra Ponte do Piauí, MG, Brazil

Dr. Nicolas Meisser
Lausanne, Switzerland

Limousinite
$BaCa[Be_4P_4O_{16}].6H_2O$
Chanteloube, France

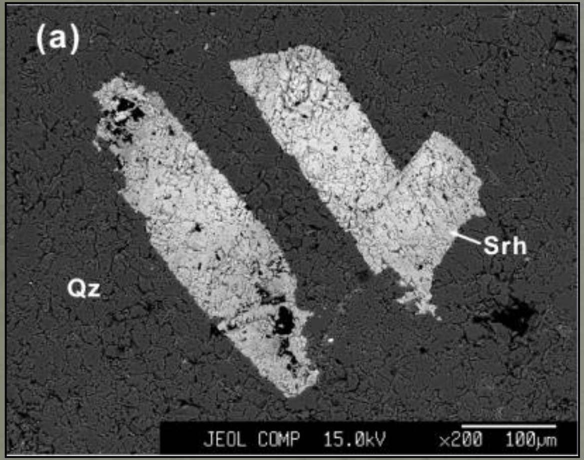
Three new Ba-Be-phosphates!

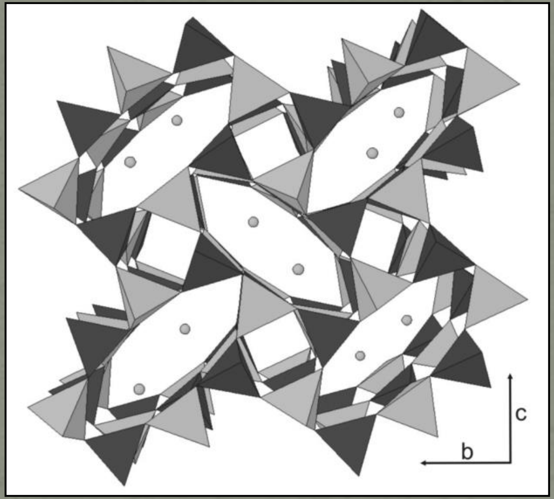
Strontiohurlbutite, $Sr[Be_2P_2O_8]$

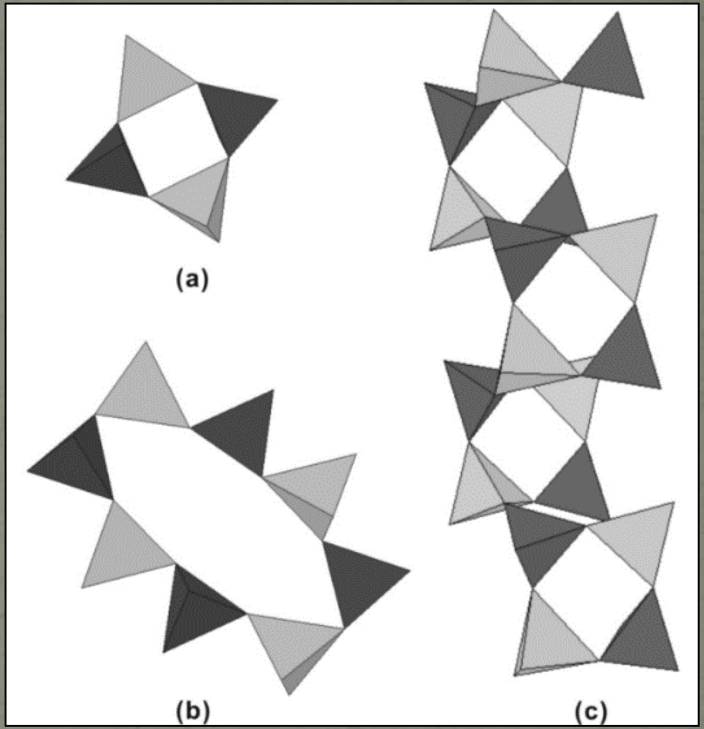
American Mineralogist, Volume 99, pages 494–499, 2014

Strontiohurlbutite, $SrBe_2(PO_4)_2$, a new mineral from Nanping No. 31 pegmatite, Fujian Province, Southeastern China

Can Rao[1,2,*], Rucheng Wang[1], Frédéric Hatert[3], Xiangping Gu[4], Luisa Ottolini[5], Huan Hu[1], Chuanwan Dong[2], Fabrice Dal Bo[3] and Maxime Baijot[3]







- *a* = 7.997(3), *b* = 8.979(2), *c* = 8.420(7) Å, β = 90.18(6)°
- SG $P2_1/c$

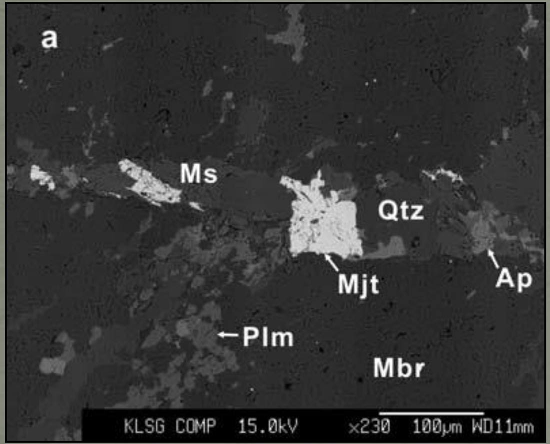
- Framework structure
- 4-membered and 8-membered rings
- Identical to the structure of synthetic $SrBe_2P_2O_8$

Minjiangite, $Ba[Be_2P_2O_8]$

Mineralogical Magazine, October 2015, Vol. 79(5), pp. 1195–1202

Minjiangite, $BaBe_2(PO_4)_2$, a new mineral from Nanping No. 31 pegmatite, Fujian Province, southeastern China

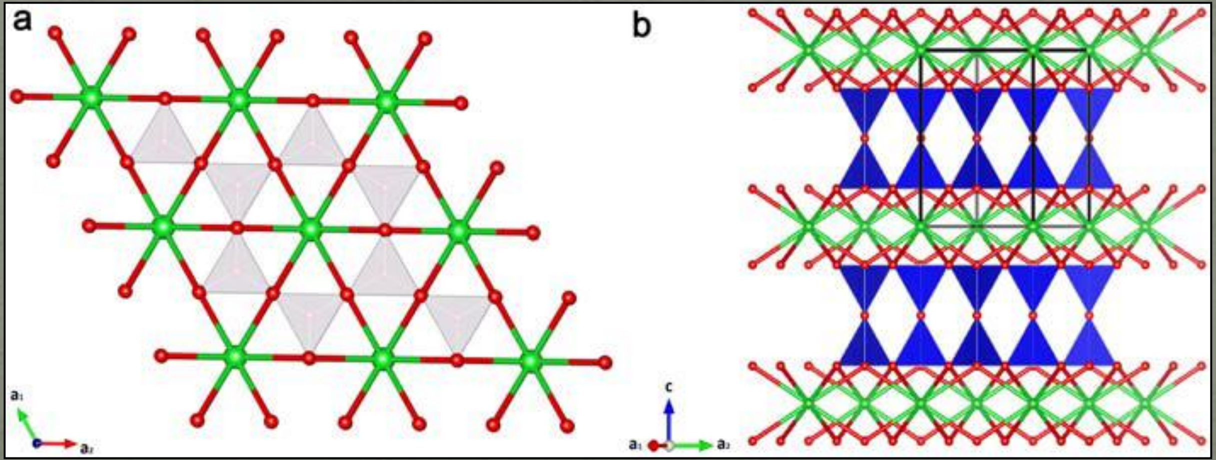
C. Rao[1,*], F. Hatert[2], R. C. Wang[3], X. P. Gu[4], F. Dal Bo[2] and C. W. Dong[1]



- Similar to synthetic $BaBe_2P_2O_8$
- Double layer of $(P_{0.5}Be_{0.5})O_4$
- Six-membered rings
- 12-coordinated Ba atoms

Minjiang river, China

- a = 5.029(1) Å
- c = 7.466(1) Å
- SG *P*6/*mmm*



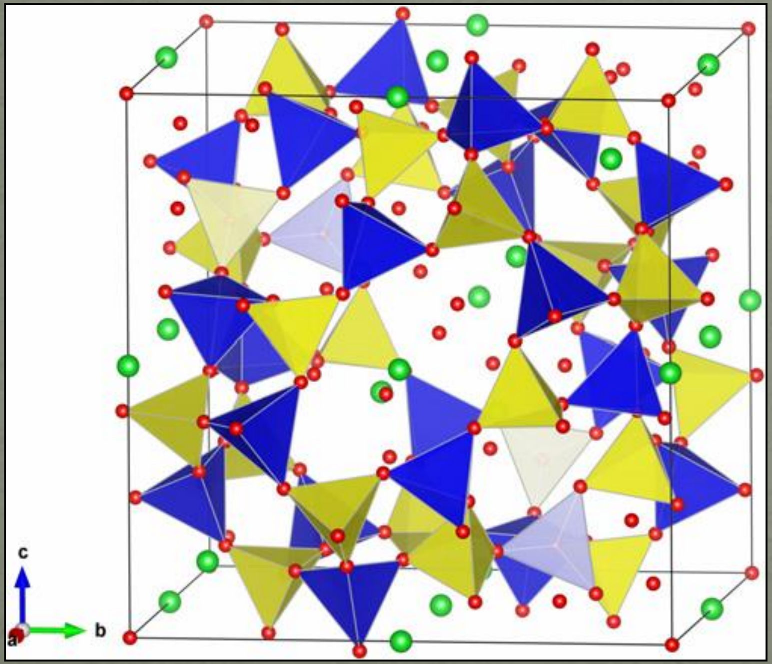
Wilancookite, $(Ba,K,Li)_8(Ba,Li,[])_6Be_{24}P_{24}O_{96}.32H_2O$

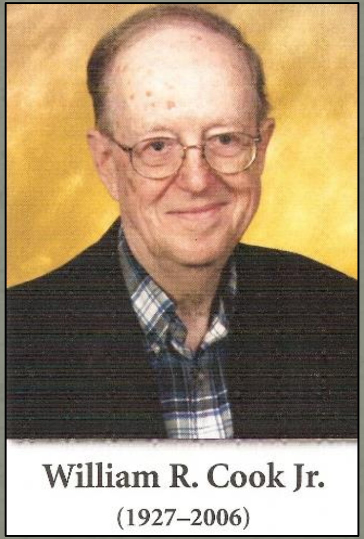
Eur. J. Mineral.
2017, **29**, 923–930
Published online 26 June 2017

Wilancookite, $(Ba,K,Na)_8(Ba,Li,\square)_6Be_{24}P_{24}O_{96}\cdot32H_2O$, a new beryllophosphate with a zeolite framework

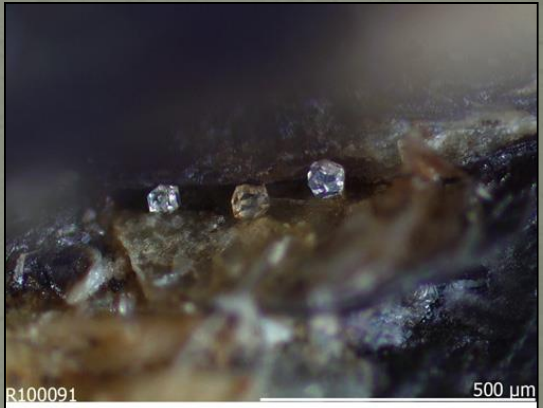
Frédéric Hatert[1,*], Simon Philippo[2], Luisa Ottolini[3], Fabrice Dal Bo[1], Ricardo Scholz[4], Mário L.S.C. Chaves[5], Hexiong Yang[6], Robert T. Downs[6] and Luiz A.D. Menezes Filho[7,a]

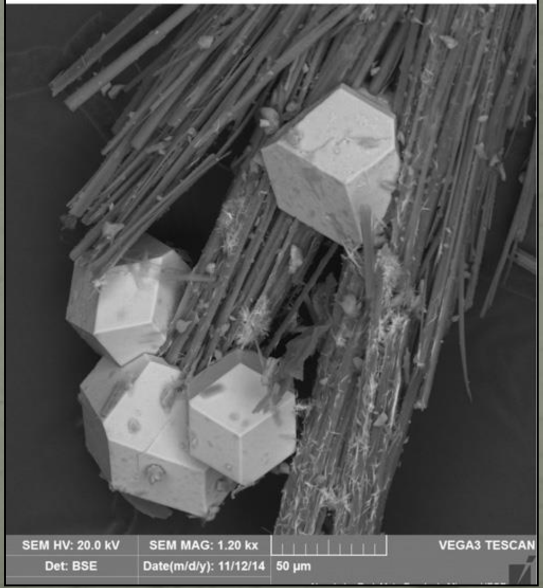
- 2nd known zeolite phosphate
- Similar to synthetic zeolite RHO
- Isostructural with pahasapaite
- 8-, 6-, and 4-membered rings



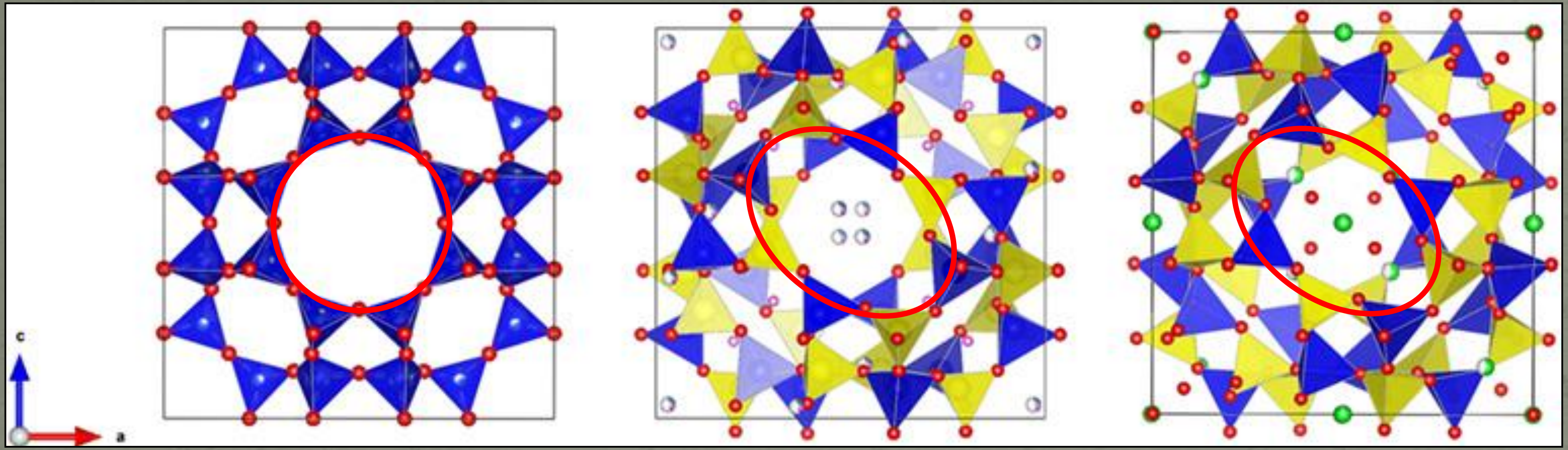


- *a* = 13.579(9) Å
- SG *I*23





Wilancookite

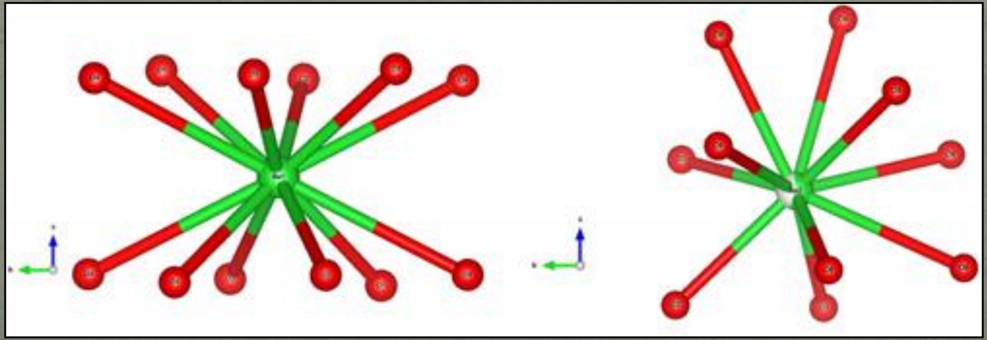


Zeolite RHO
*Im*3*m*

Pahasapaite
*I*23

Wilancookite
*I*23

$Ba(1)O_{12}$



$Ba(2)O_{10}$

Limousinite, $BaCa[Be_4P_4O_{16}].6H_2O$

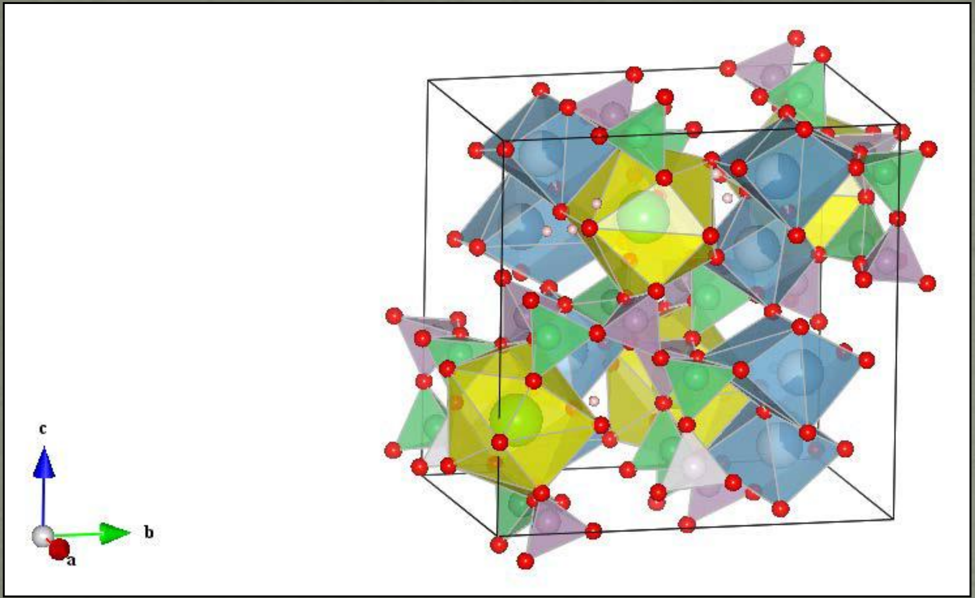
2019-011 Limousinite
Ideal chemical formula: $BaCa[Be_4P_4O_{16}]\cdot 6H_2O$
Crystal system: Monoclinic Space group: $P2_1/c$ (#14)

a = 9.4958(4) Å b = 13.6758(4) Å c = 13.4696(4) Å
β = 90.398(3)°
V = 1749.15(10) $Å^3$ Z = 4

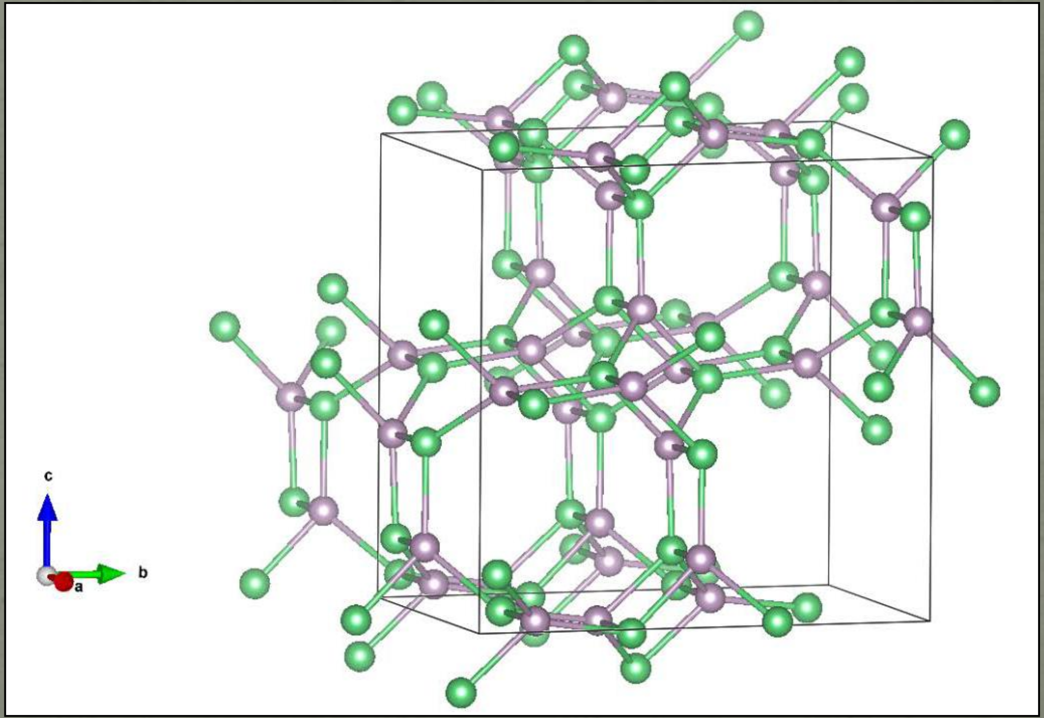
Frédéric Hatert[1]*, Nicolas Meisser[2], Fabrice Dal Bo[1], Yannick Bruni[1], Pietro Vignola[3], Andrea Risplendente[4], François-Xavier Châtenet[5] and Julien Lebocey[6].

Limousin region, France

Limousinite



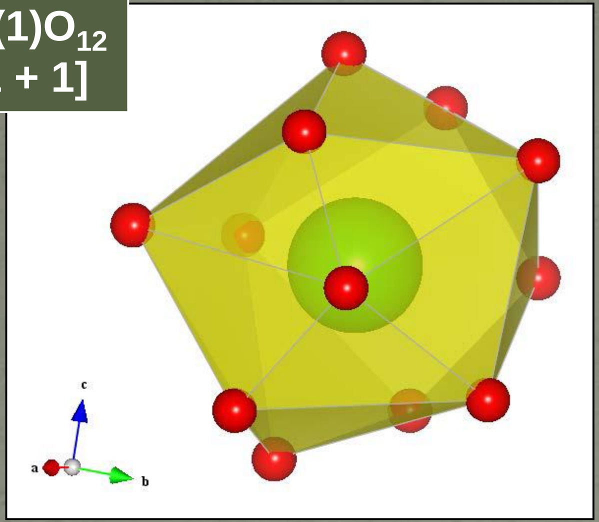
- Third known zeolite phosphate
- Framework identical to that of phillipsite-group minerals
- 8- and 4-membered rings



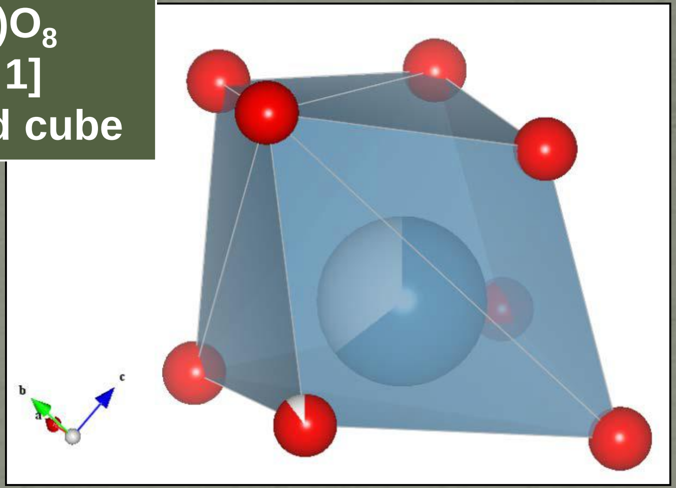
LIÈGE université

Limousinite

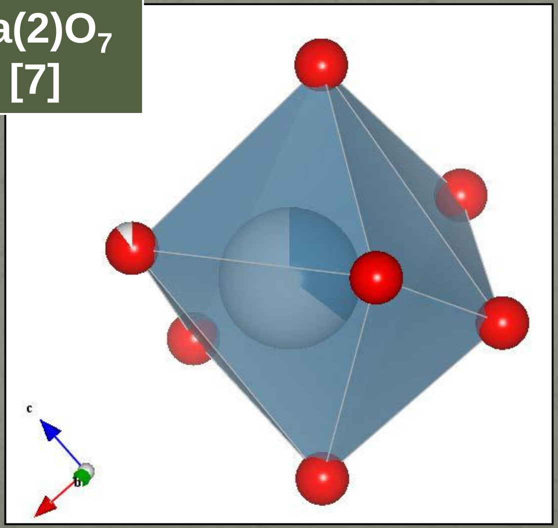
Ba(1)O_{12}
[11 + 1]

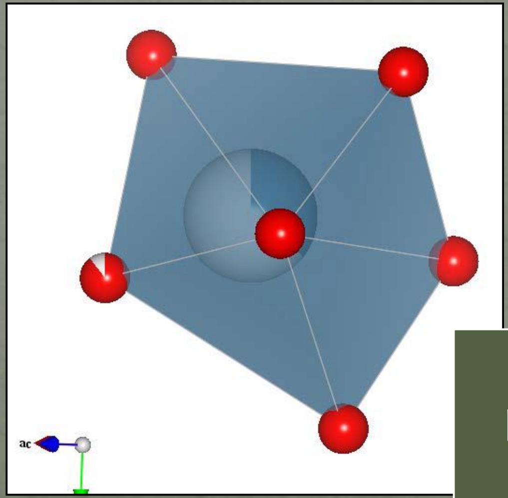


Ca(1)O_8
[7 + 1]
Distorted cube



Ca(2)O_7
[7]





Distorted pentagonal bipyramid

Step 1: Formulae modifications

IMA-CNMNC mineral list

- Fransoletite = $Ca_3Be_2(PO_4)_2(PO_3OH)_2.4H_2O$
- Herderite = $CaBe(PO_4)F$
- Hurlbutite = $CaBe_2(PO_4)_2$
- Pahasapaite = $Li_8(Ca,Li,K)_{10}Be_{24}(PO_4)_{24}.38H_2O$

Phosphate minerals are always considered as constituted by isolated (PO_4) groups

New proposed formulae

- Fransoletite = $Ca_3[Be_2P_4O_{14}(OH)_2].4H_2O$
- Herderite = $Ca[BePO_4F]$
- Hurlbutite = $Ca[Be_2P_2O_8]$
- Pahasapaite = $Li_8(Ca,Li,K)_{10}[Be_{24}P_{24}O_{96}].38H_2O$

Tetrahedral unit composition in square brackets

Step 2 : Definition of sub-classes

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Possible linkages of phosphate tetraherda

- (PO_4)-(PO_4) = Polyphosphates
- (PO_4)-(BeO_4) = Beryllophosphates
- (PO_4)-(ZnO_4) = Zincophosphates
- (PO_4)-(AlO_4) = Aluminophosphates

Huminicki & Hawthorne (2002)

Eur. J. Mineral.
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The standardisation of mineral group hierarchies: application to recent nomenclature proposals

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NESOPHOSPHATES
SOROPHOSPHATE
CYCLOPHOSPHATES
INOPHOSPHATES
PHYLLOPHOSPHATES
TECTOPHOSPHATES

- ➔ Isolated tetrahedra -triphylite – $[PO_4]$
- ➔ Finite clusters of tetrahedra – canaphite – $[P_2O_7]$
- ➔ Cyclic units – no known example
- ➔ Infinite chains - fransoletite - $[Be_2P_4O_{14}(OH)_2]$
- ➔ Infinite sheets - minjiangite – $[Be_2P_2O_8]$
- ➔ Infinite framework - limousinite – $[Be_4P_4O_{16}]$

Conclusions

• Beryllophosphates show an exciting crystal chemistry, due to the possibility of polymerization between PO_4 and BeO_4 tetrahedra

• Hydrothermal synthesis experiments were performed, showing that the hurlbutite-type structure was extremely stable. This structure is topologically related to the feldspar structure.

• Three new Ba beryllophosphates were described from pegmatites in Brazil, China and France: minjiangite, wilancookite, and limousinite.

• Wilancookite and limousinite show a zeolite framework, and limousinte is the first phosphate with a framework similar to that of a natural zeolite aluminosilicate.