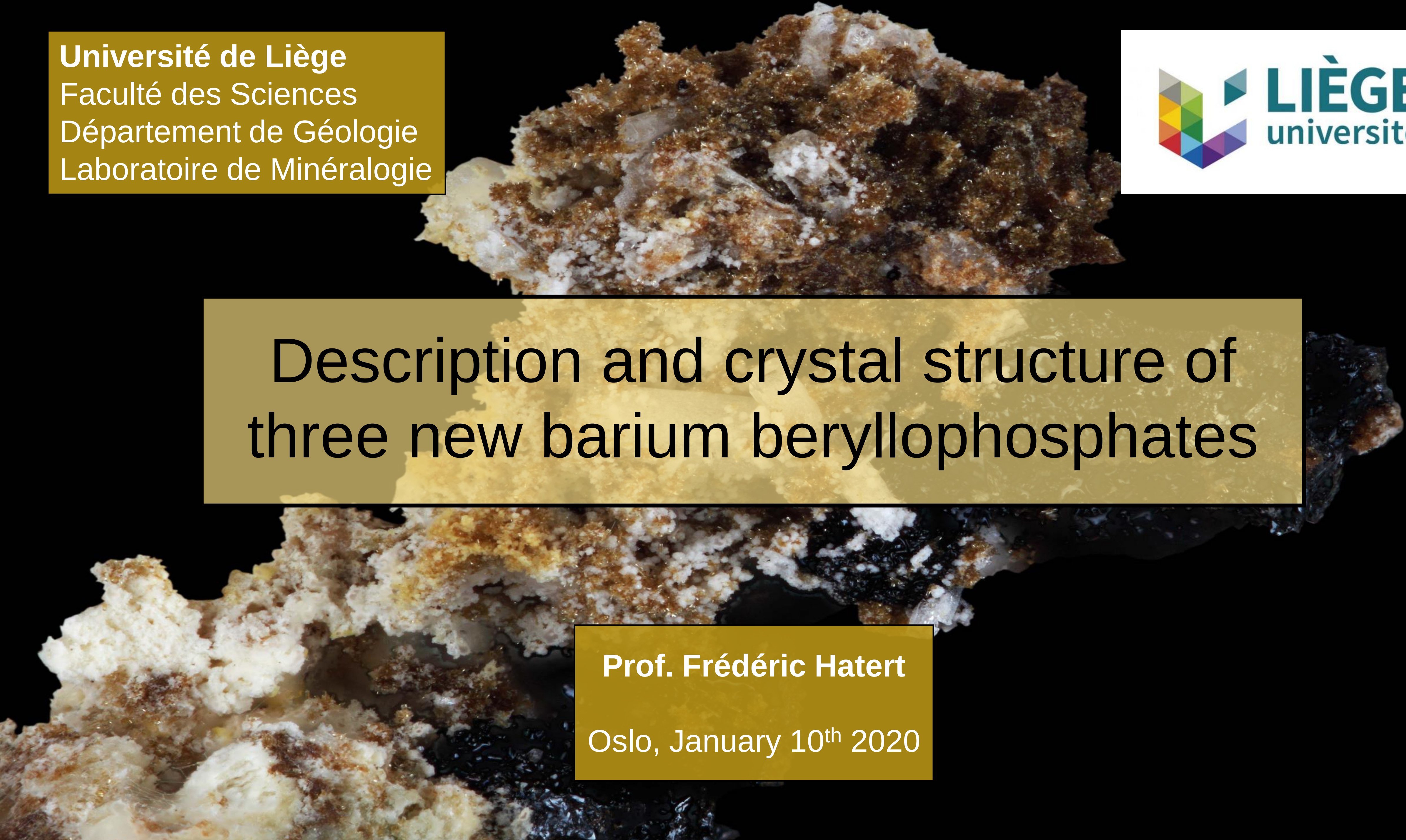

Université de Liège
Faculté des Sciences
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Laboratoire de Minéralogie

LIÈGE université

Description and crystal structure of three new barium beryllophosphates

Prof. Frédéric Hatert

Oslo, January 10th 2020

Table of contents

- **Introduction**

  Crystal chemistry of beryllophosphates

- **Wilancookite**

  $(Ba,K,Li)_8(Ba,Li,[])_6[Be_{24}P_{24}O_{96}].32H_2O$

- **Minjiangite**

  $Ba[Be_2P_2O_8]$

- **Limousinite**

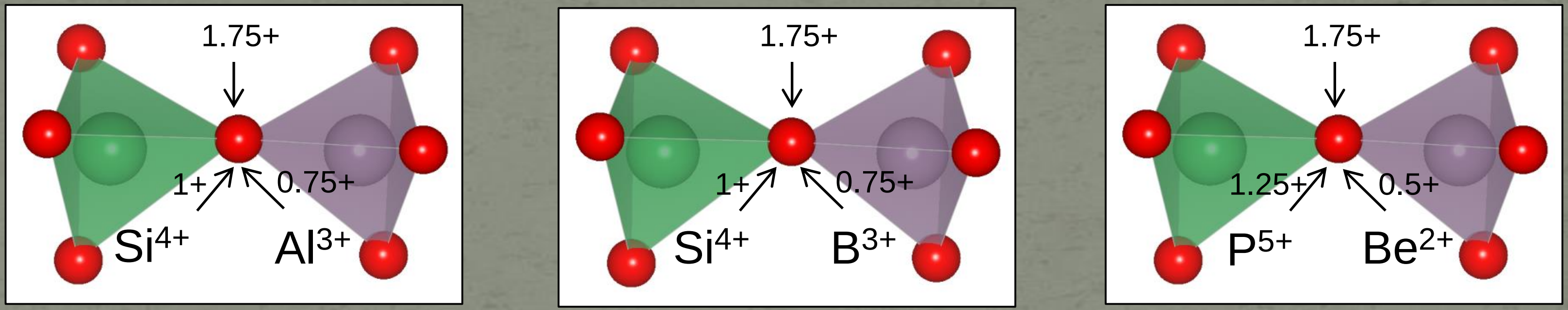
  $BaCa[Be_4P_4O_{16}].6H_2O$

- **Classification of phosphate minerals**

Natural beryllophosphates

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

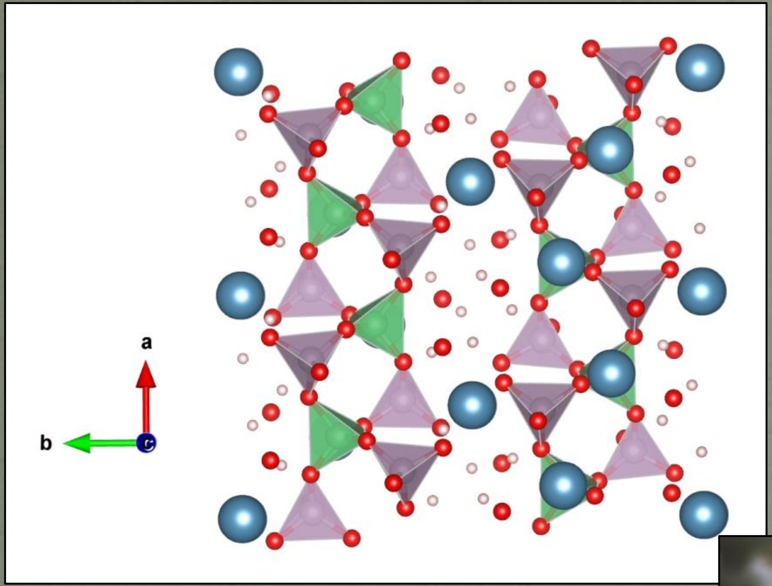
Crystal structures similar to those of aluminosilicates and borosilicates



Pauling bond-valence sum on shared oxygen = 1.75

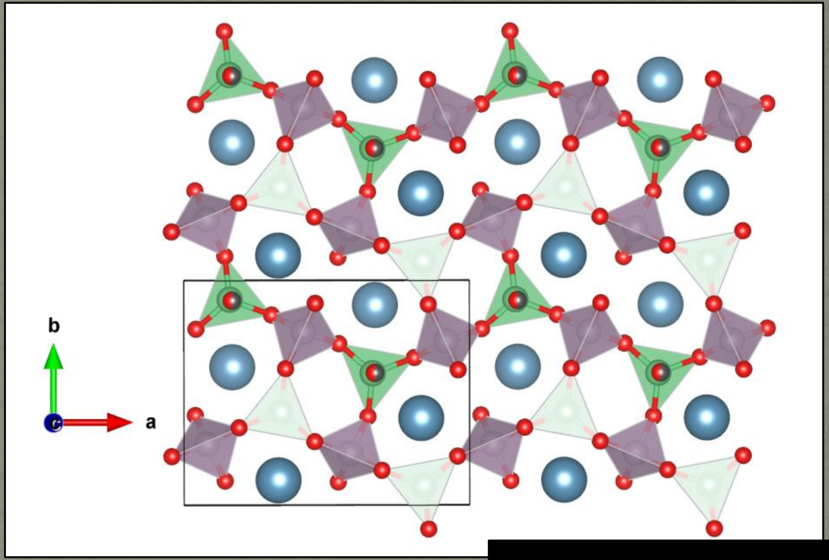
Crystal chemistry of beryllophosphates

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

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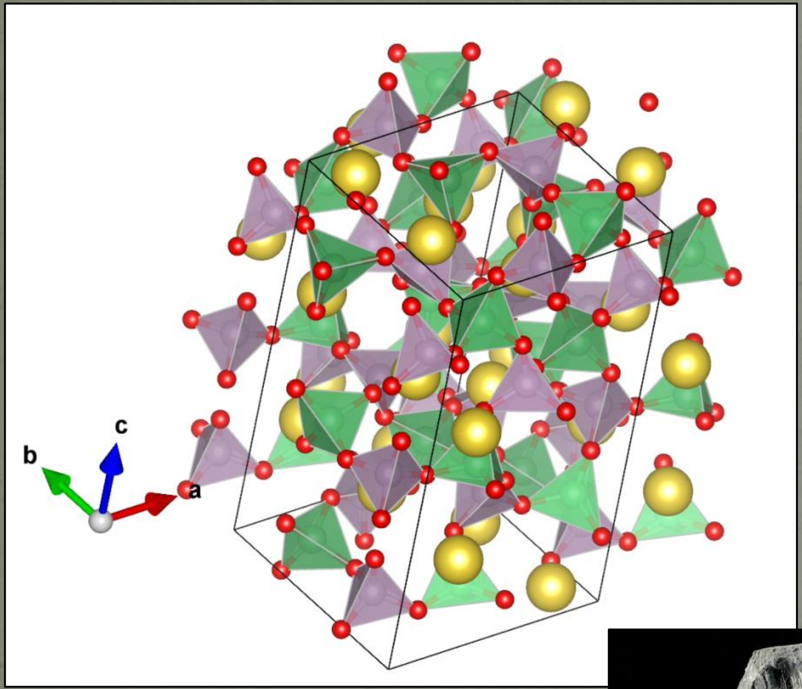
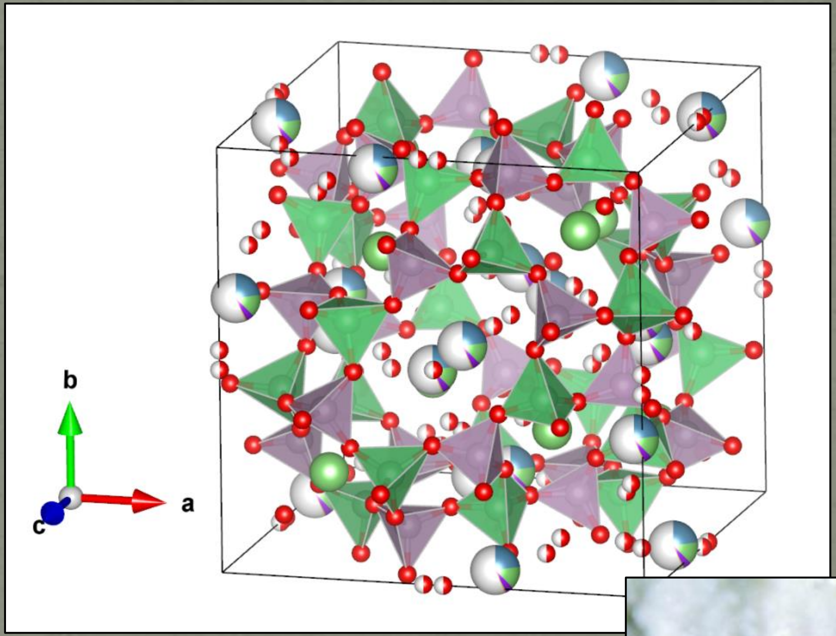
Framework structures



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)

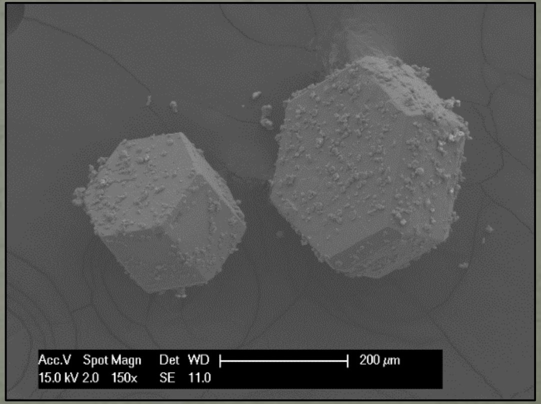
The Canadian Mineralogist
Vol. 52, pp. 337-350 (2014)
DOI: 10.3749/canmin.52.2.337

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

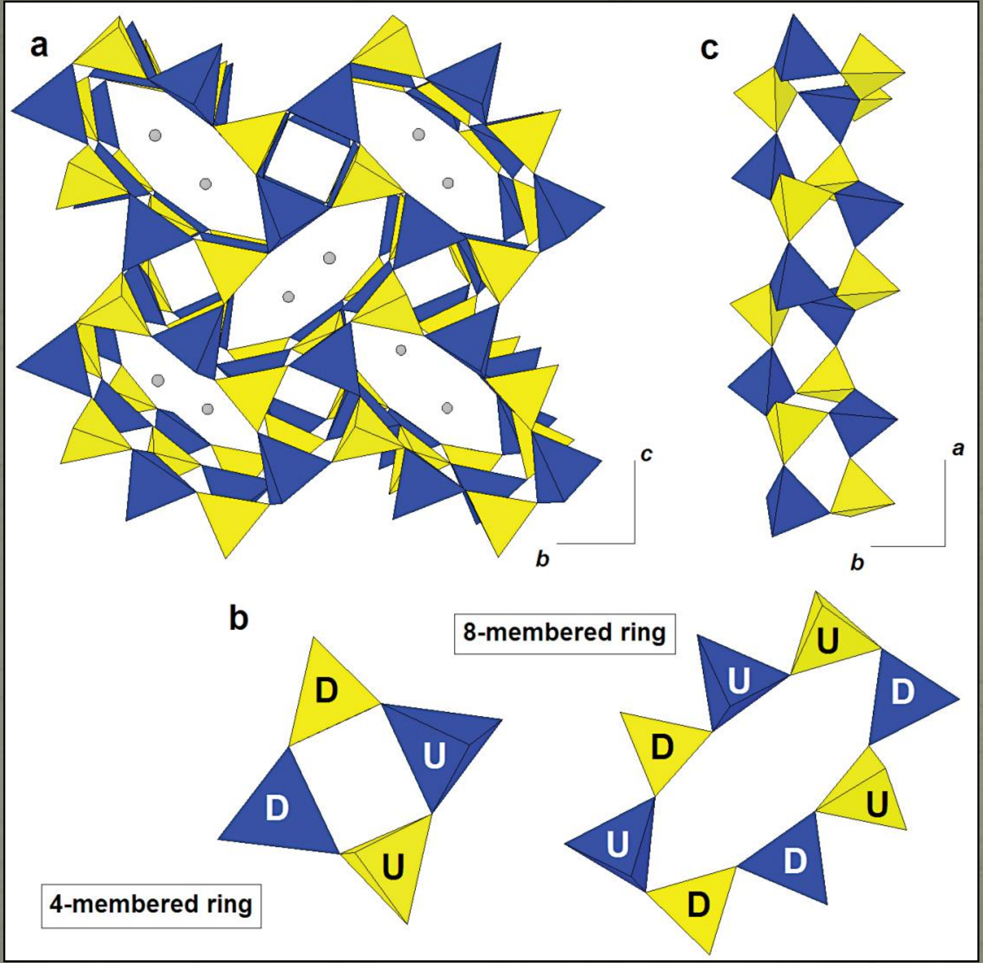
TABLE 1. HYDROTHERMAL SYNTHESIS PERFORMED IN THE M^{2+}-BE-PO_4 SYSTEM

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	$BaBe_2P_2O_8$

Hurlbutite
$CaBe_2P_2O_8$

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

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



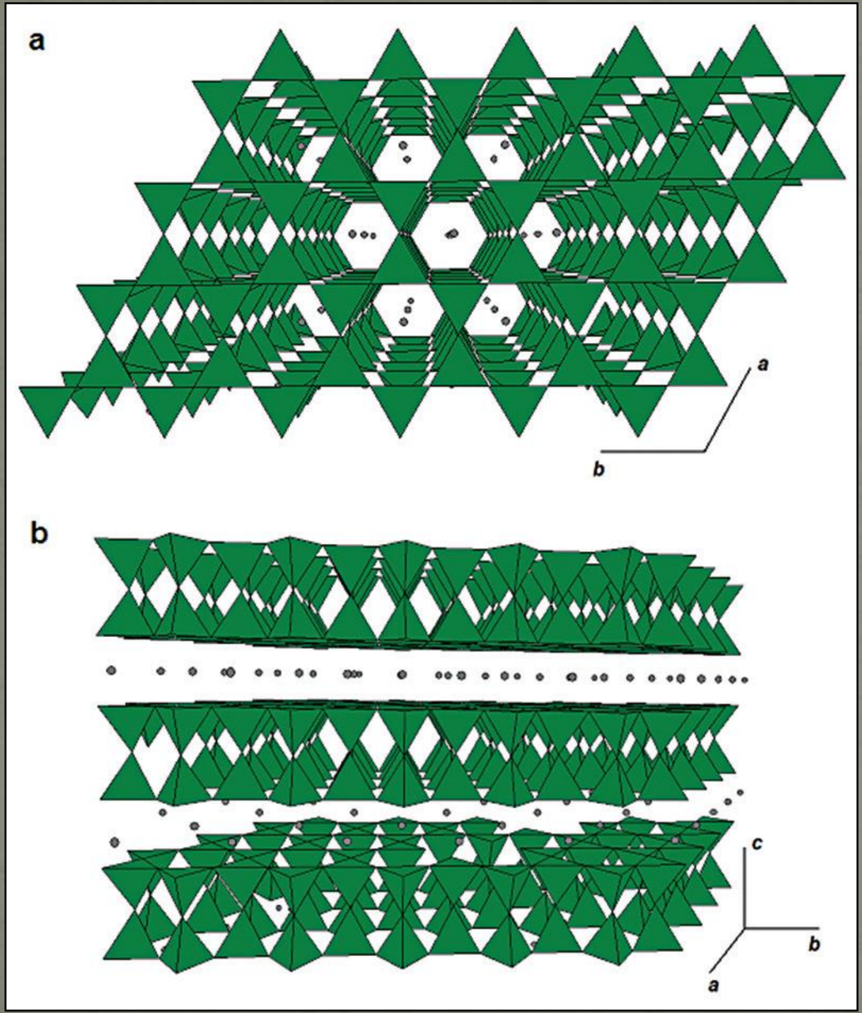
	$CaBe_2P_2O_8$	$SrBe_2P_2O_8$	$PbBe_2P_2O_8$
a (Å)	7.809(1)	8.000(1)	8.088(1)
b	8.799(1)	8.986(1)	9.019(1)
c	8.309(1)	8.418(1)	8.391(1)
β (°)	90.51(1)	90.22(1)	90.12(1)
V (Å³)	570.98(2)	605.10(6)	612.22(1)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$

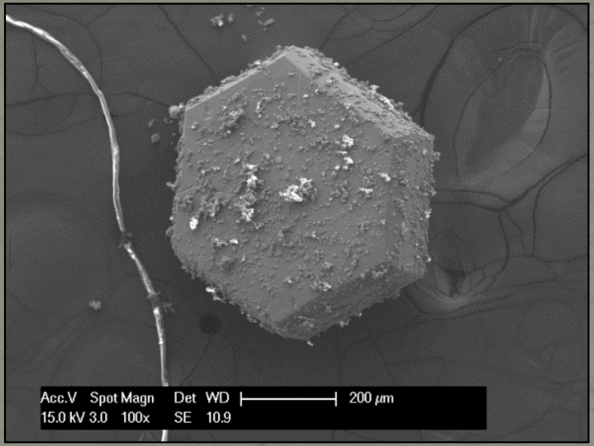
- **Framework beryllophosphates**
- **Feldspar topology**

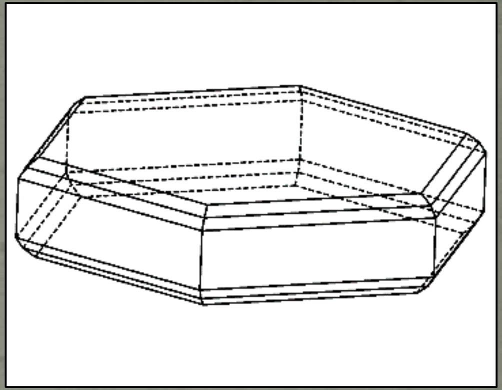
- **4-membered rings UUDD**
- **8-membered rings DDUDUUDU**
- **Double crankshaft chain parallel to *a***

Hurlbutite
$CaBe_2P_2O_8$

$BaBe_2P_2O_8$





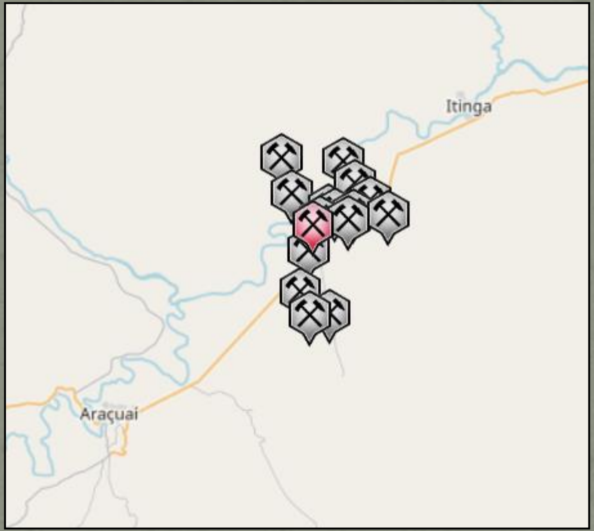


- *a* = 5.028(1), *c* = 7.466(1) Å
- SG *P6/mmm*

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

A new species from Brazil?

© Mindat



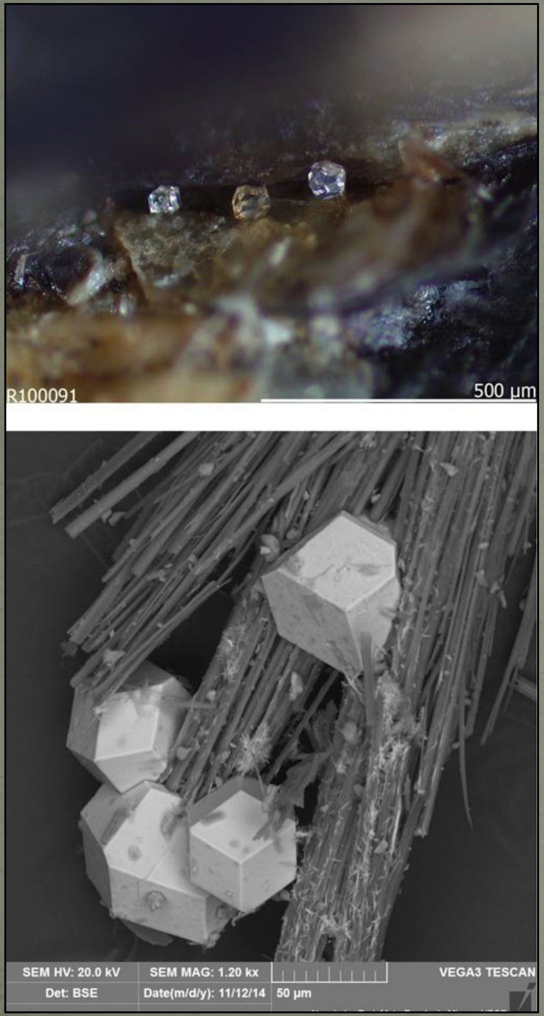
© Mindat

Lavra Ponte do Piaui pegmatite, Minas Gerais, Brazil

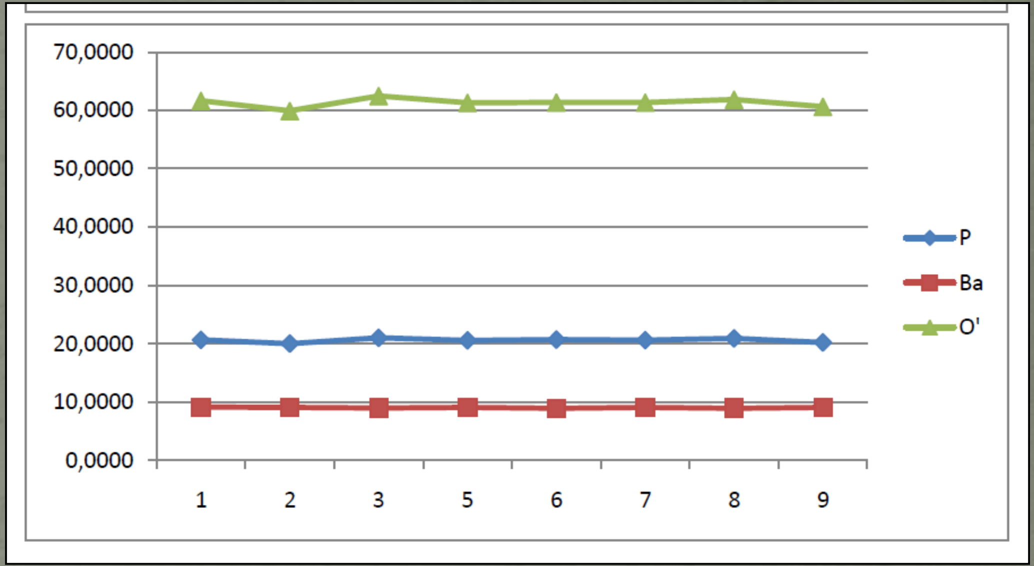
Luiz A.D. Menezes Filho
Brazil (1950-2014)

© Mineralogical Record

A Ba-bearing phosphate…



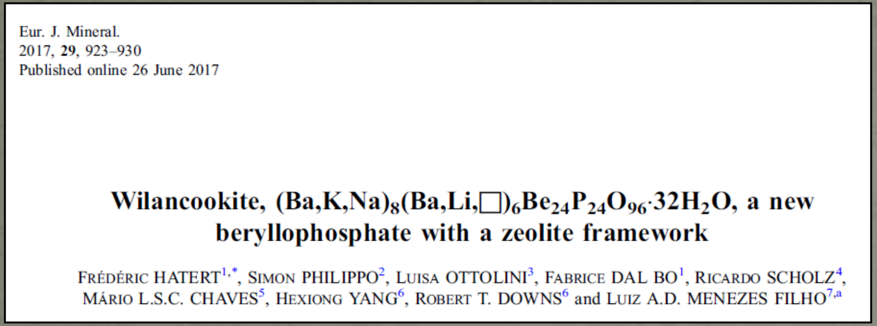
Dr. Simon Philippo
Luxembourg



EMP analyses
~ 20-21 wt. % P and ~ 9-10 wt. % Ba

- **Tiny dodecahedral colorless crystals**
- **Deposited on moraesite fibres**

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

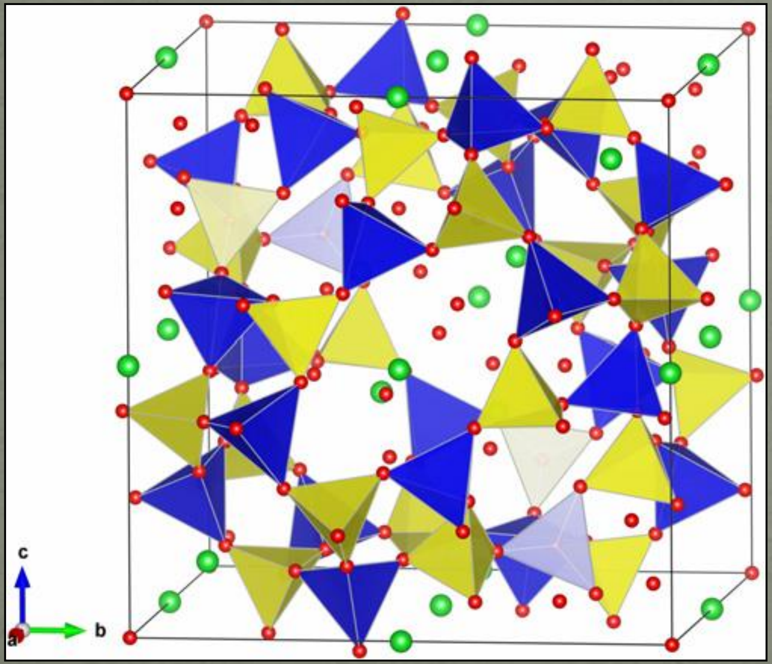

Eur. J. Mineral.
2017, 29, 923–930
Published online 26 June 2017

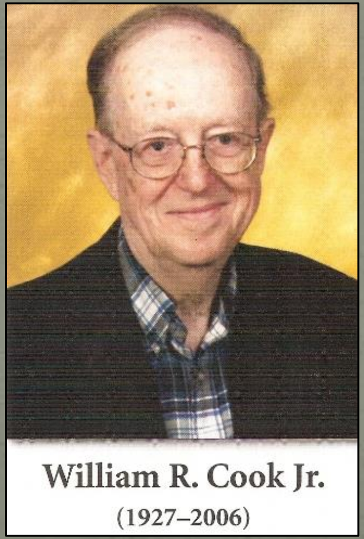
Wilancookite, $(Ba,K,Na)_8(Ba,Li,\square)_6Be_{24}P_{24}O_{96}\cdot 32H_2O$, a new beryllophosphate with a zeolite framework

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]

- *a* = 13.579(9) Å
- SG *I*23

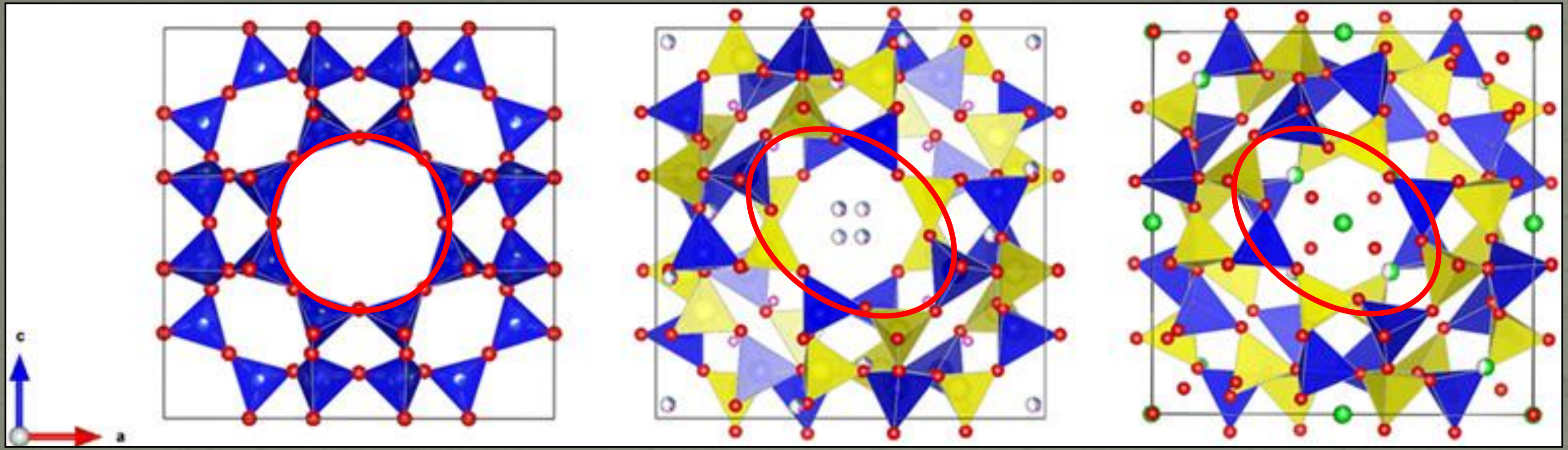
- 2[nd] known zeolite phosphate
- Similar to synthetic zeolite RHO
- Isostructural with pahasapaite
- 8-, 6-, and 4-membered rings





- Dedicated to William .R. Cook and his wife A

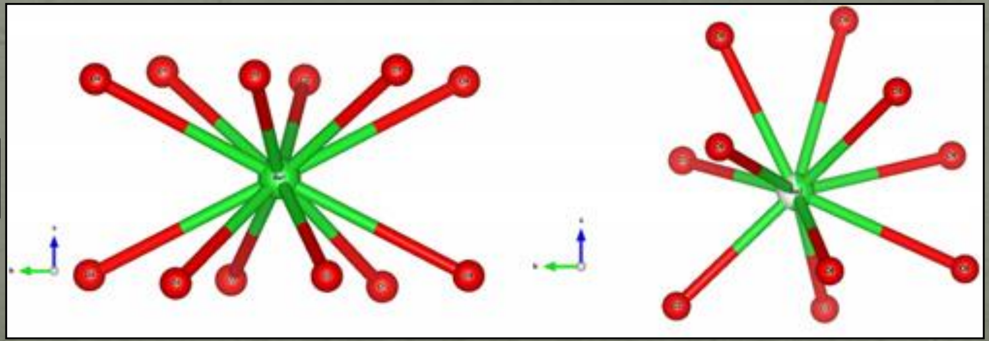
Wilancookite



Zeolite RHO
*Im*3*m*

Pahasapaite
*I*23

Wilancookite
*I*23



$Ba(1)O_{12}$

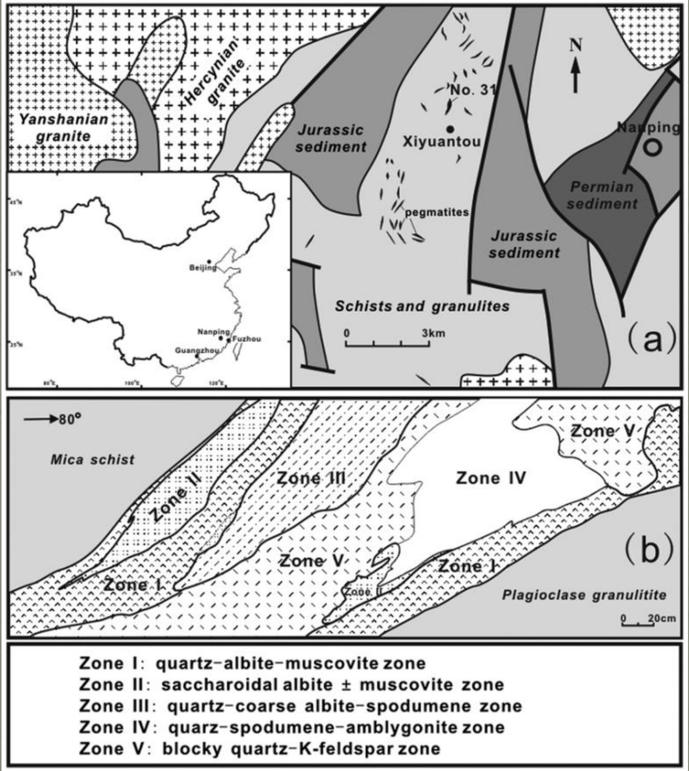
$Ba(2)O_{10}$

A second Ba-phosphate from Nanping ?

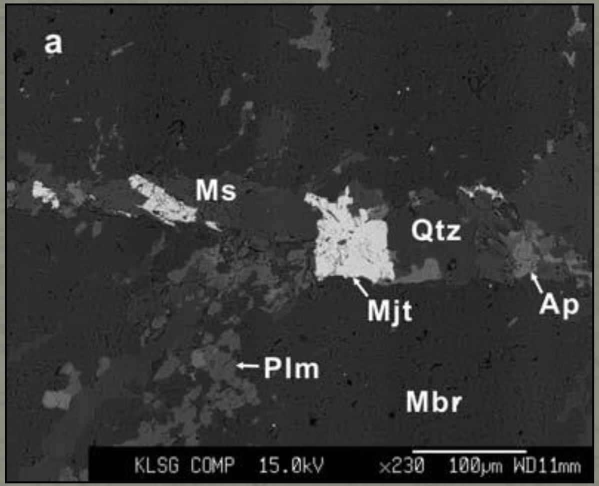
Dr. Rao Can
Hangzhou, China

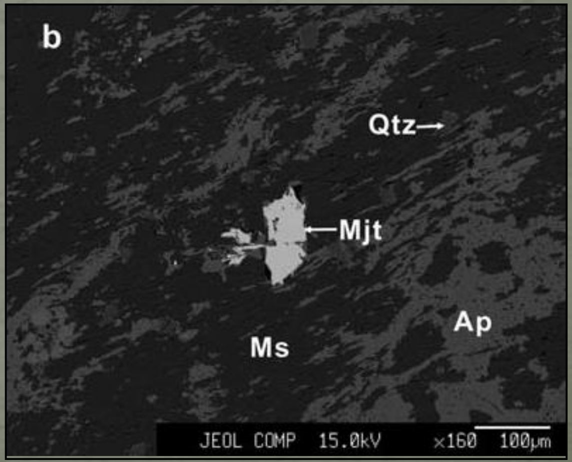
Strontiohurlbutite
$SrBe_2P_2O_8$
Nanping No. 31, China

Minjiangite
$BaBe_2P_2O_8$
Nanping No. 31, China



Rao et al. 2012





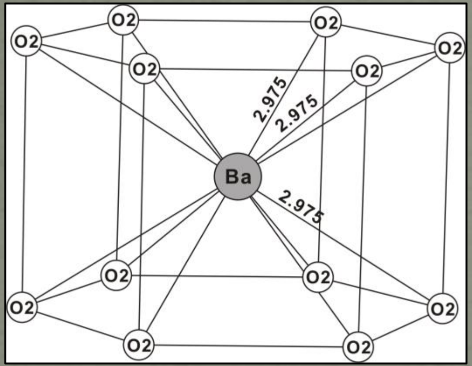
EMP analyses and X-ray powder diffraction

Minjiangite, $Ba[Be_2P_2O_8]$

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

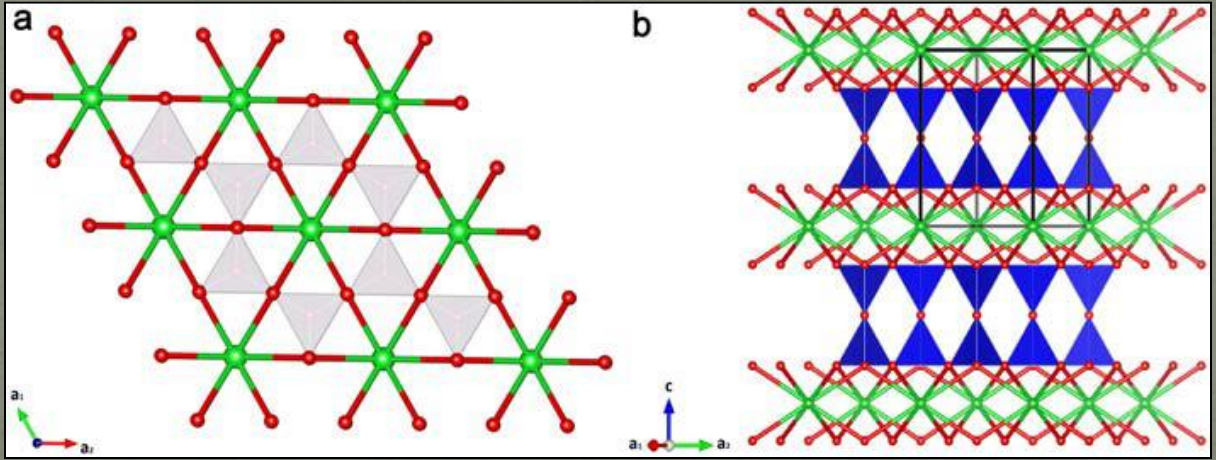
Minjiangite, $BaBe_2(PO_4)_2$, a new mineral from Nanping No. 31 pegmatite, Fujian Province, southeastern China

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



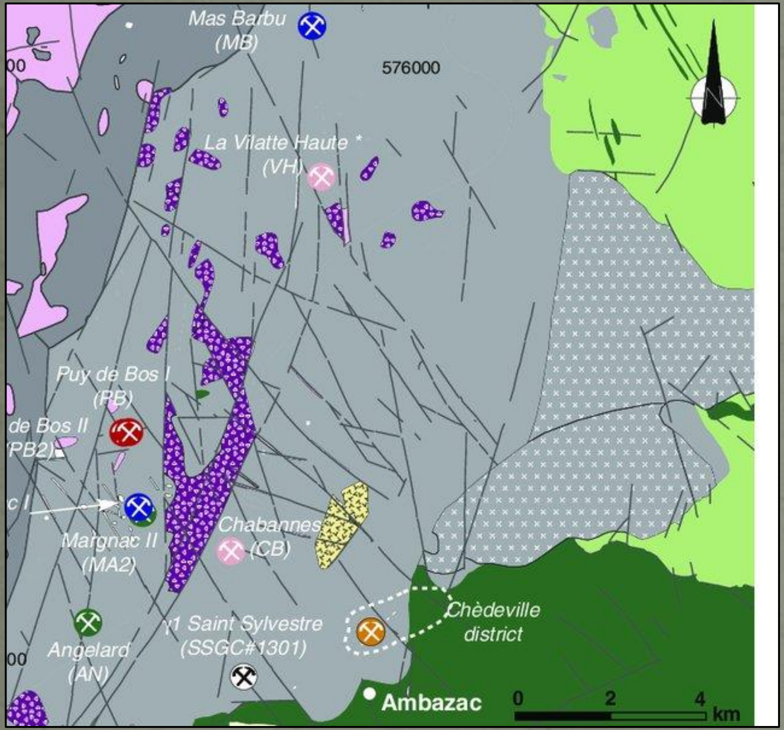
- Similar to synthetic $BaBe_2P_2O_8$
- Double layer of $(P_{0.5}Be_{0.5})O_4$
- Six-membered rings
- 12-coordinated Ba atoms

Minjiang river, China



- *a* = 5.029(1) Å
- *c* = 7.466(1) Å
- SG *P6/mmm*

A third Ba-P-bearing species from France!



Deveaud et al. 2013

© Wikipedia

Dr. Nicolas Meisser
Lausanne, Switzerland

La Villatte Haute pegmatite
Ambazac Mountains
Chanteloube, France

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

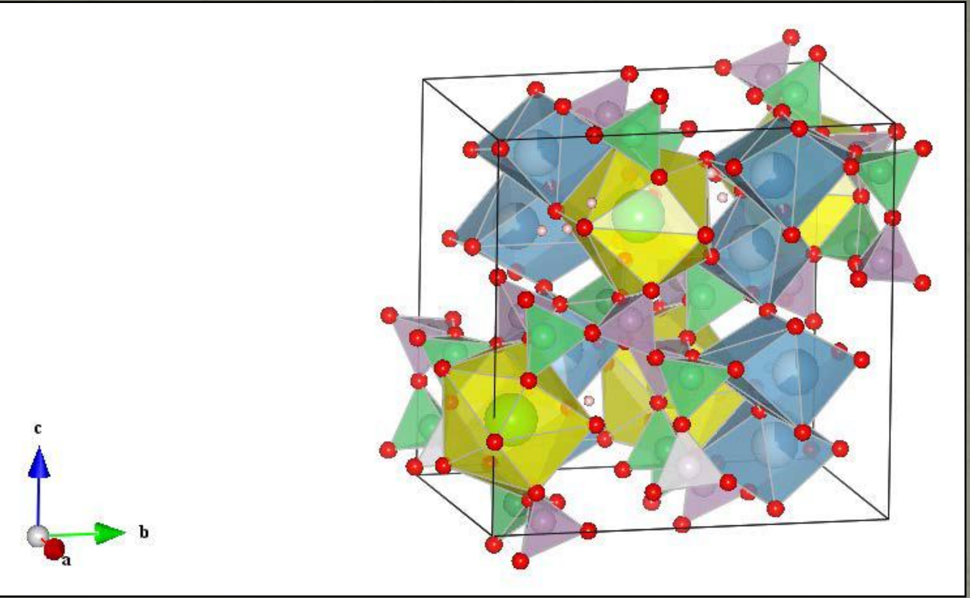
2019-011 Limousinite
Ideal chemical formula: $BaCa[Be_4P_4O_{16}]\cdot 6H_2O$
Crystal system: Monoclinic   Space group: $P2_1/c$ (#14)

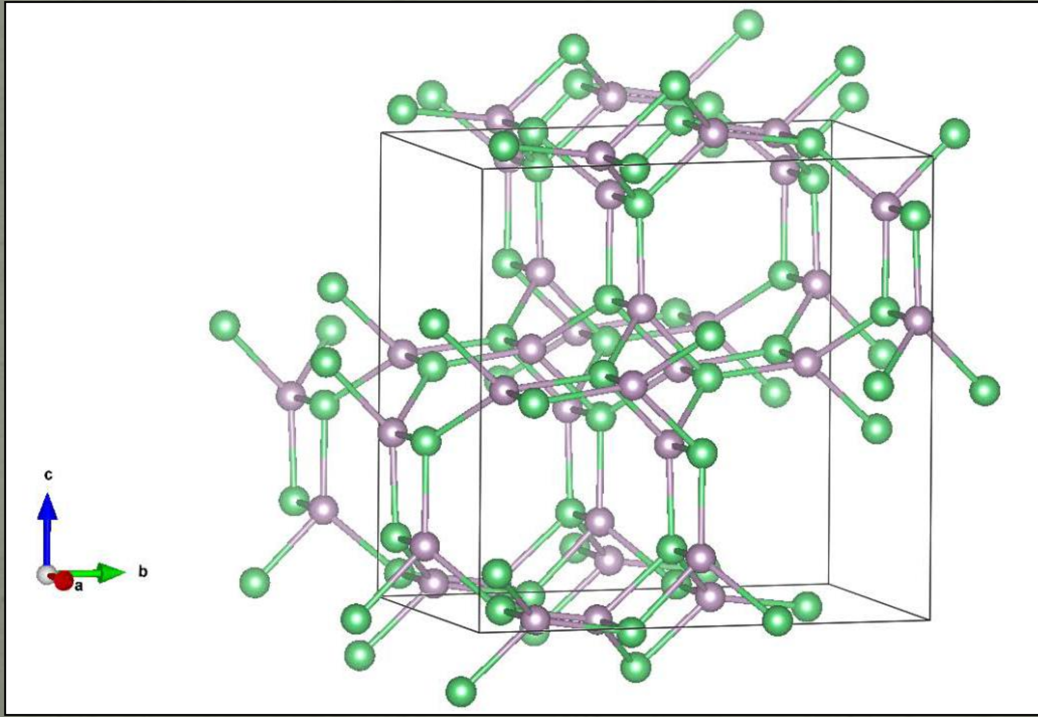
a = 9.4958(4) Å b = 13.6758(4) Å c = 13.4696(4) Å
β = 90.398(3)°
V = 1749.15(10) Å^3 Z = 4

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].

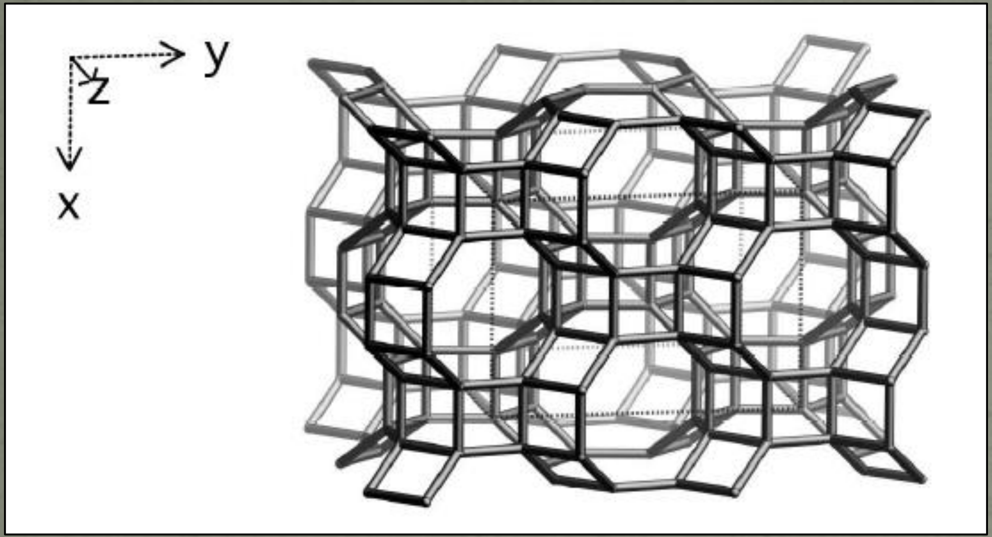
Limousin region, France

Limousinite



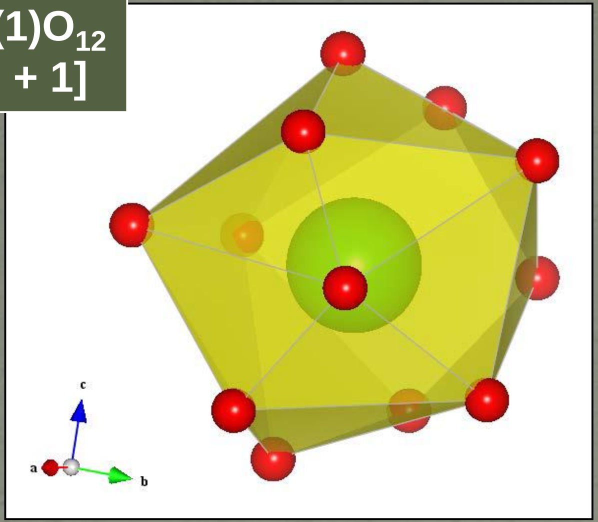


- Third known zeolite phosphate
- Framework identical to that of phillipsite-group minerals
- 8- and 4-membered rings

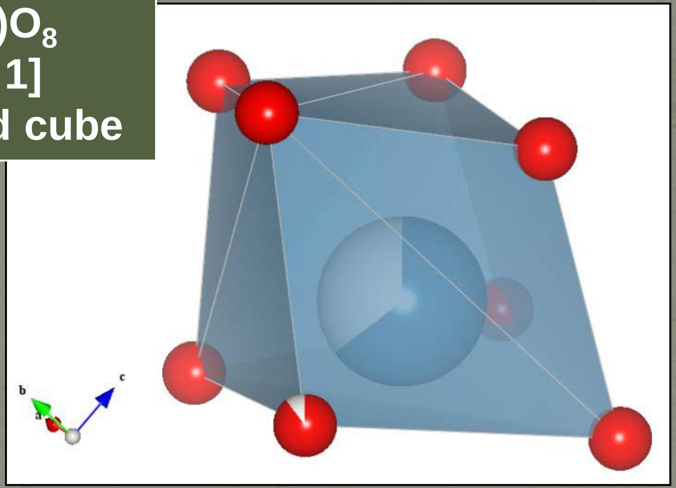

y
z
x

Limousinite

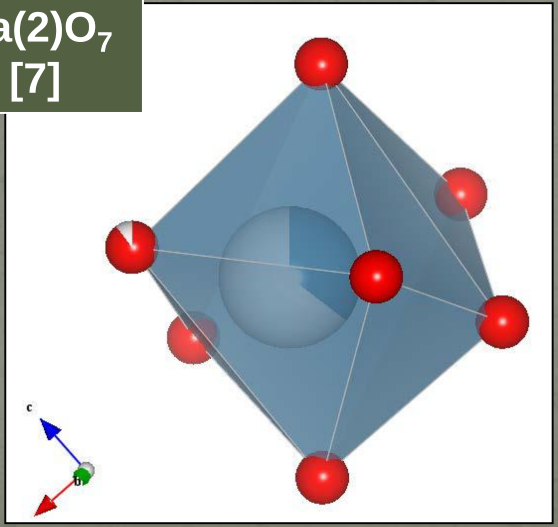
$Ba(1)O_{12}$
[11 + 1]

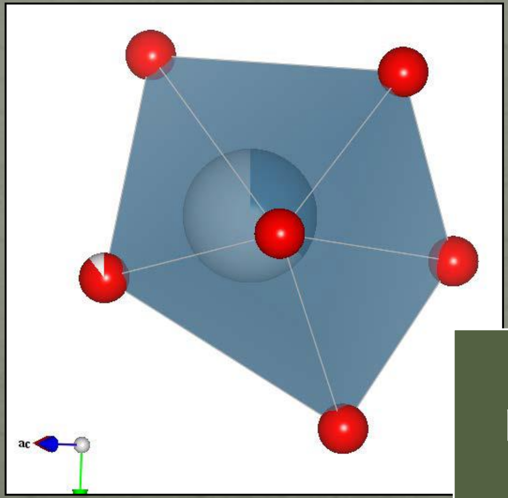


$Ca(1)O_8$
[7 + 1]
Distorted cube



$Ca(2)O_7$
[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

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.
2009, **21**, 1073–1080
Published online October 2009

The standardisation of mineral group hierarchies: application to recent nomenclature proposals

STUART J. MILLS[1,*], FRÉDÉRIC HATERT[2], ERNEST H. NICKEL[3,**] and GIOVANNI FERRARIS[4]

NESOPHOSPHATES	➔ Isolated tetrahedra -triphylite – $[PO_4]$
SOROPHOSPHATE	➔ Finite clusters of tetrahedra – canaphite – $[P_2O_7]$
CYCLOPHOSPHATES	➔ Cyclic units – no known example
INOPHOSPHATES	➔ Infinite chains - fransoletite - $[Be_2P_4O_{14}(OH)_2]$
PHYLLOPHOSPHATES	➔ Infinite sheets - minjiangite – $[Be_2P_2O_8]$
TECTOPHOSPHATES	➔ 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.