

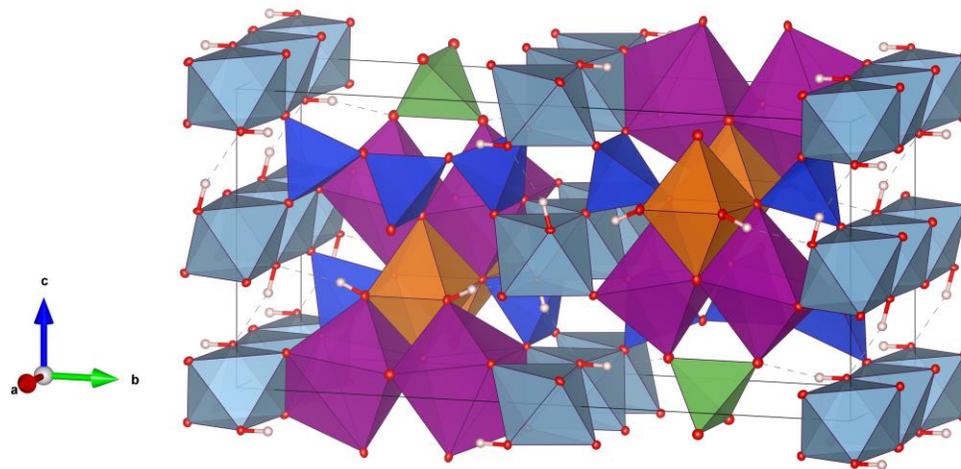


LIÈGE université
Laboratoire de Minéralogie
et de Cristallographie

emc²
18–23 August
2024
4th european mineralogical
conference • Dublin, Ireland

Crystal chemistry of Belgian ardennites

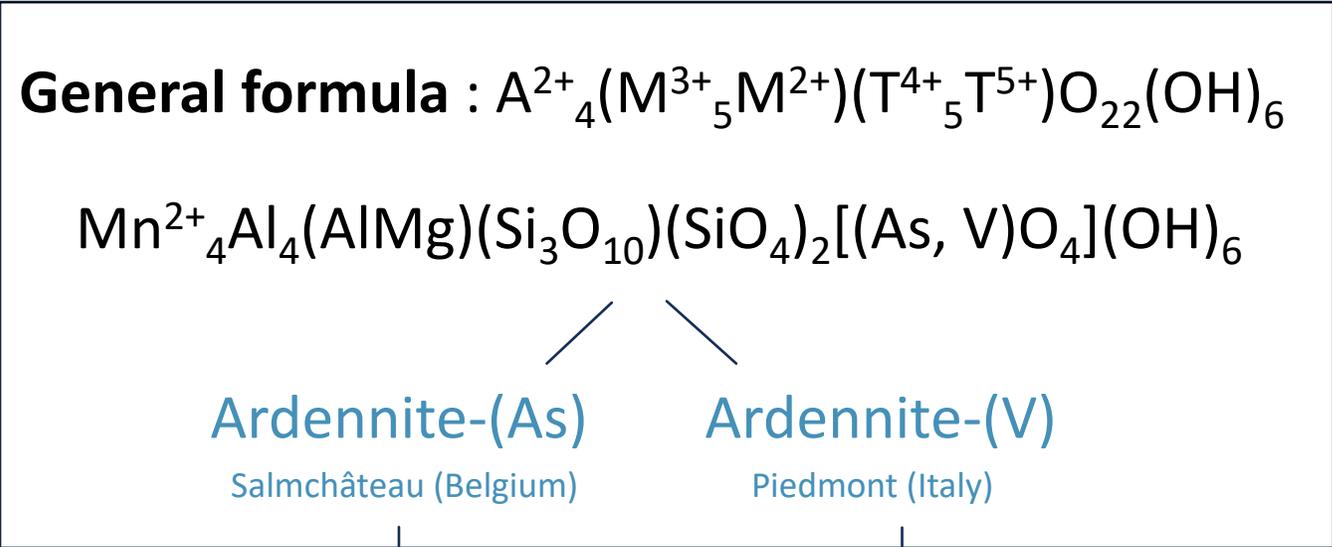
Depret, M., Hatert, F., Blondieau, M., Puccio, S., Dal Bo,
F., Erambert, M. and Bomal F.



1. Introduction

- **Mn-rich** aluminium silicate discovered in a quartz vein (Belgian Ardennes)
- Simultaneously investigated by A. von Lasaux and F. Pisani

→ Controversies between the two scientists



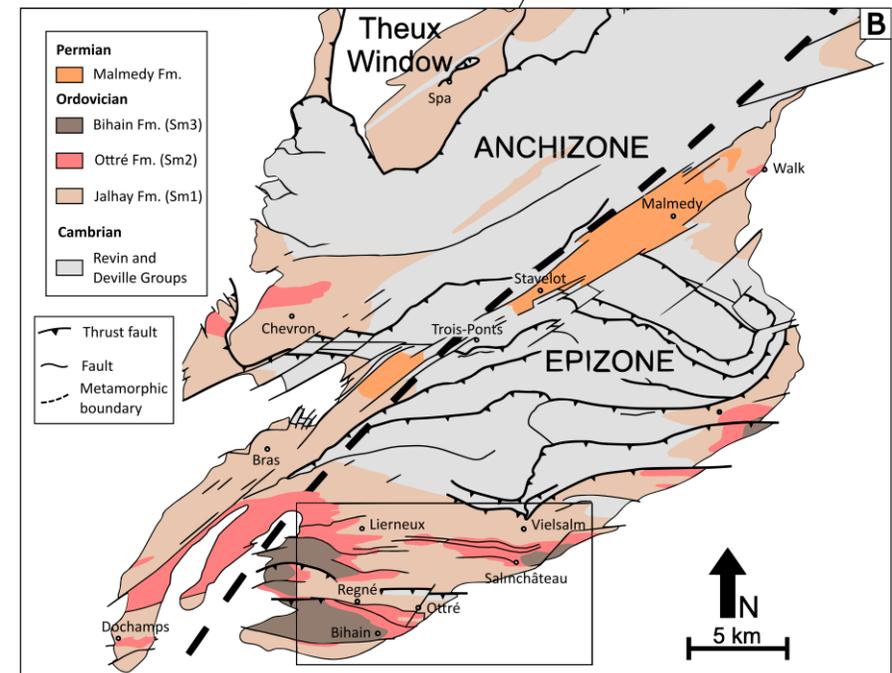
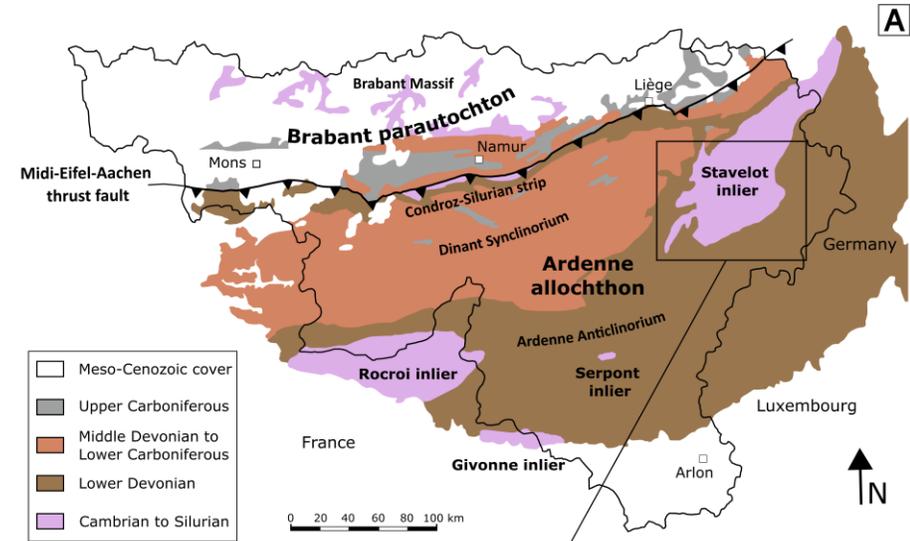
- Highly oxidized manganiferous metasediments

2. Belgian *ardennites*

- Stavelot-Venn Massif (Cambro-Ordovician inlier)
- Low-grade metamorphism

- Ottré Formation
- Unusual geochemistry with Mn and Fe enrichments

- New occurrences in the area
- Crystal-chemical study on eleven Belgian *ardennite* samples



3. Petrographic description

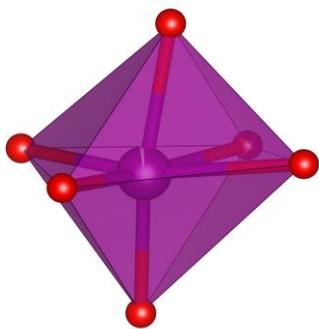
- a) Lamellar to bladed aggregates
- b) Lenticular crystals
- c) Elongated prisms
- d) Reddish needles
- e) Acicular crystals
- f) Millimetre-sized spots



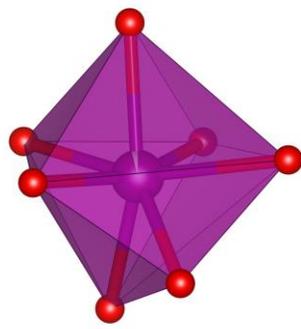
4. Crystal structure

Crystallography: orthorhombic, space group $Pn\bar{m}$,
 $a \approx 8.8 \text{ \AA}$, $b \approx 5.8 \text{ \AA}$, $c \approx 18.6 \text{ \AA}$, $Z = 2$

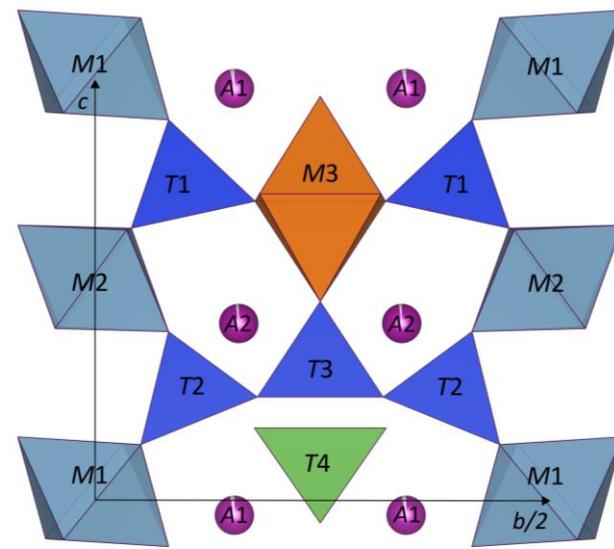
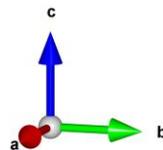
- Chains of edge-sharing octahedra
- Connected by SiO_4 and Si_3O_{10} groups
- Large cations in the cavities of the structure
- T4 tetrahedra connected to M3



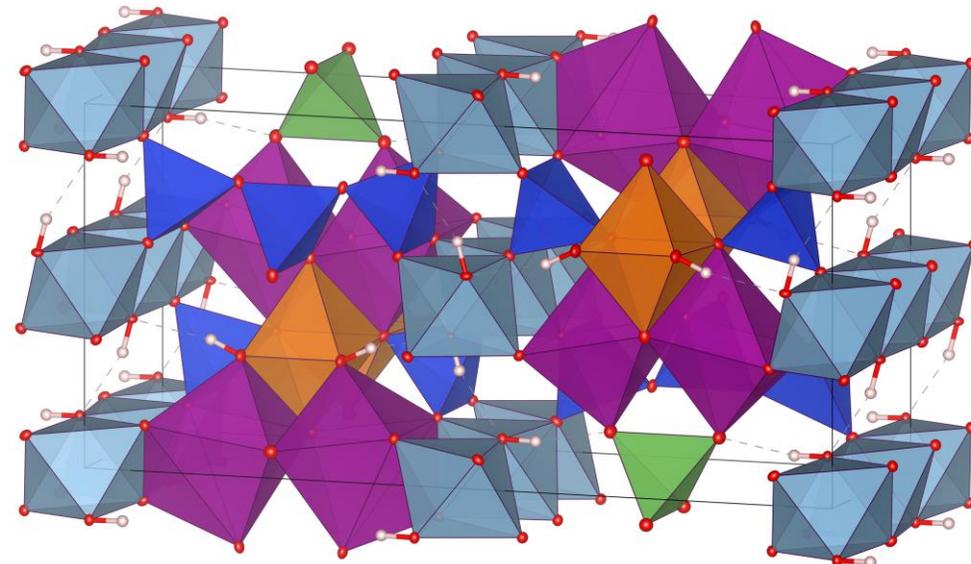
A1 six-fold coordination



A2 seven-fold coordination



- A1, A2 = Mn^{2+} , Ca^{2+}
- M1, M2 = Al
- M3 = Mg, Al
- T1, T2, T3 = Si
- T4 = As^{5+} , V^{5+} , P^{5+}



5. Chemical compositions

General formula : $A^{2+}_4(M^{3+}_5M^{2+})(T^{4+}_5T^{5+})O_{22}(OH)_6$

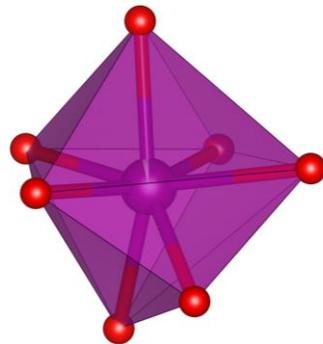
Structural formula : $A1_2A2_2(M1_2M2_2M3_2)(T1_2T2_2T3_2T4_2)O_{22}(OH)_6$

A sites → homovalent substitutions of Mn^{2+} by Ca^{2+} and Mg^{2+}

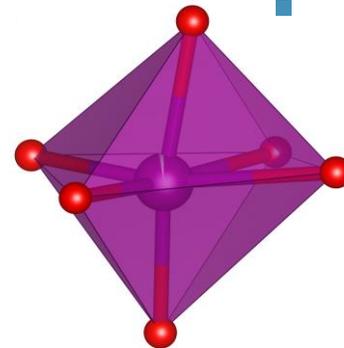
- Ca varying from 0.1 to 0.2 *apfu*
(Max. 0.48 and 0.33 *apfu*)

→ *Geochemistry of the Ottré Formation (CaO < 0.5wt.%)*

- (Ca+Mn) content < 4 *apfu*
- Mg never exceed 0.13 *apfu*



A2 seven-fold coordination

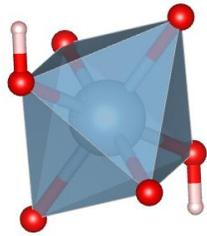


A1 six-fold coordination

General formula : $A^{2+}_4(M^{3+}_5M^{2+})(T^{4+}_5T^{5+})O_{22}(OH)_6$

Structural formula : $A1_2A2_2(\underbrace{M1_2M2_2}_{Al^{3+}}\underbrace{M3_2}_{Mg^{2+}, Al^{3+}, Fe^{3+}, \text{ and } Mn^{3+} \text{ and minor Ca, Mn}^{2+}, Cu, \text{ and } Zn}})(T1_2T2_2T_3T_4)O_{22}(OH)_6$

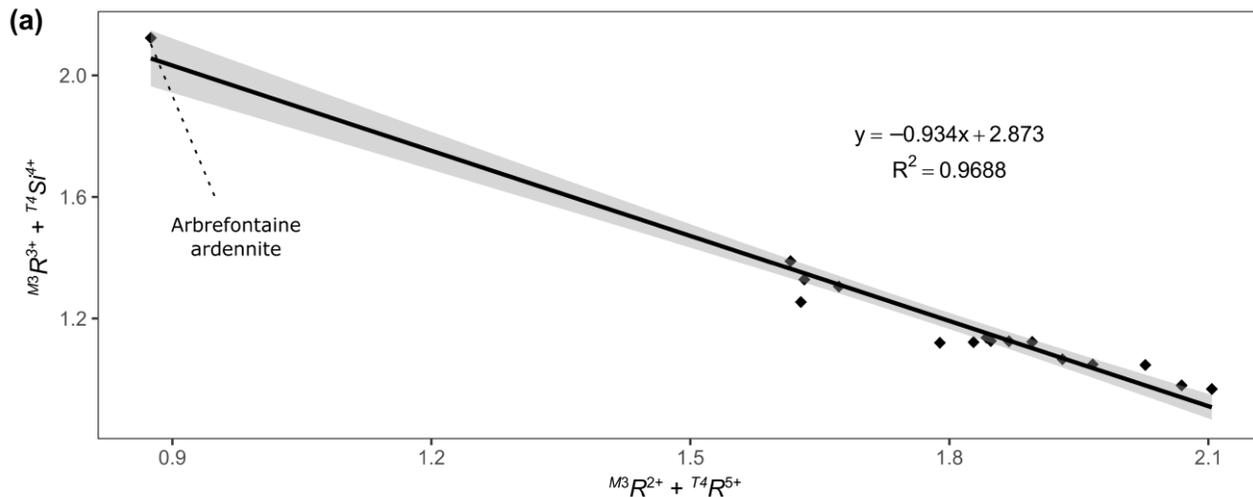
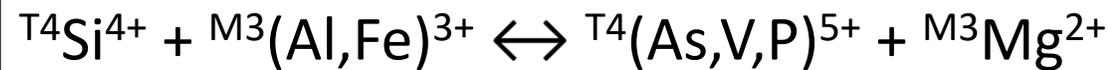
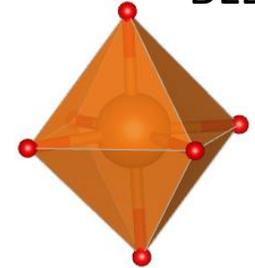
MBL ~ 1.90 Å
BLD ~ 1.80



Al^{3+}

$Mg^{2+}, Al^{3+}, Fe^{3+}$, and Mn^{3+} and minor $Ca, Mn^{2+}, Cu,$ and Zn

MBL ~ 1.99 Å
BLD ~ 3.30

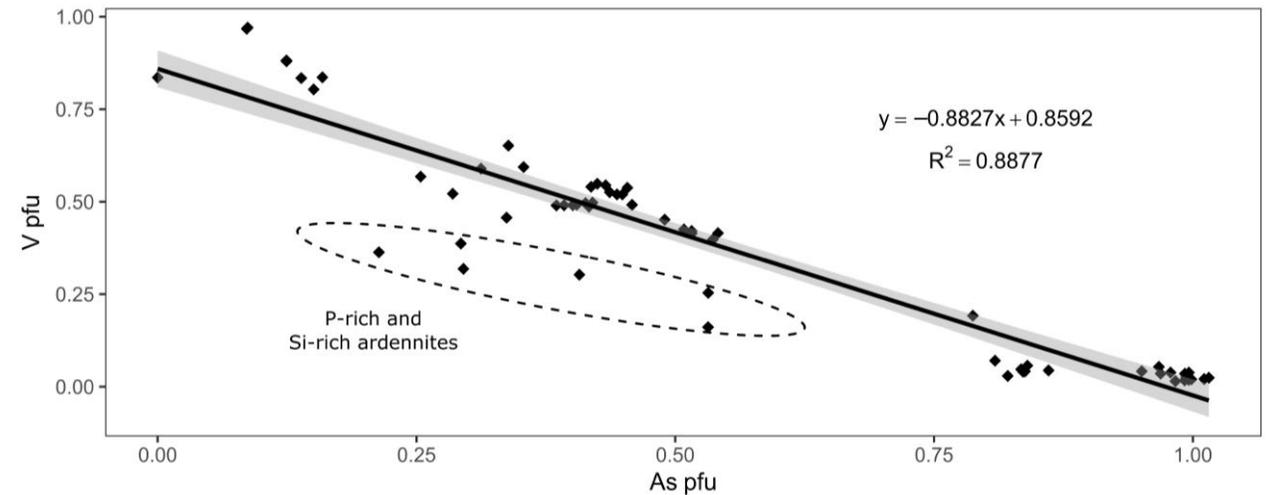
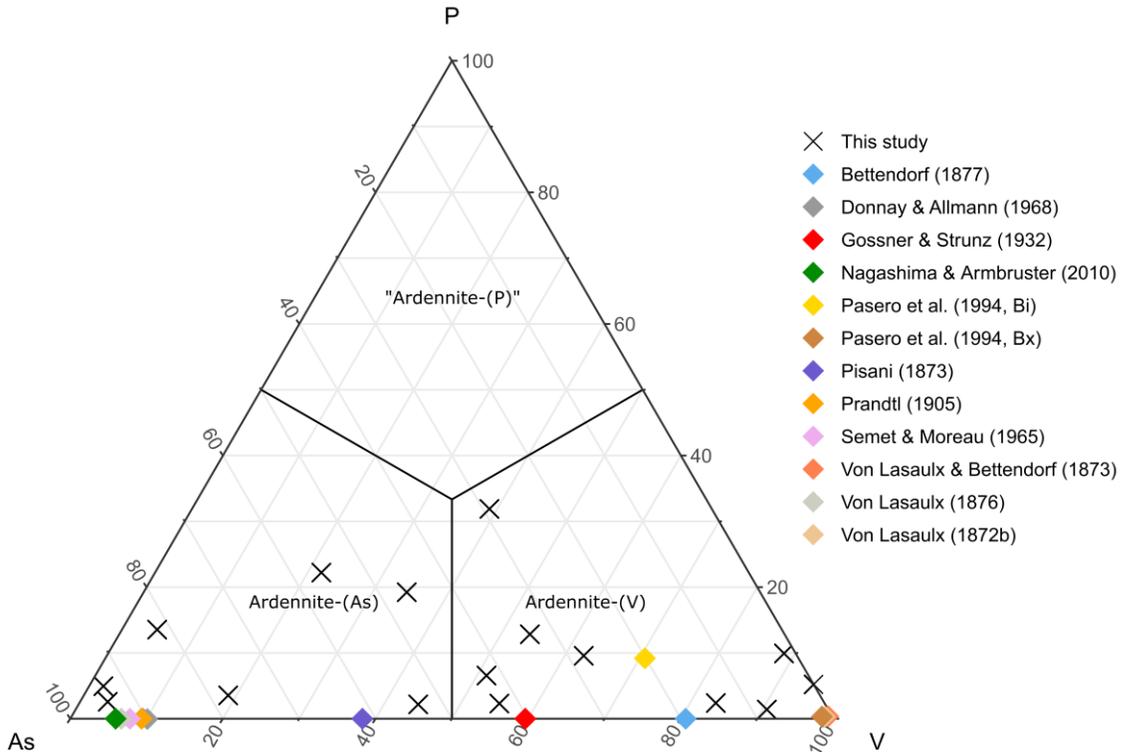


Various multiplicity \rightarrow valency-imposed double site occupancy (Hatert and Burke, 2008)

$M3 \rightarrow 50\% Mg^{2+}$ and 50% trivalent cations $(Al, Fe, Mn)^{3+}$

General formula : $A^{2+}_4(M^{3+}_5M^{2+})(T^{4+}_5T^{5+})O_{22}(OH)_6$

Structural formula : $A1_2A2_2(M1_2M2_2M3_2)(T1_2T2_2T_3T_4)O_{22}(OH)_6$



$As^{5+} \leftrightarrow V^{5+}$ homovalent substitution

→ Complete solid solution between ardennite-(As) and ardennite-(V)

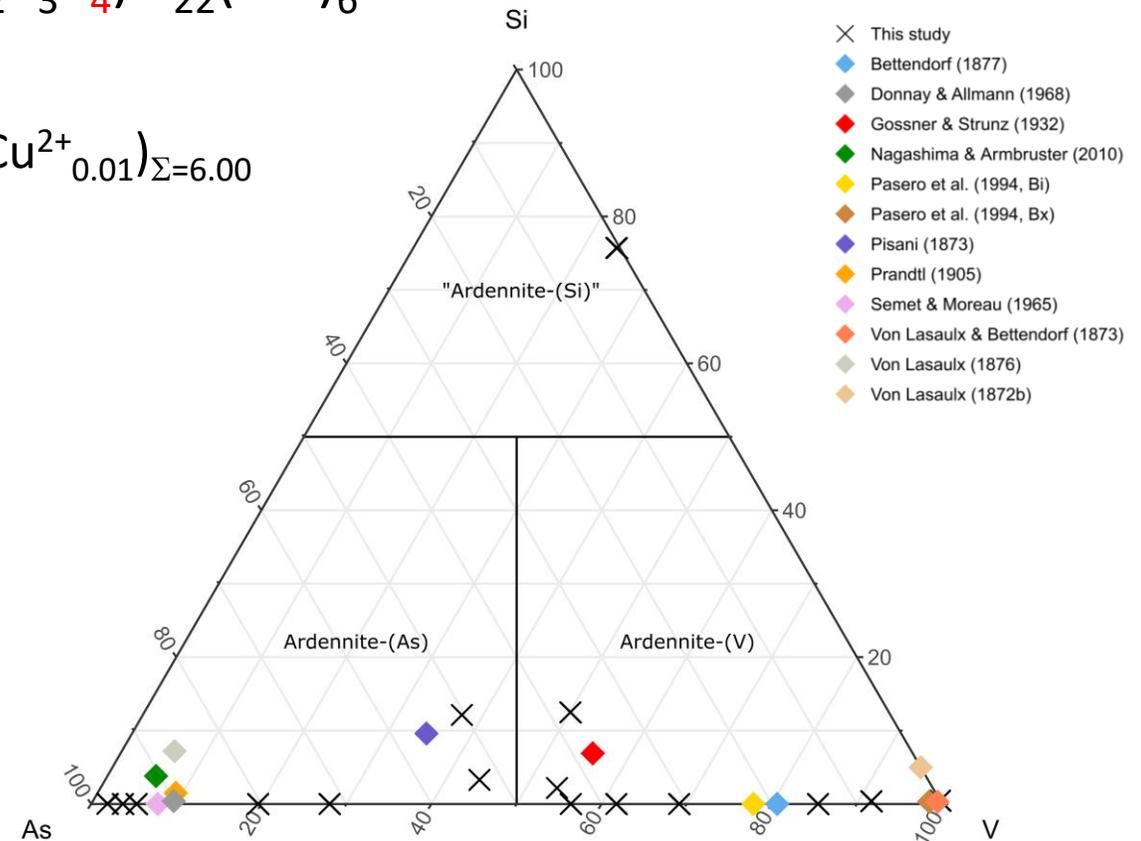
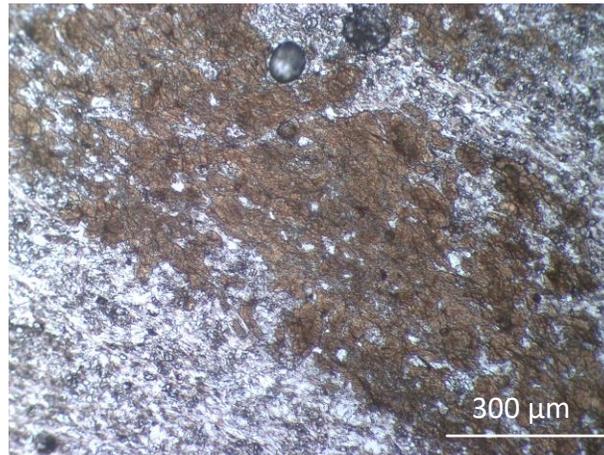
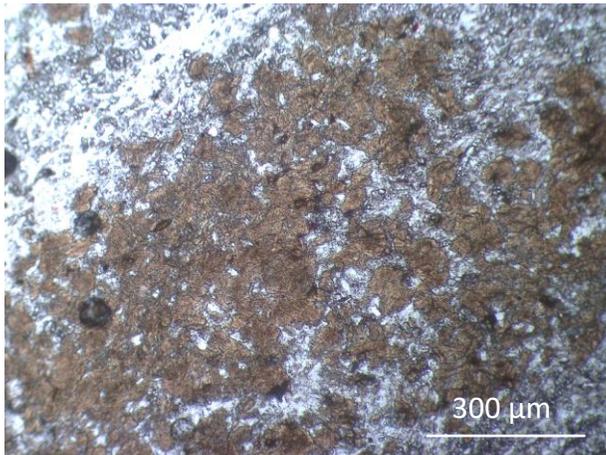
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Structural formula : $A1_2A2_2(M1_2M2_2M3_2)(T1_2T2_2T3T_4)O_{22}(OH)_6$

$(Mn^{2+}_{3.77}Ca^{2+}_{0.18}Mg^{2+}_{0.05})_{\Sigma=4.00}(Al^{3+}_{4.60}V^{3+}_{0.70}Mg^{2+}_{0.60}Fe^{3+}_{0.09}Cu^{2+}_{0.01})_{\Sigma=6.00}$

$(Si^{4+})_{\Sigma=5.00}(Si^{4+}_{0.74}V^{5+}_{0.23}P^{5+}_{0.03})_{\Sigma=1.00}O_{22}(OH)_{6.59}$

→ Possible Si- and V³⁺-rich end-member of the ardennite group

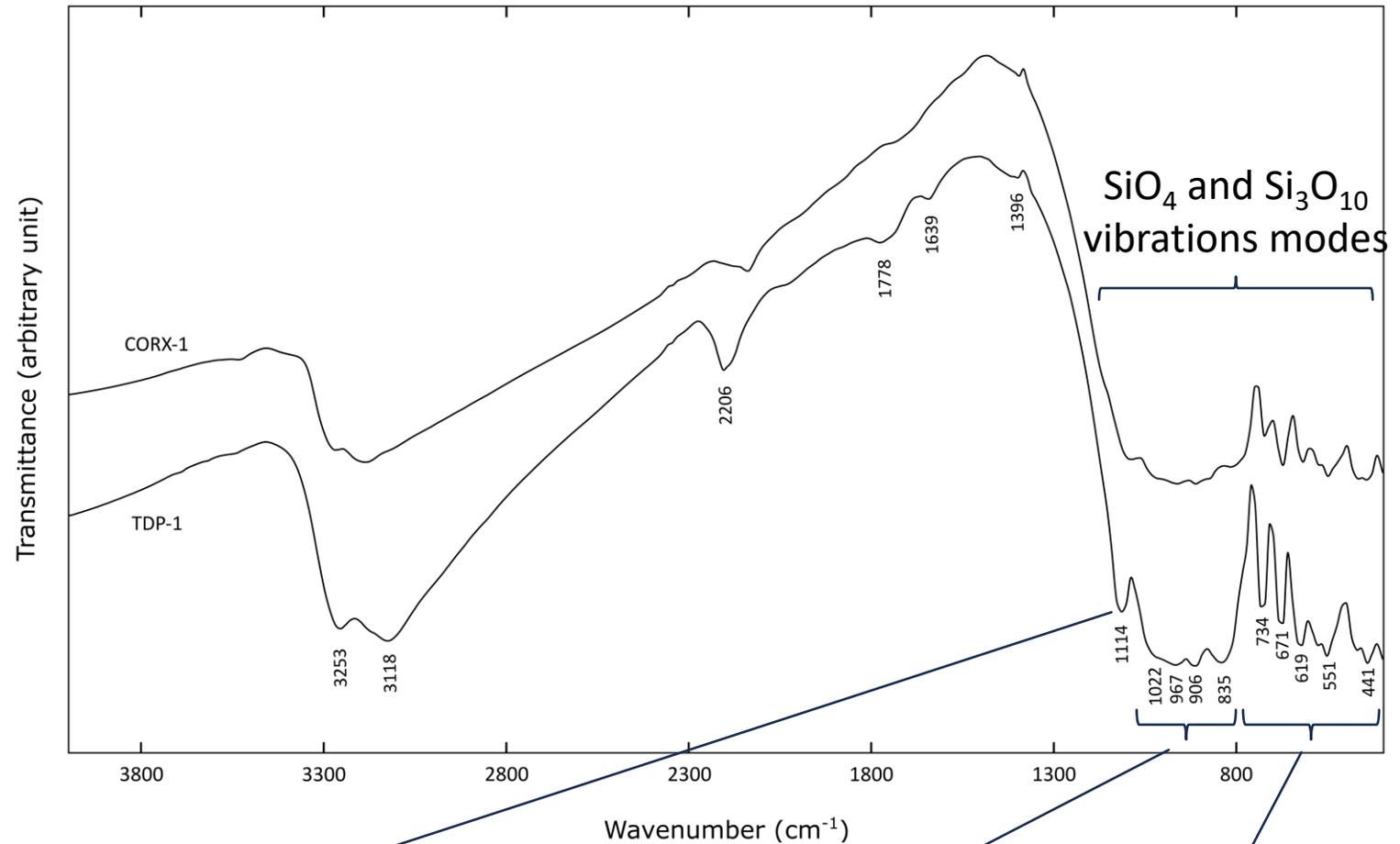


6. Infrared spectroscopy

$$d(\text{O}\cdots\text{O}) = -0.1321 \cdot \ln \left(\frac{\nu - 3592}{(-304 \cdot 10^9)} \right)$$

$$d(\text{H}\cdots\text{O}) = -0.2146 \cdot \ln \left(\frac{\nu - 3632}{(-1.79 \cdot 10^6)} \right)$$

	This study (TDP-1)	Nagashima and Armbruster (2010)	Libowitzky (1999)
O(10)-H(10)	0.79	0.98	-
O(10) \cdots O(9)	2.69	2.69	2.68
H(10) \cdots O(9)	1.9	1.72	1.75
O(11)-H(11)	0.81	0.98	-
O(11) \cdots O(10)	2.69	2.7	2.68
H(11) \cdots O(10)	1.91	1.74	1.75
O(12)-H(12)	0.83	0.98	-
O(12) \cdots O(11)	2.80	2.81	2.72
H(12) \cdots O(11)	1.98	1.84	1.82



Si-O antisymmetric stretching vibrations

Si-O stretching and bending vibrations

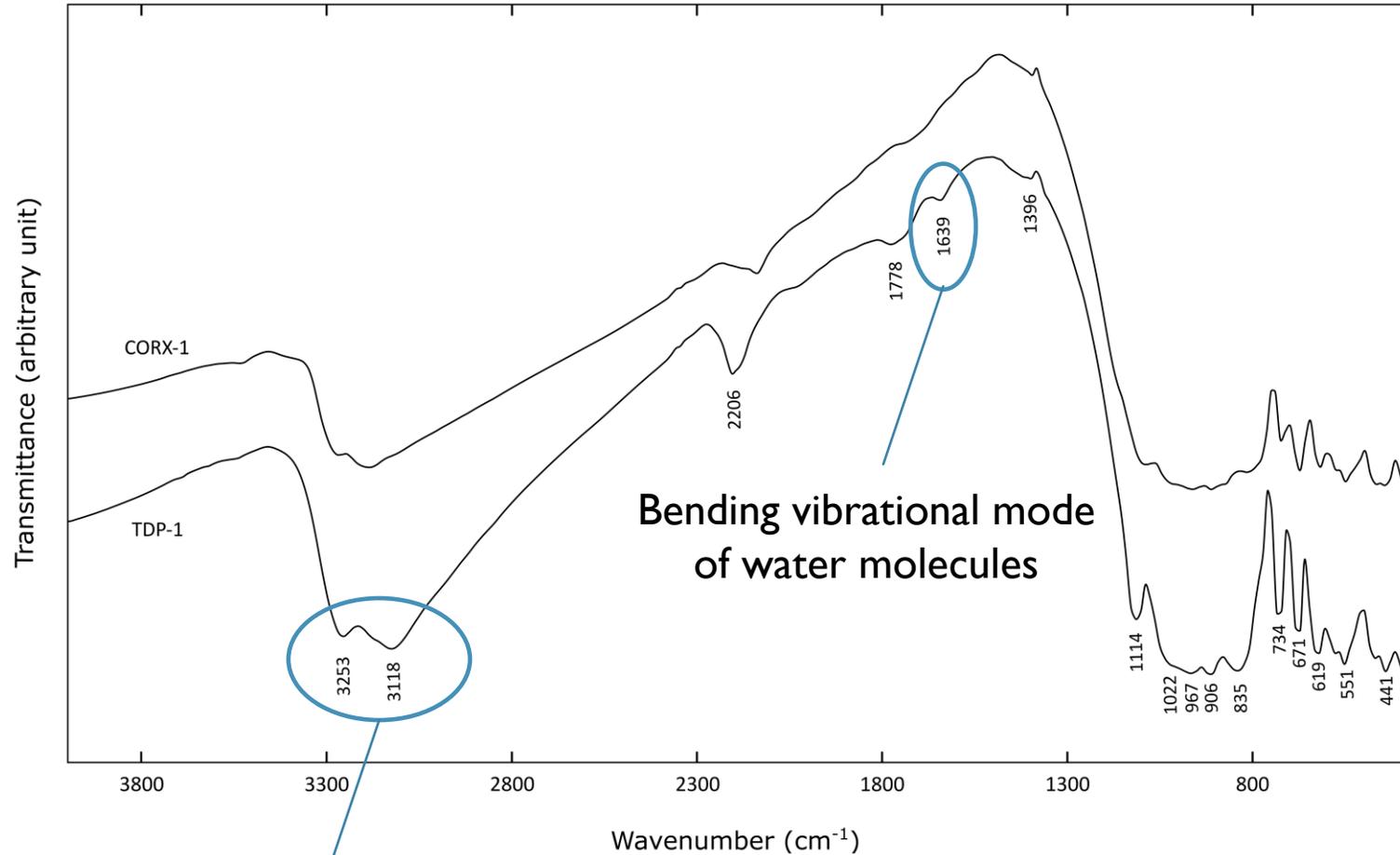
Tetrahedral bending modes and lattice vibrations

6. Infrared spectroscopy

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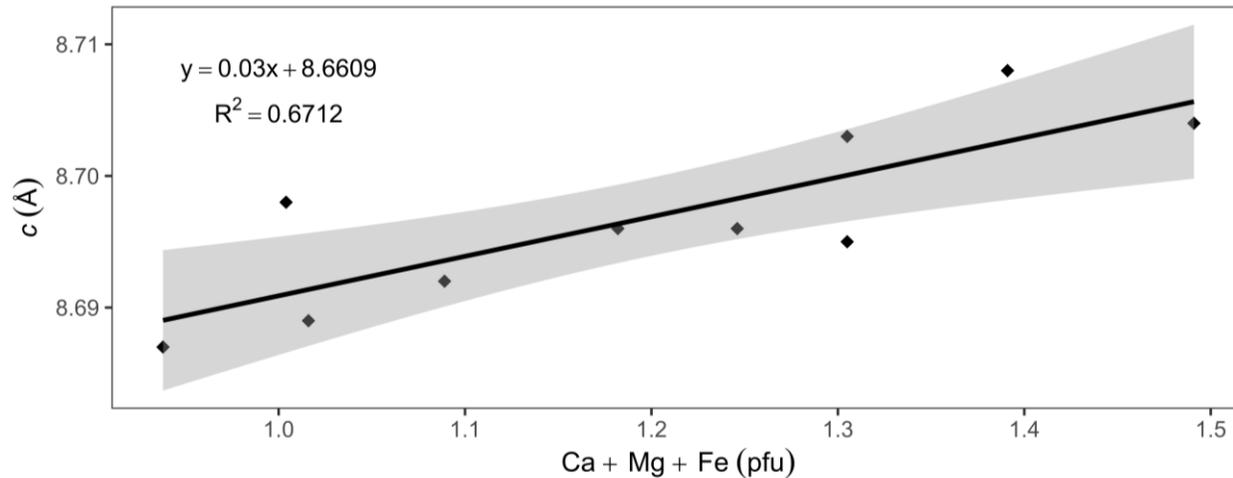


OH stretching vibrations

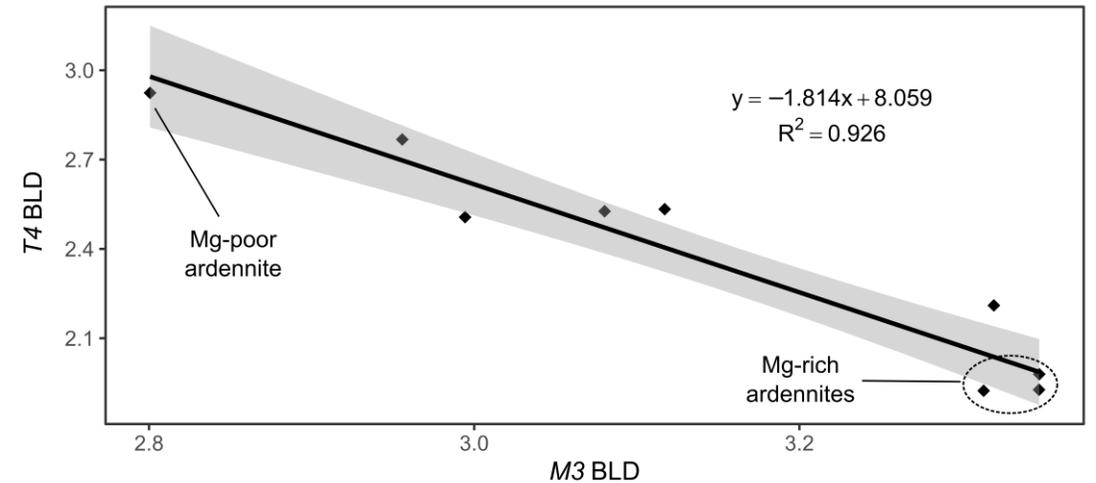
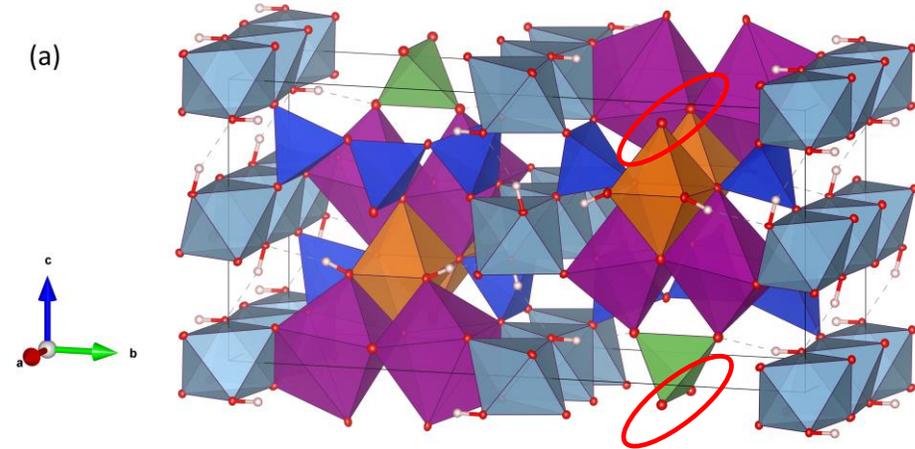
Two peaks \rightarrow various cationic coordination of the oxygens

7. Crystal chemistry

Only a few satisfactory trends
→ overall adjustment of the unit-cell ?



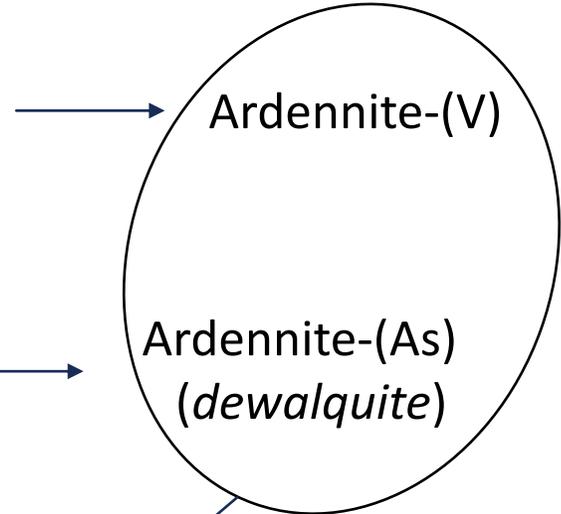
Unit-cell volume higher in Ca-rich sample
→ Chains act as rigid units



Controlled by the position of O5
→ Displacement to balance the charge in each site

8. Nomenclature of the ardennite group

- von Lasaulx (1872b)
- von Lasaulx & Bettendorf (1876)

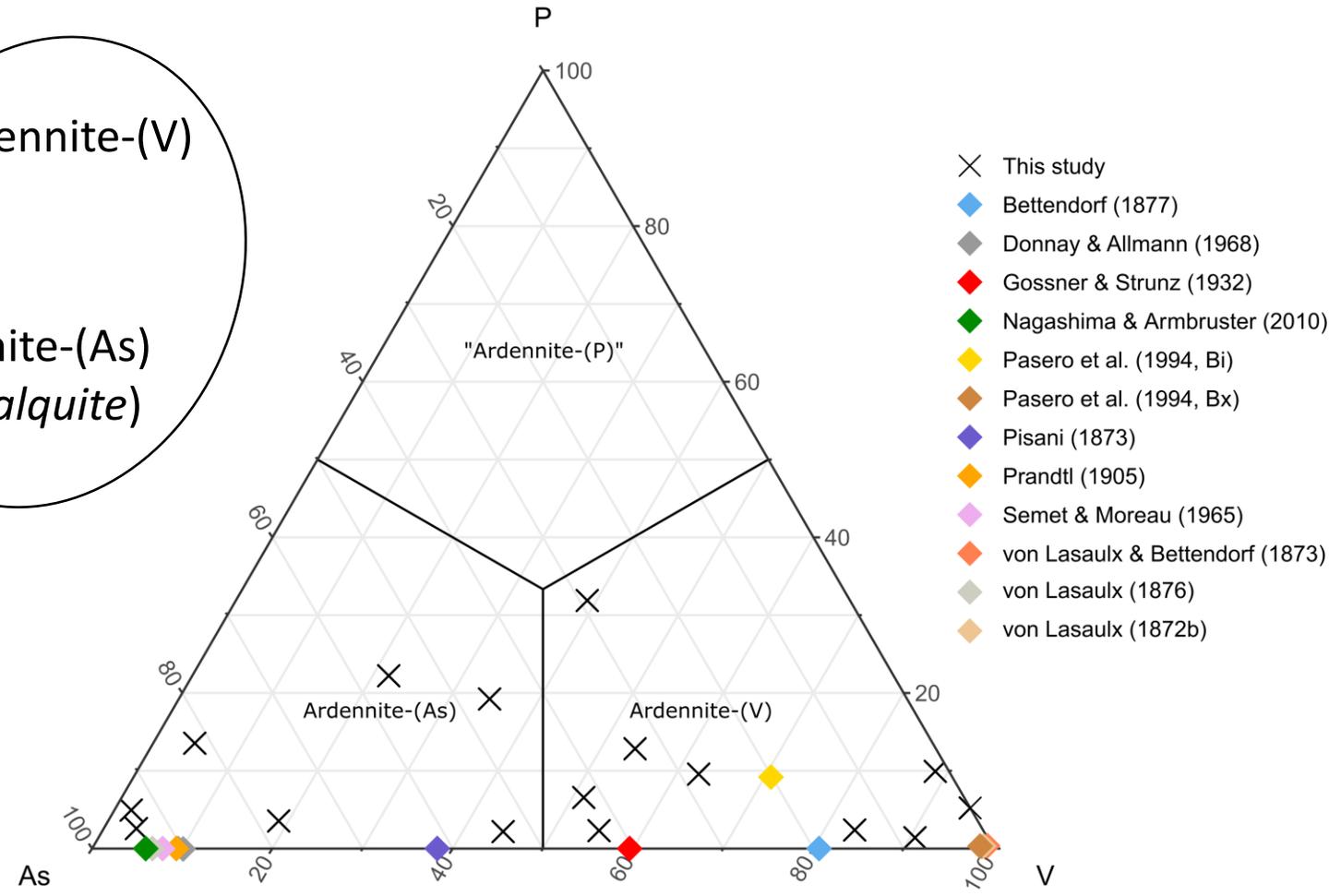


- Pisani (1873)
- von Lasaulx (1876)
- Prandtl (1905)

Both species originally present in Salmchâteau area

→ Legitimacy of the type locality for ardennite-(V) ??

Dewalquite as a “new” root-name ?





THANK YOU FOR YOUR ATTENTION!

