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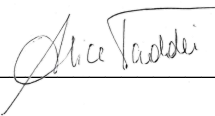
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Pyrochlore-supergroup minerals: Potential sinks for toxic elements in aqueous matrices

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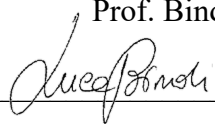
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*«The future is always built on the past,
even if we won't get to see it»*

—

*Alla mia
mamma di cristallo
brillerai per sempre
nel mio cielo
diamante tra le stelle*

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Abstract

This work deals with the crystal chemistry, structure, and ion-exchange properties of minerals belonging to the pyrochlore supergroup, with a special focus on their potential environmental applications in heavy metal sequestration. The research is centred on naturally occurring defective, hydrous species: hydropyrochlore, hydrokenopyrochlore, hydrokenomicrolite, and the newly described kenomicrolite from various localities including Lueshe (D.R. Congo), Araxá, and Nazareno (Brazil). Pyrochlores are oxides (or rarely fluorides) that mainly crystallise in the cubic system, space group $Fd\bar{3}m$, characterised by the general formula $A_{2-m}B_2X_{6-w}Y_{1-n}$ and a structure consisting of a B_2X_6 octahedral framework that forms tunnels along $[110]$, within which the A and Y sites are hosted. The samples have been investigated by means of electron microprobe analyses and single-crystal X-ray diffraction also to assess their structural response to imbibition experiments in Tl- and Pb-rich aqueous solutions. Fourier-transform infrared spectroscopy studies were also carried out to complement the obtained crystal-chemical information. The results show that hydropyrochlore and hydrokenopyrochlore can incorporate large amounts of monovalent thallium (up to $\sim 70\%$ occupancy of the A site) through an ion-exchange process involving aqueous species at tunnel sites (H^+), resulting in a unit cell expansion. Kinetic studies revealed that thallium uptake occurs rapidly (within hours). Hydrokenopyrochlore from Araxá exhibits a different Tl^+ -exchange mechanism, likely involving Ba^{2+} , which results in slower reaction kinetics. Furthermore, the thorough study of hydrokenomicrolite samples led to the identification of kenomicrolite, a new microlite-group species, expanding the known diversity of the pyrochlore supergroup. The work deepens the understanding of the ion-exchange properties of pyrochlores and highlights their potential use as sinks for toxic metals such as Tl^+ , providing valuable insights for both environmental mineralogy and the systematics of the pyrochlore supergroup.

Contents

Acknowledgements	4
Abstract.....	5
List of Tables	9
List of Figures.....	12
1. Introduction	17
1.1 Pyrochlore-supergroup minerals: an overview	17
1.2 Crystal structure of pyrochlore minerals	20
1.3 Alteration processes.....	24
1.4 Possible applications of pyrochlores	26
1.4.1 Environmental applications	27
1.5 Aims of the work	28
2. Methods and materials.....	29
2.1 Samples.....	29
2.2 Chemical analyses (EMPA-WDS).....	31
2.3 Imbibition experiments.....	32
2.3.1 Single crystals.....	32
2.3.2 Epoxy mounts	33
2.4 Single-crystal X-ray diffraction.....	33
3. Hydropyrochlore and hydrokenopyrochlore from Lueshe (D.R. Congo)	34
3.1 Imbibition experiments in water-diluted Clerici solution.....	34
3.1.1 Introduction	34
3.1.2 Experimental methods	34
3.1.3 Structural refinements.....	39
3.1.4 Results and discussion	44

3.1.5	Conclusions	53
3.2	Insights into the kinetics of the Tl-incorporation reaction	57
3.2.1	Introduction	57
3.2.2	Experimental methods.....	58
3.2.3	Results and discussion	67
3.2.4	Conclusions	75
4.	Hydrokenopyrochlore from Araxá, Minas Gerais (Brazil)	77
4.1	Imbibition experiments in Tl- and Pb-concentrated solutions	77
4.1.1	Introduction	77
4.1.2	Experimental methods.....	78
4.1.3	Results and discussion	85
4.1.4	Conclusions	95
5.	Hydrokenomicrolite and kenomicrolite from the Volta Grande pegmatite, Nazareno, Minas Gerais (Brazil).....	97
5.1	Imbibition experiments of hydrokenomicrolite crystals in Tl-rich solutions	97
5.1.1	Introduction	97
5.1.2	Experimental methods.....	98
5.1.3	Results and discussion	105
5.1.4	Conclusions	109
5.2	Kenomicrolite, a new microlite-group mineral: crystal-chemical characterisation and ion-exchange properties	111
5.2.1	Introduction	111
5.2.2	Occurrence	112
5.2.3	Appearance, physical and optical properties of kenomicrolite	114
5.2.4	Chemical data.....	114
5.2.5	X-ray diffraction.....	116

5.2.6	Infrared spectroscopy	120
5.2.7	Imbibition experiments in a Ti^{+} -rich solution	123
5.2.8	Discussion.....	123
6.	Conclusions	129
	References	131
	Appendices	143
A.	Hydropyrochlore and hydrokenopyrochlore from Lueshe (D.R. Congo): additional data	144
B.	Other pyrochlore samples datasets	148
B.1	Hydrokenoelsmoreite from Devon (United Kingdom)	173

List of Tables

TABLE 2.1. List of the investigated specimens.	29
TABLE 2.2. Standards employed for EMPA analyses.	32
TABLE 3.1. Average microprobe analyses (wt.% oxides) of untreated and treated crystals together with the crystal-chemical formulae on the basis of $\Sigma B = 2$ apfu.	37
TABLE 3.2 SC-XRD experimental details and crystal data for the selected hydroxyrochlore crystals.	39
TABLE 3.3. Selected structural parameters for the selected hydroxyrochlore crystals. Bond distances in Å, angles in °.	42
TABLE 3.4. Crystal-chemical formulae for untreated pyrochlore-supergroup minerals from Lueshe and for Tl-Imb crystal.	50
TABLE 3.5. Average microprobe analyses (wt.% oxides) of untreated Hkpcl and Hpcl along with the apfu values normalised on the basis of $\Sigma B = 2$ apfu.	60
TABLE 3.6. Single-crystal X-ray diffraction experimental details and crystal data of Hkpcl and Hpcl before and after each Tl imbibition.	61
TABLE 3.7. Selected structural parameters for Hkpcl and Hpcl, before and after Tl imbibitions. Bond distances in Å, angles in °.	65
TABLE 4.1. Average microprobe analyses (wt.% oxides) of untreated and treated crystals together with the crystal-chemical formulae on the basis of $\Sigma B = 2$ apfu.	79
TABLE 4.2. SC-XRD experimental details and crystal data for Ba-bearing hydrokenopyrochlore crystals before and after Tl and Pb imbibition experiments.	81
TABLE 4.3. Selected structural parameters for treated and untreated hydrokenopyrochlore samples from Araxá. Bond distances in Å, angles in °.	83
TABLE 4.4. Crystal-chemical formulae for BAPY_A, BAPY_B (before and after Tl-imbibition), BAPY_L, and BAPY_N. The formulae for the untreated samples were calculated with EMPA and SC-XRD data, whereas the ones for imbibed samples were calculated as specified in the text.	93

TABLE 5.1. Average microprobe analyses (wt.% oxides) and values normalised to $\Sigma B = 2$ apfu for treated and untreated HKM samples.....	100
TABLE 5.2. SC-XRD experimental details and crystal data for hydrokenomicrolite crystals before and after Tl and Pb imbibition experiments.....	102
TABLE 5.3. Selected structural parameters for treated and untreated hydrokenomicrolite. Bond distances in Å, angles in °.	104
TABLE 5.4. Crystal-chemical formulae for HKM_A (before and after Tl-incorporation), HKM_I, and HKM_J.....	109
TABLE 5.5. Analytical data (in wt.%) for kenomicrolite.....	115
TABLE 5.6. Crystal data, experimental details and refinement details for kenomicrolite and Tl-treated kenomicrolite.	117
TABLE 5.7. Atomic coordinates, Wyckoff positions, site occupancy factors (<i>s.o.f.</i>) and equivalent isotropic displacement parameters (Å ²) for kenomicrolite and Tl-treated kenomicrolite.	118
TABLE 5.8. Selected interatomic distances (Å) and angles (°) for kenomicrolite and Tl-treated kenomicrolite.	118
TABLE 5.9. Comparison between the observed and calculated mean atomic number (MAN, in number of electrons per site) for kenomicrolite and Tl-treated kenomicrolite.....	119
TABLE 5.10. Bond valence sums (BVS) for kenomicrolite (sample KM), calculated considering populations as calculated from EMPA.....	119
TABLE 5.11. X-ray powder diffraction data (<i>d</i> in Å) for kenomicrolite, sample KM.	121
TABLE A.1. SC-XRD experimental details and crystal data for the selected hydropyrochlore and hydrokenopyrochlore crystals from Lueshe.	144
TABLE A.2. Bond distances and structural parameters for the selected hydropyrochlore and hydrokenopyrochlore crystals from Lueshe.	146
TABLE B.1. Average microprobe analyses (wt.% oxides) for all the samples that were not chosen for imbibition experiments.	149

TABLE B.2. Microprobe data normalised to $\Sigma B = 2$ apfu for all the samples that were not chosen for imbibition experiments.	161
TABLE B.3. Average microprobe analyses (wt.% oxides) for treated and untreated HKE.	174
TABLE B.4. Microprobe data normalised to $\Sigma B = 2$ apfu collected from treated and untreated HKE.	175

List of Figures

- FIGURE 1.1. a) Pyrochlore structure viewed approximately along $[110]$; b) pyrochlore structure projection down $[111]$, showing alternating rings of six and three members organised in “layers”. Symbols: blue octahedra = B , green spheres = A , red spheres = Y 21
- FIGURE 1.2. a) When $x_{48f} = 0.3125$, the B octahedron is regular while A is coordinated by a trigonal scalenohedron; b) when $x_{48f} = 0.375$, the A polyhedron is a regular cube, while B flattens into a trigonal antiprism. Symbols: orange spheres = X ; the rest as in Figure 1.1. 23
- FIGURE 1.3. Comparison between the fluorite structure (on the left) and the ideal pyrochlore structure (on the right). The latter shows a vacant $8a$ position, corresponding to a pair of opposite vertices at the B site (thus removing $\frac{1}{8}$ of the anions). Symbols as in Figure 1.1. The fluorite structure was drawn using the data from Speziale and Duffy (2002) ($P = 0$ GPa). 24
- FIGURE 3.1. Structural sketch of hydropyrochlore from Lueshe. The B_2X_6 octahedral framework forms pseudo-hexagonal tunnels that host the partially occupied A (black), A' (red) and Y' (yellow) sites. Projection approximately down the $[110]$ axis. 44
- FIGURE 3.2. Unit-cell parameter plotted against the number of electrons at the A and A' sites. Empty, filled and half-filled symbols represent untreated, TI-Imb and H_2O -Imb crystals, respectively (* denotes the second imbibition in Ti^{1+} -rich solution). Crystals that underwent imbibition experiments are coloured as follows: L7 = red, L8 = orange, L9 = blue, L12 = green, L19 = purple. The black star symbol indicates $Ti^{1+}_{2-x}Ti^{3+}_xNb_2O_{6+x}$ ($x = 0.07$) (Fourquet *et al.*, 1995). Regression line (fitting the equation $y = 0.0018x + 10.550$, $R^2 = 0.91$) is calculated with samples from this thesis only. 45
- FIGURE 3.3. Unshared- and shared-octahedral edges variation as function of the A – X distance [$\Delta(X-X) = (\text{unsh. } X-X - \text{sh. } X-X)/\langle X-X \rangle$]. Symbols as in Figure 3.2, except for L7 (= red empty circle) and L19 (= purple empty circle). In the synthetic $Ti^{1+}_{2-x}Ti^{3+}_xNb_2O_{6+x}$ ($x = 0.07$) pyrochlore ($\langle A-X \rangle = 2.813$ Å;

Fourquet *et al.*, 1995), not reported in figure, the difference between unshared and shared octahedral edges is even more pronounced [$\Delta(X-X) = -0.0661$].

FIGURE 3.4. Sketch of the structural environment of the X site (view along $[100]$).

The bond valence sum on the X site was calculated considering the contribution of two B sites, two A sites, one $(\frac{1}{2} + \frac{1}{2}) A'$ site and $\frac{1}{4} Y'$ site (see text for explanation)..... 50

FIGURE 3.5. FT-IR spectra acquired from (a) KBr pellet containing untreated hydropyrochlore powder; (b) a small, untreated hydropyrochlore fragment. The weak bands in the range $4000\text{--}5100\text{ cm}^{-1}$ are attributable to water combination modes; (c) L19_Tl crystal; (d) L19_Tl-W crystal. Bands in the range $2800\text{--}3000\text{ cm}^{-1}$ are due to C–H vibrational modes, possibly due to contamination from possible glue residues on the crystal. 53

FIGURE 3.6. Relation between the amount of Tl^+ incorporated and the initial content of H_3O^+ (or H_2O) at $A' + Y'$. Symbols as in Figure 3.2. Solid line (fitting the regression equation: $y = 0.5x + 0.7$, $R^2 = 0.82$) shows the rough correlation between the two parameters. The amount of initial H_2O or H_3O^+ has been indirectly estimated from the number of electrons found at A' and Y' .

Analogously, the Tl^+ values were tentatively derived from the refined site scattering at the A site and taking into account the Sr content as found by microprobe analysis (L9_Tl)..... 55

FIGURE 3.7. Number of electrons at $A+A'$ plotted against time of imbibition. The points of both datasets (Hkpcl = black squares; Hpcl = red circles; empty symbols are untreated samples) are approximated by a logarithmic curve, analogous to a typical kinetic curve for ion-exchange reactions (*e.g.*, Inglezakis, 2005, fig. 3). Data collected at $t = 0$ were not considered for the calculation of the curves. The black dashed line (which fits data from Hkpcl) can be expressed as $y = 15.107\ln(x) - 37.339$ ($R^2 = 0.96$), while the red dashed line (fitting the Hpcl data) can be expressed as $y = 10.681\ln(x) - 16.396$ ($R^2 = 0.98$). The error bars relative to $n.e^-(A+A')$ that are not visible are contained within the data symbols..... 70

FIGURE 3.8. The $A-X$ distance plotted against the unit-cell parameter a (symbols as in Figure 3.7; the numbers indicate the duration of imbibition), showing a linear correlation trend. The black dashed line fits Hkpcl data ($y = 2.111x + 4.839$; $R^2 = 0.95$), while the red dashed line fits Hpcl data ($y = 2.326x + 4.251$; $R^2 = 0.74$). The error bars relative to a that are not visible are contained within the data symbols. 71

FIGURE 3.9. Number of electrons at Y' plotted against time of imbibition (symbols as in Figure 3.7). The curves were calculated similarly to those in Figure 3.7. The black dashed line, fitting Hkpcl data, can be expressed as $y = -4.383\ln(x) + 36.803$ ($R^2 = 0.93$); the red dashed line, which fits Hpcl data, can be expressed as $y = -3.912\ln(x) + 29.619$ ($R^2 = 0.99$). 72

FIGURE 3.10 The inverse correlation between electrons at $A+A'$ and those at Y' is approximated by a linear trend, with the slight differences possibly due to different initial compositions (especially water content). The black dashed line approximates Hkpcl data ($y = -0.309x + 26.109$; $R^2 = 0.85$), while the red dashed line fits Hpcl data ($y = -0.361x + 23.394$; $R^2 = 0.98$). Symbols as in Figure 3.8 except for the black empty squares, which represent data from the treated crystals reported in Taddei *et al.* (2024). 73

FIGURE 3.11. Unit-cell parameter a plotted against time of imbibition; Hkpcl and Hpcl show an almost identical behaviour despite the different solutions used for the treatments. Symbols as in Figure 3.7. The black dashed line fits Hkpcl data ($y = 0.013\ln(x) + 10.580$; $R^2 = 0.90$), while the red dashed line approximates Hpcl data ($y = 0.0144\ln(x) + 10.567$; $R^2 = 0.99$). The error bars relative to a that are not visible are contained within the data symbols. 75

FIGURE 4.1. Number of electrons at the $A+A'$ sites plotted against the unit-cell parameter. Symbols: red triangles are from (Taddei *et al.*, 2024); black squares are untreated and Tl-treated samples; black circles represent the untreated and Pb-treated sample. Empty symbols indicate untreated samples, full symbols indicate treated samples. The rate of expansion of the unit-cell differs between the two sets of samples probably due to the different composition at the $A+A'$ sites before the treatments. The red line fits the equation $y = 0.0018x + 10.550$

($R^2 = 0.91$) reported by Taddei *et al.* (2024), while the black line fits $y = 0.0032x + 10.494$ ($R^2 = 0.78$), calculated using the data from this chapter of the thesis..... 88

FIGURE 4.2. Number of electrons at the $A+A'$ sites plotted against the $A-X$ distance.

The black line is fitted as reported top left. Symbols as in Figure 4.1..... 89

FIGURE 4.3 Unit-cell parameter *vs.* $A-X$ distances. The black line fits the equation

reported top left. Although the sample BAPY_XTl is not strictly an outlier, it is seemingly grouped with untreated samples, as the amount of incorporated thallium could be insufficient to produce visible structural variations. Symbols as in Figure 4.1. Error bars relative to a that are not visible are contained within the symbols. 90

FIGURE 4.4. BSE image of the BAPY_X grain after undergoing an imbibition experiment in a 1M Tl-concentrated solution. The lighter, euhedral crystal on the right is mainly constituted of Tl, indicating a possible recrystallisation of thallium formate precipitated during the treatment..... 92

FIGURE 4.5. Number of electrons at $A+A'$ as a function of the time of imbibition.

The black line, fitting the equation at top left of the figure, was calculated not considering the BAPY_LPb sample, given the different behaviour of the latter. Symbols as in Figure 4.1..... 94

FIGURE 5.1. Unit-cell parameter against the number of electrons refined at $A+A'$ in different pyrochlore samples before and after imbibition in a Tl-rich solution.

The expansion of a is related to the entry of Tl^+ at the A site. Symbols: blue, downward triangle = hydrokenomicrolite (data from this chapter); green, upward triangle = hydrokenopyrochlore (data from Chapter 4); black squares = hydrokenopyrochlore and hydropyrochlore (data from Taddei *et al.*, 2024); red circles = hydrokenopyrochlore (data from Taddei and Bindi, 2025); empty symbols = untreated samples; filled symbols = Tl-treated samples..... 106

FIGURE 5.2. Back-scattered electrons (BSE) image of the investigated kenomicrolite fragment. 113

FIGURE 5.3. Transmission FT-IR spectrum of kenomicrolite. 122

- FIGURE 5.4. Comparison between the FT-IR spectra of kenomicrolite (blue) and hydrokenomicrolite (red). 122
- FIGURE 5.5. Kenomicrolite crystal structure approximately down [110]. Symbols: orange octahedra = B ; green spheres = A ; red spheres = X ; pink spheres = Y 124
- FIGURE 5.6. Linear correlation between the estimated amount of Ti^+ at the A site and the A – X distance, calculated using data from the hydrokenopyrochlore sample Hkpcl in Taddei and Bindi (2025). The number near the symbols indicate the duration (not cumulative) of the imbibition experiment in minutes; error bars that are not visible are contained within the data symbols. 127
- FIGURE 5.7. Comparison between the FT-IR spectra of untreated kenomicrolite (red) and Ti-treated kenomicrolite (black). 128

1. Introduction

1.1 Pyrochlore-supergroup minerals: an overview

Minerals belonging to the pyrochlore supergroup and their synthetic analogues have long attracted scientific interest owing to their distinctive chemical and structural features, which allow a range of applications across different fields (Wang *et al.*, 2023, and references therein).

Pyrochlores are oxides of high-charged metals (Nb, Ta, Ti, W) or Sb^{5+} , typically occurring as primary phases in highly evolved, late-stage igneous systems such as carbonatites, granitic pegmatites and nepheline syenites (Lumpkin and Ewing, 1995). Within these contexts, they crystallise during magmatic, late-magmatic or hydrothermal stages, with a stability field extending from medium P – T conditions (0.2–0.4 GPa, 450–650°C) down to ambient conditions (Lumpkin and Mariano, 1995). The pyrochlore supergroup also comprises two fluoride minerals, hydrokenoralstonite and fluornatrocoulsellite (Atencio *et al.*, 2017).

Pyrochlore supergroup minerals are usually cubic – although rhombohedral variants are also known – and are characterised by the following structural formula:

$$A_{2-m}B_2X_{6-w}Y_{1-n}$$

where m , w and n represent structural vacancies (Atencio *et al.*, 2010). The A site is 8-fold coordinated and hosts a wide range of chemical constituents of different charge and size, *e.g.*, Na^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Y^{3+} , Ce^{3+} , U^{4+} , H_2O , *etc.* (Lumpkin *et al.*, 2000). This site can be partially vacant, with $0 \leq m \leq 1.75$ vacancies per formula unit (pfu; Ercit *et al.*, 1993; Lumpkin and Ewing, 1995), although cases approaching $m \approx 2$ have also been observed (Atencio *et al.*, 2010; Taddei *et al.*, 2024). The B site, octahedrally coordinated, is typically occupied by high-field-strength cations such as Nb, Ta, Ti, W, Sb^{5+} , though it may also contain lower-

charged cations like Mg or Al (Atencio *et al.*, 2017), with minor substitutions by Sn^{4+} , Zr, Fe^{3+} , *etc.* The *X* site mainly hosts oxygen or fluorine, but in strongly leached pyrochlores it could be partially vacant ($0 \leq w \leq 0.7$ pfu; Lumpkin and Ewing, 1992, 1995; Blundred *et al.*, 2004) or partially occupied by OH^- groups substituting for O^{2-} (Ercit *et al.*, 1994; Taddei *et al.*, 2024). Finally, the *Y* site can accommodate either H_2O groups, anions (OH^- , F^- , O^{2-}) or large cations (K^+ , Cs^+). Full occupancy of *Y* by large cations requires *A*-site vacancies due to stereochemical constraints, leading to the so-called ‘inverse’ pyrochlore structure (Ercit *et al.*, 1993; Agakhanov *et al.*, 2021), having the structural formula $\square\text{B}_2\text{X}_6\text{Y}$. Whether a cation is hosted at *A* or *Y* depends on the ratio between the ionic radii of *A*- and *B*-site cations: for instance, cations with $^{\text{VIII}}r \approx 1.50\text{--}1.60$ Å (*e.g.*, K^+ , Tl^+) may occupy both *A* and *Y* simultaneously producing intermediate degrees of ‘inversion’, whereas larger cations such as Cs^+ ($^{\text{VIII}}r = 1.74$ Å) tend to order preferentially at *Y* (Ercit *et al.*, 1993).

Members of the pyrochlore supergroup are numerous and complex, and despite being known for nearly two centuries – the first scientific paper reporting a pyrochlore mineral is attributable to Wöhler (1826), while the earliest structural descriptions of pyrochlores date back to the 1930s (von Gaertner, 1930; Zedlitz, 1932) –, the classification and nomenclature of the pyrochlore supergroup remain subjects of debate. Several attempts to create a simple yet effective nomenclature system were made in the past (Van Der Veen, 1963; Hogarth, 1977), in an effort to avoid unnecessary proliferation of species names. The current nomenclature, accepted by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-CNMNC), is that proposed by Atencio *et al.* (2010), later expanded by Atencio (2021). This system is based on the *yaroot* rule: the name of each species consists of two prefixes, reflecting the dominant constituents of the *Y* and *A* sites, and a root assigned according to the content of *B*. As of today, the roots are seven, and each individuates a group of minerals according to the dominant-valency rule (Hatert and Burke, 2008; Bosi *et al.*, 2019): the root is defined by the most abundant valence group of cations at *B* and the dominant cation within it. Thus, the roots are:

- *elsmoreite* if M^{6+} cations are dominant at B , W is dominant among them, and O^{2-} is dominant at X ;
- *pyrochlore* if M^{5+} cations are dominant at B , Nb is dominant among them, and O^{2-} is dominant at X ;
- *microlite* if M^{5+} cations are dominant at B , Ta is dominant among them, and O^{2-} is dominant at X ;
- *roméite* if M^{5+} cations are dominant at B , Sb^{5+} is dominant among them, and O^{2-} is dominant at X ;
- *betafite* if M^{4+} cations are dominant at B , Ti^{4+} is dominant among them, and O^{2-} is dominant at X ;
- *ralstonite* if M^{3+} cations are dominant at B , Al is dominant among them, and F^- is dominant at X ;
- *coulsellite* if M^{2+} cations are dominant at B , Mg is dominant among them, and F^- is dominant at X .

Since a ‘group’ must consist of two or more species, betafite, ralstonite and coulsellite cannot be considered proper mineral groups, as each is currently represented by a single species: oxyttriobetafite-(Y) (Nishio–Hamane *et al.*, 2022), hydrokenoralstonite, and fluornatrocoulsellite (Atencio *et al.*, 2017), respectively, which remain unassigned species within the pyrochlore supergroup.

The dominant-valency rule is also applied for the assignment of the two prefixes, where the first one refers to the Y -site content and the second one refers to the A -site content. Vacancies or neutral species define the “zero-charge group”, expressed by the prefixes *keno-* (vacancy) or *hydro-* (H_2O). Repetition is omitted if the same prefix applies to both sites. Other prefixes directly indicate the dominant species: for Y , these include *hydroxy-* (OH), *fluor-* (F), *oxy-* (O), or even *cesio-* (Cs), where cesiokenopyrochlore represents the only known natural pyrochlore to have a fully inverse configuration (Agakhanov *et al.*, 2021). For the A site, a larger variety of prefixes is possible, given that the number of species that can dominate this position is considerable. The most common are *natro-* (Na), *calcio-* (Ca), *plumbo-* (Pb), *etc.*

This nomenclature requires an in-depth knowledge of the chemical composition of the samples to be classified, particularly regarding the occupancy of the *A*, *B*, and *Y* sites. However, ambiguities often arise. The choice of the *Y*-site prefix can be particularly problematic, as it can host O^{2-} , OH^- and/or H_2O , and their speciation can be difficult to resolve. Usually, the choice is made based on charge-balance considerations. Even more challenging is the application of the dominant-valency rule for the *A*-site prefix assignment, given the wide range of possible substituents. In fact, in certain cases ambiguity cannot be avoided. For instance, a pyrochlore of composition $(Na_{1.15}Ca_{0.70}Bi_{0.15})Ta_2O_6F$ would be classified as “fluornatromicrolite”, implying the presence of the $Na_2Ta_2O_6F$ end-member. It is not charge-balanced and therefore cannot exist. Attempts to fix this issue using electrically neutral end-members such as $NaCaTa_2O_6F$ or $Na_{1.5}Bi_{0.5}O_6F$ (Hawthorne, 2002) remain problematic: in the first case, Na^+ and Ca^{2+} belong to equally dominant valence groups, making both *calcio*- and *natro*- *A*-prefixes correct. In the second case, the possible presence of additional substituents renders the species name insufficient to properly describe its content, let alone unambiguously convey genetic or petrological information (see also Bhattacharjee *et al.*, 2022). Atencio *et al.* (2010) proposed the use of the ‘#’ symbol to denote all charge-balancing species. Nevertheless, the issues raised with this nomenclature are still being discussed and the solution proposed by Atencio *et al.* (2010) should be considered provisional.

1.2 Crystal structure of pyrochlore minerals

The pyrochlore structure, usually cubic (space group $Fd\bar{3}m$), is distinctive for its ability to host a wide variety of cations and anions of different sizes and charges, favouring a remarkable ion-exchange capacity. Rhombohedral pyrochlores are also known: *e.g.*, hydrokenomicrolite (Andrade *et al.*, 2013a) and hydrokenoelsmoreite (Mills *et al.*, 2016) can both occur as either cubic or rhombohedral polytypes (Atencio, 2016). The structure can be described as a framework of corner-sharing BX_6 octahedra forming tunnels along $[110]$, which host the interstitial *A* and *Y* sites (*e.g.*, Subramanian *et al.*, 1983; Figure 1.1a). The structure can thus be regarded as the interpenetration of two sub-networks: the B_2X_6 framework and the interstitial

A_2Y network, the latter being analogous to that of anticitobalite-type Cu_2O (Vanderah *et al.*, 2005). When viewed down the $[111]$ direction, the octahedra are configured as layers consisting of rings, alternating between six- and three-membered units (Figure 1.1b).

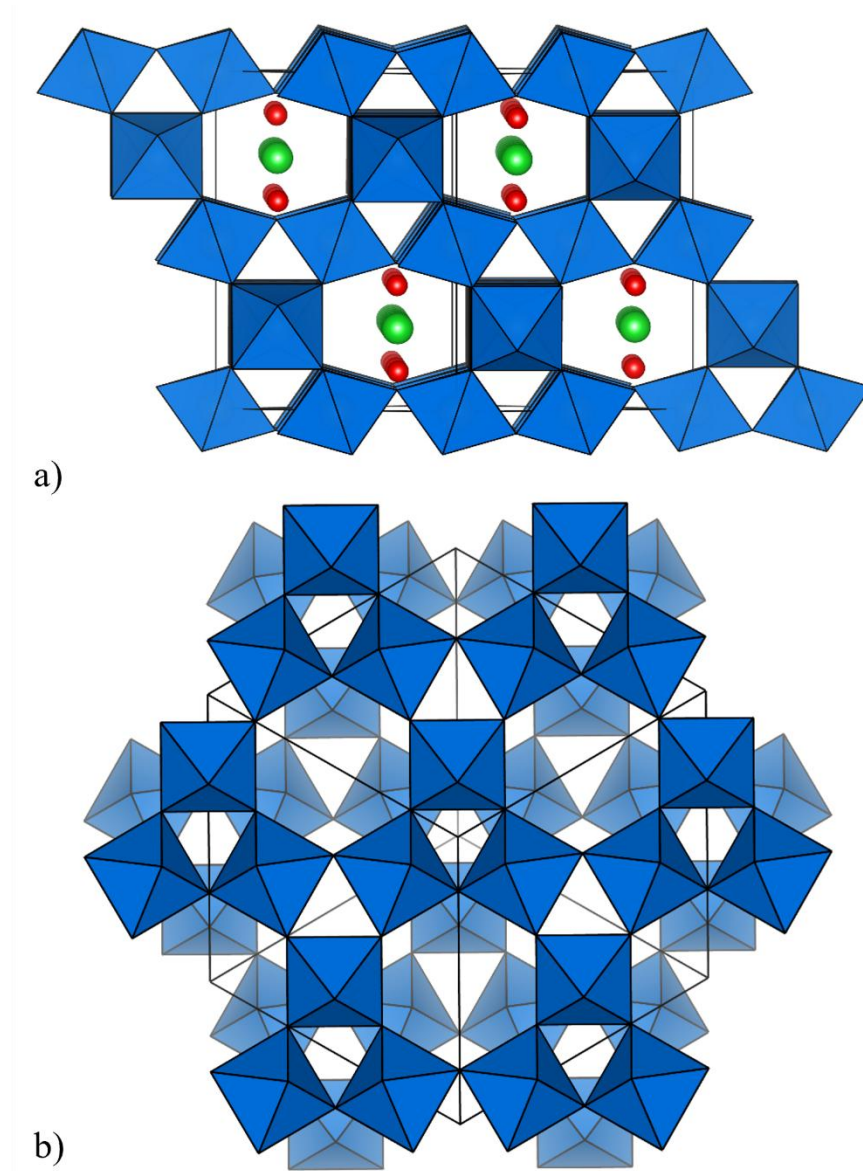


FIGURE 1.1. **a)** Pyrochlore structure viewed approximately along $[110]$; **b)** pyrochlore structure projection down $[111]$, showing alternating rings of six and three members organised in “layers”. Symbols: blue octahedra = B , green spheres = A , red spheres = Y .

The tunnel sites A and Y can range from fully occupied to completely vacant. The limiting case corresponds to the end-member $\square_2B_2X_6\square$ (Groult *et al.*, 1982; Taddei *et al.*, 2025), which highlights the role of the octahedral framework as the building block of the whole structure (Lumpkin and Ewing, 1988). Such variability provides the basis for the wide range of possible chemical compositions, even broader in synthetic pyrochlore-type compounds, and ultimately explains the diversity of the physical and chemical properties of each species.

A peculiarity of the crystal structure of pyrochlores is that all atoms occupy special Wyckoff positions: A at $16d$, B at $16c$, X at $48f$ and Y at $8b$. The origin of the unit cell can be positioned at any of these positions (Subramanian *et al.*, 1983), but is usually set at $16c$ (choice 2 in the *International Tables for Crystallography*; Wilson, 1992), with atoms in $16d = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, $16c = 0, 0, 0$, $48f = x, \frac{1}{8}, \frac{1}{8}$, and $8b = \frac{3}{8}, \frac{3}{8}, \frac{3}{8}$. It is immediately clear that the only free coordinate is the x coordinate of the X site (x_{48f}). Although this might suggest an overall rigid framework, both the geometry and size of the A and B polyhedra are strongly affected by x_{48f} (Subramanian *et al.*, 1983), resulting in a very flexible structure which enables the accommodation of a large variety of cationic and anionic species in different combinations. In particular, a few distinct cases need to be pointed out: (i) when $x_{48f} = 0.3125$, A is coordinated by a trigonal scalenohedron with $A-X$ bonds longer than $A-Y$, while B is a regular octahedron (Figure 1.2a); (ii) when $x_{48f} = 0.375$, A is in perfect cubic coordination, whereas the B octahedron flattens along its threefold axis (Figure 1.2b); (iii) for $x_{48f} < 0.3125$, the B octahedron elongates along its threefold axis, and the A polyhedron becomes a hexagonal bipyramid (Chakoumakos, 1984).

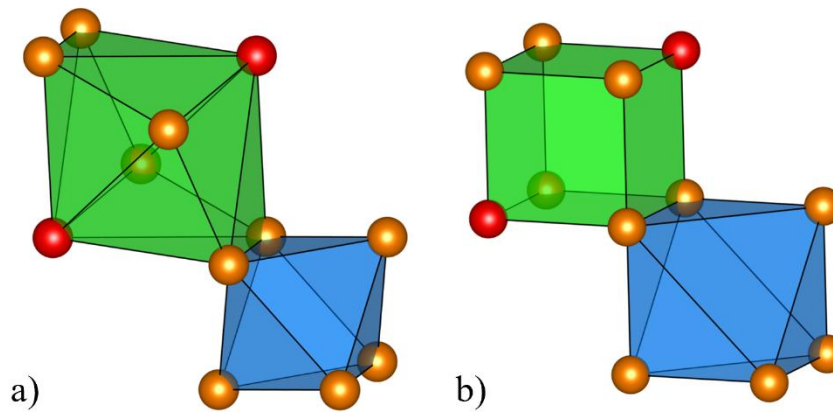


FIGURE 1.2. **a)** When $x_{48f} = 0.3125$, the B octahedron is regular while A is coordinated by a trigonal scalenohedron; **b)** when $x_{48f} = 0.375$, the A polyhedron is a regular cube, while B flattens into a trigonal antiprism. Symbols: orange spheres = X ; the rest as in Figure 1.1.

The pyrochlore structure can alternatively be described as a “defect fluorite” structure (Subramanian *et al.*, 1983; Lumpkin and Ewing, 1988). The unit-cell parameter a of pyrochlores is twice that of fluorite (AX_2 , space group $Fm\bar{3}m$), from which the pyrochlore structure is derived by removing one-eighth of the anions. The latter correspond to the atoms positioned at the $8a$ position, which remains vacant in pyrochlores (Figure 1.3). This kind of description, however, best applies when the x_{48f} coordinate gets closer to 0.375, a rare occurrence in natural species (Subramanian *et al.*, 1983), but easily achieved in synthetic compounds having the pyrochlore structure with A and B cations showing fairly similar ionic radii (Wang *et al.*, 2018). For this reason, in the present thesis preference will be given to the structural description based on the two interpenetrating networks – the octahedral framework and the tunnel sites –, making it easier to understand the ion-exchange mechanisms involving the structure of these minerals and investigated in the present thesis work.

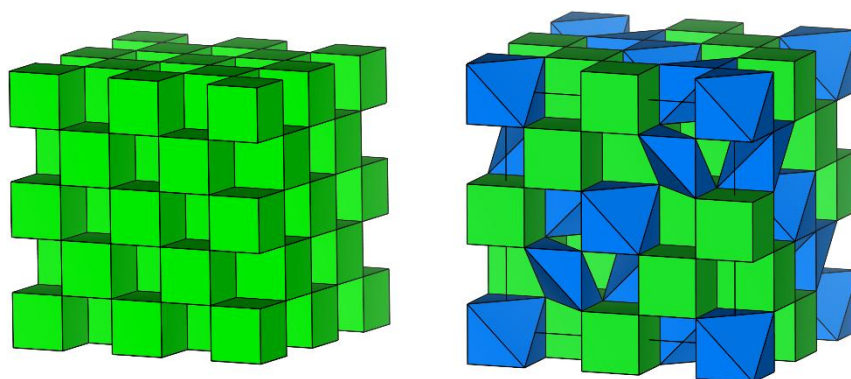


FIGURE 1.3. Comparison between the fluorite structure (on the left) and the ideal pyrochlore structure (on the right). The latter shows a vacant $8a$ position, corresponding to a pair of opposite vertices at the B site (thus removing $\frac{1}{8}$ of the anions). Symbols as in Figure 1.1. The fluorite structure was drawn using the data from Speziale and Duffy (2002) ($P = 0$ GPa).

1.3 Alteration processes

Minerals belonging to the pyrochlore and microlite groups mainly occur as primary phases in carbonatitic or pegmatitic deposits, where they may undergo both primary and secondary alteration. These processes have been thoroughly described by Lumpkin and Ewing (1992, 1995, 1996). Primary (hydrothermal) alteration of pyrochlores typically takes place during the late magmatic to hydrothermal stages of granitic pegmatites, at pressures of 0.2–0.4 GPa and temperatures of 300–650°C, and is often associated with the emplacement of the host rocks. In contrast, in carbonatites and nepheline syenites, hydrothermal alteration occurs under different conditions due to the usually shallower emplacement depths ($P = 0$ –0.2 GPa) and the persistence of a relatively low-temperature hydrothermal activity during the period of uplift and erosion. Primary alteration predominantly involves large-scale intracrystalline diffusion, which is the dominant process of alteration at higher temperatures, with limited fracture control. Conversely, secondary alteration (weathering) takes place under near-surface conditions ($T < 100^\circ\text{C}$ and $P < 0.1$ GPa) and is driven by the circulation of meteoric water through voids and preexisting

cracks in the crystals. The development of microfractures is generally related to radiation damage, since it is not rare that pyrochlores incorporate minor but significant amounts of U and Th. Secondary alteration often occurs after the crystal structure has become partially or completely metamict. Both alteration processes involve more-or-less pronounced ion-exchange, which occurs at the tunnel positions within the structure, along with an increase of structural vacancies at the *A*, *Y*, and possibly *X* sites. On the contrary, the *B* site usually remains unaffected, except for minor substitution mechanisms mainly involving Fe^{3+} , which further corroborate the physicochemical stability of the octahedral framework.

Most unaltered, magmatic compositions of pyrochlore- and microlite-group minerals cluster near the $\text{NaCaTa}_2\text{O}_6\text{F}$ – CaTa_2O_6 or $\text{NaCaNb}_2\text{O}_6\text{F}$ – CaNb_2O_6 joins, or within the $\text{NaCaTa}_2\text{O}_6\text{F}$ – $\text{Ca}_2\text{Ta}_2\text{O}_7$ – CaTa_2O_6 or $\text{NaCaNb}_2\text{O}_6\text{F}$ – $\text{Ca}_2\text{Nb}_2\text{O}_7$ – CaNb_2O_6 compositional fields. Primary alteration leads to a decrease in the more mobile monovalent cations and anions and a concomitant increase in divalent cations, following substitution schemes such as: ${}^A\text{Na}^Y\text{F} \rightarrow {}^A\text{Ca}^Y\text{O}$, ${}^A\Box^Y\Box \rightarrow {}^A\text{Ca}^Y\text{O}$ and ${}^A\text{Na}^Y\text{F} \rightarrow {}^A\Box^Y\Box$ (where “unaltered” $\rightarrow$ “altered”, and the arrow stands for “goes to”; Lumpkin and Ewing, 1995). This process is also associated with a typical estimated increase of 2–5 wt.% H_2O .

Secondary alteration produces more pronounced changes in the chemistry of the tunnel sites. In addition to the loss of monovalent cations, divalent cations are also depleted, accompanied by a notable increase in both structural vacancies and water content (8–14 wt.%). The corresponding substitution schemes are: ${}^A\text{Ca}^Y\text{O} \rightarrow {}^A\Box^Y\Box$, ${}^A\text{Na}^Y\text{F} \rightarrow {}^A\Box^Y\Box$ and ${}^A\text{Ca}^X\text{O} \rightarrow {}^A\Box^X\Box$. Minor uptake of cations such as Ba, Sr, K, Pb, and rare earth elements (REEs) may also occur: these elements are typically supplied by the dissolution of feldspars and carbonates during laterite formation.

Transitional alteration stages are also recognised, characterised by a major loss of Na and F, moderate Ca loss, and an increase in REEs and Fe. In these cases, hydration reaches intermediate levels between the two main alteration processes, ranging from 4 to 12 wt.% H_2O .

Understanding the alteration pathways of minerals of the pyrochlore supergroup is crucial, as they provide direct evidence of the enhanced ion-exchange properties of these species. Moreover, altered pyrochlores represent the most promising candidates for environmental applications, especially the weathered ones, as they host large amounts of H₂O at the tunnel sites, which is highly mobile and readily exchangeable.

1.4 Possible applications of pyrochlores

Members of the pyrochlore supergroup and their synthetic analogues are well known for their versatility across a wide spectrum of technological and industrial applications. This flexibility arises from their peculiar crystal structure, and the remarkable variety of chemical species that it can accommodate. As a result, pyrochlores have been extensively investigated over the past decades for their magnetic, dielectric, electrical, photocatalytic, and ion-exchange capacities (Fukina *et al.*, 2024, and references therein). Minerals belonging to the pyrochlore and microlite groups also represent major sources for niobium and tantalum, critical metals essential to high-tech and industrial applications; in fact, most of the world's niobium resources occur as pyrochlore in carbonatite deposits (Friedline, 2025).

Natural and synthetic pyrochlores have been explored for a range of applications, including photocatalyst materials (Jitta *et al.*, 2015), thermal barrier coatings (Sankar and Kumar, 2021), and fast ionic conductors (Kreller *et al.*, 2019) among others. Notably, thallium-bearing pyrochlore-type synthetic compounds have shown promising results as electrocatalyst in aqueous Na-air batteries (Kim *et al.*, 2019) and have been studied for the mobility of Tl⁺ ions within the tunnels, suggesting potential ionic conductivity properties (Fourquet *et al.*, 1979).

Within the scope of this thesis, the most relevant feature of pyrochlore is their ion-exchange capability, which has the potential to be exploited for environmental remediation applications.

1.4.1 Environmental applications

A variety of materials with the pyrochlore structure have been examined for applications in the environmental field because of their capability to immobilise toxic elements such as Pb or Sb (Han *et al.*, 2014; Radková *et al.*, 2017; Jurkovič *et al.*, 2019) or, more commonly, actinides and other hazardous radionuclides (Koivula *et al.*, 2002; Ewing *et al.*, 2004; McMaster *et al.*, 2018). Although some authors have previously reported that monovalent thallium can be incorporated in natural, hydrated, defective pyrochlores by soaking them in Tl-rich solutions (Jäger *et al.*, 1959; Van Der Veen, 1963; Harris, 1965; Bindi *et al.*, 2006), there are few studies on their potential use as sinks for Tl⁺ (Zoppi, 2004). It is thus crucial to further pursue the issue, since pollution from thallium is rapidly becoming a concerning matter due to its high toxicity and enhanced mobility in aqueous solutions, especially when it is present in its reduced state (*e.g.*, Biagioni *et al.*, 2017; George *et al.*, 2019). Numerous methods for Tl removal from wastewater have been developed in the recent years, including the exploitation of adsorption and ion-exchange properties of various materials (Xu *et al.*, 2019; Zhao *et al.*, 2020), but most of them have shown greatly reduced uptake efficiency in the presence of competitors such as H⁺, Na⁺, K⁺, and Ca²⁺.

Ion-exchange processes may indeed take place at the interstitial sites located within the tunnels of pyrochlores, especially when these sites are occupied by highly mobile species (*e.g.*, H₂O or H₃O⁺) or when they are partially vacant, which are common features for natural, strongly weathered species (*e.g.*, hydropyrochlore, Ercit *et al.*, 1994; Lumpkin and Ewing, 1995; and hydrokenopyrochlore; Biagioni *et al.*, 2018). Defective, hydrous pyrochlores thus represent the most suitable candidates for environmental applications. Therefore, assessing the potential suitability of pyrochlores as sinks for heavy metals, with a focus on monovalent thallium among others, is both scientifically interesting and environmentally significant.

1.5 Aims of the work

The aim of this thesis is to carry out a preliminary investigation to assess the suitability of natural pyrochlores for environmentally oriented applications, in particular their ability to incorporate and retain toxic cations such as monovalent thallium and lead dispersed in aqueous systems. Since these heavy metals pose serious risks to both human health and ecosystems, this research seeks to identify the optimal crystal-chemical characteristics of pyrochlores that maximise their ion-exchange capacity and selectivity towards these elements.

To this end, various imbibition experiments in Tl- and Pb-rich solutions were performed on single crystals from a selected set of defective, hydrous pyrochlores, which represent the most promising candidates for incorporation processes. Highly concentrated solutions were chosen to enhance and emphasize the structural modifications induced by the uptake of these large cations. This approach allows a more accurate assessment of the structural parameters that favour ion exchange, with the goal of tailoring synthetic pyrochlore-like compounds that replicate these features. Furthermore, it enables the evaluation of possible consequences on the stability of these minerals associated with the entry of Tl and Pb in the structure. For this reason, single-crystal X-ray diffraction (SC-XRD) was chosen as the primary analytical method, as it provides detailed and reliable three-dimensional structural information.

The examined samples that yielded satisfactory results include hydropyrochlore and hydrokenopyrochlore from Lueshe (D.R. Congo), hydrokenopyrochlore from Araxá (Brazil), and hydrokenomicrolite from Minas Gerais (Brazil). During the investigation of the latter, a new mineral species, kenomicrolite, was discovered and characterised. Although its ion-exchange capacity was also tested, it was found to be very limited due to the lack of exchangeable species at the tunnel sites. Additional data obtained from hydropyrochlore and hydrokenopyrochlore from Lueshe and from pyrochlore samples that were later deemed unsuitable for the purpose of this thesis work are reported in Appendices A and B, respectively.

2. Methods and materials

2.1 Samples

Minerals belonging to the pyrochlore supergroup mainly crystallise in the cubic hexoctahedral class, typically displaying an octahedral habit, sometimes associated with other simple forms. Not seldom they are found as granular or saccharoidal aggregates. Their colour ranges from colourless, to greenish-yellowish, reddish, brown, or even black. Lustre is usually resinous but can be vitreous to adamantine in well-developed crystals. Fracture is irregular to conchoidal, with a hardness ranging from 4 to 6 on the Mohs scale; density varies from ~ 3 to ~ 8 g/cm³ depending on the chemical composition.

The samples studied for this thesis come from different localities and were obtained from museums or private collections as specified in Table 2.1.

TABLE 2.1. List of the investigated specimens.

Sample	Locality	Collection	Catalogue number
Hydropyrochlore and hydrokenopyrochlore (×3 specimens)	Lueshe, Bwito, Rutshuru Territory, North Kivu, D.R. Congo	Private collection of Dr. M. Batoni	-
		<i>Naturhistoriska Riksmuseet</i> (Stockholm)	GEO-NRM 20060253
		<i>Muséum National d'Histoire Naturelle</i> (Paris)	GGM-LC 205.174

TABLE 2.1 (continued)

“Ceriopyrochlore”	Fensfältet Söve gruvor, Norway	<i>Naturhistoriska Riksmuseet</i> (Stockholm)	GEO-NRM 19970269
“Pyrochlore” (×2 specimens)	Langesundsford Brevik (Brevig), Norway	<i>Naturhistoriska Riksmuseet</i> (Stockholm)	GEO-NRM g26838 GEO-NRM g26870
Kenoplumbomicrolite	Mount Ploskaya, Western Keivy Massif, Russia	<i>Naturhistoriska Riksmuseet</i> (Stockholm)	GEO-NRM 20060246
“Pyrochlore”	Ilmenberget, Russia	<i>Naturhistoriska Riksmuseet</i> (Stockholm)	GEO-NRM 18620111
“Pyrochlore”	Långharsholmen (Långörsholmen), Alnön, Sweden	<i>Naturhistoriska Riksmuseet</i> (Stockholm)	GEO-NRM g26834
“Uranpyrochlore”	MacDonald mine, Hybla, Canada	<i>Naturhistoriska Riksmuseet</i> (Stockholm)	GEO-NRM 19270116
“Bariopyrochlore”	Araxá, Minas Gerais, Brazil	<i>Muséum National d’Histoire Naturelle</i> (Paris)	GGM-LC 175.67
“Plumbopyrochlore”	Keivy, Murmansk Oblast, Russia	A.E. Seaman Museum (Michigan Technological University)	DM 28428
Hydrokenoelsmoreite	Hemerdon (Drakelands) mine, Plymouth, Devon, United Kingdom	Natural History Museum (London)	BM 2006,119
Hydrokenomicrolite and kenomicrolite	Volta Grande, Nazareno, Minas Gerais, Brazil	Received from Prof. Daniel Atencio (<i>Universidade de São Paulo</i>)	—*

TABLE 2.1 (continued)

“Pyrochlore”	Val Vigezzo (VB), Orcesco, Piedmont, Italy	<i>Museo di Storia Naturale “La Specola” (Florence)</i>	MSN-Fi 3706-Z, Brizzi collection
“Microlite” (×5 specimens)	Grotta d’Oggi, Elba, Tuscany, Italy	<i>Museo di Storia Naturale “La Specola” (Florence)</i>	MSN-Fi 4820-E, Elbana collection
	Facciatoia, San Piero in Campo, Elba, Tuscany, Italy		MSN-Fi 4825-E, Elbana collection MSN-Fi 4827-E, Elbana collection MSN-Fi 4828-E, Elbana collection
	Le Fate, San Piero in Campo, Elba, Tuscany, Italy		MSN-Fi 4831-E, Elbana collection

Notes: *sample studied by Andrade *et al.* (2013a).

2.2 Chemical analyses (EMPA-WDS)

Quantitative chemical analyses were carried out on all samples, priorly embedded in polished epoxy resin mounts, by means of a JEOL JXA-8230 electron microprobe operated in WDS mode at 10 nA and 15 kV. Counting times are different for each specimen, given their wide chemical variability, and thus separately listed in the *Experimental methods* paragraphs of each chapter. The standards employed for analyses are reported in Table 2.2. ZAF correction was always applied for absorption and matrix effects.

An overlap correction factor was calculated and applied to take into account the interference between $TlM\alpha$ and $NbL\beta$. Given this interference issue, thallium values were measured again by increasing the voltage to 20 kV; no variations were observed.

TABLE 2.2. Standards employed for EMPA analyses.

Element	Standard material	Line
F	Fluorite	FK α
Na	Albite	NaK α
Al	Plagioclase	AlK α
Si	Albite	SiK α
K	Sanidine	KK α
Ca	Diopside	CaK α
Ti	Ilmenite	TiK α
Mn	Bustamite	MnK α
Fe	Ilmenite	FeK α
As	As-metal	AsL α
Sr	Celestine	SrL α
Zr	Zirconia	ZrL α
Nb	Nb-metal	NbL α
Sn	Cassiterite	SnL α
Sb	Sb-metal	SbL α
Ba	Baryte	BaL α
La	Monazite	LaL α
Ce	Monazite	CeL α
Ta	Ta-metal	TaM α
w	W-metal	WM α
Tl	Lorándite	TlM α
Pb	Crocoite	PbM α
Th	Th-metal	ThM α
U	U-metal	UM α

2.3 Imbibition experiments

2.3.1 *Single crystals*

The imbibition experiments of single crystals were performed in specific containers built for this purpose. The containers consist of closable cylinders hosting the

sample holders for single crystals. The latter are metal pins with a Kapton loop at the top, where the crystal is mounted, and have a magnetic cap. In the cylinders, the cap is placed upside down, with the pin pointing towards the ground; inside the cap, a small conical vial is kept in place by tape and is filled with the solutions used for the treatments. The pin is then placed into the cap, making sure the Kapton loop at the top is completely covered by the solution.

The used solutions consist of a 1:1 deionised water-diluted Clerici solution, a 1M and 0.1M TI^+ concentrated solutions prepared by dissolving thallium(I) formate in deionised water, and lastly a 1M Pb^{2+} concentrated solution prepared by dissolving lead(II) nitrate in deionised water. The duration of each experiment is variable and is reported for each chapter in the respective section.

2.3.2 *Epoxy mounts*

The same solutions prepared for the single crystals were used to treat samples directly from within the polished epoxy mount. The imbibition experiments were carried out by placing a droplet of solution upon the exposed sample surfaces, making sure to reposition it if complete evaporation occurs. Upon evaporation, thallium(I) formate tends to precipitate on the surface of the epoxy mount, making it necessary to rapidly clean it with deionised water (in which the compound is highly soluble) after the treatment.

2.4 **Single-crystal X-ray diffraction**

Unit-cell parameters and intensity data of all the samples investigated through this technique were collected using a Bruker D8 Venture diffractometer equipped with a Photon III detector, using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All intensity data were corrected for Lorentz-polarisation effects and for absorption with APEX3 (Bruker, 2016; see Chapter 3.1.2) or APEX5 (Bruker, 2023).

3. Hydropyrochlore and hydrokenopyrochlore from Lueshe (D.R. Congo)

3.1 Imbibition experiments in water-diluted Clerici solution

3.1.1 Introduction

In this chapter, following preliminary indications obtained by Zoppi (2004), imbibition experiments were carried out on hydropyrochlore from Lueshe (Bwito, Rutshuru Territory, North Kivu, D.R. Congo), ideally $(\text{H}_2\text{O}, \square)_2\text{Nb}_2(\text{O}, \text{OH})_6(\text{H}_2\text{O})$. This mineral was firstly described by Van Wambeke (1978) as kalipyrochlore (hydropyrochlore, following the current nomenclature; (Atencio *et al.*, 2010; Christy and Atencio, 2013; Atencio *et al.*, 2017; Atencio, 2021) and fully characterised by Ercit *et al.* (1994), who pointed out the partially inverse character of this structure and provided insights into the role of H_2O in the tunnels.

At Lueshe, (Sr,K)-bearing hydropyrochlore occurs as a secondary leached product of primary $(\text{Ca}, \text{Na})_2\text{Nb}_2\text{O}_6(\text{OH}, \text{F})$ pyrochlores within the lateritic soils overlapping a syenite-carbonatite complex associated with secondary phosphates of the crandallite-goyazite series, Fe-Ti oxides and clays (Wall *et al.*, 1996; Nasraoui and Bilal, 2000). In the deposit, the supergene alteration causes chemical modifications involving a major leaching of the *A* cations and *Y* anions, the formation of structural vacancies, the incorporation of minor quantities of K^+ , Sr^{2+} , Ba^{2+} , Ce^{3+} , and hydration (Lumpkin and Ewing, 1995; Nasraoui and Bilal, 2000).

3.1.2 Experimental methods

From a large hydropyrochlore octahedral fragment, several single crystals (labelled L#) were extracted for single-crystal and powder X-ray diffraction (SC-XRD,

PXRD) investigations, electron microprobe analyses (EMPA) and imbibition experiments in a thallium-bearing solution (Tl-Imb), followed by desorption tests in deionised water (H₂O-Imb). The uptake/release mechanisms were also investigated through Fourier transform infrared spectroscopy (FT-IR).

Chemical analyses

Chemical analyses were carried out on crystals L1, L11, L14 and L9_Tl after Tl-Imb, as well as some grains not characterised by X-ray diffraction. Counting times were 30 s (Fe, Pb, Ca, Sb, Ba, U, Na, F), 20 s (Ti, Sr), 15 s (K, Tl, Ce, La), and 10 s (Nb, Ta).

F (fluorite; $FK\alpha$), Si (albite; $SiK\alpha$), Sb (Sb-metal; $SbL\alpha$) and Ta (Ta-metal; $TaM\alpha$) were sought but found below the detection limits (0.01–0.02 wt.%). In order to check for the possible presence of NH_4^+ , the λ range (3.0000–3.3214 nm) was scanned but no peak ascribable to N was observed.

Chemical data were normalised on the basis of ΣB cations = 2 atoms per formula unit (apfu) with all the iron considered to be trivalent. Average values are reported in Table 3.1. Low EMPA analytical totals probably indicate the presence of significant amounts of H₂O (see below).

Single-crystal X-ray diffraction

Unit-cell parameters and intensity data were collected before and after each imbibition experiment (Table 3.2). Intensity data were corrected for Lorentz-polarisation effects and for absorption with APEX3 (Bruker, 2016).

Imbibition experiments

Five selected crystals (L7, L8, L9, L12, L19) were soaked for five days in a 1:1 H₂O-diluted Clerici solution. For L8_Tl, an additional Tl-Imb was performed for three days (L8_2Tl). L8_2Tl and L19_Tl were subsequently soaked in deionised water for seven days (L8_2Tl-W and L19_Tl-W). A further water imbibition led to a major fracturing of L8_2Tl-2W into several domains.

Powder X-ray diffraction

In order to check the purity of the sample for the FT-IR investigations, about 4 mg of material were crushed in an agate mortar and the resulting powder was analyzed with a PANalytical X'Pert PRO diffractometer using $\text{CuK}\alpha$ radiation (2θ range = $5\text{--}70^\circ$, step size = 0.017° , scan step time = 114.3 s). The powdered material was found to consist mainly of hydropyrochlore with minor amounts of ilmenite, a member of the crandallite-goyazite series, and likely very minor magnesian calcite.

FT-IR spectroscopy

Spectroscopic analyses were carried out using a Bruker Vertex 70 attached to a Hyperion 2000 microscope and equipped with a glowbar source, KBr beamsplitter and an MCT detector. IR spectra were acquired in transmission mode by placing the sample on a KBr plate and adjusting the aperture size to that of the sample. Measures were obtained from L19_Tl, L19_Tl-W and from small fragments of untreated sample (50–100 μm). The acquired IR spectra represent an average of 64 scans, with a spectral range between 6000 and 600 cm^{-1} and a resolution of 4 cm^{-1} . Additional measurements on untreated sample were taken using the KBr pellet method, by mixing 2 mg of the mineral with 200 mg of KBr in an agate mortar and then pressing the mixture to a 12 mm diameter disc under a load of 4.5 tonnes.

TABLE 3.1. Average microprobe analyses (wt.% oxides) of untreated and treated crystals together with the crystal-chemical formulae on the basis of $\Sigma B = 2$ apfu.

	A	B	C	D	E	L1	L11	L14	Mean	L9_Tl
<i>n</i>	2	4	4	6	4	6	6	9		5
Nb ₂ O ₅	77.53	74.46	75.86	74.12	75.14	74.42	74.03	73.03	74.82	43.21
TiO ₂	4.00	3.59	3.49	3.97	3.80	4.18	3.84	3.93	3.85	2.38
Fe ₂ O ₃	-	0.03	0.06	0.11	0.06	0.04	0.04	0.03	0.05	0.01
Na ₂ O	0.53	1.55	0.08	0.11	0.40	0.84	0.09	0.49	0.51	0.03
K ₂ O	1.18	1.74	1.42	1.59	1.24	1.51	1.53	1.28	1.44	0.51
CaO	0.13	0.15	0.11	0.24	0.10	0.09	0.11	0.12	0.13	0.03
SrO	5.55	5.46	5.49	5.44	5.57	5.83	5.65	5.56	5.57	3.14
Ce ₂ O ₃	-	0.04	0.03	0.05	0.02	0.02	0.03	0.12	0.04	0.05
La ₂ O ₃	-	0.05	-	0.04	0.04	-	-	0.01	0.02	-
UO ₂	-	0.03	0.07	0.06	0.06	0.04	0.05	0.03	0.04	-
BaO	0.14	0.14	0.15	0.17	0.14	0.17	0.19	0.17	0.16	0.07
PbO	0.29	0.33	0.33	0.31	0.35	0.36	0.33	0.33	0.33	-
Tl ₂ O	-	-	-	-	-	-	-	-	-	49.63
Total	89.35	87.57	87.09	86.21	86.92	87.50	85.89	85.10	86.96	99.06
H ₂ O*						12.43	14.19	13.90		0.70
TOTAL						99.93	100.08	99.00		99.76

TABLE 3.1 (*continued*)

	A	B	C	D	E	L1	L11	L14	Range n.e ⁻	Mean	L9_Tl
Nb ⁵⁺	1.84	1.85	1.86	1.83	1.85	1.83	1.84	1.84	75.0–76.3	1.84	1.83
Ti ⁴⁺	0.16	0.15	0.14	0.16	0.15	0.17	0.16	0.16	3.1–3.7	0.16	0.17
Fe ³⁺	-	-	-	0.01	-	-	-	-	0.0–0.3	-	-
Na ⁺	0.05	0.17	0.01	0.01	0.04	0.09	0.01	0.05	0.1–1.9	0.05	0.01
K ⁺	0.08	0.12	0.10	0.11	0.09	0.11	0.11	0.09	1.5–2.3	0.10	0.06
Ca ²⁺	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.2	0.01	-
Sr ²⁺	0.17	0.17	0.17	0.17	0.18	0.18	0.18	0.18	6.5–6.8	0.18	0.17
Ce ³⁺	-	-	-	-	-	-	-	-	-	-	-
La ³⁺	-	-	-	-	-	-	-	-	-	-	-
U ⁴⁺	-	-	-	-	-	-	-	-	-	-	-
Ba ²⁺	-	-	-	-	-	-	-	-	-	-	-
Pb ²⁺	-	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.0–0.8	0.01	-
Tl ⁺	-	-	-	-	-	-	-	-	-	-	1.32

Notes: n = number of analytical points; *H₂O calculated on the basis of the formulae reported in Table 3.4.

TABLE 3.2 SC-XRD experimental details and crystal data for the selected hydropyrochlore crystals.

	L1	L8	L8_2Ti	L8_2Ti-W
a (Å)	10.555(2)	10.5567(8)	10.6444(8)	10.6397(6)
V (Å ³)	1175.7(5)	1176.5(3)	1206.0(3)	1204.4(2)
size (μm)	65 × 60 × 40	60 × 60 × 50	60 × 60 × 50	60 × 60 × 50
$\theta_{\max}$ (°; MoK α)	32	32	32	32
R_{int} (%)	9.24	5.60	5.38	5.14
indep. refl.	125	124	129	129
obs. refl.	97	108	103	105
$[F_o > 4\sigma(F_o)]$				
ref. param.	13	12	11	14
$R1_{\text{all}}$ (%)	4.85	3.33	4.74	5.32
$R1_{\text{obs}}$ (%)	3.28	2.74	3.74	3.99
$\Delta\rho_{\max}$ (e/Å ³)	0.69	0.41	1.16	1.68
$\Delta\rho_{\min}$ (e/Å ³)	−0.55	−0.79	−0.77	−0.96

	L9	L9_Ti	L11	L14
a (Å)	10.5712(3)	10.6531(3)	10.585(4)	10.5578(3)
V (Å ³)	1181.3(1)	1209.0(1)	1186(1)	1176.9(1)
size (μm)	70 × 60 × 40	70 × 60 × 40	80 × 70 × 50	95 × 95 × 90
$\theta_{\max}$ (°; MoK α)	32	32	32	32
R_{int} (%)	5.27	4.25	13.16	4.80
indep. refl.	124	126	129	123
obs. refl.	108	97	77	109
$[F_o > 4\sigma(F_o)]$				
ref. param.	12	13	13	12
$R1_{\text{all}}$ (%)	3.05	6.27	9.39	3.39
$R1_{\text{obs}}$ (%)	2.46	4.09	4.81	2.98
$\Delta\rho_{\max}$ (e/Å ³)	0.53	1.04	0.96	0.37
$\Delta\rho_{\min}$ (e/Å ³)	−0.58	−1.81	−1.00	−0.94

3.1.3 Structural refinements

Structural refinements were carried out in the space group $Fd\bar{3}m$ using SHELXL (Sheldrick, 2015), setting the origin at $\bar{3}m$ (origin choice 2), which involves the A site at the Wyckoff position $16d$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), the B site at $16c$ (0, 0, 0), the Y site at $8b$ ($\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$) and the X site at $48f(x, \frac{1}{8}, \frac{1}{8})$. The x_{48f} coordinate was refined starting

from the value reported by Ercit et al. (1994). Convergence was achieved adopting an anisotropic model. With these sites alone, the atomic displacement parameter of the Y site, invariably extremely large, suggested intense positional disorder. A careful analysis of the ΔF map revealed the presence of a peak analogous to the ϕ'' site observed by Ercit et al. (1994). This peak corresponds to a partially occupied site here named Y' . The replacement of Y (8b) with Y' (32e) led to an improvement of the overall refinement. In both untreated and H₂O-Imb crystals an additional A' peak (32e) in the vicinity of the A site was observed. However, first attempts to model the positional disorder of the tunnel sites (A , A' , Y') without constraints still led to rather high displacement parameters along with a strong correlation with their occupancy factors. Thus, following the procedure of Ercit et al. (1994), some constraints were applied based on the following assumptions: *i*) the A site was considered to be occupied by (Sr+Na+Ca+Pb) only, and its occupancy factor was fixed accordingly; *ii*) the occupancy of A' was refined, and its atomic displacement parameter was constrained to be equal to that of the A site; *iii*) it was assumed that all K^+ is located at Y' along with the aqueous species to complete $\frac{1}{4}$ of the 32e position occupancy. When available, the cationic content was taken from EMPA data; in the other cases, given the low variability of the chemical composition among the selected crystals, the chemical constraints were assigned considering the overall averaged values (Table 3.1). All atoms but B and X were refined isotropically. For H₂O-Imb treated crystal (L8_2Tl-W), the same constraints were applied, but the occupancies of the A and Y' sites were refined. For Tl-Imb treated crystals, where A' is no longer observed, it was possible to model the A site using anisotropic displacement parameters. The occupancy of both A and Y' sites was refined leading to a satisfactory match between the number of electrons obtained by the refinement ($A = 56.8$, $Y' = 4.6$) and that calculated on the basis of chemical composition ($A = 55.5$, $Y' = 3.8$, see L9_Tl crystal in Table 3.1). The X site was refined using isotropic displacement parameters only for the L8_2Tl refinement.

Scattering curves for neutral atoms, taken from the *International Tables for Crystallography* (Wilson, 1992), were used as follows: $A = \text{Sr}$ vs. $\square$ (untreated crystals) or Tl vs. $\square$ (Tl-Imb and H₂O-Imb); $A' = \text{O}$ vs. $\square$ (untreated crystals) or Tl vs. $\square$ (H₂O-Imb); $B = \text{Nb}$ vs. Ti; $X = \text{O}$; $Y' = \text{K}$ vs. O (untreated crystals) or K vs. $\square$

(Tl-Imb and H₂O-Imb). Details of the data collections and structure refinements (Table 3.2) as well as bond distances and structural parameters (Table 3.3) are given for a selected set of crystals. Data related to the other crystals are given in Appendix A.

TABLE 3.3. Selected structural parameters for the selected hydropyrochlore crystals. Bond distances in Å, angles in °.

	L1	L8	L8_2Ti	L8_2Ti-W	L9	L9_Ti	L11	L14
n.e ⁻ (<i>A</i>)	4.4	4.2	61.0	22.8	4.2	56.8	4.0	4.2
n.e ⁻ (<i>A'</i>)	2.3	2.5	-	15.5	1.8	-	3.6	3.3
n.e ⁻ (<i>Y'</i>)	9.2	9.1	5.3	11.3	9.1	4.6	9.2	9.0
x_{48f} (<i>X</i>)	0.3126(4)	0.3130(3)	0.3102(9)	0.3114(6)	0.3129(3)	0.3104(8)	0.3137(7)	0.3135(3)
x_{32e} (<i>A'</i>)	0.518(2)	0.5178(16)	-	0.5235(7)	0.519(4)	-	0.516(3)	0.5149(12)
x_{32e} (<i>Y'</i>)	0.392(10)	0.396(4)	0.409(7)	0.436(3)	0.382(10)	0.404(5)	0.401(4)	0.401(2)
<i>A</i> - <i>X</i> (×6)	2.719(3)	2.717(2)	2.761(7)	2.751(5)	2.721(2)	2.761(7)	2.718(6)	2.713(2)
<i>A</i> - <i>Y'</i> (×2)	2.40(8)	2.44(4)	2.58(7)	2.88(4)	2.34(7)	2.54(5)	2.49(3)	2.49(2)
< <i>A</i> -O>	2.639	2.648	2.716	2.783	2.626	2.706	2.659	2.657
<i>B</i> - <i>X</i> (×6)	1.979(2)	1.981(1)	1.988(3)	1.991(2)	1.983(1)	1.990(3)	1.989(3)	1.983(1)
<i>A'</i> - <i>X</i> (×3)	2.78(3)	2.78(2)	-	2.842(9)	2.79(5)	-	2.78(4)	2.765(13)
(×3)	2.69(3)	2.69(2)	-	2.725(10)	2.69(5)	-	2.69(4)	2.688(13)
<i>A'</i> - <i>Y'</i> (×2)	2.73(11)	2.76(5)	-	3.29(4)	2.68(12)	-	2.78(6)	2.75(3)
< <i>A'</i> -O>	2.73	2.74	-	2.920	2.73	-	2.75	2.732
<i>Y'</i> - <i>X</i> (×3)	3.13(9)	3.09(4)	3.03(6)	2.84(4)	3.23(11)	3.07(4)	3.04(3)	3.04(2)
(×3)	3.49(11)	3.53(5)	3.75(8)	4.09(4)	3.38(11)	3.69(6)	3.59(3)	3.58(3)
< <i>Y'</i> - <i>X</i> >	3.31	3.31	3.39	3.47	3.31	3.38	3.32	3.31
<i>X</i> - <i>X</i> (u.)	2.800(6)	2.807(5)	2.788(14)	2.805(10)	2.809(5)	2.793(13)	2.825(11)	2.814(5)
<i>X</i> - <i>X</i> (s.)	2.798(3)	2.797(2)	2.834(5)	2.827(4)	2.801(2)	2.836(5)	2.801(4)	2.795(2)
< <i>X</i> - <i>X</i> >	2.799	2.802	2.811	2.816	2.805	2.815	2.813	2.805

TABLE 3.3 (*continued*)

$X-B-X$	90.0(2)	90.2(1)	89.0(4)	89.5(3)	90.1(1)	89.2(3)	90.5(3)	90.4(1)
$(X-B-X)'$	90.0(2)	89.8(1)	91.0(4)	90.5(3)	89.9(1)	90.8(3)	89.5(3)	89.6(1)
$B-X-B$	141.0(2)	140.8(2)	142.4(5)	141.7(4)	140.9(2)	142.3(5)	140.3(4)	140.5(2)
$B-X-A$	104.06(7)	104.12(5)	103.6(2)	103.8(1)	104.10(5)	103.7(2)	104.2(1)	104.21(5)
$A-X-A$	86.7(1)	86.78(8)	85.9(3)	86.3(2)	86.74(8)	86.0(3)	87.0(2)	86.94(9)
$\sigma^2(B)$	0.00	0.05	0.97	0.22	0.03	0.81	0.26	0.18

Notes: u. = unshared edge of the octahedron; s. = shared edge between *B* and *A* polyhedra. Bond angle variance (σ^2) was computed according to the formula proposed by Robinson *et al.* (1971).

3.1.4 Results and discussion

The crystal structure of hydropyrochlore from Lueshe here studied is topologically identical to that of cubic ($Fd\bar{3}m$) pyrochlores having a partially inverse character, and in particular it is rather similar to the one described by Ercit *et al.* (1994) for a sample from the same locality. Figure 3.1 shows the B_2X_6 framework of corner-linked octahedra forming tunnels along $[110]$, wherein the A , A' and Y' sites are located.

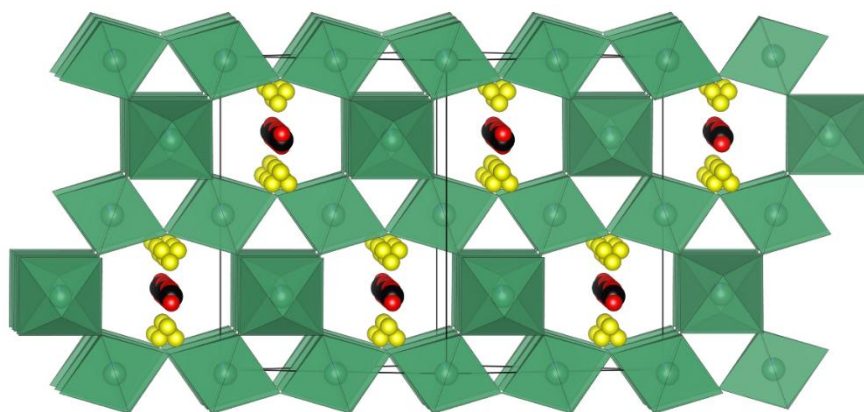


FIGURE 3.1. Structural sketch of hydropyrochlore from Lueshe. The B_2X_6 octahedral framework forms pseudo-hexagonal tunnels that host the partially occupied A (black), A' (red) and Y' (yellow) sites. Projection approximately down the $[110]$ axis.

Before imbibition all the tested crystals yielded a unit-cell parameter a ranging from 10.536 to 10.585 Å (Table 3.2), a range of values consistent with previous literature (Van Wambeke, 1978; Ercit *et al.*, 1994). Following Tl^+ imbibition, the first structural evidence of the Tl^+ uptake is an expansion of the unit-cell parameter ($a = 10.644$ – 10.672 Å; Figure 3.2) towards the value of 10.6829 Å measured for the synthetic $Tl^{+}_{2-x}Tl^{3+}_xNb_2O_{6+x}$ ($x = 0.07$) pyrochlore (Fourquet *et al.*, 1995). Accordingly, EMPA data obtained after Tl^+ imbibition showed a high Tl content accompanied by a high analytical total (99.06 wt.%; Table 3.1), suggesting a substantial dehydration consequent to Tl^+ incorporation.

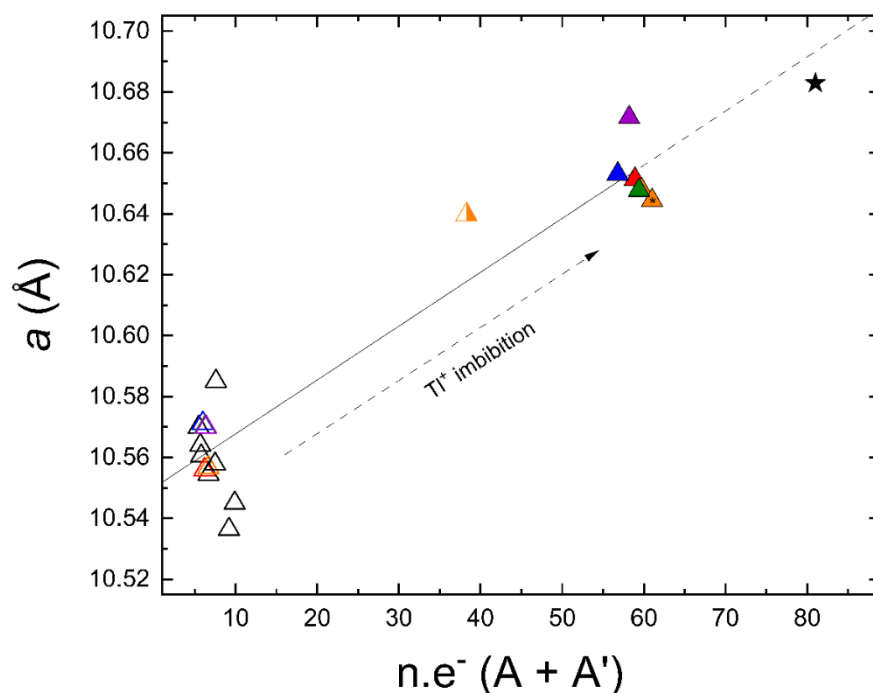


FIGURE 3.2. Unit-cell parameter plotted against the number of electrons at the A and A' sites. Empty, filled and half-filled symbols represent untreated, Tl-Imb and H_2O -Imb crystals, respectively (* denotes the second imbibition in Tl^{+} -rich solution). Crystals that underwent imbibition experiments are coloured as follows: L7 = red, L8 = orange, L9 = blue, L12 = green, L19 = purple. The black star symbol indicates $Tl^{+}_{2-x}Tl^{3+}_xNb_2O_{6+x}$ ($x = 0.07$) (Fourquet *et al.*, 1995). Regression line (fitting the equation $y = 0.0018x + 10.550$, $R^2 = 0.91$) is calculated with samples from this thesis only.

The A site is located in the centre of the tunnels, exhibiting a trigonal scalenohedral coordination determined by six oxygen atoms at X and other two at Y' , when the latter is occupied by aqueous species. In hydropyrochlore from Lueshe, A is dominated by structural vacancies with a mixed (Sr , Na , Ca , Pb^{2+}) cationic population ranging from 0.20 to 0.36 apfu. Sr is the most abundant cation and shows similar values in each measured grain (0.17–0.18 apfu), constantly higher than those reported in the literature (Van Wambeke, 1978; Ercit *et al.*, 1994). On the other hand, given its high leachability, the Na content is rather variable (0.01–0.17 apfu). Minor amounts of Ca (0.01 apfu) and Pb^{2+} (up to 0.01 apfu) are also observed.

After TI^+ imbibition, a dramatic increase of the site scattering ($n.e^-$ from ~ 4 to ~ 60) indicates the entry of a conspicuous amount of TI^+ at the A site (up to about 70%), leading to a lengthening of the $A-X$ distance (Table 3.3). After desorption experiments (L8_2TI-W), a remarkable decrease of electrons at the A site (from 61.0 to 38.3) is observed, suggesting partial TI^+ loss. Nonetheless, the cell parameter decreases less than expected (Figure 3.2). Further imbibition experiments in deionised water (L8_2TI-2W) led to a fracturing of the crystal, preventing any further SC-XRD investigation.

The additional A' peak in the vicinity of the A site, present in untreated crystals, is no longer observed after TI^+ imbibition. Interestingly, it occurs again after the final treatment in water thus corroborating the hypothesis that A' hosts mainly an aqueous species even if the presence of a minor amount of TI^+ at this site in the water-imbibed crystal cannot be completely ruled out. Given the high positional disorder of A and A' , atomic displacement parameters are strongly correlated with the site scattering. The disappearance of A' could then be related to the increase of the electrons number at the A site, which is in turn associated with an almost quadruple atomic displacement parameter (U_{iso} going from 0.0137 to 0.0415 $\text{\AA}^2$). Thus, this could explain either why A' is not observed after TI^+ imbibition and the new appearance of the extra site after the treatment in water.

As shown by chemical data, the B site exhibits a quite constant composition, with Nb as the main constituent (1.83–1.86 apfu) partially replaced by Ti (0.14–0.17 apfu). Such a limited chemical variation well reflects the very narrow range of the $B-X$ octahedral distances, either before (1.979–1.989 $\text{\AA}$) and after (1.988–1.995 $\text{\AA}$) the imbibition experiments. Although the B octahedron is not directly involved in the accommodation of TI^+ , it is affected by some geometrical variations, since it shares an edge with the A polyhedron. When the large TI^+ cation induces an increase of the $\langle A-X \rangle$ distance, the shared $X-X$ edge lengthens, becoming longer than the unshared one (Figure 3.3). Consequently, the B octahedron, extremely regular ($\langle \sigma^2 \rangle = 0.12$) before the TI^+ incorporation at A , slightly stretches along the 3-fold axis ($\langle \sigma^2 \rangle = 0.70$; Table 3.3). In principle, if A is occupied by a relatively highly charged, small cation (*e.g.*, Ce^{3+} or Ce^{4+}), the shared edge should shorten, and the octahedron should exhibit a slight flattening along its 3-fold axis.

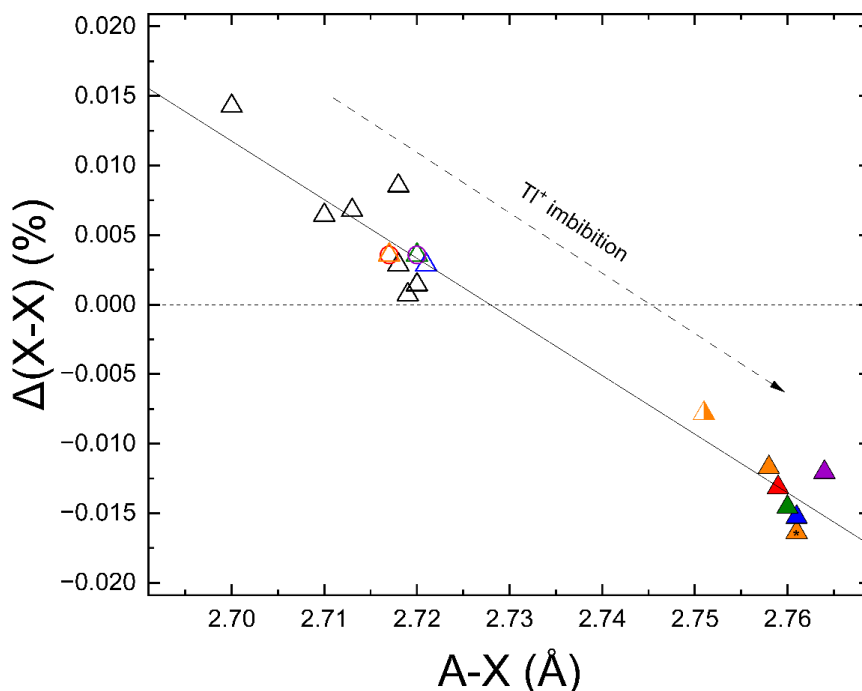


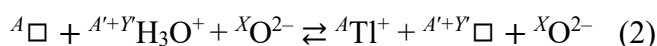
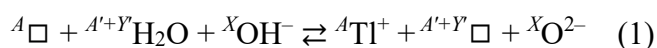
FIGURE 3.3. Unshared- and shared-octahedral edges variation as function of the $A-X$ distance [$\Delta(X-X) = (\text{unsh. } X-X - \text{sh. } X-X) / \langle X-X \rangle$]. Symbols as in Figure 3.2, except for L7 (= red empty circle) and L19 (= purple empty circle). In the synthetic $\text{Ti}^{+}_{2-x}\text{Ti}^{3+}_x\text{Nb}_2\text{O}_{6+x}$ ($x = 0.07$) pyrochlore ($\langle A-X \rangle = 2.813 \text{ \AA}$; Fourquet *et al.*, 1995), not reported in figure, the difference between unshared and shared octahedral edges is even more pronounced [$\Delta(X-X) = -0.0661$].

The Y' site, in untreated crystals, is assumed as completely occupied by aqueous species and K. Such an assignment is based on the hypothesis that the cation hosted at Y' , if any, should be the largest one (Ercit *et al.*, 1993), thus implying a certain degree of inversion already inferred by Ercit *et al.* (1994) for hydropyrochlore from Lueshe. The coordination sphere around Y' when it hosts K is achieved by six oxygen atoms at X (Table 3.3) and, if H_2O occupies the A' site, by two additional oxygen atoms ($Y'\text{K}-A'\text{O}$ distance from 2.68 to 2.86 $\text{\AA}$). Noteworthy, the $Y'-A$ distance is far too short to justify a cation-cation separation: consequently, when Y' is occupied by K, the A site must be vacant. The number of vacancies at A calculated for all the X-rayed crystals satisfies this requirement rather well, taking into

consideration the uncertainty of the indirect determination method, especially in the presence of heavy elements (Table 3.1). Constraints also exist when Y' is occupied by aqueous species: the site is surrounded by eight partially occupied A' sites, but only three $A'-Y'$ distances are suitable for $O\cdots O$ separations. Moreover, the occupancy of A' is also prevented by the occurrence of cations at A . Thus, even in the case of a completely empty A site, the maximum amount of H_2O at the A' site cannot exceed $\frac{3}{8}$, and the maximum total amount of H_2O pfu can be described as follows: $H_2O_{\max} = Y'1 + 3/8A\Box$, where $A\Box$ represents the vacancies (pfu) at A (Ercit *et al.*, 1994). Such a configuration allows $O\cdots O$ bridges between oxygen atoms belonging to aqueous species ($A'O-Y'O$ in the range 2.68–2.86 Å).

After the incorporation of thallium, the number of electrons at the Y' site decreases to about half of that in untreated crystals. At this point, Y' should be predominantly vacant, hosting most of the initial K together with very minor Tl^+ , as deduced from a comparison between the refined site scattering and the EMPA data. Moreover, the persistence of a small number of H_2O groups at this site cannot be ruled out, being also confirmed by FT-IR investigations (*vide infra*). Indeed, the large amount of Tl^+ incorporated at A requires a vacancy-dominated Y' site, because of the above discussed stereochemical reasons ($A-Y'$ distance ranging from 2.51 to 2.58 Å). In particular, Y' , which can be occupied up to $\frac{1}{4}$ (= 1 pfu) if A is completely vacant, must have additional vacancies at least equal to $1/32$ (= $\frac{1}{8}$ pfu) of the sum of the A cations pfu ($Y'\Box \geq \frac{3}{4} + \Sigma_{Acat.}/8$). This is verified also for L9_Tl, within the experimental uncertainty (Table 3.1).

The entry of the above-described amounts of Tl^+ requires necessarily a loss of positive charge to achieve charge neutrality. The cations that could potentially exchange with Tl^+ , in particular Sr^{2+} and K^+ , are not enough and tend to be retained in the structure after Tl^+ incorporation (Table 3.1). Thus, charge neutrality must be achieved mainly by H^+ loss. To account for the site scattering decrease at the Y' and A' sites, as well as the high analytical total after Tl^+ imbibition, the following two balancing mechanisms are plausible:



In the hypothesis that the aqueous species at A' and Y' before Tl^+ incorporation is represented by water molecules, a dehydrogenation should occur at the anionic X site (1) concurrently with the entry of Tl^+ . As shown in Table 3.4, the two mechanisms lead to formulae with different degrees of $OH^- \rightarrow O^{2-}$ substitution at X , even before Tl^+ incorporation. In the hypothesis that the untreated mineral contains H_2O [mechanism (1)], a very large amount of OH^- should replace O^{2-} at the X site, which should thus show a very low bond-valence sum if the contribution of the covalent O–H bond is neglected. The bond-valence sums on the X site [parameters from Brese and O’Keeffe (1991) and Ferraris and Ivaldi (1988)] were calculated on the basis of the formulae derived from both mechanism (1) and (2) (Table 3.4, Figure 3.4). In both cases, the obtained values (1.84/1.93, 1.86/1.98, 1.88/2.00 valence units for L1, L11 and L14 respectively) are hardly compatible with the large extent of hydrogenation at the X site required by the balancing mechanism (1). This may constitute an indirect proof of the presence of H_3O^+ in the structure.

It can be noted that in L1 and L14 crystals (Table 3.4) the structural vacancies rather than the aqueous species are dominant at $(A+A')$. Therefore, on the basis of the current nomenclature system (Atencio *et al.*, 2010; Atencio, 2021), they are to be referred to as hydrokenopyrochlore [ideal formula $(\square, \#)_2Nb_2O_6 \cdot H_2O$ (Biagioni *et al.*, 2018)].

TABLE 3.4. Crystal-chemical formulae for untreated pyrochlore-supergroup minerals from Lueshe and for Tl-Imb crystal.

L1	$[\square_{1.13}(\text{H}_2\text{O})_{0.58}\text{Sr}_{0.18}\text{Na}_{0.09}\text{Ca}_{0.01}\text{Pb}_{0.01}]_{\Sigma 2.00}(\text{Nb}_{1.83}\text{Ti}_{0.17})$ [O _{4.43} (OH) _{1.57}][(H ₂ O) _{0.89} K _{0.11}]	(1)
	$[\square_{1.13}(\text{H}_3\text{O})_{0.58}\text{Sr}_{0.18}\text{Na}_{0.09}\text{Ca}_{0.01}\text{Pb}_{0.01}]_{\Sigma 2.00}(\text{Nb}_{1.83}\text{Ti}_{0.17})$ [O _{5.90} (OH) _{0.10}][(H ₃ O) _{0.89} K _{0.11}]	(2)
L11	$[(\text{H}_2\text{O})_{0.90}\square_{0.89}\text{Sr}_{0.18}\text{Na}_{0.01}\text{Ca}_{0.01}\text{Pb}_{0.01}]_{\Sigma 2.00}(\text{Nb}_{1.84}\text{Ti}_{0.16})$ [O _{4.36} (OH) _{1.64}][(H ₂ O) _{0.89} K _{0.11}]	(1)
	$[(\text{H}_3\text{O})_{0.90}\square_{0.89}\text{Sr}_{0.18}\text{Na}_{0.01}\text{Ca}_{0.01}\text{Pb}_{0.01}]_{\Sigma 2.00}(\text{Nb}_{1.84}\text{Ti}_{0.16})$ O ₆ [(H ₃ O) _{0.74} (H ₂ O) _{0.15} K _{0.11}]	(2)
L14	$[\square_{0.92}(\text{H}_2\text{O})_{0.83}\text{Sr}_{0.18}\text{Na}_{0.05}\text{Ca}_{0.01}\text{Pb}_{0.01}]_{\Sigma 2.00}(\text{Nb}_{1.84}\text{Ti}_{0.16})$ [O _{4.38} (OH) _{1.62}][(H ₂ O) _{0.91} K _{0.09}]	(1)
	$[\square_{0.92}(\text{H}_3\text{O})_{0.83}\text{Sr}_{0.18}\text{Na}_{0.05}\text{Ca}_{0.01}\text{Pb}_{0.01}]_{\Sigma 2.00}(\text{Nb}_{1.84}\text{Ti}_{0.16})$ O ₆ [(H ₃ O) _{0.79} (H ₂ O) _{0.12} K _{0.09}]	(2)
L9_Tl	$(\text{Tl}_{1.29}\square_{0.53}\text{Sr}_{0.17}\text{Na}_{0.01})_{\Sigma 2.00}(\text{Nb}_{1.83}\text{Ti}_{0.17})[\text{O}_{5.56}(\text{OH})_{0.44}](\square_{0.91}\text{K}_{0.06}\text{Tl}_{0.03})$	

Notes: crystal-chemical formulae were obtained assuming that the initial aqueous species in untreated crystals is H₂O (1) or mainly H₃O⁺ (2).

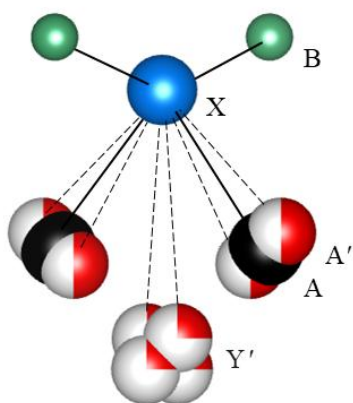


FIGURE 3.4. Sketch of the structural environment of the *X* site (view along [100]). The bond valence sum on the *X* site was calculated considering the contribution of two *B* sites, two *A* sites, one (½ + ½) *A'* site and ¼ *Y'* site (see text for explanation).

The IR spectrum of untreated sample acquired with the KBr pellet method (Figure 3.5a) is similar to that obtained by Nasraoui *et al.* (1999), yielding a large absorption band from 3600 to 3000 cm^{-1} in the O–H stretching zone. In particular, at least two peaks at 3400 and 3230 cm^{-1} due to O–H stretching in different crystal-chemical environments are observed. The H–O–H bending mode occurs at 1634 cm^{-1} . An additional peak at 1404 cm^{-1} in the spectrum could be assigned to C–O vibration modes, possibly due to relict carbonate minerals included in the studied sample. The two bands visible at 1035 and 883 cm^{-1} are due to the vibration modes of P–O bonds, confirming the presence of phosphates inclusions (crandallite–goyazite series). The band at 1035 cm^{-1} exhibits a shoulder at 960 cm^{-1} , that together with a very intense peak at around 650 cm^{-1} (out of scale in Figure 3.5a) can be attributed to the stretching vibrations of the octahedral bonds (Nb–O, Ti–O) (Geisler *et al.*, 2004).

The spectrum directly acquired from a minute fragment of untreated pyrochlore (Figure 3.5b) shows a similar profile to that obtained from KBr pellet, but the intensities of the peaks are stronger, enough to make the band in the O–H stretching zone severely out of scale. However, there is a key difference between these spectra, namely the presence of an unusual peak at 1729 cm^{-1} . According to Chukanov (2014), an anomalous band in the range between 1700–1800 cm^{-1} , usually observed in the IR spectra of hydronium-bearing minerals, is interpreted as the ν_4 bending mode of H_3O^+ [*e.g.*, 1730 cm^{-1} in IR spectrum of larisaite, $\text{Na}(\text{H}_3\text{O}^+)(\text{UO}_2)_3(\text{SeO}_3)_2\text{O}_2 \cdot 4(\text{H}_2\text{O})$, Chukanov *et al.* (2004); 1725 cm^{-1} in IR spectrum of chernikovite, $(\text{H}_3\text{O}^+)(\text{UO}_2)(\text{PO}_4) \cdot 4(\text{H}_2\text{O})$, Armstrong and Clark (2010)]. It is important to remark that none of the minerals associated with hydropyrochlore from Lueshe exhibits a peak close to that observed at 1729 cm^{-1} . On the other hand, the signal ascribable to other vibrational modes of the hydronium ion ($\nu_1 = 3160 \text{ cm}^{-1}$; $\nu_2 = 1050\text{--}1140 \text{ cm}^{-1}$; $\nu_3 = 3320 \text{ cm}^{-1}$), in particular ν_2 , may be hidden by the presence of strong O–H bands and significant inclusions of phosphates and carbonates in the sample.

The IR spectrum of L19_Tl shows much less intense and broader bands corresponding to the O–H stretching (3550–3000 cm^{-1}) and the H–O–H bending mode (1641 cm^{-1} ; Figure 3.5c), indicating a much lower water content, which can

be estimated as roughly 5% of that originally present in the untreated sample, in good agreement with the crystal-chemical formula obtained for the L9_Tl crystal (Table 3.4), which requires $\text{H}_2\text{O} = 0.70$ wt.% whereas in the untreated crystals the calculated H_2O ranges from 12.43 to 14.19 wt.%. Noteworthy, the peak at 1729 cm^{-1} is no longer observed in the spectrum of the Tl^+ -rich crystal, suggesting loss of H_3O^+ in favour of Tl^+ .

Imbibition experiments in deionised water cause an increase in intensity of the bands ascribed to the aqueous species (Figure 3.5d), although it does not reach the values observed in untreated samples, in agreement with the entry of aqueous species (H_2O or H_3O^+) concomitant with Tl^+ partial loss. Interestingly, the peak at 3281 cm^{-1} in the O–H stretching zone is much sharper than the corresponding bands observed in the other spectra, possibly indicating a partial ordering of the molecules in the tunnels of the pyrochlore structure. The occurrence of an additional peak at 1539 cm^{-1} remains unexplained.

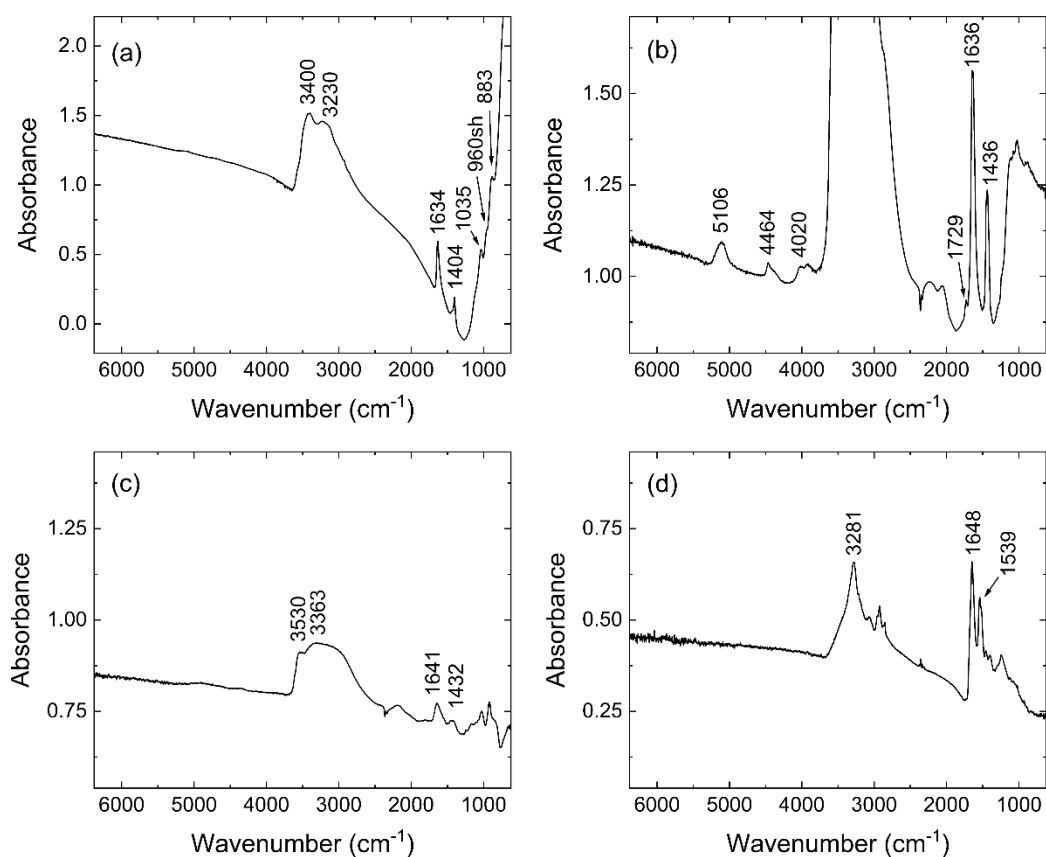


FIGURE 3.5. FT-IR spectra acquired from **(a)** KBr pellet containing untreated hydropyrochlore powder; **(b)** a small, untreated hydropyrochlore fragment. The weak bands in the range 4000–5100 cm^{-1} are attributable to water combination modes; **(c)** L19_Tl crystal; **(d)** L19_Tl-W crystal. Bands in the range 2800–3000 cm^{-1} are due to C–H vibrational modes, possibly due to contamination from possible glue residues on the crystal.

3.1.5 Conclusions

This chapter focused on the structural variations subsequent to imbibition experiments and unequivocally demonstrated that this cation is not merely adsorbed on the surface of the crystal, instead it enters the structure. In particular, the considerable structural changes observed are consistent with the entry of conspicuous amounts of Tl^+ at the *A* site (up to about 70%), leading to a significant increase of the volume of the *A* polyhedron, which in turn causes the expansion of the unit cell and minor adjustments in the edge-sharing *B* octahedron. Tl^+

incorporation appears strongly linked to the initial amount of aqueous species (namely hydronium ions) rather than the amount of structural vacancies (Figure 3.6). Although the predominance of neutral H₂O molecules at the interstitial sites of hydropyrochlore from the Lueshe deposit is widely accepted by the mineralogical community, both FT-IR and crystal-chemical data here obtained provide evidence that the dominant species could actually be the hydronium ion, with significant implications also on the nomenclature of the pyrochlore supergroup. Nonetheless, the choice between H₂O or H₃O⁺ is far from obvious. The presence of hydronium in minerals has been investigated with different spectroscopical methods (IR, Raman, ¹H and ²H NMR, *etc.*) through the years, but the proof of its actual presence is, in many cases, weak or indirect (Ripmeester *et al.*, 1986). Interestingly, neutron powder diffraction studies on antimonic acid having a pyrochlore-like structure demonstrated the occurrence of interstitial hydronium ions (Slade *et al.*, 1996; Alonso and Turrillas, 2005), confirming that H₃O⁺ can be actually hosted within the pyrochlore tunnels.

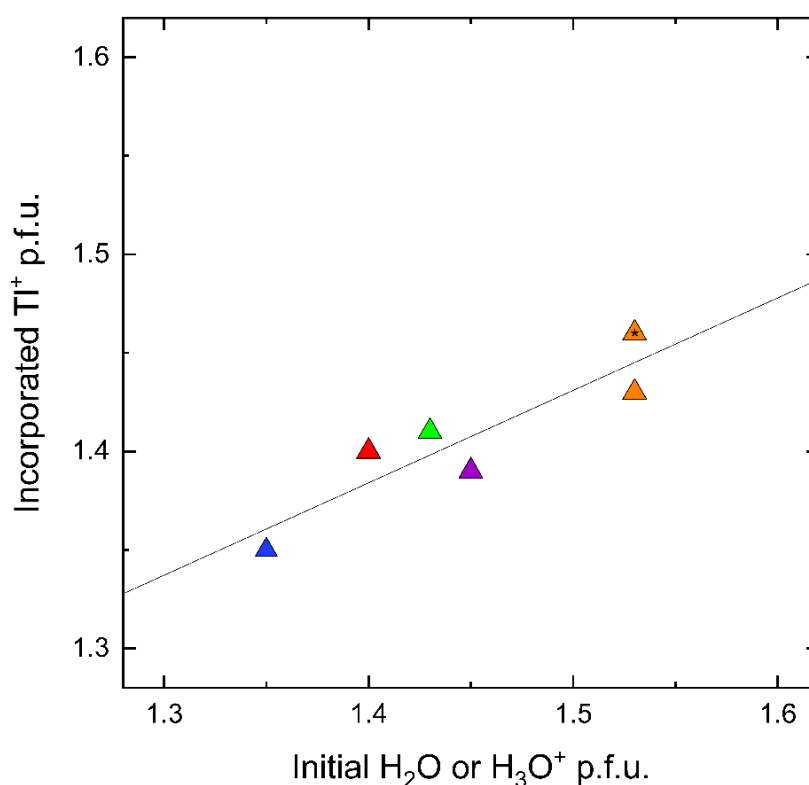


FIGURE 3.6. Relation between the amount of TI^+ incorporated and the initial content of H_3O^+ (or H_2O) at $A'+Y'$. Symbols as in Figure 3.2. Solid line (fitting the regression equation: $y = 0.5x + 0.7$, $R^2 = 0.82$) shows the rough correlation between the two parameters. The amount of initial H_2O or H_3O^+ has been indirectly estimated from the number of electrons found at A' and Y' . Analogously, the TI^+ values were tentatively derived from the refined site scattering at the A site and taking into account the Sr content as found by microprobe analysis (L9_Tl).

In summary, this study underlines the capabilities of the mineral from Lueshe to incorporate remarkable amounts of TI^+ , although there are still some open questions about the actual suitability of hydropyrochlore as a sink for thallium dispersed in polluted natural or industrial aqueous solutions. Worthy to note, imbibition in deionised water caused the loss of about one third of the total TI^+ previously incorporated, thus it will still be necessary to investigate the effect of other parameters (*i.e.*, pH of the solution, temperature, pressure) on the capability of the structure to retain the thallium incorporated as well as the influence of other

variables (*e.g.*, duration of the imbibition experiments, concentration of TI^+ in the solutions, presence of competing cations in the solution, *etc.*) on the performance of the uptake/release process.

3.2 Insights into the kinetics of the Tl-incorporation reaction

3.2.1 Introduction

It is known that pyrochlore minerals that host large amounts of highly mobile species such as water in their tunnel sites exhibit significant ion-exchange properties (Zoppi, 2004), because water molecules are only weakly bonded to tunnel walls (Ercit *et al.*, 1994). In nature, strongly hydrated pyrochlores exist as alteration products of usually anhydrous magmatic pyrochlores, *e.g.*, hydropyrochlore (Ercit *et al.*, 1994), hydrokenopyrochlore (Biagioni *et al.*, 2018), and hydrokenomicrolite (Andrade *et al.*, 2013a).

All these considerations have recently driven research towards a promising application in the environmental field: the use of hydropyrochlore and hydrokenopyrochlore, which contain substantial amounts of water, as mineral sinks for hazardous water pollutants like monovalent thallium (Taddei *et al.*, 2024). The rising concern over increasing thallium pollution, which poses severe environmental and health risks due to its high toxicity and enhanced mobility in aqueous matrices, underlines the importance of pursuing this research. This issue is further exacerbated by the progressive discovery of new and unexpected sources of Tl pollution, *e.g.*, in lithium ores, whose exploitation is necessary for green energy production (Liu *et al.*, 2023). Taddei *et al.* (2024) observed that the structures of hydropyrochlore and hydrokenopyrochlore can incorporate large amounts of Tl^+ in a relatively short time (≤ 5 days), with an ion-exchange mechanism involving an aqueous species (either $\text{H}_2\text{O} + \text{OH}^-$ or H_3O^+). In the present chapter, further investigations on this mechanism were pursued, focusing on the kinetics of the ion-exchange process. The experiments were carried out using the same starting material, namely hydropyrochlore and hydrokenopyrochlore from the Lueshe carbonatitic deposit (Bwito, Rutshuru Territory, North Kivu, D.R. Congo), with ideal formulae $(\text{H}_2\text{O}, \square)_2\text{Nb}_2(\text{O}, \text{OH})_6(\text{H}_2\text{O})$ and $(\square, \text{H}_2\text{O})_2\text{Nb}_2(\text{O}, \text{OH})_6(\text{H}_2\text{O})$, respectively. Notably, the hydrokenopyrochlore sample used in this chapter, as well as those investigated by Taddei *et al.* (2024), represent the first occurrence of this mineral at the Lueshe carbonatite. Hydropyrochlore and hydrokenopyrochlore from

Lueshe display a partially inverse character, with a unique enrichment in K^+ which is fully ordered at Y (Ercit *et al.*, 1993, 1994). Due to this unusually high K^+ content, the mineral was originally named *kalipyrochlore* (Van Wambeke, 1978), long before the current nomenclature was approved by IMA-CNMNC (Atencio *et al.*, 2010; Atencio, 2021).

3.2.2 *Experimental methods*

Electron microprobe analyses (EMPA)

The composition of two small single crystals (Hkpcl and Hpcl) was determined by means of a JEOL JXA-8230 electron microprobe, operated at 10 nA and 15 kV in wavelength-dispersive mode. Counting times were 30 s (Na, Si, Ca, Mn, Fe, Zr, Sn, Sb, Ba, Pb, Th, U, F), 20 s (Ti, Sr, Ta) and 15 s (Al, K, Nb, Ce, La, Tl).

Chemical data were normalised on the basis of 2 B cations pfu, with all iron considered as Fe^{3+} . The H_2O content was inferred from chemical and structural data. Average values for both crystals are listed in Table 3.5.

Imbibition experiments

The two single crystals were immersed in a solution of thallium(I) formate dissolved in deionised water. The Tl^+ concentration used was 1M for Hkpcl and 0.1M for Hpcl. The crystals were soaked for increasing durations (30, 60, 120, 240 and 480 minutes), with cumulative soaking times of 30, 90, 210, 450 and 930 minutes. After the fourth imbibition experiment (240 minutes, or 450 minutes cumulatively), Hpcl fractured and detached from the Kapton loop; only a small fragment ($10 \times 10 \times 5 \mu m$) remained attached to the sample holder, preventing further analysis. Subsequently to the treatments, the crystals underwent a gradual colour change, shifting from colourless to pale yellow, bright orange and eventually to dark brown.

Single-crystal X-ray diffraction (SC-XRD)

Hkpcl and Hpcl were handpicked from the polished mount used for the microprobe study to undergo X-ray diffraction data collection, which was repeated after each

imbibition experiment. Unit-cell parameters and other details of the data collections are listed in Table 3.6. Due to the fracture of Hpcl after the 240-minute imbibition experiment, only unit-cell parameters could be obtained using 42 reflections within the range $6.63^{\circ} < \theta < 20.28^{\circ}$ (exposure time = 11 s, step size = 1.5°).

TABLE 3.5. Average microprobe analyses (wt.% oxides) of untreated Hkpcl and Hpcl along with the apfu values normalised on the basis of $\Sigma B = 2$ apfu.

	Hkpcl	σ	Hpcl	σ	Element	Hkpcl	Hpcl
<i>n</i>	4		4		apfu		
<i>B</i> _{cations}							
Al ₂ O ₃	n.d.	-	0.01	0.02	Al	-	-
Fe ₂ O ₃	0.06	0.05	0.12	0.06	Fe ³⁺	-	0.01
TiO ₂	3.49	0.21	3.95	0.31	Ti	0.14	0.16
Nb ₂ O ₅	75.86	2.04	74.20	0.61	Nb	1.86	1.83
Sb ₂ O ₅	0.03	0.02	0.02	0.02	Sb ⁵⁺	-	-
<i>A</i> _{cations}							
Na ₂ O	0.08	0.04	0.06	0.01	Na	0.01	0.01
K ₂ O	1.42	0.29	1.74	0.35	K	0.10	0.12
Tl ₂ O	n.d.	-	0.06	0.07	Tl ⁺	-	-
CaO	0.11	0.02	0.07	0.01	Ca	0.01	-
MnO	n.d.	-	0.01	0.02	Mn ²⁺	-	-
SrO	5.49	0.19	5.81	0.22	Sr	0.17	0.18
BaO	0.15	0.03	0.15	0.02	Ba	-	-
PbO	0.34	0.02	0.25	0.04	Pb	0.01	-
Ce ₂ O ₃	0.03	0.05	0.07	0.07	Ce	-	-
ThO ₂	n.d.	-	0.04	0.04	Th	-	-
UO ₂	0.07	0.04	0.09	0.06	U ⁴⁺	-	-
Total	87.13		86.65				
H ₂ O*	8.17		9.93		H ₂ O	2.95	3.62
TOTAL	95.30		96.58				

Notes: σ = standard deviation; *n* = number of analytical points; n.d. = not detected; *H₂O calculated on the basis of the formulae (1) and (3).

TABLE 3.6. Single-crystal X-ray diffraction experimental details and crystal data of Hkpcl and Hpcl before and after each Tl imbibition.

	Hkpcl	Hkpcl_30min	Hkpcl_60min	Hkpcl_120min	Hkpcl_240min	Hkpcl_480min
a (Å)	10.5674(3)	10.6159(12)	10.6496(14)	10.6491(16)	10.6614(9)	10.6673(9)
V (Å ³)	1180.06(10)	1196.4(4)	1207.8(5)	1207.6(5)	1211.8(3)	1213.8(3)
size (μm)	60 × 50 × 30	60 × 50 × 30	60 × 50 × 30	60 × 50 × 30	60 × 50 × 30	60 × 50 × 30
$\theta_{\max}$ (°; MoK α)	32.0	32.0	31.9	31.9	31.9	31.9
R_{int} (%)	4.58	9.68	9.63	7.68	6.32	10.45
indep. refl.	123	129	129	129	129	129
obs. refl.	109	101	85	109	95	77
$[F_o > 4\sigma(F_o)]$						
Ref. param.	13	14	15	16	15	15
$R1_{\text{all}}$ (%)	3.30	10.27	9.31	5.34	4.08	8.08
$R1_{\text{obs}}$ (%)	2.79	8.85	5.78	4.72	2.59	3.69
$\Delta\rho_{\max}$ (e/Å ³)	0.46	1.81	0.97	1.52	1.35	0.74
$\Delta\rho_{\min}$ (e/Å ³)	−0.72	−1.05	−1.24	−0.99	−0.71	−1.36

TABLE 3.6 (*continued*)

	Hpcl	Hpcl_30min	Hpcl_60min	Hpcl_120min
a (Å)	10.5807(5)	10.6171(9)	10.6312(10)	10.6413(7)
V (Å ³)	1184.52(17)	1196.8(3)	1201.6(3)	1205.0(2)
size (μm)	40 × 40 × 40	40 × 40 × 40	40 × 40 × 40	40 × 40 × 40
$\theta_{\max}$ (°; MoK α)	31.9	32.0	32.0	31.9
R_{int} (%)	4.58	7.42	9.73	7.42
indep. refl.	123	129	129	129
obs. refl.	107	105	92	96
$[F_o > 4\sigma(F_o)]$				
Ref. param.	13	15	16	16
$R1_{\text{all}}$ (%)	2.94	7.75	7.86	5.73
$R1_{\text{obs}}$ (%)	2.35	6.54	4.98	4.26
$\Delta\rho_{\max}$ (e/Å ³)	0.48	1.02	0.86	0.88
$\Delta\rho_{\min}$ (e/Å ³)	−0.46	−1.24	−0.80	−1.14

Notes: after the 240 minutes long TI imbibition of Hpcl, the collected unit-cell parameter was $a = 10.657(6)$ Å [$V = 1210.3(2)$ Å³].

Structure refinements

Structure refinements were carried out in the space group $Fd\bar{3}m$ (origin choice 2) using SHELXL (Sheldrick, 2015). The starting atomic positions were assigned as follows: the A site at Wyckoff position $16d$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), the B site at $16c$ ($0, 0, 0$), the Y site at $8b$ ($\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$) and the X site at $48f$ ($x, \frac{1}{8}, \frac{1}{8}$). The only free coordinate was that of the X site, initially set to the value reported by Ercit *et al.* (1994). All refinements were performed under the assumption that the X site is fully occupied by oxygen, while the Nb/Ti ratio at the B site was fixed to that obtained with the EMPA analyses. The refinement procedure followed the approach described by Taddei *et al.* (2024), with some differences between untreated and Tl-treated samples.

For untreated crystals, the occupancy of the A site was fixed to the values obtained from EMPA, without accounting for potential water content. Instead, the latter was assigned to an A' site displaced to a $32e$ position nearby A , whose occupancy was refined, with its displacement parameters constrained to be equal to those of A .

Extremely large displacement parameter values, indicating significant positional disorder at $8b$ and its vicinity, led to the replacement of this site by a slightly displaced one located at a $32e$ position (Y'), corresponding to the ϕ'' site identified by Ercit *et al.* (1994). This adjustment yielded more reasonable displacement parameters. In the models of untreated crystals, Y' was assumed to host all K^+ (as determined via microprobe analysis), along with an aqueous species (either H_2O or H_3O^+) to complete $\frac{1}{4}$ of the occupancy of the $32e$ position.

Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992) and used as follows: $A = Sr$ vs. $\square$ (untreated crystals) or Tl vs. $\square$ (Tl-treated crystals); $A' = O$ vs. $\square$ (untreated crystals) or Tl vs. $\square$ (Tl-treated crystals); $B = Nb$ vs. Ti; $X = O$; $Y' = K$ vs. O (untreated crystals) or O vs. $\square$ (Tl-treated crystals).

The refinement methods for the Tl-treated samples were the same used for untreated ones, except for the refinement of the occupancies of A , A' , and Y' .

Finally, convergence was achieved by refining anisotropic atomic displacement parameters (ADPs) for all atoms except *Y* (all refinements), *A* and *A'* (Hpcl and Hkpc1_30min refinements), which were refined with isotropic ADPs.

Details of data collection and structural refinements are summarised in Table 3.6, while bond distances and structural parameters are provided in Table 3.7.

TABLE 3.7. Selected structural parameters for Hkpc1 and Hpcl, before and after Tl imbibitions. Bond distances in Å, angles in °.

	Hkpc1	Hkpc1_30 min	Hkpc1_60 min	Hkpc1_ 120min	Hkpc1_ 240min	Hkpc1_ 480min	Hpcl	Hpcl_30 min	Hpcl_60 min	Hpcl_120 min
n.e ⁻ (A)	3.8	10.0	26.7	33.8	42.9	58.3	3.4	17.3	26.2	29.2
n.e ⁻ (A')	1.6	4.1	4.2	6.3	17.8	4.9	4.2	4.2	6.0	7.6
n.e ⁻ (Y')	9.1	23.7	14.7	12.5	10.9	7.4	9.3	16.6	11.2	9.3
x_{48f} (X)	0.3132(3)	0.3130(13)	0.3118(11)	0.3120(4)	0.3106(6)	0.3108(8)	0.3126(3)	0.3118(10)	0.3131(8)	0.3117(6)
x_{32e} (A')	0.516(8)	0.531(3)	0.542(11)	0.539(3)	0.5214(15)	0.528(10)	0.5131(8)	0.554(5)	0.548(3)	0.538(3)
x_{32e} (Y')	0.396(4)	0.327(3)	0.418(7)	0.425(4)	0.440(5)	0.439(8)	0.3491(16)	0.333(3)	0.333(3)	0.413(6)
A–X (×6)	2.718(2)	2.732(10)	2.750(8)	2.748(3)	2.762(5)	2.762(6)	2.7258(19)	2.741(8)	2.735(6)	2.749(5)
A–Y' (×2)	2.44(5)	3.18(4)	2.68(8)	2.75(5)	2.94(6)	2.92(9)	2.765(16)	3.07(4)	3.08(4)	2.62(6)
<A–O>	2.649	2.844	2.733	2.749	2.807	2.802	2.736	2.823	2.820	2.717
B–X (×6)	1.9837(11)	1.992(5)	1.994(4)	1.9950(16)	1.992(2)	1.994(3)	1.9843(9)	1.988(3)	1.996(3)	1.992(2)
A'–X (×3)	2.69(9)	2.710(12)	2.75(3)	2.742(8)	2.737(5)	2.738(11)	2.703(9)	2.78(2)	2.752(14)	2.741(9)
(×3)	2.77(9)	2.87(4)	2.96(12)	2.94(4)	2.842(17)	2.743(11)	2.770(9)	3.04(6)	2.99(4)	2.93(4)
A'–Y' (×2)	2.73(10)	2.70(5)	3.43(14)	3.44(6)	3.30(6)	3.41(14)	3.00(3)	3.12(7)	3.02(5)	3.30(8)
<A'–O>	2.73	2.77	3.00	2.99	2.92	2.91	2.805	2.96	2.91	2.95
Y'–X (×3)	3.09(5)	2.89(4)	2.95(8)	2.90(5)	2.83(6)	2.84(9)	3.056(13)	2.95(4)	2.94(4)	2.98(5)
(×3)	3.53(5)	3.04(4)	3.32(8)	3.24(5)	3.11(6)	3.12(4)	3.38(2)	3.13(4)	3.13(4)	3.37(5)
<Y'–X>	3.31	2.97	3.14	3.07	2.97	2.98	3.218	3.04	3.04	3.18
X–X (u.)	2.813(5)	2.822(19)	2.813(17)	2.816(7)	2.798(10)	2.803(13)	2.807(3)	2.805(16)	2.828(13)	2.810(10)
X–X (s.)	2.7986(15)	2.812(6)	2.827(6)	2.826(3)	2.837(4)	2.837(5)	2.8051(11)	2.819(6)	2.816(4)	2.826(4)
<X–X>	2.806	2.817	2.820	2.821	2.818	2.820	2.806	2.812	2.822	2.818

TABLE 3.7 (*continued*)

$X-B-X$	90.27(12)	89.8(5)	89.7(4)	89.80(18)	89.2(2)	89.3(3)	90.04(10)	89.7(4)	89.8(3)	89.7(2)
$X-B-X'$	89.73(12)	90.2(5)	90.3(4)	90.20(18)	90.8(2)	90.7(3)	89.96(10)	90.3(4)	90.2(3)	90.3(2)
$B-X-B$	140.68(18)	140.7(7)	141.5(8)	141.3(3)	142.2(3)	142.0(5)	141.00(14)	141.4(6)	140.7(5)	141.5(3)
$B-X-A$	104.15(5)	104.1(2)	103.91(18)	103.95(7)	103.72(10)	103.75(14)	104.05(4)	103.92(17)	104.14(13)	103.90(10)
$A-X-A$	86.83(9)	86.8(4)	86.4(3)	86.48(13)	86.06(18)	86.1(2)	86.66(8)	86.4(3)	86.8(2)	86.37(18)
$\sigma^2(B)$	0.09	0.05	0.09	0.05	0.66	0.53	0.00	0.09	0.06	0.12

Notes: u. = unshared edge of the octahedron; s. = shared edge between B and A polyhedra. Bond angle variance (σ^2) was computed according to the formula proposed by Robinson *et al.* (1971).

3.2.3 Results and discussion

Crystal-chemistry of the untreated samples

The two studied crystals are almost topologically identical to the samples reported in Taddei *et al.* (2024), which were extracted from the same sample. Minor differences in crystal-chemical features arise from the inherent chemical variability of these species, especially considering that the fragment underwent severe, heterogeneous weathering at the Lueshe carbonatitic deposit (Wall *et al.*, 1996; Nasraoui and Bilal, 2000).

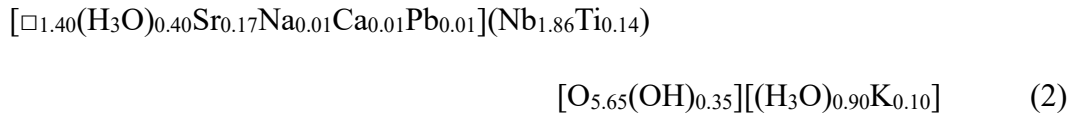
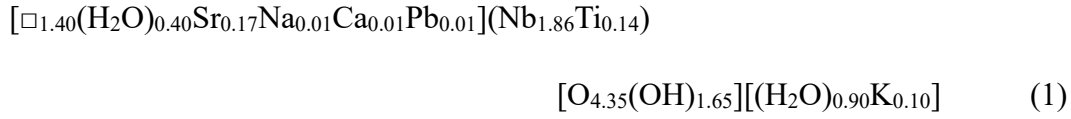
Before the imbibition experiments in Tl-rich solutions, the *a*-parameter of Hkpcl and Hpcl (Table 3.6) is comparable to that of other hydropyrochlores from the same locality (Van Wambeke, 1978; Ercit *et al.*, 1994; Taddei *et al.*, 2024). The *B* site is dominated by Nb (1.83–1.86 apfu), with a partial substitution by Ti (0.14–0.16 apfu) and Fe³⁺ (0.01 apfu in Hpcl), in agreement with the octahedral distances determined by SC-XRD investigations (Table 3.7). The dominant *A*-site cation is Sr (0.17–0.18 apfu), with very minor amounts of Na in both crystals (0.01 apfu) and, in Hkpcl, Ca and Pb (0.01 apfu).

The *A'* site in untreated crystals was assumed to mainly host an aqueous species (either H₂O or H₃O⁺), accommodating 0.40 apfu in Hkpcl and 1.05 apfu in Hpcl. This assumption is based on stereochemical considerations: in Hkpcl, the *A*–*Y'* distances are too short for stable O–H···O bonds (2.44 Å), whereas the slightly displaced *A'* site exhibits a more suitable *A'*–*Y'* distance (2.73 Å) for at least three out of eight possible positions. In Hpcl, the *A*–*Y'* distance is 2.765 Å, representing a reasonable separation for H-bridges; nonetheless, the amount of water hosted at 16*d* (and its vicinity) is more than double that of Hkpcl.

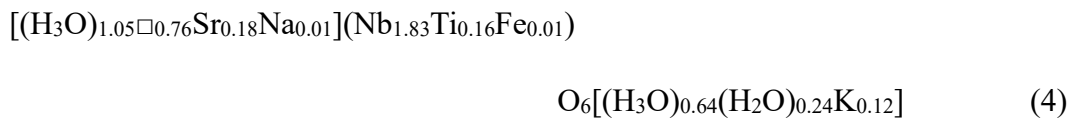
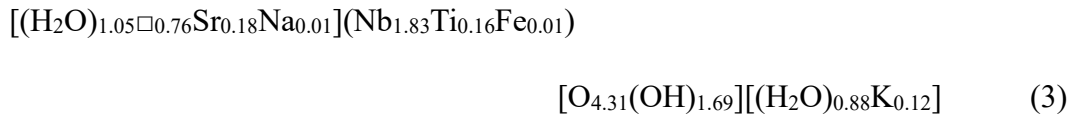
The *Y'* site, slightly displaced around the ideal 8*b* position, was considered fully occupied by minor K⁺ (0.10–0.12 apfu) and an aqueous species, assuming a moderately inverse character of the structure (Ercit *et al.*, 1993, 1994) for this species.

Lastly, a partial substitution of O by (OH)[−] at *X* was taken into account to achieve charge neutrality, with the extent of this substitution depending on whether H₂O or H₃O⁺ are hosted at the tunnel sites.

Based on the discussed data and the current nomenclature system (Atencio *et al.*, 2010; Atencio, 2021) both samples belong to the pyrochlore group, as the *B* site is dominated by Nb. Specifically, Hkpcl can be classified as a hydrokenopyrochlore, with a vacancy-dominated *A* site and a water-dominated *Y* site. Its crystal-chemical formula can be written either considering H₂O (1) or H₃O⁺ (2) at the tunnel sites:



On the other hand, Hpcl hosts mainly water at both tunnel sites – thus it is a hydropyrochlore. Similarly to Hkpcl, the crystal-chemical formula of Hpcl can be written assuming H₂O (3) or mainly H₃O⁺ (4) at *A+A'* and *Y'*:



Consequences of Tl⁺ incorporation and ion-exchange reaction kinetics

The first observable effect of imbibition experiments in Tl-rich solutions is a progressive colour change in the initially colourless crystals. Their colour shifts from colourless to pale yellow, to bright orange and lastly to dark brown as the treatment duration increases. This phenomenon was observed in other studies on natural pyrochlores that incorporated thallium after treatments in various Tl-concentrated solutions (Jäger *et al.*, 1959; Harris, 1965; Zoppi, 2004; Bindi *et al.*,

2006; Taddei *et al.*, 2024). English *et al.* (1980) described the same colour transition in synthetic pyrochlore-like Nb-compounds, where increasing Tl^+ amounts in the crystal lattice induced a colour shift from colourless to light yellow and then to dark brown. These authors suggested that the colouration depends on Tl concentration and is probably related to Tl–Tl interactions.

After just 30 minutes of treatment, Hkpcl and Hpcl exhibit an increase in electron density at both the $A+A'$ and the Y' sites (Table 3.7) caused by the entry of Tl^+ , as it can be accommodated at A , A' and/or Y' (Ercit *et al.*, 1993). This increase in electron density is accompanied by a slight lengthening of the $A-X$, $A-Y'$, $A'-X$ and $A'-Y'$ bond lengths (Table 3.7), leading to an overall expansion of the unit cell (Table 3.6). Given the large ionic radius of Tl^+ ($r = 1.59 \text{ \AA}$ in eight-fold coordination; Shannon, 1976), its incorporation induces an expansion of the A site and, consequently, of the unit cell (Taddei *et al.*, 2024).

As the number of electrons at $A+A'$ continues to rise with longer imbibition times (Figure 3.7), the $A-X$ bond length also progressively increases in both Hkpcl and Hpcl, resulting in an expansion of the unit cell linearly correlated with the $A-X$ lengthening (Figure 3.8). The increase in electron density at $A+A'$ follows a logarithmic trend, approaching a saturation limit corresponding to the maximum occupancy of available sites for Tl^+ within the crystal structure. The upper limit for Tl^+ incorporation could be controlled by factors such as the initial water content in the crystals and, more importantly, stereochemical constraints: the $^{A+A'}\text{Tl}^+ - ^{Y'}\text{Tl}^+$ interaction would be very unfavourable on electrostatic grounds, thus the coexistence of Tl^+ at $A+A'$ and Y' is improbable (English *et al.*, 1980). According to Taddei *et al.* (2024), this limit appears to be reached when the cumulative occupancy of the sites at the $16d$ position and its surroundings approaches ~70–75% (~1.40–1.50 Tl^+ pfu), consistently with the present findings (Figure 3.7).

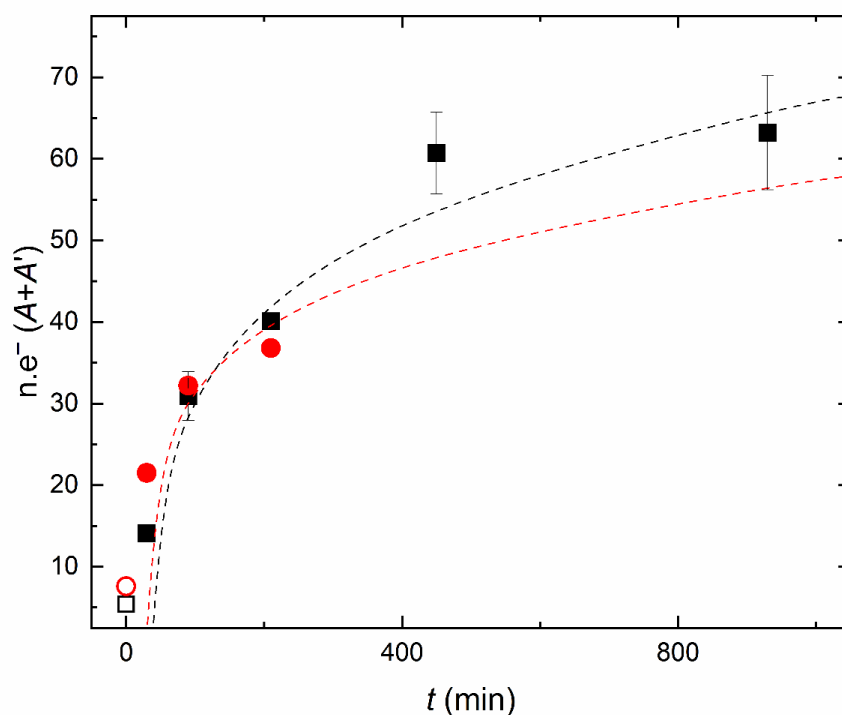


FIGURE 3.7. Number of electrons at $A+A'$ plotted against time of imbibition. The points of both datasets (Hkpcl = black squares; Hpcl = red circles; empty symbols are untreated samples) are approximated by a logarithmic curve, analogous to a typical kinetic curve for ion-exchange reactions (*e.g.*, Inglezakis, 2005, fig. 3). Data collected at $t = 0$ were not considered for the calculation of the curves. The black dashed line (which fits data from Hkpcl) can be expressed as $y = 15.107\ln(x) - 37.339$ ($R^2 = 0.96$), while the red dashed line (fitting the Hpcl data) can be expressed as $y = 10.681\ln(x) - 16.396$ ($R^2 = 0.98$). The error bars relative to $n.e^- (A+A')$ that are not visible are contained within the data symbols.

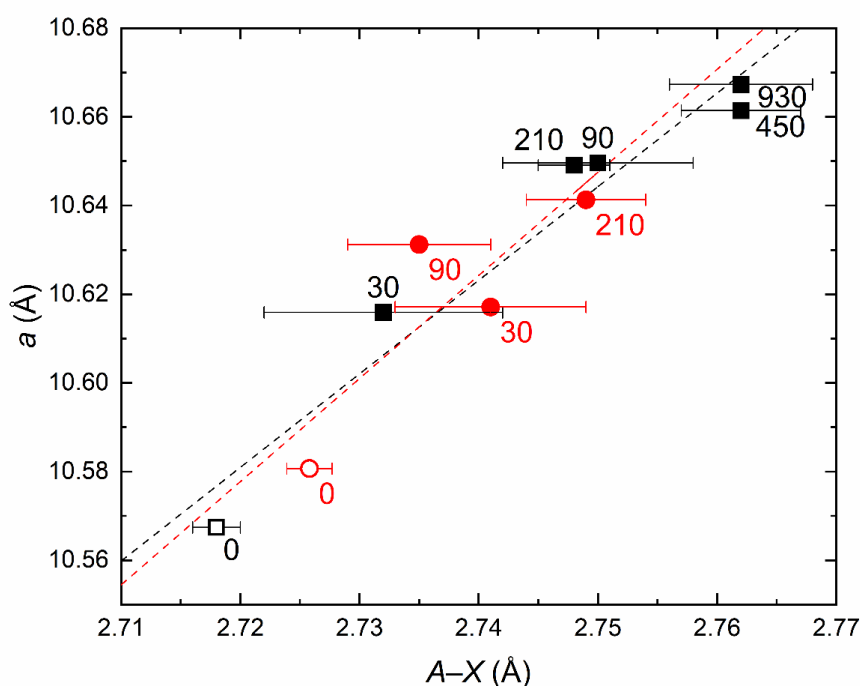


FIGURE 3.8. The $A-X$ distance plotted against the unit-cell parameter a (symbols as in Figure 3.7; the numbers indicate the duration of imbibition), showing a linear correlation trend. The black dashed line fits HkpcI data ($y = 2.111x + 4.839$; $R^2 = 0.95$), while the red dashed line fits Hpcl data ($y = 2.326x + 4.251$; $R^2 = 0.74$). The error bars relative to a that are not visible are contained within the data symbols.

Neither the $Y'-X$ nor the $A-Y'$ distances exhibit similar correlations, as the x coordinate of the Y' site can vary considerably, possibly due to positional disorder affecting this site. In the structural model, only one Y' site was included for the sake of simplicity, but the presence of multiple, slightly displaced sites in the $8b$ neighbourhood cannot in fact be ruled out (Ercit *et al.*, 1994). After the initial increase of electrons at Y' occurring during the first 30 minutes of treatment, a subsequent logarithmic decrease of electron density occurs for longer imbibition times (≥ 90 minutes; Table 3.7), as opposed to the trend observed at $A+A'$ (Figure 3.9). Notably, the rate of electron loss at Y' is slower than the rate of electron gain at $A+A'$. This trend is in keeping with the progressive ordering of Tl^+ at $16d$ (and its neighbourhood) as it enters the structure: the more thallium is incorporated, the more it preferentially occupies the $A+A'$ sites at the expense of Y' . A similar

behaviour was predicted by Grins *et al.* (1980) and English *et al.* (1980) in synthetic K^+ - and Tl^+ -bearing pyrochlore-like compounds with (Ta,W) or Nb at the octahedral site. These studies underline that tunnel cations with ionic radii in the range $1.50 \leq r \leq 1.60$ Å (e.g., K, Tl^+ in eight-fold coordination) tend to order at A and/or Y depending on the $A:B$ occupancy ratio. At high $A:B$ ratios the normal pyrochlore structure is stable, and (K,Tl) order at the A site; conversely, at low $A:B$ ratios (namely when A is largely vacant), (K,Tl) preferentially occupy the Y' site, stabilising the inverse pyrochlore structure. This behaviour is evident in both Hkpcl and Hpcl (Figure 3.10): as thallium incorporation increases with longer imbibition times, the $A:B$ ratio rises, leading to a redistribution of Tl^+ and/or K^+ from Y' to $A+A'$. Upon approaching the saturation limit (Hkpcl_450min and Hkpcl_930min), the global number of electrons at $(A+A'+Y')$ remains approximately the same, while a slight migration of Tl^+ and/or K^+ from Y' towards $A+A'$ is observed.

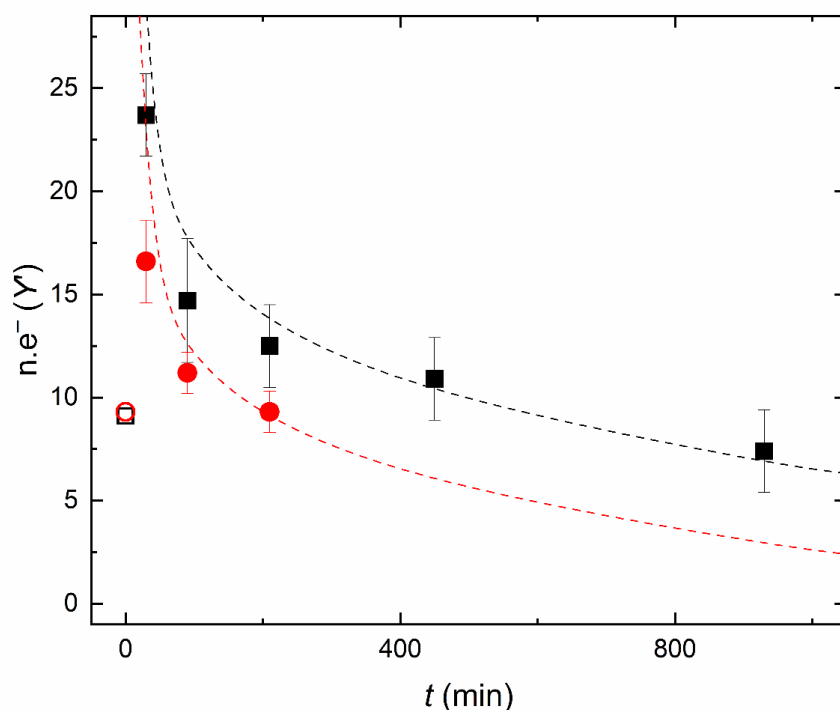


FIGURE 3.9. Number of electrons at Y' plotted against time of imbibition (symbols as in Figure 3.7). The curves were calculated similarly to those in Figure 3.7. The black dashed line, fitting Hkpcl data, can be expressed as $y = -4.383\ln(x) + 36.803$ ($R^2 = 0.93$); the red dashed line, which fits Hpcl data, can be expressed as $y = -3.912\ln(x) + 29.619$ ($R^2 = 0.99$).

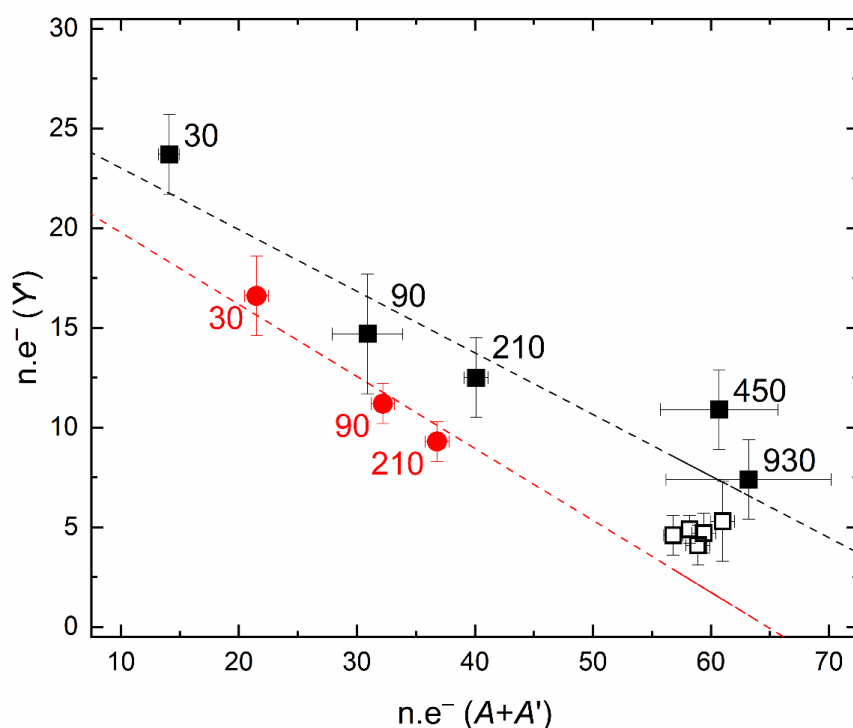


FIGURE 3.10 The inverse correlation between electrons at $A+A'$ and those at Y' is approximated by a linear trend, with the slight differences possibly due to different initial compositions (especially water content). The black dashed line approximates Hkpcl data ($y = -0.309x + 26.109$; $R^2 = 0.85$), while the red dashed line fits Hpcl data ($y = -0.361x + 23.394$; $R^2 = 0.98$). Symbols as in Figure 3.8 except for the black empty squares, which represent data from the treated crystals reported in Taddei *et al.* (2024).

The octahedral bond length also exhibits a slight but significant increase, confirming the trend reported by Taddei *et al.* (2024). The B and A polyhedra share an edge, thus remarkable geometrical modifications occurring at the A polyhedron are expected to produce distortions in the octahedron. In fact, the bond angle variance (σ^2) of the octahedron increases with Tl^+ incorporation, indicating accordingly greater distortion at B with the entry of Tl^+ ; however, this effect becomes significant only for longer imbibition durations (≥ 450 minutes), when σ^2 jumps to 0.53, a value comparable to those observed in Tl -treated hydropyrochlore crystals by Taddei *et al.* (2024). This ‘jump’ never occurs in Hpcl, whose structural data were collected only up to 210 minutes of imbibition, suggesting that substantial

octahedral distortion occurs only after the uptake of remarkable amounts of Tl^+ , nearing the saturation limit.

Despite differences in the Tl concentration of the solutions used for the imbibition experiments, the variations affecting the structural parameters observed in HkpcI and Hpcl are readily comparable, following analogous trends. This seems to be related to the ‘concentration-valency effect’ described by Pabalan and Bertetti (2001) for ion-exchange reactions occurring in natural zeolites. According to these authors, the selectivity of zeolites for a particular ion seems to be independent of the total concentration of the aqueous solution, when the ion-exchange mechanism involves homovalent ions.

Nevertheless, minor deviations can be observed, such as a slight difference in the rate of Tl incorporation. The crystal soaked in the 1 M Tl solution seems to incorporate thallium more rapidly than the one soaked in the 0.1 M Tl solution (Figure 3.7). For HkpcI, near-complete saturation is reached after just 450 minutes of treatment, whereas no equivalent data are available for Hpcl. However, based on the unit-cell parameter vs. imbibition duration trend (Figure 3.11), Hpcl is expected to follow an analogous pattern.

The relative amounts of Tl^+ and H^+ pfu were tentatively calculated based on the refined number of electrons at the $A+A'$ and Y' sites, following the ion-exchange mechanism described by Taddei *et al.* (2024), and assuming that Sr, Na, Ca, Pb and K were not involved in the exchange process. To isolate the contribution of Tl^+ and H^+ , a fixed number of electrons (corresponding to that assigned to Sr, Na, Ca and Pb) was subtracted from the total electrons refined at $A+A'$. Likewise, the electrons assigned to K^+ were subtracted from the total refined at Y' . Tl^+ and H^+ pfu were then estimated from the remaining number of electrons at each site. According to this method, the calculated bulk Tl^+ content confirms a progressive increase with soaking time. For sample HkpcI, it reached 0.44 apfu (~22 wt.% Tl_2O) after 30 minutes, 0.79 apfu (~35 wt.%) after 90 minutes, 1.02 apfu (~42 wt.%) after 210 minutes, 1.52 apfu (~53 wt.%) after 450, and 1.54 apfu (~53 wt.%) after 930 minutes. For sample Hpcl, the values were 0.48 apfu (~25 wt.%) after 30 minutes, 0.70 (~33 wt.%) apfu after 90 minutes, and 0.80 apfu (~36 wt.%) after 210 minutes;

no data are available for longer durations. As previously discussed, the incorporation of these quantities of Ti^+ leads to the loss of an equal amount of H^+ .

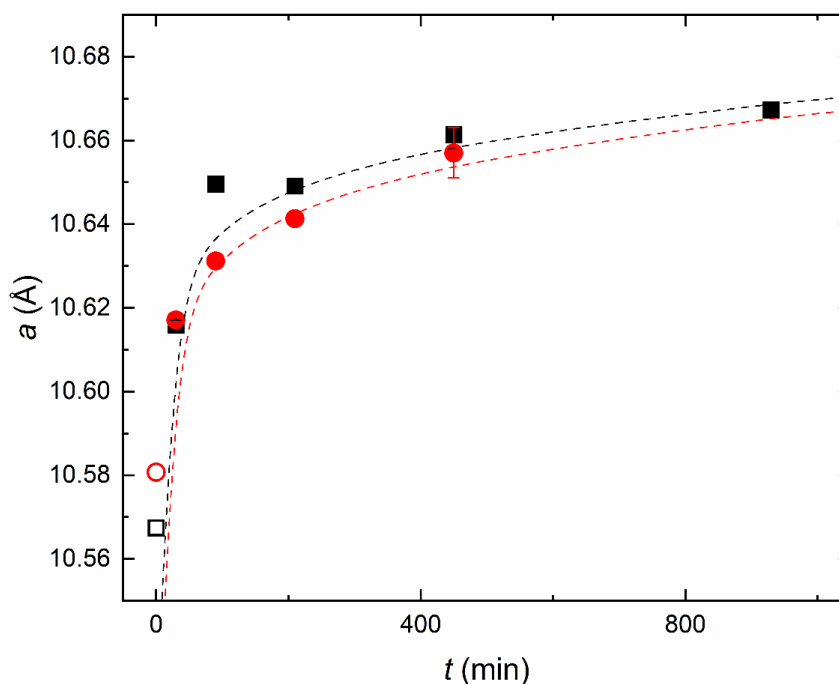
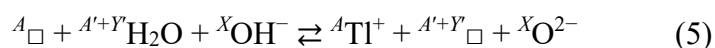
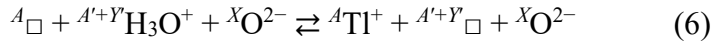


FIGURE 3.11. Unit-cell parameter a plotted against time of imbibition; Hkpcl and Hpcl show an almost identical behaviour despite the different solutions used for the treatments. Symbols as in Figure 3.7. The black dashed line fits Hkpcl data ($y = 0.013\ln(x) + 10.580$; $R^2 = 0.90$), while the red dashed line approximates Hpcl data ($y = 0.0144\ln(x) + 10.567$; $R^2 = 0.99$). The error bars relative to a that are not visible are contained within the data symbols.

3.2.4 Conclusions

Concerning the extent of Ti^+ incorporation into the structure of hydropyrochlore and hydrokenopyrochlore, all the results are consistent with those presented by Taddei *et al.* (2024), confirming that Ti^+ enters the structure at the tunnel sites according to one of the following two ion-exchange reactions, either involving $\text{H}_2\text{O} + \text{OH}^-$ (5) or H_3O^+ (6):





The data reported in this study are not able to solve the conundrum of whether the hydronium ion is actually present in the structure of natural, weathered pyrochlores, and thus, which of the two ion-exchange mechanisms takes place during the imbibition experiments in the Tl-rich solutions. However, the presented results provide greater depth to the research, with an improved time resolution necessary to shed light on the reaction kinetics. A key finding of this work is that significant Tl^+ incorporation occurs within very short timescales: while Taddei *et al.* (2024) performed five days long imbibition experiments in a more concentrated solution, the present results make it safe to assume that ~450 minutes are sufficient to induce the entry of Tl^+ at most of the available sites, regardless of its concentration in solution. Effective Tl-uptake and high incorporation rates suggest that both hydropyrochlore and hydrokenopyrochlore are promising candidates for thallium sequestration, particularly in dynamic environments where rapid immobilisation is essential. However, it is important to note that Taddei *et al.* (2024) pointed out the loss of approximately one third of the incorporated Tl after a seven days long imbibition experiment in deionised water, underlining the need for more insight into the factors that might affect the capability of the structure to retain Tl or that could trigger its release, such as the presence of competing cations in solution along with Tl^+ , temperature and pressure conditions and the pH of the solutions used for the treatments.

4. Hydrokenopyrochlore from Araxá, Minas Gerais (Brazil)

4.1 Imbibition experiments in Tl- and Pb-concentrated solutions

4.1.1 Introduction

Among the various properties characterizing pyrochlore minerals, their remarkable ion-exchange capacity is particularly relevant for potential applications in the environmental field. Several studies have pointed out their ability to incorporate and retain toxic cations such as Tl⁺ (Zoppi, 2004; Bindi *et al.*, 2006; Taddei *et al.*, 2024; Taddei and Bindi, 2025) and Pb²⁺ (Han *et al.*, 2014) from solutions enriched in these elements. This property is enhanced when pyrochlores contain large amounts of highly mobile species, such as water, large, monovalent cations (*e.g.*, K⁺), and structural vacancies.

This chapter focuses on hydrokenopyrochlore from Araxá, Minas Gerais (Brazil), formerly referred to as bariopyrochlore (Hogarth, 1977) due to the significant Ba content at the tunnel sites. Hydrokenopyrochlore was first described as a distinct species by Biagioni *et al.* (2018); however, the type material corresponds to an Sb-rich phase from the Antandrokomby pegmatite (Madagascar), chemically quite different from the Araxá ‘variety’ of hydrokenopyrochlore. Several earlier studies on ‘bariopyrochlore’ or other kinds of Ba-rich pyrochlores, actually described hydrokenopyrochlore (*e.g.*, Jäger *et al.*, 1959; Harris, 1965; Zoppi, 2004; Bindi *et al.*, 2006). The mineral from Araxá has been of particular interest given its accidental thallium contamination after treatment with Clerici solution (Zoppi, 2004; Bindi *et al.*, 2006); this study aims to further investigate the capacity of this mineral to incorporate heavy metals, inducing their incorporation via imbibition experiments conducted with Tl- and Pb-concentrated solutions.

4.1.2 *Experimental methods*

Electron microprobe analyses (EMPA)

Several hydrokenopyrochlore single crystals were selected and embedded in epoxy (a single mount) for chemical analyses, each labelled as BAPY_#, where # stands for a letter. A second epoxy mount was prepared with three additional single crystals, labelled as previously stated, and it was checked before and after a one-day long treatment in a 1M Tl solution. The chemical composition was determined with counting times of 30 s (Na, Si, Ca, Tl, Pb, U), 20 s (Fe, Sr, Ta, Th) and 15 s (K, Ti, Nb, Ba, Ce, La).

Chemical data were normalised on the basis of $\Sigma B_{\text{cat}} = 2.00$ apfu, with all iron considered as Fe^{3+} . Average values for selected samples are listed in Table 4.1.

Imbibition experiments

Two single crystals (BAPY_A and BAPY_B) were selected to undergo an imbibition experiment in a thallium(I) formate and deionised water solution, with a 1M Tl^+ concentration. Another sample, BAPY_L, was soaked in a solution of lead(II) nitrate dissolved in deionised water; Pb^{2+} concentration was 1M. The duration of the treatments was four days for BAPY_A and five days for BAPY_B and BAPY_L.

Additionally, three single crystals (BAPY_X, BAPY_Y, BAPY_Z) were soaked in the 1M Tl^+ solution for one day, while still embedded in the epoxy mount.

Single-crystal X-ray diffraction

Diffraction data were collected from some of the crystals previously analysed with the electron microprobe; samples that underwent treatments in Tl^+ or Pb^{2+} solutions were measured both before and after the imbibition experiments except for BAPY_XTl, which was checked only after the soaking experiment. Intensity data and unit-cell parameters are listed in Table 4.2. The data were integrated and corrected for absorption and for Lorentz-polarisation effects via the APEX5 software suite (Bruker, 2023).

TABLE 4.1. Average microprobe analyses (wt.% oxides) of untreated and treated crystals together with the crystal-chemical formulae on the basis of $\Sigma B = 2$ apfu.

	BAPY_A	BAPY_B	BAPY_L	BAPY_N	BAPY_X	BAPY_XTI	BAPY_Y	BAPY_YTI	BAPY_Z	BAPY_ZTI
<i>n</i>	4	5	4	4	4	2	4	2	3	2
SiO ₂	0.01	0.05	-	0.07	0.04	-	-	0.01	0.02	-
TiO ₂	3.47	3.53	3.61	4.34	3.85	3.63	3.29	2.73	3.74	3.42
Fe ₂ O ₃	0.62	0.37	0.05	0.14	0.04	0.03	0.07	0.11	0.53	0.32
Nb ₂ O ₅	62.43	61.70	64.02	62.51	62.13	50.94	64.34	53.09	61.14	50.73
Ta ₂ O ₅	1.05	0.89	0.01	-	0.03	-	0.17	0.06	-	0.02
Na ₂ O	0.06	0.22	0.12	0.09	0.13	0.13	0.09	0.06	0.14	0.10
K ₂ O	-	0.01	-	-	-	-	-	-	-	-
CaO	-	0.16	0.03	0.02	0.03	-	0.01	0.01	0.02	0.01
SrO	0.03	0.02	0.03	0.01	-	-	0.06	0.10	-	0.04
BaO	16.53	18.74	20.66	19.77	15.83	8.73	20.42	11.25	13.31	7.36
Ce ₂ O ₃	4.42	2.60	3.05	4.79	6.09	4.70	2.24	2.11	7.18	6.27
La ₂ O ₃	0.33	0.07	0.29	0.36	0.82	0.27	0.11	0.06	0.84	0.51
Tl ₂ O	0.04	0.04	0.05	0.12	0.09	27.12	0.10	28.37	0.18	28.11
PbO	0.06	-	0.03	0.07	0.09	-	-	-	0.28	-
ThO ₂	3.11	2.98	0.73	1.07	2.49	2.39	1.18	1.15	3.67	2.89
UO ₂	0.78	0.41	0.05	0.02	0.06	0.09	0.20	0.10	0.03	-
Total	92.94	91.79	92.73	93.38	91.72	98.03	92.28	99.21	91.08	99.78
H ₂ O*	5.14	3.96	5.37	3.89	-	-	-	-	-	-
TOTAL	98.08	95.75	98.10	97.27	-	-	-	-	-	-

TABLE 4.1 (*continued*)

	BAPY_A	BAPY_B	BAPY_L	BAPY_N	BAPY_X	X_Tl	BAPY_Y	Y_Tl	BAPY_Z	Z_Tl
Si ⁴⁺	-	-	-	-	-	-	-	-	-	-
Ti ⁴⁺	0.17	0.17	0.17	0.21	0.19	0.21	0.16	0.16	0.18	0.20
Fe ³⁺	0.03	0.02	-	0.01	-	-	-	0.01	0.03	0.02
Nb ⁵⁺	1.79	1.79	1.83	1.78	1.81	1.79	1.84	1.83	1.79	1.78
Ta ⁵⁺	0.02	0.02	-	-	-	-	-	-	-	-
Na ⁺	0.01	0.03	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.01
K ⁺	-	-	-	-	-	-	-	-	-	-
Ca ²⁺	-	0.01	-	-	-	-	-	-	-	-
Sr ²⁺	-	-	-	-	-	-	-	-	-	-
Ba ²⁺	0.41	0.47	0.51	0.49	0.40	0.27	0.51	0.34	0.34	0.22
Ce ³⁺	0.10	0.06	0.07	0.11	0.14	0.13	0.05	0.06	0.17	0.18
La ³⁺	0.01	-	0.01	0.01	0.02	0.01	-	-	0.02	0.01
Tl ⁺	-	-	-	-	-	0.60	-	0.61	-	0.62
Pb ²⁺	-	-	-	-	-	-	-	-	-	-
Th ⁴⁺	0.04	0.04	0.01	0.02	0.04	0.04	0.02	0.02	0.05	0.05
U ⁴⁺	0.01	0.01	-	-	-	-	-	-	-	-
Σ _{cat}	2.59	2.61	2.61	2.64	2.62	3.06	2.60	3.05	2.61	3.10
H ₂ O*	2.17	1.70	2.26	1.64	-	-	-	-	-	-

Notes: n = number of analytical points; *H₂O calculated on the basis of the formulae reported in Table 4.4.

TABLE 4.2. SC-XRD experimental details and crystal data for Ba-bearing hydrokenopyrochlore crystals before and after Tl and Pb imbibition experiments.

	BAPY_A	BAPY_ATI	BAPY_B	BAPY_BTI
a (Å)	10.5530(4)	10.5881(6)	10.5623(4)	10.6318(8)
V (Å ³)	1175.24(13)	1187.0(2)	1178.35(13)	1201.8(3)
size (μm)	80 × 70 × 60	80 × 70 × 60	60 × 50 × 40	60 × 50 × 40
$\theta_{\max}$ (°; MoK α)	32	32	32	32
R_{int} (%)	4.19	6.51	4.90	7.02
indep. refl.	120	125	125	129
obs. refl.	105	109	97	98
$[F_o > 4\sigma(F_o)]$				
Ref. param.	14	15	15	15
$R1_{\text{all}}$ (%)	2.65	6.67	3.81	8.47
$R1_{\text{obs}}$ (%)	2.25	5.95	2.98	6.81
$\Delta\rho_{\max}$ (e ⁻ /Å ³)	0.39	1.25	0.56	1.27
$\Delta\rho_{\min}$ (e ⁻ /Å ³)	-0.38	-2.01	-0.78	-1.59
	BAPY_L	BAPY_LPb	BAPY_N	BAPY_XTI
a (Å)	10.5300(13)	10.5270(14)	10.5637(4)	10.5592(17)
V (Å ³)	1167.6(4)	1166.6(5)	1178.82(13)	1177.3(6)
size (μm)	60 × 50 × 30	60 × 50 × 30	70 × 70 × 70	80 × 50 × 40
$\theta_{\max}$ (°; MoK α)	32	32	32	31
R_{int} (%)	12.01	11.43	5.33	7.09
indep. refl.	123	123	125	118
obs. refl.	72	70	101	93
$[F_o > 4\sigma(F_o)]$				
Ref. param.	14	14	14	15
$R1_{\text{all}}$ (%)	9.06	8.93	3.93	5.55
$R1_{\text{obs}}$ (%)	4.58	4.47	3.15	3.94
$\Delta\rho_{\max}$ (e ⁻ /Å ³)	0.95	1.09	0.83	1.17
$\Delta\rho_{\min}$ (e ⁻ /Å ³)	-1.06	-1.09	-0.68	-0.77

Structure refinements

Structure refinements were carried out in the space group $Fd\bar{3}m$ (origin choice 2) with SHELXL (Sheldrick, 2015). The starting atomic positions were the following: the A site at Wyckoff position $16d$ ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), the B site at $16c$ (0, 0, 0), the Y site at

8b ($\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$) and the X site at 48f ($x, \frac{1}{8}, \frac{1}{8}$). The only free coordinate, namely the x coordinate of the X site, was initially set to the value reported by Taddei *et al.* (2024), obtained from a reasonably similar hydrokenopyrochlore sample from Lueshe (D.R. Congo). The X site was found fully occupied in all refinements, while the occupancy factor of the B site was fixed to match EMPA data.

At this point, the ΔF of the model showed an anomalously high positive residue in the vicinity of the A site; moreover, the isotropic displacement parameter of the Y site was exceedingly large, indicating high local disorder. The first issue was addressed by adding a new A' site, displaced at a $32e$ position in the neighbourhood of A , with its displacement parameters forced to be equal to those of A . As for Y , it was replaced with the nearby Y' site, also in a $32e$ position, yielding lower atomic displacement parameters.

Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992) and were used as follows: $A = \text{Ba}$ vs. $\square$ (untreated crystals and the Pb-treated crystal) or Tl vs. $\square$ (Tl-treated crystals); $A' = \text{O}$ vs. $\square$ (untreated crystals and the Pb-treated crystal) or Tl vs. $\square$ (Tl-treated crystals); $B = \text{Nb}$ vs. Ti; $X = \text{O}$; $Y' = \text{O}$ vs. $\square$ (untreated crystals and the Pb-treated crystal) or Tl vs. $\square$ (Tl-treated crystals). Except for the different scattering curves, the method used for the refinements of the treated samples did not differ from that used for the untreated ones.

Lastly, anisotropic atomic displacement parameters (ADPs) were refined for all atoms except Y' (in all refinements), A and A' (BAPY_L), which were refined with isotropic ADPs, and convergence was achieved.

Bond distances and other structural parameters are listed in Table 4.3.

TABLE 4.3. Selected structural parameters for treated and untreated hydrokenopyrochlore samples from Araxá. Bond distances in Å, angles in °.

	BAPY_A	BAPY_ATI	BAPY_B	BAPY_BTI	BAPY_L	BAPY_LPb	BAPY_N	BAPY_XTI
n.e ⁻ (<i>A</i>)	12.0	31.2	11.2	34.8	17.7	16.9	9.7	19.9
n.e ⁻ (<i>A'</i>)	6.4	1.5	5.8	4.5	1.0	0.9	6.7	2.9
n.e ⁻ (<i>Y'</i>)	8*	10.4	6.9	9.3	8*	8*	6.7	14.9
x_{48f} (<i>X</i>)	0.3130(3)	0.3136(13)	0.3135(3)	0.3127(14)	0.3130(7)	0.3133(7)	0.3130(3)	0.3125(7)
x_{32e} (<i>A'</i>)	0.5170(16)	0.55(2)	0.517(3)	0.537(11)	0.567(8)	0.545(16)	0.5147(18)	0.540(5)
x_{32e} (<i>Y'</i>)**	0.3484(8)	0.335(4)	0.3486(12)	0.338(9)	0.350(2)	0.350(2)	0.3491(10)	0.3370(18)
<i>A</i> – <i>X</i> (×6)	2.715(2)	2.720(10)	2.714(3)	2.738(11)	2.710(5)	2.707(5)	2.718(2)	2.721(6)
<i>A</i> – <i>Y'</i> (×2)	2.771(15)	3.02(8)	2.77(2)	2.98(10)	2.739(4)	2.74(4)	2.761(18)	2.98(2)
< <i>A</i> –O>	2.729	2.80	2.73	2.80	2.717	2.72	2.729	2.79
<i>B</i> – <i>X</i> (×6)	1.9805(10)	1.989(5)	1.9840(12)	1.994(5)	1.976(2)	1.977(2)	1.9825(10)	1.980(3)
<i>A'</i> – <i>X</i> (×3)	2.777(16)	2.74(7)	2.78(4)	2.73(3)	2.81(9)	2.71(17)	2.77(2)	2.718(13)
(×3)	2.689(17)	3.0(3)	2.69(4)	2.91(12)	3.13(9)	2.94(17)	2.69(2)	2.91(6)
<i>A'</i> – <i>Y'</i> (×2)	3.082(18)	3.0(4)	3.08(4)	3.66(16)	3.38(9)	3.56(18)	3.03(3)	3.71(6)
< <i>A'</i> –O>	2.820	2.9	2.82	3.03	3.07	3.01	2.805	3.04
<i>X</i> – <i>X</i> (u.)	2.806(5)	2.824(18)	2.816(5)	2.82(3)	2.800(9)	2.803(9)	2.809(5)	2.800(11)
<i>X</i> – <i>X</i> (s.)	2.7958(15)	2.802(6)	2.7958(15)	2.818(7)	2.790(3)	2.787(3)	2.7986(15)	2.800(4)
< <i>X</i> – <i>X</i> >	2.801	2.813	2.806	2.82	2.795	2.795	2.804	2.800

TABLE 4.3 (*continued*)

$X-B-X$	90.21(11)	89.5(5)	90.41(13)	89.9(6)	90.2(4)	90.3(3)	90.21(11)	90.00(3)
$(X-B-X)'$	89.79(11)	90.5(5)	89.59(13)	90.1(6)	89.8(4)	89.7(3)	89.79(11)	90.00(3)
$B-X-B$	140.76(16)	140.4(7)	140.47(19)	140.9(8)	140.8(4)	140.6(4)	140.76(16)	141.1(4)
$B-X-A$	104.12(4)	104.2(2)	104.21(5)	104.1(2)	104.12(11)	104.17(11)	104.12(5)	104.04(12)
$A-X-A$	86.79(8)	87.0(4)	86.94(10)	86.7(4)	86.8(2)	86.9(2)	86.78(9)	86.6(2)
$\sigma^2(B)$	0.05	0.22	0.18	0.01	0.05	0.12	0.05	0.00

Notes: *fixed to full occupancy; **refined as $x^{+1/2}$, $-x^{+3/4}$, $-x^{+1/4}$ ($1/2, 1/2, 0$)+; u. = unshared edge of the octahedron; s. = shared edge between B and A polyhedra. Bond angle variance (σ^2) was computed according to the formula proposed by Robinson *et al.* (1971).

4.1.3 Results and discussion

Hydrokenopyrochlore from Araxá: crystal-chemistry and comparison with samples of the same species from different localities

The topology of the studied hydrokenopyrochlore is consistent with that of other cubic pyrochlores. Compared to samples from other localities, such as the Antandrokomby pegmatite (Madagascar) and the Lueshe carbonatite (D.R. Congo), some crystal-chemical differences can be observed. The studied crystals show an a parameter ranging from 10.5300(13) Å to 10.5637(4) Å (Table 4.2), slightly lower than that reported for hydrokenopyrochlore from Lueshe [10.555(2)–10.585(4) Å, Taddei *et al.*, 2024], but larger than that of the type material from Antandrokomby [10.4887(8) Å, Biagioni *et al.*, 2018]. This variability within the same species likely reflects compositional differences related to different minerogenetic conditions and subsequent alteration processes.

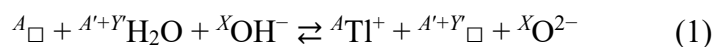
Despite being zero-valent-dominant species in all three cases – *i.e.*, with the A site (and nearby sites) dominated by structural vacancy, the B site by Nb, and the Y site (and neighbouring sites) by an aqueous species –, the cationic population at each site varies considerably among samples from different localities. The Araxá hydrokenopyrochlore crystals investigated here are compositionally quite homogeneous, with Ba as the most abundant cation at the $A+A'$ sites (0.40–0.51 apfu, Table 4.1) followed by Ce (0.05–0.17 apfu), Th (≤ 0.04 apfu), along with minor Ca, La and U. Due to the enrichment in barium, this species was formerly known as bariopyrochlore (Hogarth, 1977). At the B site, Ti substitutes for Nb (0.17–0.21 apfu), together with minor Fe^{3+} (≤ 0.03 apfu) and Ta (≤ 0.02 apfu). Lastly, the Y site is mainly occupied by an aqueous species, with only minor vacancies (up to ~15%). This indicates a ‘normal’ character of these samples, rather than the partially ‘inverse’ configuration observed for hydrokenopyrochlores from Lueshe and Antandrokomby.

Indeed, hydrokenopyrochlores from both Lueshe and Antandrokomby show fundamentally different chemistries and, consequently, slightly different arrangements of the tunnel cations. The Lueshe samples are relatively enriched in

Sr, which is the most abundant cation at *A* (0.17–0.18 apfu; Taddei *et al.*, 2024), and in K, assumed to order at the *Y* site (0.08–0.12 apfu). As mentioned above, this makes them partially ‘inverse’ pyrochlores and explains their former classification as ‘kalipyrochlore’ (Ercit *et al.*, 1994). On the other hand, in the hydrokenopyrochlore described by Biagioni *et al.* (2018), Sb^{3+} represents the most abundant cation at the *A* site (0.35 apfu), followed by Na (0.24 apfu) and Ca (0.07). The stereoactive Sb^{3+} cation requires a split *A'* position at 96g coexisting with the *A* site at 16d, which however differs from the *A'* position (32e) observed in the Araxá and Lueshe samples. The Ba enrichment in hydrokenopyrochlore from Araxá, which has a larger ionic radius than both Sr and Sb^{3+} , results in slightly longer $\langle A-O \rangle$ distances (~ 2.72 – 2.73 Å, Table 4.3). At the *B* site, the main substituents differ as well: whereas the Araxá and Lueshe varieties show comparable Nb/Ti ratios, the Antandrokomby sample also contain Ta and W, with minor Sb^{5+} and, possibly, Si, accounting for the slightly shorter *B*–*X* bond lengths observed in the latter sample (~ 1.97 Å vs. ~ 1.98 Å). With 45% of the *Y* site occupied by Cs^+ , the Sb^{3+} -rich hydrokenopyrochlore also shows the highest degree of inversion among the three, representing an intermediate member between ideal hydrokenopyrochlore and cesiokenopyrochlore (Agakhanov *et al.*, 2021).

Another key difference lies in the hydration degree of the three minerals. Hydrokenopyrochlore from Antandrokomby appears the least hydrated, not even requiring OH^- groups at *X* to achieve charge balance: its calculated H_2O content does not exceed 2.2 wt.% (Biagioni *et al.*, 2018). The (Sr,K)-rich samples from Lueshe, by contrast, is the most hydrated, with water molecules at *A* nearly equalling out structural vacancies (had water dominated, the species would have been classified as hydropyrochlore). The calculated H_2O content for these samples ranges from 12.4 to 14.2 wt.% (Taddei *et al.*, 2024). The present samples show intermediate hydration, including OH^- groups at *X*, with 3.9–5.4 wt.% H_2O . Given the high mobility of H_2O and the possibility that part of it could be occurring, in fact, as H_3O^+ , it is safe to assume that the most suitable candidate as a sink for Ti^+ would be the most hydrated pyrochlore, namely hydrokenopyrochlore from Lueshe. Indeed, this was confirmed by previous studies (Taddei *et al.*, 2024; Taddei and

Bindi, 2025), which proposed that the TI^+ incorporation reaction involves H^+ [either as $\text{H}_2\text{O} + \text{OH}^-$ (1) or H_3O^+ (2)]:



Although less hydrated, the here investigated samples still display a significant ion-exchange capacity (see below; Zoppi, 2004; Bindi *et al.*, 2006), though not as effective as that of hydrokenopyrochlore from Lueshe.

Ion-exchange reactions in hydrokenopyrochlore from Araxá

The incorporation of monovalent thallium into Ba-rich hydrokenopyrochlore produces several changes in its crystal-chemical features. The first observable effect is the expansion of the unit-cell parameter, which increases by $\sim 3\%$ in BAPY_A and $\sim 7\%$ in BAPY_B (Table 4.2). This expansion reflects the entry of TI^+ ($r^{\text{VIII}} = 1.59 \text{ \AA}$; Shannon, 1976), as shown by a marked increase in electron density at the $A+A'$ sites (Figure 4.1), which nearly doubles compared to the initial value. The unit-cell expansion is linked to the lengthening of the $A-X$ distance (Taddei *et al.*, 2024), also observed in the samples soaked for four and five days (Figures 4.2–4.3), within experimental uncertainty. As in hydropyrochlore and hydrokenopyrochlore from Lueshe, the expansion of the A polyhedron also affects the B octahedron, causing a slight increase in the $B-X$ distance (Table 4.3).

The sample BAPY_XTI, soaked for only one day, displays structural parameters closer to those of untreated crystals, although structural evidence of incorporation is still visible. In this case, TI^+ seems to order at both Y' (14.9 e^-) and $A+A'$ (22.8 e^-), consistently with the observation that the lower the A/B occupancy ratio is, the more large monovalent cations tend to order at the Y' site (Grins *et al.*, 1980; Taddei and Bindi, 2025). Comparing the untreated crystals (quite constant in composition; mean number of electrons at $A+A' = 17.9 \text{ e}^-$) with the one-day-treated sample highlights a modest but detectable increase of electron density at the $16d$ and neighbouring positions, although less pronounced than in crystals that were soaked for longer times. Chemical data collected from TI-treated crystals are only available for BAPY_XTI among the samples that underwent SC-XRD, seemingly

supporting the occurrence of Tl incorporation. While most components remain unchanged before and after the imbibition experiment, Ba seems to decrease by about 30% (Table 4.1), suggesting a possible $2\text{Tl}^+ \rightarrow \text{Ba}^{2+}$ partial substitution; moreover, analytical totals approach 100 wt.% after the experiment, possibly indicating dehydration.

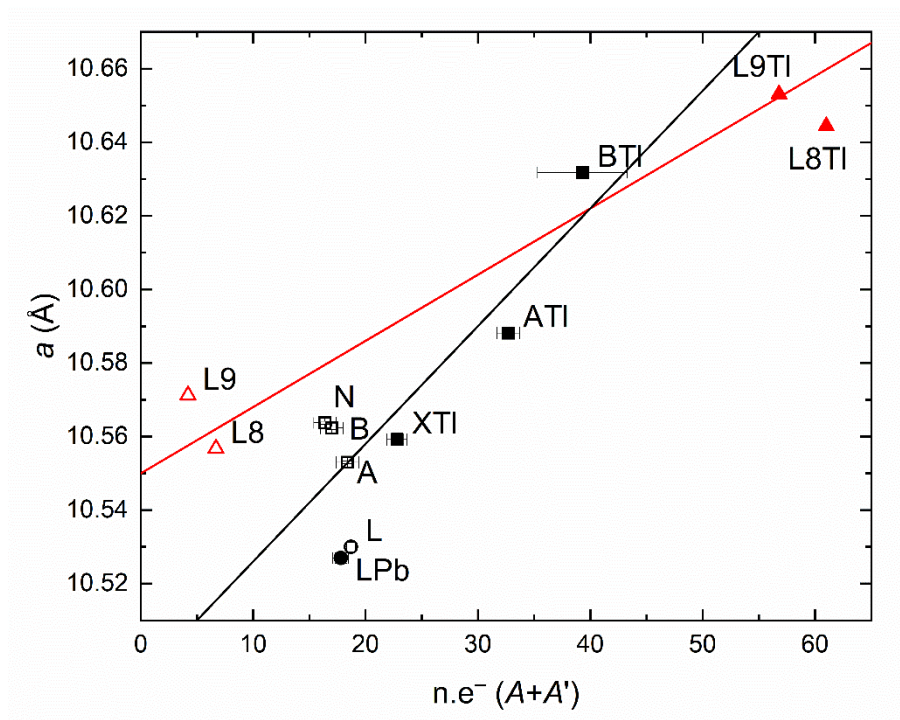


FIGURE 4.1. Number of electrons at the $A+A'$ sites plotted against the unit-cell parameter. Symbols: red triangles are from (Taddei *et al.*, 2024); black squares are untreated and Tl-treated samples; black circles represent the untreated and Pb-treated sample. Empty symbols indicate untreated samples, full symbols indicate treated samples. The rate of expansion of the unit cell differs between the two sets of samples probably due to the different composition at the $A+A'$ sites before the treatments. The red line fits the equation $y = 0.0018x + 10.550$ ($R^2 = 0.91$) reported by Taddei *et al.* (2024), while the black line fits $y = 0.0032x + 10.494$ ($R^2 = 0.78$), calculated using the data from this chapter of the thesis.

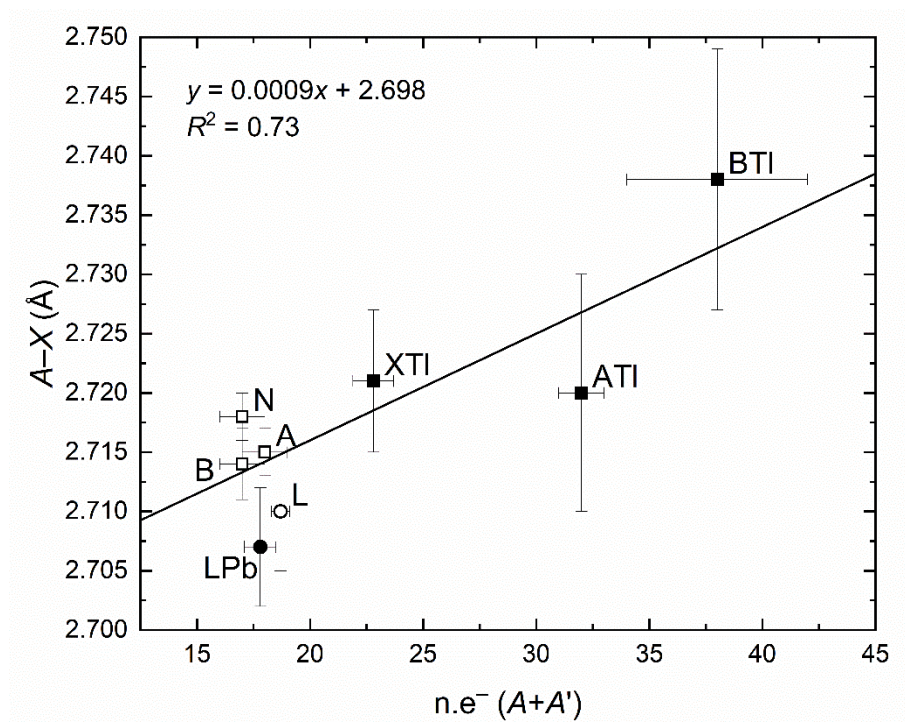


FIGURE 4.2. Number of electrons at the $A+A'$ sites plotted against the $A-X$ distance. The black line is fitted as reported top left. Symbols as in Figure 4.1.

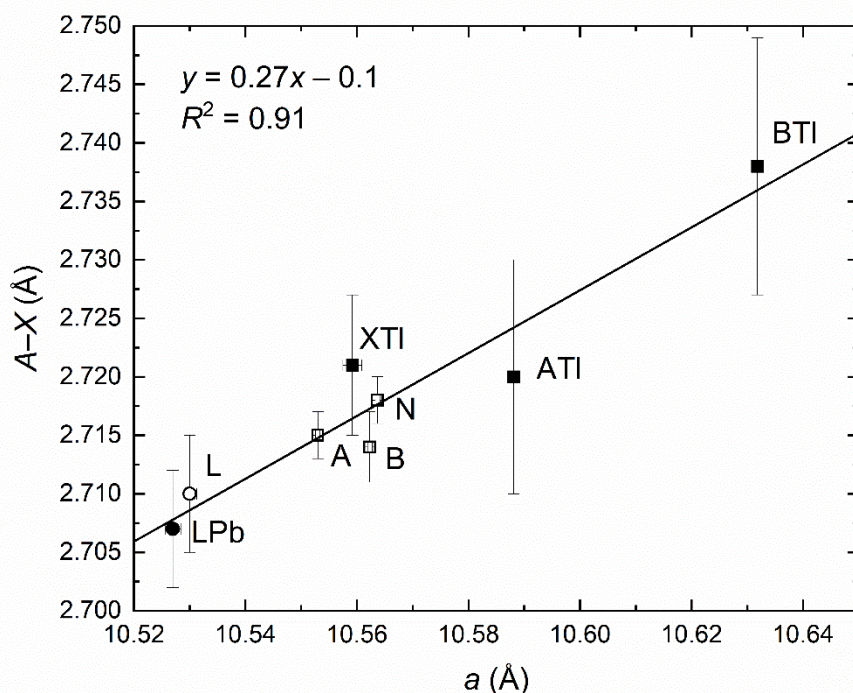


FIGURE 4.3 Unit-cell parameter vs. $A-X$ distances. The black line fits the equation reported top left. Although the sample BAPY_XTI is not strictly an outlier, it is seemingly grouped with untreated samples, as the amount of incorporated thallium could be insufficient to produce visible structural variations. Symbols as in Figure 4.1. Error bars relative to a that are not visible are contained within the symbols.

However, two issues arise. First, the ratio of incorporated Tl to lost Ba is not 2:1, as required for charge neutrality, but closer to 3:1, implying additional processes at play (e.g., involving H^+) and/or analytical artefacts. Second, a discrepancy exists between the total electron count calculated from the microprobe data ($n.e^-$ at $A+A'+Y' = \sim 75 e^-$) and that observed from the structure refinement ($\sim 61 e^-$). Since SC-XRD results were reproduced in two independent refinements, they are considered reliable, pointing that EMPA data overestimate Tl. Possible explanations for this mismatch include (i) partial adsorption of Tl on the surface of the crystal, (ii) occurrence of thallium(I) formate nanocrystals, which could have been trapped in the superficial asperities of the crystal (the presence of a well-formed microcrystal near the hydrokenopyrochlore fragment supports this hypothesis; Figure 4.4), or (iii) intergrowth of two pyrochlore types at the nanoscale with

different exchange capacities. Although the SC-XRD data are considered reliable, a fourth possibility may account for the observed discrepancy, involving an underestimation of Tl incorporation by SC-XRD. The bias could stem from the way the imbibition experiments were carried out on this sample, where only the polished surface of the crystal was exposed to the Tl^+ -rich solution. As a result, Tl incorporation may have been limited in the portions of the sample embedded in epoxy and not in direct contact with the solution. Consequently, in this case EMPA would provide accurate data collected on the treated surface, while SC-XRD would yield averaged data that also include regions of the crystal where Tl could not diffuse. Each of these scenarios, possibly being verified simultaneously, severely complicate a precise quantification of the incorporated Tl. Even so, the minimum amount of entered thallium can be estimated following the approach of Taddei and Bindi (2025). Assuming exchange according to reactions (1) or (2) and that no $A+A'$ cations are directly involved in the reaction, the mean number of electrons of untreated crystals was subtracted from that of BAPY_XTl, isolating the contribution of Tl^+ at $A+A'$, corresponding to $\sim 0.12 \text{ Tl}^+$ pfu. Given the nearly complete dehydration of the sample (Taddei *et al.*, 2024; Table 4.1), the Y' site was instead assumed to host $\sim 0.18 \text{ Tl}^+$ pfu after soaking, with the remainder vacant. This gives a total of $\sim 0.30 \text{ Tl}^+$ pfu, roughly half of that measured with EMPA. Importantly, unlike the samples from Lueshe (where only H^+ participates in the exchange mechanism; Taddei *et al.*, 2024), the Araxá hydrokenopyrochlore shows significant Ba involvement. This suggests that the true Tl content could well exceed the estimated 0.30 apfu. Crystal-chemical formulae for BAPY_A and BAPY_B, before and after the Tl imbibition, are reported in Table 4.4, with Tl^+ contents calculated using the procedure described above.

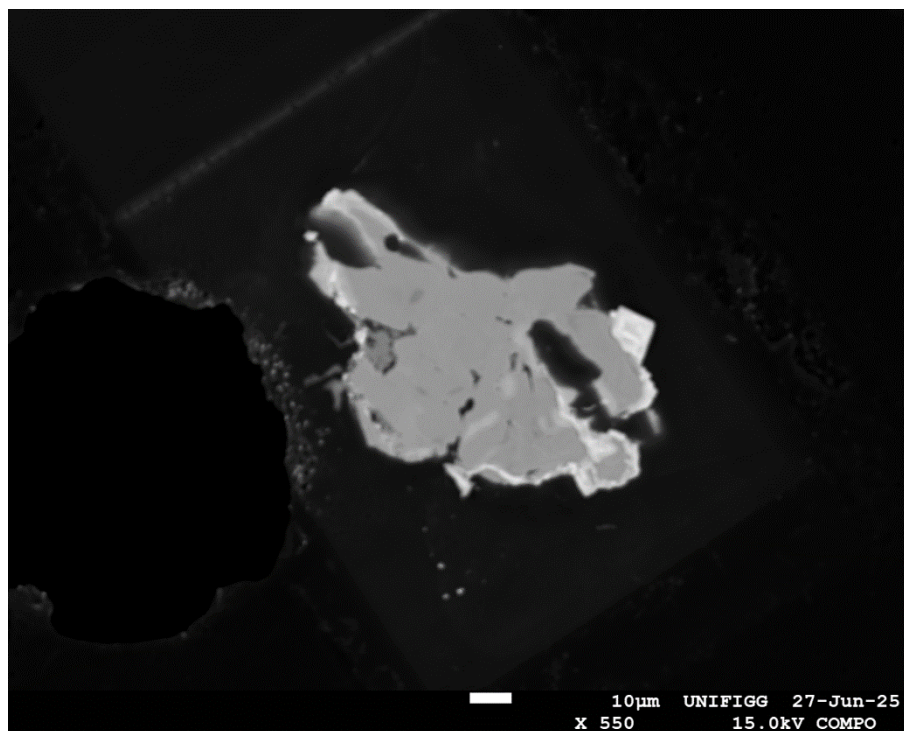


FIGURE 4.4. BSE image of the BAPY_X grain after undergoing an imbibition experiment in a 1M Tl-concentrated solution. The lighter, euhedral crystal on the right is mainly constituted of Tl, indicating a possible recrystallisation of thallium formate precipitated during the treatment.

TABLE 4.4. Crystal-chemical formulae for BAPY_A, BAPY_B (before and after Tl-imbibition), BAPY_L, and BAPY_N. The formulae for the untreated samples were calculated with EMPA and SC-XRD data, whereas the ones for imbibed samples were calculated as specified in the text.

BAPY_A	$[\square_{1.07}\text{Ba}_{0.41}(\text{H}_2\text{O})_{0.35}\text{Ce}_{0.10}\text{Th}_{0.04}\text{Na}_{0.01}\text{La}_{0.01}\text{U}_{0.01}]$ $(\text{Nb}_{1.79}\text{Ti}_{0.17}\text{Fe}^{3+}_{0.03}\text{Ta}_{0.02})[\text{O}_{5.18}(\text{OH})_{0.82}](\text{H}_2\text{O})$
BAPY_ATl	$[\square_{1.03}\text{Ba}_{0.41}\text{Tl}_{0.39}\text{Ce}_{0.10}\text{Th}_{0.04}\text{Na}_{0.01}\text{La}_{0.01}\text{U}_{0.01}]$ $(\text{Nb}_{1.79}\text{Ti}_{0.17}\text{Fe}^{3+}_{0.03}\text{Ta}_{0.02})[\text{O}_{5.61}(\text{OH})_{0.39}][(\text{H}_2\text{O})_{0.92}\text{Tl}_{0.04}\square_{0.04}]$
BAPY_B	$(\square_{1.38}\text{Ba}_{0.47}\text{Ce}_{0.06}\text{Th}_{0.04}\text{Na}_{0.03}\text{Ca}_{0.01}\text{U}_{0.01})$ $(\text{Nb}_{1.79}\text{Ti}_{0.17}\text{Fe}^{3+}_{0.02}\text{Ta}_{0.02})[\text{O}_{5.16}(\text{OH})_{0.84}][(\text{H}_2\text{O})_{0.86}\square_{0.14}]$
BAPY_BTl	$(\square_{0.84}\text{Tl}_{0.54}\text{Ba}_{0.47}\text{Ce}_{0.06}\text{Th}_{0.04}\text{Na}_{0.03}\text{Ca}_{0.01}\text{U}_{0.01})$ $(\text{Nb}_{1.79}\text{Ti}_{0.17}\text{Fe}^{3+}_{0.02}\text{Ta}_{0.02})[\text{O}_{5.79}(\text{OH})_{0.21}][\square_{0.79}(\text{H}_2\text{O})_{0.23}\text{Tl}_{0.09}]$
BAPY_L	$[\square_{0.99}\text{Ba}_{0.51}(\text{H}_2\text{O})_{0.40}\text{Ce}_{0.07}\text{Na}_{0.01}\text{La}_{0.01}\text{Th}_{0.01}]$ $(\text{Nb}_{1.83}\text{Ti}_{0.17})[\text{O}_{5.14}(\text{OH})_{0.86}](\text{H}_2\text{O})$
BAPY_N	$(\square_{1.36}\text{Ba}_{0.49}\text{Ce}_{0.11}\text{Th}_{0.02}\text{Na}_{0.01}\text{La}_{0.01})$ $(\text{Nb}_{1.78}\text{Ti}_{0.21}\text{Fe}^{3+}_{0.01})[\text{O}_{5.20}(\text{OH})_{0.80}][(\text{H}_2\text{O})_{0.84}\square_{0.16}]$

As shown in Table 4.4, the highest Tl^+ content calculated for Ba-bearing hydrokenopyrochlore is 0.63 apfu, ~44% of the amount incorporated by (Sr,K)-bearing hydrokenopyrochlore treated in Tl-rich solutions for equal or shorter durations (Taddei *et al.*, 2024; Taddei and Bindi, 2025). The reduced uptake efficiency could be due to the different exchange mechanisms: in hydrokenopyrochlore from Lueshe, H^+ is the main exchanger, whereas in hydrokenopyrochlore from Araxá it seems to be Ba^{2+} (with suspected additional H^+ involvement as previously discussed). This difference not only reduces the overall ion-exchange capacity, which is dramatically higher for hydrokenopyrochlore from Lueshe, but also slows down reaction kinetics. In fact, as shown by Taddei and Bindi (2025), the Lueshe sample reaches saturation in less than one day of imbibition in a 1 M Tl^+ solution, while the Araxá sample reacts more slowly (Figure 4.5). The slower kinetics may rise from Ba, a divalent cation, which is exchanged instead of the much more mobile H^+ .

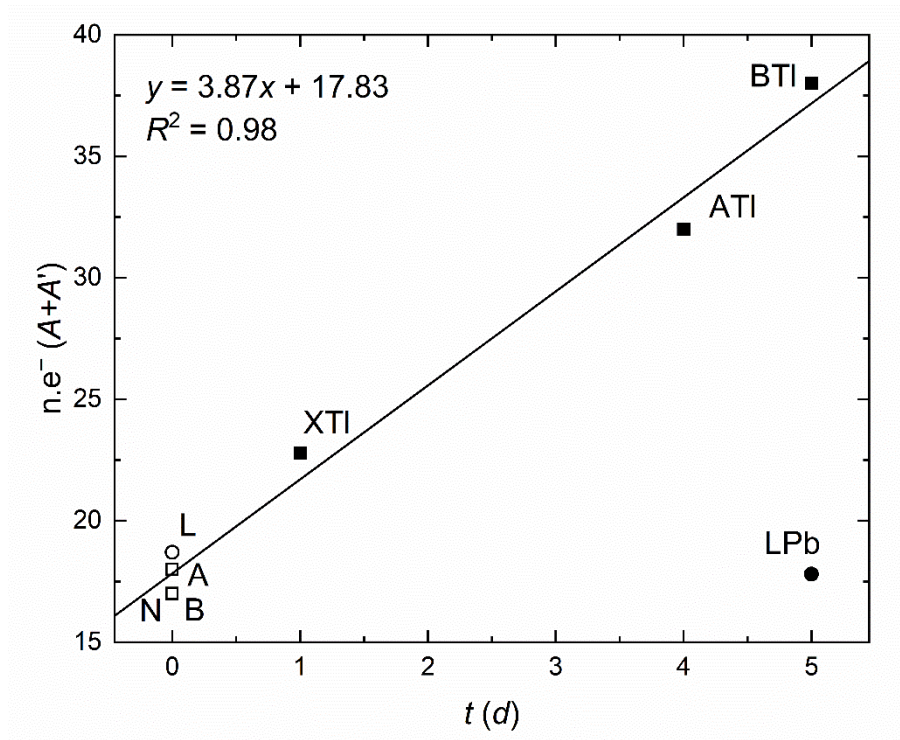


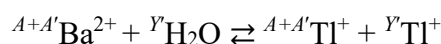
FIGURE 4.5. Number of electrons at $A+A'$ as a function of the time of imbibition. The black line, fitting the equation at top left of the figure, was calculated not considering the BAPY_LPb sample, given the different behaviour of the latter. Symbols as in Figure 4.1.

By contrast, imbibition in Pb-rich solutions, produced no major changes in the BAPY_L sample, making it extremely difficult to confirm the incorporation of Pb^{2+} without further investigations. The only observable effect was a slight shortening of the $A-X$ distance (Table 4.3) and a corresponding small contraction of the unit-cell parameter (Table 4.2), consistent with the smaller ionic radius of Pb^{2+} in 8-fold coordination ($r^{\text{VIII}} = 1.29 \text{ \AA}$, Shannon, 1976). However, no increase of electrons at any tunnel site was observed, indicating minimal incorporation (if any). Pb may instead accumulate at grain rims, as already observed for synthetic hydrokenoelsmoreite single crystals (S. Margheri, personal communication, June 2025), which would hardly be detectable by single crystal X-ray diffraction and would need deeper investigation, possibly at a smaller scale.

4.1.4 Conclusions

Investigating the ion-exchange properties of different hydrated pyrochlores raises interesting questions that extend beyond the strictly environmental scope of this study. In particular, this chapter highlights a potential issue in the current classification of this supergroup of minerals, which relies on the dominant valence rule (Atencio *et al.*, 2010; Atencio, 2021). As already noted by Bhattacharjee *et al.* (2022), previously established species (*e.g.*, kalipyrochlore, bariopyrochlore, strontipyrochlore, *etc.*) are now all grouped as zero-valent-dominant species, leading to a loss of petrogenetic information. This also affects the evaluation of possible candidates for environmental applications, as hydrokenopyrochlores from different genetic environments may display significantly different ion-exchange capacities depending not only on their hydration degree but also on the cationic population at the tunnel sites.

Hydrokenopyrochlore from Araxá, formerly known as bariopyrochlore, appears to exhibit a different ion-exchange mechanism compared to hydrokenopyrochlore or hydropyrochlore from Lueshe (Taddei *et al.*, 2024; Taddei and Bindi, 2025), where only H⁺ seems to be involved. For the here studied samples, the proposed reaction is the following:



where water molecules are released from the structure to accommodate monovalent thallium, in agreement with the high analytical totals measured after the imbibition experiments. The reactions hypothesised for the Lueshe samples likely play only a minor role in the Tl-incorporation mechanism occurring for Ba-rich hydrokenopyrochlore, although the relative contributions of the two processes remain difficult to quantify.

A key issue in this chapter arises from the discrepancy between SC-XRD and EMPA data in one of the samples, which complicates the assessment of the Tl⁺-uptake efficiency. Further investigations are therefore necessary to better understand this mechanism. Noteworthy, a TEM study would be valuable to identify possible nanoscale causes, also allowing to determine the actual

distribution of Tl within the crystal, and providing a more detailed picture of the incorporation process. Given the growing concern over pollution from hazardous elements, especially heavy metals as toxic as thallium or lead dispersed in aqueous systems, comprehensive studies on potential sinks such as pyrochlores are not only relevant, but necessary to sift through all possible ways to counter the issue.

5. Hydrokenomicrolite and kenomicrolite from the Volta Grande pegmatite, Nazareno, Minas Gerais (Brazil)

5.1 Imbibition experiments of hydrokenomicrolite crystals in Ti-rich solutions

5.1.1 Introduction

Among the hydrous, defective members of the pyrochlore supergroup, representing ideal candidates to play a role in sequestration of heavy metals, hydrokenomicrolite is characterised by Ta-dominant octahedra, a vacancy-dominated *A* site, and a *Y* site primarily occupied by H₂O molecules, consistent with the ideal formula $\square_2\text{Ta}_2[\text{O}_4(\text{OH})_2](\text{H}_2\text{O})$. Like most minerals belonging to this supergroup, hydrokenomicrolite crystallises in the cubic system, space group $Fd\bar{3}m$; it is however worth noting that a rhombohedral polytype, hydrokenomicrolite-3*R* (space group $R\bar{3}m$), has also been reported. The former species *parabariomicrolite* (Ercit *et al.*, 1986), initially excluded from the pyrochlore supergroup (then referred to as a group) due to its rhombohedral symmetry – despite the structural analogies –, was later discredited, having been demonstrated to be identical to hydrokenomicrolite-3*R* (Atencio, 2016). The lowering of symmetry in the 3*R* polytype is attributed to the ordering of Ba and vacancies on split *A* sites.

The studied hydrokenomicrolite sample, representing the type material for this species, occurs as an accessory phase and as an alteration product of Na-Ca-dominant microlites within the Volta Grande pegmatite, Nazareno, Minas Gerais, Brazil (Andrade *et al.*, 2013a). Detailed investigation of this material, consisting of octahedral grains of 1–2 mm in size, led to the discovery of kenomicrolite (IMA 2024-097; Taddei *et al.*, 2025), the first pyrochlore-supergroup species to exhibit

predominantly vacant tunnel sites. The crystal-chemical features and ion-exchange properties of this new species are described and discussed in Paragraph 5.2. This finding corroborates the high variability in the degree of hydration among microlites at the Volta Grande pegmatite, which likely reflects subtle variations in the alteration environment and/or the presence or absence of microfractures at the microscale during the transformation of primary Na-Ca-microlites. These, in turn, commonly occur as small, relict inclusions within the larger octahedral grains.

5.1.2 Experimental methods

Chemical analyses

EMPA analyses were performed on several single crystals of hydrokenomicrolite, labelled HKM_# where “#” stands for a letter. Chemical analyses were also carried out on grains that were soaked in a Tl-rich solution directly from the epoxy mount as well. Counting times were 30 s (Fe, Pb, Ca, Sb, Ba, U, Na, F, Sn, Tl, Th, Mn, Zr, Si), 20 s (Ti, Sr, Ta), and 15 s (K, Ce, La, Nb, Al).

Chemical data were normalised based on ΣB cations = 2 apfu with all the iron considered to be trivalent. Average values are reported in Table 5.1. Low analytical totals indicate the presence of H₂O, which was calculated according to the structural formula where possible.

Imbibition experiments

One single crystal, sample HKM_A, was chosen to be treated in a thallium(I) formate and deionised water solution having a 1M Tl⁺ concentration. The duration of the imbibition experiment was five days.

Additionally, a hydrokenomicrolite small fragment (HKM_Tl) was soaked in the 1M Tl⁺ solution for one day, while still embedded in the epoxy mount.

Single-crystal X-ray diffraction

Diffraction data were collected from the crystals previously investigated via electron microprobe; data related to the sample that underwent treatments in the

Tl⁺-rich solution were collected both before and after the imbibition experiment. Intensity data and unit-cell parameters are listed in Table 5.2. The data were integrated and corrected for Lorentz-polarisation effects and for absorption via the APEX5 software suite (Bruker, 2023). All the studied crystals yielded poor-quality data due to the partial metamictisation (leading to poor crystallinity) and the difficulty in finding single-crystals that were not ‘powderish’ (leading to the presence of quite intense diffraction rings in the frames); several samples did not yield acceptable structural results and were thus discarded for this thesis work.

TABLE 5.1. Average microprobe analyses (wt.% oxides) and values normalised to $\Sigma B = 2$ apfu for treated and untreated HKM samples.

wt.%	HKM_A	HKM_I	HKM_J	HKM_XTI	apfu	HKM_A	HKM_I	HKM_J	HKM_XTI
<i>n</i>	6	5	5	8					
Al ₂ O ₃	0.05	0.07	0.04	0.07	Al	-	0.01	-	0.01
SiO ₂	0.36	0.36	0.37	0.41	Si	0.03	0.03	0.03	0.04
TiO ₂	0.17	0.19	0.11	0.03	Ti	0.01	0.01	0.01	-
Fe ₂ O ₃	0.08	0.03	0.07	0.27	Fe ³⁺	-	-	-	0.02
ZrO ₂	0.01	0.02	0.04	n.d.	Zr	-	-	-	-
Nb ₂ O ₅	3.36	3.04	3.48	3.85	Nb	0.13	0.11	0.13	0.15
SnO ₂	2.88	2.76	3.68	2.49	Sn	0.09	0.09	0.12	0.08
Sb ₂ O ₅	0.05	0.02	0.05	n.d.	Sb	-	-	-	-
Ta ₂ O ₅	76.90	77.06	75.92	73.28	Ta	1.73	1.74	1.70	1.70
Na ₂ O	0.01	0.01	0.02	0.01	Na	-	-	-	-
K ₂ O	0.20	0.07	0.10	0.20	K	0.02	0.01	0.01	0.02
CaO	0.11	0.01	n.d.	0.04	Ca	0.01	-	-	-
MnO	0.32	0.17	0.13	0.26	Mn ²⁺	0.02	0.01	0.01	0.02
SrO	0.39	0.60	0.11	0.47	Sr	0.02	0.03	0.01	0.02
BaO	4.52	8.15	7.04	6.26	Ba	0.15	0.27	0.23	0.21
Ce ₂ O ₃	0.76	0.91	0.89	0.42	Ce	0.02	0.03	0.03	0.01

TABLE 5.1 (*continued*)

La ₂ O ₃	0.24	0.02	0.05	0.21	La	0.01	-	-	0.01
Tl ₂ O	0.05	0.07	0.14	4.17	Tl ⁺	-	-	-	0.10
PbO	2.32	1.48	0.15	0.70	Pb	0.05	0.03	-	0.02
ThO ₂	0.01	n.d.	0.04	n.d.	Th	-	-	-	-
UO ₂	2.34	1.90	2.36	1.98	U	0.04	0.04	0.04	0.04
F	0.35	0.28	0.27	0.24	F	0.09	0.07	0.07	0.06
= O	-0.15	-0.12	-0.12	-0.10					
Total	95.33	97.10	94.94	95.26					
H ₂ O*	5.13	4.07	5.80			2.83	2.26	3.19	
TOTAL	100.46	101.17	100.74						

Notes: *calculated from the structural formula; *n* = number of analytical points; n.d. = not detected.

TABLE 5.2. SC-XRD experimental details and crystal data for hydrokenomicrolite crystals before and after Tl and Pb imbibition experiments.

	HKM_A	HKM_ATI	HKM_I	HKM_J
a (Å)	10.553(2)	10.614(2)	10.5633(16)	10.565(3)
V (Å ³)	1175.4(7)	1195.9(8)	1178.7(5)	1179.2(9)
size (µm)	160 × 130 × 130	60 × 60 × 50*	160 × 90 × 80	120 × 80 × 70
$\theta_{\max}$ (°; MoK α)	32	32	33	32
R_{int} (%)	13.96	10.31	12.39	11.84
indep. refl.	123	125	130	125
obs. refl.	82	76	88	87
$[F_o > 4\sigma(F_o)]$				
Ref. param.	14	15	15	13
$R1_{\text{all}}$ (%)	9.45	14.01	7.80	8.65
$R1_{\text{obs}}$ (%)	5.56	9.34	4.98	5.83
$\Delta\rho_{\max}$ (e ⁻ /Å ³)	3.68	4.37	2.14	1.64
$\Delta\rho_{\min}$ (e ⁻ /Å ³)	-4.17	-4.11	-3.86	-2.75

Notes: *the crystal broke after the imbibition experiment, decreasing significantly its size.

Structure refinements

Structure refinements were carried out in the space group $Fd\bar{3}m$ (origin choice 2) using SHELXL (Sheldrick, 2015). The initial model was based on the following atomic positions: A at the Wyckoff position $16d$ ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), B at $16c$ (0, 0, 0), Y at $8b$ ($\frac{3}{8}$, $\frac{3}{8}$, $\frac{3}{8}$), and X at $48f$ (x , $\frac{1}{8}$, $\frac{1}{8}$). The only variable coordinate, x of the X site, was initially set to the value reported by Andrade *et al.* (2013a), refined from the holotype material for hydrokenomicrolite. The X site was found to be fully occupied in all samples, while the site occupancy factor of the B site was fixed to match EMPA data.

At this stage, the ΔF of the models revealed an unusually large isotropic displacement parameter of the Y site, indicating high local disorder; moreover, in two out of three refinements related to untreated samples an anomalously high positive residue in the vicinity of the A site was observed. To address these issues, a supplementary A' site, displaced at a $32e$ position in the neighbourhood of A , was added for HKM_A and HKM_I, restraining its displacement parameters to be equal

to those of A . In both cases, the s.o.f. of A was fixed to account for the contribution of the cationic population at this site observed through chemical analysis, while A' was assumed to host mostly water molecules (Ercit *et al.*, 1994; Taddei *et al.*, 2024). The Y atom was then relocated to a nearby $32e$ position, named Y' , which resulted in lower atomic displacement parameters. In the treated sample (HKM_ATI), this last operation was not necessary, keeping the atom at its original $8b$ position.

Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). They were applied as follows: $A = \text{Ba}$ vs. $\square$ (untreated crystals) or Tl vs. $\square$ (treated crystal); $A' = \text{O}$ vs. $\square$ (where present, untreated crystals) or Tl vs. $\square$ (treated crystal); $B = \text{Ta}$ vs. Nb ; $X = \text{O}$; $Y, Y' = \text{O}$ vs. $\square$ (all refinements).

Lastly, anisotropic atomic displacement parameters (ADPs) were refined for all atoms except Y' , which was isotropically refined, and convergence was achieved.

Bond distances and other structural parameters are listed in Table 5.3.

*Hydrokenomicrolite and kenomicrolite from the Volta Grande pegmatite,
Nazareno, Minas Gerais (Brazil)*

TABLE 5.3. Selected structural parameters for treated and untreated hydrokenomicrolite. Bond distances in Å, angles in °.

	HKM_A	HKM_ATI	HKM_I	HKM_J
n.e ⁻ (A)	9.7	30.8	14.4	12.7
n.e ⁻ (A')	1.9	8.1	1.7	-
n.e ⁻ (Y')	10.3	2.7*	4.8	10.3
x_{48f} (X)	0.317(2)	0.313(4)	0.317(2)	0.314(2)
x_{32e} (A')	0.558(12)	0.547(7)	0.563(17)	-
x_{32e} (Y')	0.336(8)**	-	0.354(6)	0.352(17)**
A-X (×6)	2.689(19)	2.73(3)	2.686(16)	2.709(15)
A-Y' (×2)	3.00(14)	-	2.67(7)	2.7(3)
A-Y (×2)	-	2.2980(5)	-	-
<A-O>	2.77	2.33	2.68	2.71
B-X (×6)	1.994(9)	1.991(15)	1.998(8)	1.987(7)
A'-X (×3)	2.73(13)	2.75(5)	2.76(19)	-
(×3)	3.03(13)	2.98(8)	3.08(18)	-
A'-Y' (×2)	3.18(16)	-	3.3(2)	-
A'-Y (×2)	-	3.16(8)	-	-
<A'-O>	2.96	2.94	3.02	-
X-X (u.)	2.87(3)	2.82(7)	2.87(3)	
X-X (s.)	2.777(10)	2.81(2)	2.779(10)	2.794(10)
<X-X>	2.82	2.82	2.82	2.82(3)
X-B-X	88.4(10)	89.9(17)	88.1(8)	89.3(8)
(X-B-X)'	91.6(10)	90.1(17)	91.9(8)	90.7(8)
B-X-B	138.7(14)	140(2)	138.4(12)	140.0(11)
B-X-A	104.7(4)	104.1(7)	104.8(3)	104.3(3)
A-X-A	87.9(8)	86.7(13)	88.1(7)	87.2(6)
σ^2 (B)	3.55	0.05	3.55	0.40

Notes: *refined at the Y site (8b); **refined as $x+1/2, -x+3/4, -x+1/4$ ($1/2, 1/2, 0$)+; u. = unshared edge of the octahedron; s. = shared edge between B and A polyhedra. Bond angle variance (σ^2) was computed according to the formula proposed by Robinson *et al.* (1971).

5.1.3 Results and discussion

The topology of the studied hydrokenomicrolite crystals is analogous to that of other cubic pyrochlores. The unit-cell parameter a , ranging from 10.553 to 10.565 Å, is consistent with that of other hydrous and defective members of the pyrochlore and microlite group, such as hydropyrochlore (10.555–10.604 Å; Ercit *et al.*, 1994; Taddei *et al.*, 2024), hydrokenopyrochlore (10.5300–10.5637 Å; see Chapter 4), and kenomicrolite (10.5707–10.5911 Å; Taddei *et al.*, 2025). Rijkeboerite, first described by Van Der Veen (1963) and later renamed *bariomicrolite* (Hogarth, 1977), is now believed to correspond to hydrokenomicrolite (Atencio *et al.*, 2010), displaying an a parameter of 10.570 Å, in agreement with the present findings. Interestingly, the single crystal of hydrokenomicrolite analysed by Andrade *et al.* (2013b) yielded a markedly shorter unit-cell parameter (10.454 Å), in contrast with the value obtained from powder data collected on the same material (10.5733 Å), which closely matches that of the present samples. After the imbibition experiment in the Tl-rich solution, the unit-cell parameter expanded by approximately 6%, reaching $a = 10.614$ Å. This behaviour, also observed for other Tl-treated pyrochlores (Zoppi, 2004; Taddei *et al.*, 2024; Figure 5.1), is a direct consequence of the incorporation of significant amounts of monovalent thallium at the tunnel sites, preferentially occupying the $A+A'$ positions as the amount of incorporated Tl^+ gradually increases (Taddei and Bindi, 2025).

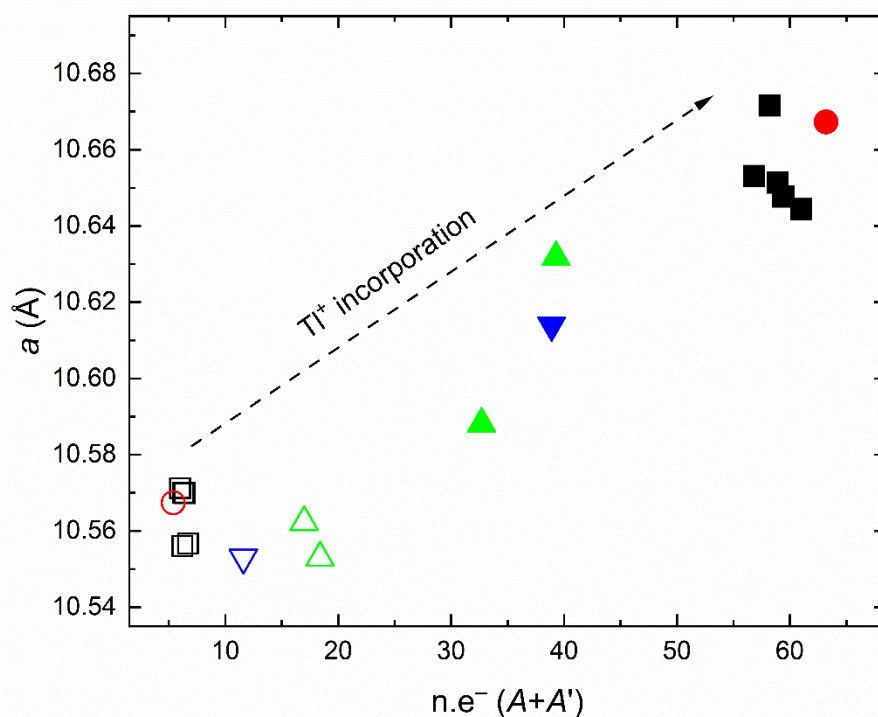


FIGURE 5.1. Unit-cell parameter against the number of electrons refined at $A+A'$ in different pyrochlore samples before and after imbibition in a Tl-rich solution. The expansion of a is related to the entry of Tl^+ at the A site. Symbols: blue, downward triangle = hydrokenomicrolite (data from this chapter); green, upward triangle = hydrokenopyrochlore (data from Chapter 4); black squares = hydrokenopyrochlore and hydropyrochlore (data from Taddei *et al.*, 2024); red circles = hydrokenopyrochlore (data from Taddei and Bindi, 2025); empty symbols = untreated samples; filled symbols = Tl-treated samples.

Indeed, the $A-X$ distance ranges from 2.686 to 2.709 Å prior to the imbibition, while after the experiment it lengthens to 2.73 Å, in keeping with an increase of electrons at the $A+A'$ sites from 11.6 to 38.9 e^- . Before the treatment, the cationic population at $A+A'$ involve Ba, which is by far the most abundant cation (0.15–0.27 apfu), followed by U (0.04 apfu in all samples) and Pb (0.03–0.05 apfu in HKM_A and HKM_J), with minor amounts (<0.03 apfu) of Ca, Mn, Sr, La, and Ce. These cations are retained after Tl uptake (Table 5.1), suggesting that Tl^+ is exchanged at the expense of an aqueous species (either H_2O+OH^- or H_3O^+) according to one of the two mechanisms proposed by Taddei *et al.* (2024) for hydropyrochlore and

hydrokenopyrochlore (see Chapter 3). However, the chemically analysed treated grain (HKM_XTl) appears to contain less Ti^+ than that calculated for HKM_ATl (Table 5.4). This discrepancy likely reflects the shorter duration of the HKM_XTl imbibition experiment (one day) compared to HKM_ATl (five days), as well as the influence of pre-existing or radiation-induced microfractures. Indeed, crystal HKM_ATl exhibits a dense network of microfractures that would have facilitated Ti^+ diffusion, while HKM_XTl appears more compact and less damaged.

The *B* site is dominated by Ta, which is substituted to a limited extent by Nb, Sn, Ti, and possibly minor amounts of Si and Al (Andrade *et al.*, 2013a), maintaining a quite constant composition across samples. The *B*–*X* distance well reflects the low compositional variability, showing a narrow range (1.987–1.998 Å). Although the *B* octahedron is not directly involved in the Ti^+ -incorporation process, it still experiences geometric adjustments due to its shared edge with the *A* polyhedron, where Ti^+ is mainly hosted. As the *A* polyhedron expands, the shared *X*–*X* edge lengthens and becomes slightly longer than the unshared one. According to Taddei *et al.* (2024), the entry of Ti^+ causes a distortion of the *B* octahedron, initially nearly regular in geometry ($x_{48f} = 0.3125$; Chakoumakos, 1984). This holds true for hydrokenopyrochlore and hydropyrochlore, where the octahedron starts from a regular geometry. In hydrokenomicrolite, however, the *B* octahedron is initially slightly flattened along its 3-fold axis ($x_{48f} = 0.317$; $\sigma^2 = 3.55$). Upon Ti-incorporation, the *X* atom shifts slightly along [100] ($x_{48f} = 0.313$), resulting in an almost regular octahedron ($\sigma^2 = 0.05$), although the shared edge remains marginally shorter than the unshared one (Table 5.3). It therefore can be inferred that further Ti^+ -incorporation would push the x_{48f} coordinate below the ideal 0.3125 value, producing an elongation of the octahedron along its 3-fold axis, analogously to what observed for hydrokenopyrochlore and hydropyrochlore. Thus, the effect of Ti-incorporation is not to introduce distortion of the *B* octahedron *per se*, but to simply shift the x_{48f} coordinate towards lower values regardless of the starting geometry of *B*.

Before treatment, the *Y'* site hosts minor amounts of F (0.06–0.09 apfu) and K (0.01–0.02 apfu), as well as variable H_2O , which dominates the site in all samples.

In crystals HKM_A and HKM_J, the refined number of electrons suggests a fully occupied Y' site, though the oxygen from the aqueous species (plus F and K) does not fully account for the refined electron density; the values would match perfectly by assuming at this site a small quantity of Cs (0.04–0.05 apfu), undetected during microprobe analyses but reported in the type material by Andrade *et al.* (2013b). As a large, low-charge cation ($^{VI}\text{Cs}^+ = 1.67 \text{ \AA}$; Shannon, 1976), Cs can only be hosted at Y or nearby positions (Ercit *et al.*, 1993). On the other hand, the sample HKM_I appears only slightly more than half-occupied, pointing towards an intermediate composition between hydrokenomicrolite and kenomicrolite (Taddei *et al.*, 2025); nonetheless, the aqueous species remains dominant over vacancy. After the imbibition experiment, most of the water seems to have been lost from this site, as the number of electrons drops to $2.7 e^-$, whereas K and F are retained (Table 5.1). The amount of exchanged water closely matches the amount of incorporated Tl^+ , reinforcing the ion-exchange mechanisms proposed by Taddei *et al.* (2024). It is also noteworthy that, following Tl incorporation, the displaced Y' site shifts towards the $8b$ position. In highly hydrated pyrochlores, such displacement guarantees adequate separations between water molecules in the tunnels, otherwise too close to each other (Ercit *et al.*, 1994). As most of $^v\text{H}_2\text{O}$ is lost after the treatment, the adjustment is no longer needed, and the remaining atoms tend to prefer the centred, ideal $8b$ position.

Lastly, it was necessary to assume partial substitution of O^{2-} for OH^- at the X site to achieve charge neutrality. Table 5.4 reports the empirical formulae of the hydrokenomicrolite samples, both treated and untreated, derived by combining chemical and structural data. In particular, the H_2O content was calculated from the refined number of electrons after subtracting the contributions of other cations and anions at both tunnel sites; the same method was applied to calculate the amount of thallium pfu, where the initial electron density value was subtracted from the final one, and the remainder was considered to represent the contribution of Tl^+ .

*Hydrokenomicrolite and kenomicrolite from the Volta Grande pegmatite,
Nazareno, Minas Gerais (Brazil)*

TABLE 5.4. Crystal-chemical formulae for HKM_A (before and after Tl-incorporation), HKM_I, and HKM_J.

HKM_A	$[\square_{1.20}(\text{H}_2\text{O})_{0.48}\text{Ba}_{0.15}\text{Pb}_{0.05}\text{U}_{0.04}\text{Mn}_{0.02}\text{Sr}_{0.02}\text{Ce}_{0.02}\text{Ca}_{0.01}\text{La}_{0.01}]$ $(\text{Ta}_{1.73}\text{Nb}_{0.13}\text{Sn}_{0.09}\text{Si}_{0.03}\text{Ti}_{0.01})[\text{O}_{4.50}(\text{OH})_{1.50}][(\text{H}_2\text{O})_{0.89}\text{F}_{0.09}\text{K}_{0.02}]$
HKM_ATl	$[\text{Tl}_{0.68}\square_{0.52}(\text{H}_2\text{O})_{0.48}\text{Ba}_{0.15}\text{Pb}_{0.05}\text{U}_{0.04}\text{Mn}_{0.02}\text{Sr}_{0.02}\text{Ce}_{0.02}\text{Ca}_{0.01}\text{La}_{0.01}]$ $(\text{Ta}_{1.73}\text{Nb}_{0.13}\text{Sn}_{0.09}\text{Si}_{0.03}\text{Ti}_{0.01})[\text{O}_{5.18}(\text{OH})_{0.82}][\square_{0.68}(\text{H}_2\text{O})_{0.21}\text{F}_{0.09}\text{K}_{0.02}]$
HKM_I	$[\square_{1.16}(\text{H}_2\text{O})_{0.43}\text{Ba}_{0.27}\text{U}_{0.04}\text{Sr}_{0.03}\text{Ce}_{0.03}\text{Pb}_{0.03}\text{Mn}_{0.01}]$ $(\text{Ta}_{1.74}\text{Nb}_{0.11}\text{Sn}_{0.09}\text{Si}_{0.03}\text{Al}_{0.01}\text{Ti}_{0.01})[\text{O}_{4.67}(\text{OH})_{1.33}][(\text{H}_2\text{O})_{0.50}\square_{0.42}\text{F}_{0.07}\text{K}_{0.01}]$
HKM_J	$[\square_{0.88}(\text{H}_2\text{O})_{0.80}\text{Ba}_{0.23}\text{U}_{0.04}\text{Ce}_{0.03}\text{Mn}_{0.01}\text{Sr}_{0.01}]$ $(\text{Ta}_{1.70}\text{Nb}_{0.13}\text{Sn}_{0.12}\text{Si}_{0.03}\text{Ti}_{0.01})[\text{O}_{4.48}(\text{OH})_{1.52}][(\text{H}_2\text{O})_{0.92}\text{F}_{0.06}\text{K}_{0.02}]$

5.1.4 Conclusions

The structural behaviour exhibited by hydrokenomicrolite is comparable to that of other hydrous, defective pyrochlore-supergroup members, confirming its capacity to accommodate large monovalent cations such as Tl^+ within its tunnel sites. The crystal-chemical variations are consistent with a Tl^+ -incorporation mechanism involving an aqueous species (either $\text{H}_2\text{O}+\text{OH}^-$ or H_3O^+ ; Taddei *et al.*, 2024). These findings further validate the ion-exchange processes previously described for hydropyrochlore and hydrokenopyrochlore, and further highlight the key role of water molecules and structural vacancies in controlling cation uptake in these minerals; it is important to also remark that, in this case, Ba seems to be not involved, contrary to what happens to hydrokenopyrochlore from Araxá (see Chapter 4).

Hydrokenomicrolite demonstrates a decent potential for the sequestration of toxic monovalent cations, specifically Tl^+ . However, due to its partially metamict nature, the long-term stability of hydrokenomicrolite may be limited. Radiation-induced amorphization results in increased microfracturing and enhanced permeability, which could in turn facilitate the release of previously incorporated cations. Therefore, while hydrokenomicrolite provides a natural specimen to evaluate ion-exchange properties and assess their efficiency, its metamict state and the overall poor quality of hydrokenomicrolite crystals may render it less suitable

for direct environmental applications compared to structurally intact or synthetic pyrochlore-like materials. Given the hazard posed by heavy metals such as Tl^+ , it is mandatory that the materials designated for their immobilisation are stable under ambient conditions and resistant to alteration processes that could lead to the release of the incorporated elements into the environment.

5.2 Kenomicrolite, a new microlite-group mineral: crystal-chemical characterisation and ion-exchange properties

5.2.1 Introduction

Kenomicrolite, ideally $\square_2\text{Ta}_2[\text{O}_4(\text{OH})_2]\square$, is a new mineral (IMA 2024-097) from the Volta Grande pegmatite, Nazareno, Minas Gerais, Brazil. The general formula of pyrochlore-supergroup minerals is $A_{2-m}B_2X_{6-w}Y_{1-n}$, where m (0–1.7 apfu), w (0–0.7 apfu) and n (0–1 apfu) represent the number of vacancies at each site (Lumpkin and Ewing, 1995): kenomicrolite is the first mineral belonging to the pyrochlore supergroup having both A and Y dominated by vacancy and the B site dominated by Ta, making it, ideally, a tantalum oxyhydroxide. Kenomicrolite was allegedly observed at the María Elena pegmatite, Sierra de San Luis, Argentina (Galliski *et al.*, 2021) and at the São João Del Rei Pegmatite Province, Minas Gerais, Brazil (Menezes da Silva, 2018; Alves *et al.*, 2021), where the present sample was also found; however, none of these authors provided exhaustive data. The chosen name complies to the currently approved nomenclature system for pyrochlore-supergroup minerals (*yaroot* rule, Atencio *et al.*, 2010; Atencio, 2021). The root name is microlite, as Ta dominates B ; both tunnel sites (A and Y) are dominated by structural vacancy, thus the prefix ‘keno-’. Where the first and second prefixes are equal, then only one prefix is applied. The recommended mineral symbol is kmic (Warr, 2021).

Holotype material, consisting of two small kenomicrolite crystals, is deposited in the mineralogical collection of the Museo di Storia Naturale, Sezione di Mineralogia e Litologia, Università di Firenze, Firenze (Italy), under catalogue number MSN-MIN 3747-I.

Kenomicrolite was discovered during a systematic study of hydrokenomicrolite crystals with the aim of investigating their ion-exchange capacity. Indeed, pyrochlore minerals and their synthetic analogues exhibit significant ion-exchange properties (Möller *et al.*, 2002; Zoppi, 2004; Han *et al.*, 2014; Taddei *et al.*, 2024), due to the easy leachability of the A and Y species, especially when they are large and have low charge (K^+ , Cs^+ , Tl^+ , *etc.*) and/or highly

mobile (H₂O). This property has significant environmental implications, since pyrochlores can represent promising candidates as sinks for toxic metals such as Tl or Pb. The number of possible exchangers at the tunnel sites in kenomicrolite is very limited, given that both sites are vacancy-dominated, and they are mainly represented by aqueous species (H₂O + OH⁻ or H₃O⁺); for this reason, kenomicrolite should not be regarded as the best choice for heavy metals immobilisation. Nonetheless, the incorporation mechanism involving Tl⁺ in the structure of kenomicrolite was hereby investigated in order to have more insights on the limits of critical features of the crystal structure of pyrochlore minerals.

5.2.2 Occurrence

The new mineral (Figure 5.2) occurs at the Volta Grande pegmatite (21°10'08.6"S, 44°36'01.3"W), Nazareno, Minas Gerais, Brazil as an accessory phase. The pegmatite belongs to the Sn-Ta-rich São João del Rei Pegmatite Province (Heinrich, 1964; Lagache and Quemeneur, 1997). The Volta Grande granitic pegmatite is associated with Transamazonian granites (Early Proterozoic) hosted by the Archean greenstone belt of the Rio das Mortes Valley, which is situated at the southern border of the São Francisco Craton, in Minas Gerais, Brazil (Lagache and Quemeneur, 1997). The pegmatite bodies, which are usually large (up to 1200 × 40 m), show a dominant intermediate zone containing spodumene, microcline, albite and quartz, with an irregular border of an aplitic facies surrounded by an extensive metasomatic aureole with 'zinnwaldite', phlogopite and holmquistite. The spodumene-rich core zone is continuous or segmented and also contains lenses of 'lepidolite'. The main rock type that hosts the pegmatite is an amphibole schist. This pegmatite is characterised by their high Rb and Li content (Lagache and Quemeneur, 1997). The paragenetic position of the mineral could not be determined, as it was found in a large octahedral fragment collected in a heavy mineral concentrate (see Andrade *et al.*, 2013b). The octahedral fragments are formed by an association of kenomicrolite and hydrokenomicrolite together with Na-rich fluorcalciomicrolite, pointing to a possible secondary origin of kenomicrolite. The leaching of Ca, Na and F from primary fluorcalciomicrolite can be a consequence of weathering (Lumpkin and Ewing, 1992), followed by a subsequent limited uptake of locally enriched cations

(in this case, Ba, Ce, U, Pb, Mn, Sr) as well as water molecules. Depending on the entity of the hydration process, either hydrokenomicrolite or kenomicrolite can form this way.

Other associated minerals within the pegmatite are albite, fluorapatite, beryl, bityite, cassiterite, epidote, fluorite, ‘garnet’, gahnite, hydroxycalciumicrolite, ‘lepidolite’, magnetite, microcline, monazite-(Ce), muscovite, quartz, rutile, spodumene, tantalite-(Mn), ‘tourmaline’ and zircon.

Nazareno is the type locality for hydrokenomicrolite (Andrade *et al.*, 2013a), fluorcalciumicrolite (Andrade *et al.*, 2013b), hydroxycalciumicrolite (Andrade *et al.*, 2017) and oxycalciumicrolite (Menezes Da Silva *et al.*, 2020).

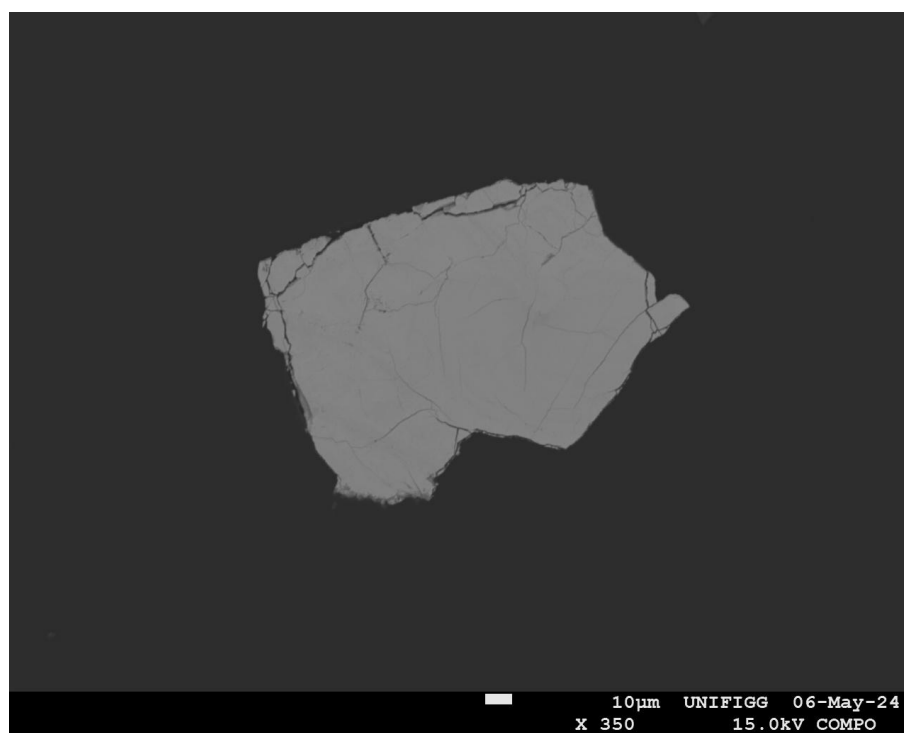


FIGURE 5.2. Back-scattered electrons (BSE) image of the investigated kenomicrolite fragment.

5.2.3 *Appearance, physical and optical properties of kenomicrolite*

Kenomicrolite is hypothesized to form small domains up to 200 μm in size in hydrokenomicrolite euhedral octahedral crystals, probably pseudomorph after fluorcalciomicrolite (Figure 5.2). The colour is pale orange, with a white streak; the crystals are transparent with an adamantine to resinous lustre, and they have an altered appearance, hardly distinguishable from hydrokenomicrolite grains. Kenomicrolite is brittle and displays a conchoidal fracture, while no cleavage or parting are observed; estimated Mohs hardness is 6. It shows no fluorescence under UV-light. The density was not measured because of the size of available grains. The calculated value of $5.599 \text{ g}\cdot\text{cm}^{-3}$ was obtained on the basis of the empirical chemical formula and the unit-cell volume obtained from single-crystal XRD data (see below).

Kenomicrolite is isotropic, with $n_{\text{calc}} = 1.880$ (from the Gladstone-Dale relationship for the empirical formula; Mandarino, 1981). Other optical data were not collected given the availability of only two small crystals.

5.2.4 *Chemical data*

Chemical analyses were carried out on the fragment from which the crystal used for the structural study was extracted, using a Jeol JXA-8230 electron microprobe (EMPA; tungsten cathode) in wavelength dispersion mode (WDS) at 15 kV acceleration voltage, 10 nA beam current and 2 μm beam size. The total number of spot analyses on the investigated crystal was 5. Based on standard deviation values, the crystal was found to be homogeneous (with slightly variable degrees of hydration from point to point). The occurrence of H_2O was confirmed by infrared spectroscopy and was calculated in accordance with the results of the crystal structure refinement; a direct measurement was prevented by dearth of material. All Fe was assumed to be Fe^{3+} and all Sn to be Sn^{4+} . Th and Zr were measured but were found to be below the detection limit (0.01 wt.%). Mean analytical results are given in Table 5.5.

*Hydrokenomicrolite and kenomicrolite from the Volta Grande pegmatite,
Nazareno, Minas Gerais (Brazil)*

The empirical formula, calculated on the basis of 2 *B* cations pfu, can be written as

${}^A(\square_{1.61}\text{Ba}_{0.29}\text{Ce}_{0.03}\text{U}_{0.03}\text{Pb}_{0.02}\text{Mn}_{0.01}\text{Sr}_{0.01})_{\Sigma 2.00}{}^B(\text{Ta}_{1.74}\text{Nb}_{0.11}\text{Sn}_{0.08}\text{Si}_{0.05}\text{Al}_{0.01}\text{Ti}_{0.01})_{\Sigma 2.00}{}^X[\text{O}_{4.65}(\text{OH})_{1.35}]_{\Sigma 6.00}{}^Y[\square_{0.57}(\text{H}_2\text{O})_{0.35}\text{F}_{0.07}\text{K}_{0.01}]_{\Sigma 1.00}$. The ideal chemical formula of kenomicrolite is thus $\square_2\text{Ta}_2[\text{O}_4(\text{OH})_2]\square$, which requires Ta_2O_5 96.09, H_2O 3.91, total 100.00 wt.%.

TABLE 5.5. Analytical data (in wt.%) for kenomicrolite.

Constituent	wt.%	Range	Stand. dev.
Nb ₂ O ₅	2.88	2.15–3.05	0.44
Sb ₂ O ₅	0.02	0.00–0.04	0.04
Ta ₂ O ₅	77.63	76.00–78.46	1.08
SiO ₂	0.66	0.20–1.27	0.43
TiO ₂	0.17	0.00–0.24	0.10
SnO ₂	2.48	1.89–2.76	0.38
UO ₂	1.89	1.75–1.99	0.09
Al ₂ O ₃	0.13	0.04–0.28	0.10
Fe ₂ O ₃	0.02	0.00–0.09	0.04
La ₂ O ₃	0.02	0.00–0.12	0.06
Ce ₂ O ₃	1.00	0.96–1.08	0.04
CaO	0.01	0.00–0.05	0.02
MnO	0.19	0.00–0.28	0.12
SrO	0.18	0.08–0.25	0.08
BaO	9.07	8.16–10.43	0.89
PbO	1.07	0.53–1.46	0.38
Na ₂ O	0.01	0.00–0.02	0.01
K ₂ O	0.10	0.08–0.14	0.02
Tl ₂ O	0.14	0.00–0.49	0.20
F	0.27	0.15–0.46	0.16
H ₂ O*	3.10		
O=F	–0.11		
TOT	100.93		

Notes: *calculated from structural formula – the value in atoms per formula unit (apfu; 1.35 at *X* + 0.35 at *Y*) was converted to H₂O wt.% as follows: the value in apfu was divided by the normalisation parameter ($\Sigma B = 2$ apfu) and then multiplied by two to obtain H₂O mol.%. The latter was then multiplied by the molecular weight of H₂O, resulting in H₂O wt.%.

5.2.5 *X-ray diffraction*

Single crystal data

Single-crystal X-ray diffraction investigations were performed on two single crystals (labelled KM and KM2) extracted from the fragment in Figure 5.2, with a Bruker D8 Venture diffractometer equipped with a Photon III detector. Unit-cell parameters and intensity data were collected using graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å). Crystal data and experimental conditions are listed in Table 5.6. Intensity data were integrated by means of the APEX5 software suite (Bruker, 2023) and corrected for Lorentz-polarisation effects and for absorption (multi-scan method – SADABS). Given the close relation to other cubic pyrochlore minerals, the structure was refined in the space group $Fd\bar{3}m$ (origin choice 2) using the program SHELXL (Sheldrick, 2015). The refinement was carried out starting from the atomic coordinates reported for hydrokenomicrolite (Andrade *et al.*, 2013a) for *A*, *B*, *X* and *Y*. All these sites are located at special Wyckoff positions: *A* = 16*d*, *B* = 16*c*, *X* = 48*f* and *Y* = 8*b*. Site occupancy factors (s.o.f.s) were refined using the following scattering curves for neutral atoms (from the *International Tables for Crystallography*; Wilson, 1992): Ba vs. $\square$ (*A*), Ta vs. Nb (*B*), O (*X*), O vs. $\square$ (*Y*). The s.o.f. value of the *B* site was fixed to EMPA values. Final coordinates and equivalent isotropic displacement parameters are given in Table 5.7, while selected interatomic distances are reported in Table 5.8.

Table 5.9 contains a comparison between the electron numbers calculated from microprobe data and those obtained from the structural model of sample KM; lastly, the bond valence sums (BVSs), calculated for the KM crystal considering the site populations as obtained from microprobe data and using the parameters given by Brese and O’Keeffe (1991), are reported in Table 5.10.

TABLE 5.6. Crystal data, experimental details and refinement details for kenomicrolite and Tl-treated kenomicrolite.

Crystal data	KM	KM2	KM2_Tl
Crystal size (mm)	0.070 × 0.070 × 0.050	0.120 × 0.110 × 0.100	0.120 × 0.110 × 0.100
Cell setting, space group	Cubic, $Fd\bar{3}m$	Cubic, $Fd\bar{3}m$	Cubic, $Fd\bar{3}m$
a (Å)	10.5911(6)	10.5707(17)	10.574(3)
V (Å ³)	1188.0(2)	1181.2(6)	1182.3(10)
Z	8	8	8
Data collection details			
Radiation, wavelength (Å)	MoK α , $\lambda = 0.71073$	MoK α , $\lambda = 0.71073$	MoK α , $\lambda = 0.71073$
Temperature (K)	298	298	298
$2\theta_{\max}$ (°)	63.79	63.93	63.91
Measured reflections	4155	1955	1571
Unique reflections	125	125	125
Reflections with $F_o > 4\sigma(F_o)$	95	93	93
R_{int} (%)	7.24	7.56	7.73
Range of h, k, l	$-15 \leq h \leq 15$	$-13 \leq h \leq 15$	$-15 \leq h \leq 12$
	$-15 \leq k \leq 15$	$-13 \leq k \leq 15$	$-11 \leq k \leq 13$
	$-15 \leq l \leq 15$	$-15 \leq l \leq 13$	$-10 \leq l \leq 15$
Refinement details			
$R1$ [$F_o > 4\sigma(F_o)$]	0.0291	0.0447	0.0648
$R1$ (all data)	0.0420	0.0621	0.0792
GoF	1.194	1.278	1.161
Number of least-square parameters	12	12	13

*Hydrokenomicrolite and kenomicrolite from the Volta Grande pegmatite,
Nazareno, Minas Gerais (Brazil)*

TABLE 5.7. Atomic coordinates, Wyckoff positions, site occupancy factors (*s.o.f.*) and equivalent isotropic displacement parameters ($\text{\AA}^2$) for kenomicrolite and Tl-treated kenomicrolite.

site	Wyckoff	<i>s.o.f.</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
KM						
<i>A</i>	16 <i>d</i>	Ba _{0.197(9)} □ _{0.803}	½	½	½	0.013(2)
<i>B</i>	16 <i>c</i>	Ta _{0.85} *Nb _{0.15} *	0	0	0	0.0193(4)
<i>X</i>	48 <i>f</i>	O _{1.00}	0.3130(9)	⅛	⅛	0.0208(17)
<i>Y</i>	8 <i>b</i>	O _{0.45(11)} □ _{0.55}	⅜	⅜	⅜	0.07(4)**
KM2						
<i>A</i>	16 <i>d</i>	Ba _{0.193(17)} □ _{0.807}	½	½	½	0.013(4)
<i>B</i>	16 <i>c</i>	Ta _{0.85} *Nb _{0.15} *	0	0	0	0.0204(7)
<i>X</i>	48 <i>f</i>	O _{1.00}	0.3145(16)	⅛	⅛	0.026(3)
<i>Y</i>	8 <i>b</i>	O _{0.22(12)} □ _{0.78}	⅜	⅜	⅜	0.02(4)**
KM2_Tl						
<i>A</i>	16 <i>d</i>	Ba _{0.32(4)} □ _{0.68}	½	½	½	0.040(6)
<i>B</i>	16 <i>c</i>	Ta _{0.85} *Nb _{0.15} *	0	0	0	0.0309(16)
<i>X</i>	48 <i>f</i>	O _{1.00}	0.315(2)	⅛	⅛	0.037(5)
<i>Y</i>	8 <i>b</i>	O _{0.36(18)} □ _{0.64}	⅜	⅜	⅜	0.04(5)**

Notes: *fixed to EMPA values; ** U_{iso} .

TABLE 5.8. Selected interatomic distances ($\text{\AA}$) and angles ($^\circ$) for kenomicrolite and Tl-treated kenomicrolite.

	KM	KM2	KM2_Tl
<i>A</i> – <i>X</i> (×6)	2.725(7)	2.707(12)	2.71(2)
<i>A</i> – <i>Y</i> (×2)	2.2930(1)	2.2886(4)	2.2894(7)
< <i>A</i> –O>	2.617	2.602	2.601
<i>B</i> – <i>X</i> (×6)	1.988(3)	1.990(6)	1.992(8)
<i>X</i> – <i>B</i> – <i>X</i>	90.2(4)	90.9(7)	91.0(9)
<i>X</i> – <i>B</i> – <i>X'</i>	89.8(4)	89.1(7)	89.0(9)
<i>B</i> – <i>X</i> – <i>B</i>	140.8(5)	139.8(9)	139.6(13)
<i>B</i> – <i>X</i> – <i>A</i>	104.13(15)	104.4(3)	104.4(4)
<i>A</i> – <i>X</i> – <i>A</i>	86.8(3)	87.3(5)	87.4(7)

*Hydrokenomicrolite and kenomicrolite from the Volta Grande pegmatite,
Nazareno, Minas Gerais (Brazil)*

TABLE 5.9. Comparison between the observed and calculated mean atomic number (MAN, in number of electrons per site) for kenomicrolite and Tl-treated kenomicrolite.

KM			
Site	MAN _{obs}	Site occupancy	MAN _{calc}
<i>A</i>	11.0	$\square_{1.61}\text{Ba}_{0.29}\text{Ce}_{0.03}\text{U}_{0.03}\text{Pb}_{0.02}\text{Mn}_{0.01}\text{Sr}_{0.01}$	11.5
<i>B</i>	68.2*	$\text{Ta}_{1.74}\text{Nb}_{0.11}\text{Sn}_{0.08}\text{Si}_{0.05}\text{Al}_{0.01}\text{Ti}_{0.01}$	68.3
<i>X</i>	8.0	$\text{O}_{1.00}$	8.0
<i>Y</i>	3.6	$\square_{0.56}(\text{H}_2\text{O})_{0.35}\text{F}_{0.07}\text{K}_{0.01}$	3.6
KM2			
<i>A</i>	10.8	$\square_{1.61}\text{Ba}_{0.29}\text{Ce}_{0.03}\text{U}_{0.03}\text{Pb}_{0.02}\text{Mn}_{0.01}\text{Sr}_{0.01}$	11.5
<i>B</i>	68.2*	$\text{Ta}_{1.74}\text{Nb}_{0.11}\text{Sn}_{0.08}\text{Si}_{0.05}\text{Al}_{0.01}\text{Ti}_{0.01}$	68.3
<i>X</i>	8.0	$\text{O}_{1.00}$	8.0
<i>Y</i>	1.8	$\square_{0.56}(\text{H}_2\text{O})_{0.13}\text{F}_{0.07}\text{K}_{0.01}$	1.8
KM2_Tl			
<i>A</i>	17.9	$\square_{1.45}\text{Ba}_{0.29}\text{Tl}_{0.16}\text{Ce}_{0.03}\text{U}_{0.03}\text{Pb}_{0.02}\text{Mn}_{0.01}\text{Sr}_{0.01}$	11.5
<i>B</i>	68.2*	$\text{Ta}_{1.74}\text{Nb}_{0.11}\text{Sn}_{0.08}\text{Si}_{0.05}\text{Al}_{0.01}\text{Ti}_{0.01}$	68.3
<i>X</i>	8.0	$\text{O}_{1.00}$	8.0
<i>Y</i>	2.9	$\square_{0.89}\text{F}_{0.07}\text{Tl}_{0.03}\text{K}_{0.01}$	2.9

Notes: *fixed occupancy. MAN_{calc} always refers to the whole kenomicrolite fragment before the imbibition experiments.

TABLE 5.10. Bond valence sums (BVS) for kenomicrolite (sample KM), calculated considering populations as calculated from EMPA.

	<i>A</i>	<i>B</i>	SUM
<i>X</i>	$\downarrow \times 6 \rightarrow \times 2$ 0.053	$\downarrow \times 6 \rightarrow \times 2$ 0.815	1.74*
<i>Y</i>	$\downarrow \times 2 \rightarrow \times 4$ 0.069		0.28
SUM	0.46	4.89	
Expected value	0.44	4.92	

Notes: *in agreement with the partial substitution of O for OH at *X*.

Powder diffraction data

X-ray powder diffraction data were collected with a Gandolfi-like experiment on KM, using $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Unit-cell parameters refined from powder data (space group $Fd\bar{3}m$) are $a = 10.5628(3) \text{ \AA}$ and $V = 1178.52(10) \text{ \AA}^3$. A comparison of the measured powder diffraction data and those calculated from the structural model is given in Table 5.11.

5.2.6 Infrared spectroscopy

Fourier-transform infrared (FT-IR) data were collected in transmission mode by placing the KM crystal on an IR-transparent BaF_2 plate. The analyses were carried out by means of a Nicolet RaptIR microscope attached to a Nicolet iS50 FT-IR spectrometer (Thermo Fisher), equipped with a Polaris IR source, KBr beam splitter and a LN2 MCT detector. The spectrum (Figure 5.3) was collected adjusting the aperture size to that of the crystal; sixty-four scans were averaged, with a spectral range between $5000\text{--}650 \text{ cm}^{-1}$ and a resolution of 4 cm^{-1} .

Spectral features are observed at 893sh, 1009sh, 1077, 1236w, 1442, 1644, ~ 2700 to ~ 3600 , 3730w, 4023w, 4469w cm^{-1} . The large band occurring between 2700 and 3600 cm^{-1} and the small peak at 3730 cm^{-1} can be interpreted as due to O–H stretching vibrations, while H–O–H bending vibrations can be observed at 1644 cm^{-1} . A comparison with the spectrum of a hydrokenomicrolite single crystal (Figure 5.4), collected under identical instrumental conditions, shows a weaker H_2O bending mode band in kenomicrolite. This agrees with the lower amount of H_2O groups in kenomicrolite compared to hydrokenomicrolite. Bands between 840 and 1240 cm^{-1} are probably related to $\text{Ta}\cdots\text{O}\text{--H}$ bending vibrations (Andrade *et al.*, 2013a). Lastly, the weak bands above 4000 cm^{-1} can be ascribed to H_2O combination modes.

*Hydrokenomicrolite and kenomicrolite from the Volta Grande pegmatite,
Nazareno, Minas Gerais (Brazil)*

TABLE 5.11. X-ray powder diffraction data (d in Å) for kenomicrolite, sample KM.

<i>hkl</i>	<i>d_{calc}</i>	<i>I_{calc}</i>	<i>d_{meas}</i>	<i>I_{meas}</i>
111	6.1148	100	6.1	70
311	3.1933	52	3.18	40
222	3.0574	95	3.04	100
400	2.6478	32	2.637	28
331	2.4298	11	2.423	8
511,333	2.0383	16	2.032	16
440	1.8723	40	1.866	51
531	1.7902	16	1.784	16
533	1.6151	7	1.611	8
622	1.5967	37	1.593	40
444	1.5287	10	1.528	9
551,711	1.4831	10	1.479	8
553,731	1.3788	10		
800	1.3239	5		
751	1.2230	3		
662	1.2149	12		
840	1.1841	11		
753	1.1625	2		
931	1.1102	3		
844	1.0809	7		
<u>1022,666</u>	1.0191	9		
880	0.9361	3		
973	0.8983	2		
<u>1062</u>	0.8951	11		
884	0.8826	7		
<u>1151</u>	0.8735	2		
<u>1240</u>	0.8373	7		

Notes: calculated d -values were obtained by XPOW (Downs *et al.*, 1993) using the atomic coordinates and site occupancies reported in Table 5.7 (KM line).

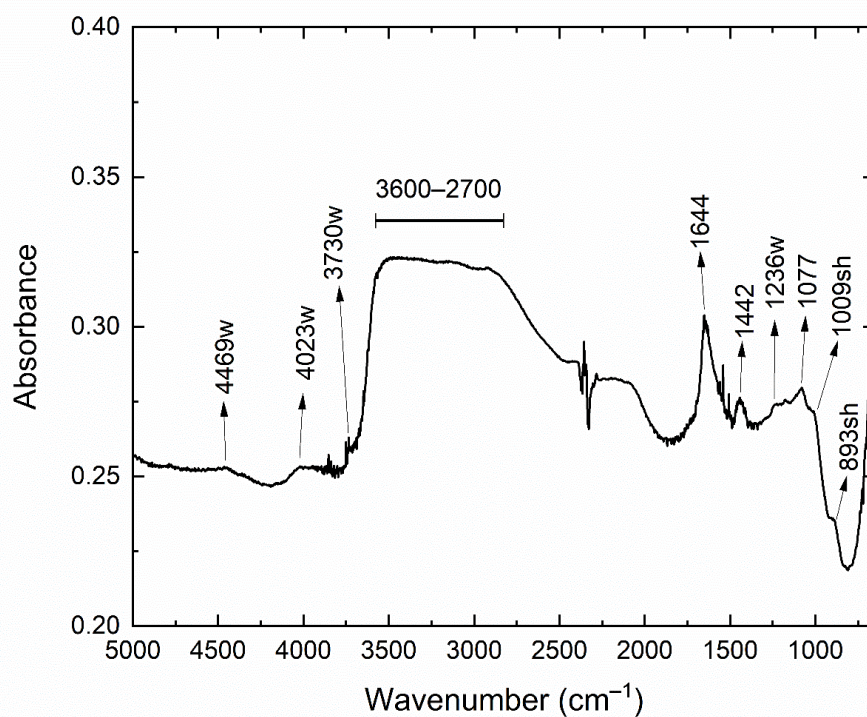


FIGURE 5.3. Transmission FT-IR spectrum of kenomicrolite.

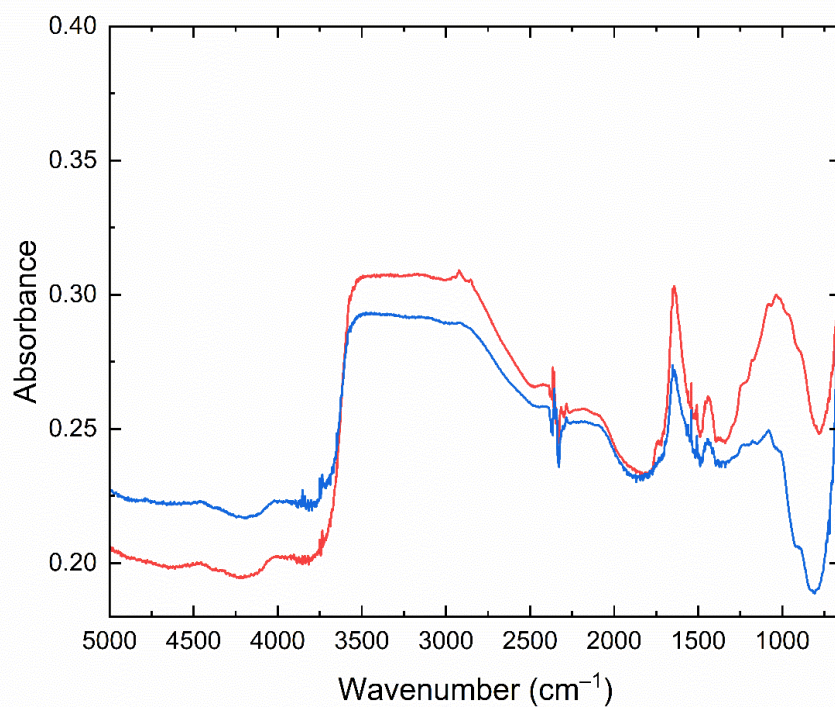


FIGURE 5.4. Comparison between the FT-IR spectra of kenomicrolite (blue) and hydrokenomicrolite (red).

5.2.7 Imbibition experiments in a Tl^+ -rich solution

KM2 was soaked for five days in a thallium(I) formate-deionised water solution having a concentration of 1M Tl^+ . SC-XRD data were collected before and after the imbibition experiment (Tables 5.6–5.7) as described above.

5.2.8 Discussion

Crystal-chemistry of kenomicrolite

The crystal structure of kenomicrolite (Figure 5.5) is topologically identical to that of other pyrochlore minerals crystallising in the space group type $Fd\bar{3}m$, showing a framework of corner-linked BX_6 octahedra that forms tunnels running parallel to $[110]$. The tunnels host the interstitial A and Y sites. In kenomicrolite, Ta is dominant at the B site, along with minor Nb, Sn, Si, Al and Ti. The A site has been found mainly vacant, having Ba as the most abundant cation (0.29 apfu) accompanied by minor (≤ 0.03 apfu) Ce, U^{4+} , Pb^{2+} , Mn^{2+} and Sr. The total cationic population at this site is 0.39 apfu. In both crystals (KM and KM2), no H_2O groups were observed at A , as the refined electron number (11.0 e^- and 10.8 e^- , respectively) well matches that calculated from microprobe data (11.5 e^-), even without additional water. The Y site was also found to be dominated by structural vacancy: the number of electrons refined at this site was 3.6 e^- for KM. Taking into account the contribute of minor F + K (~ 0.8 e^-), the remaining 2.8 e^- were assigned to O, corresponding to 0.35 H_2O pfu (the presence of which was confirmed by infrared spectroscopic analyses).

For KM2, the number of electrons refined at Y was even lower, 1.8 e^- , yielding 0.13 H_2O pfu; this discrepancy can be explained considering the slight difference in totals for the different spots, ranging from 96.24 wt.% up to 99.08 wt.% (mean 97.84 wt.%). KM2 was handpicked in a part of the fragment particularly depleted in aqueous species. Potassium was assumed at Y due to the relatively large ionic radius and low charge (see Ercit *et al.*, 1993, 1994). Finally, the charge balance was achieved by replacing O for $(OH)^-$ at the X site $[O_{4.65}(OH)_{1.35}]_{\Sigma 6.00}$.

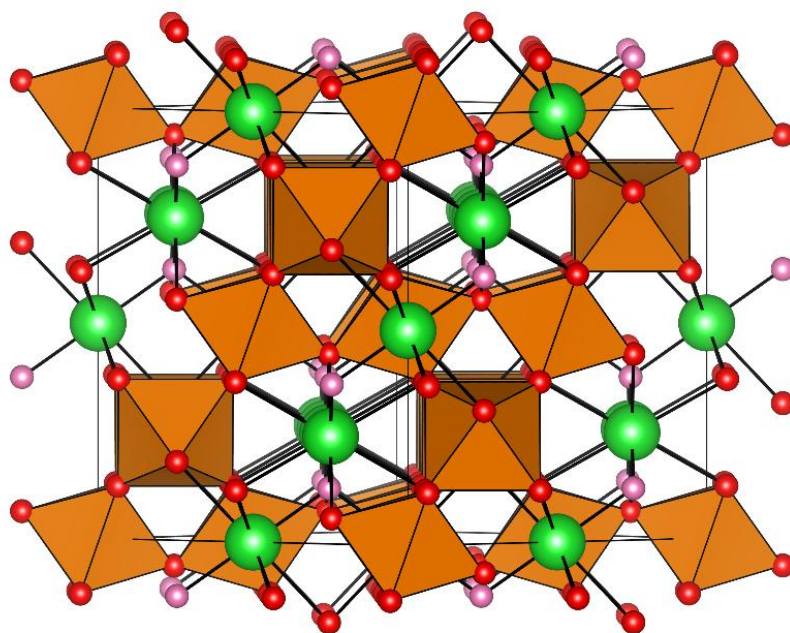


FIGURE 5.5. Kenomicrolite crystal structure approximately down [110]. Symbols: orange octahedra = *B*; green spheres = *A*; red spheres = *X*; pink spheres = *Y*.

Kenomicrolite displays a larger *a*-parameter (10.591 Å) than other zero-valent-dominant microlite-group minerals, *e.g.*, hydroxykenomicrolite (*a* = 10.526 Å, formerly known as ‘cesstibtantite’; Ercit *et al.*, 1993; Atencio *et al.*, 2010) or hydrokenomicrolite (*a* = 10.454 Å; Andrade *et al.*, 2013b). The latter, however, shows a unit-cell parameter refined from powder XRD data much closer to that of kenomicrolite, namely 10.573 Å; furthermore, a Pb-bearing microlite mineral with the *A* site dominated by H₂O or vacancy was described by Zoppi (2004), having an *a*-parameter of 10.569 Å. Among the hydrous pyrochlore-group minerals (thus having dominant Nb at *B*), the closest values are those of hydroxykenopyrochlore (*a* = 10.590 Å; Miyawaki *et al.*, 2021) and hydropyrochlore (*a* = 10.54–10.60 Å; Van Wambeke, 1978; Ercit *et al.*, 1994; Philippo *et al.*, 1995; Taddei *et al.*, 2024). The numerous data available for hydropyrochlore (formerly named ‘kalipyrochlore’) make evident a marked variability of the unit cell in samples from the same locality, or even from the same fragment, possibly due to a certain degree of variability in composition. This could justify the slight difference observed

between the unit-cell parameter of KM and that of KM2, which are reasonably similar anyway.

Small deviations in the crystal structure among different pyrochlore mineral species usually occur due to positional disorder at the tunnel sites, which could give rise to split sites located in the vicinity of the ideal A ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and Y ($\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$) positions. The comparison between the kenomicrolite structure and that of hydrokenomicrolite (Andrade *et al.*, 2013a), fairly similar in composition, highlights one of the aforementioned differences: hydrokenomicrolite, containing relatively large amounts of H₂O at both tunnel sites, shows a partially occupied site near Y (Y' , 32e). This slight displacement from the ideal Y position is, in principle, necessary to maintain a physically sound distance between the oxygens when H₂O groups are simultaneously present at both A and Y (Ercit *et al.*, 1994). The distance between the two ideal positions is indeed ~ 2.3 Å, too short for acceptable O–O separations. In kenomicrolite this displacement does not occur, consistently with the absence of H₂O groups at A .

Ion-exchange properties of kenomicrolite

Pyrochlore minerals that host leachable cations (*e.g.*, Na⁺, K⁺, *etc.*) or aqueous species (H₂O, H₃O⁺) at the tunnel sites, can usually show enhanced ion-exchange capacity, especially for large-radius, low-charge cations (*e.g.*, Tl⁺). Taddei *et al.* (2024) pointed out two possible Tl⁺ incorporation mechanisms, involving either (H₂O + OH[−]) or H₃O⁺. In kenomicrolite, none of the cations hosted at A and Y are monovalent (except a very minor amount of K⁺ at Y) and the water content in the structure is low and limited to the Y site; therefore, a poor ion-exchange capacity is expected for this mineral. Indeed, after the imbibition experiment in a Tl-rich solution, only a slight increase of electron density is observed at both the A (17.9 e[−]) and Y (2.9 e[−]) sites, corresponding to an incorporation of approximately 0.16 Tl⁺ pfu at A and ~ 0.03 Tl⁺ pfu at Y . Considering the ion-exchange mechanisms proposed by Taddei *et al.* (2024), these values are consistent – within analytical error – with the total amount of H₂O + K⁺ calculated for KM2, namely 0.14 apfu. Nevertheless, no substantial structural changes occur, in contrast with hydropyrochlore crystals subjected to the same imbibition experiments (Taddei *et al.*, 2024): in

hydropyrochlore, Tl^+ incorporation induces an expansion of the unit cell due to the increase of the $A-X$ distances, as Tl preferentially orders at the A site. However, hydropyrochlore can ideally host up to 1.75 apfu of water at both tunnel sites (Ercit *et al.*, 1994), making its ion-exchange capacity significantly higher; in fact, the amount of incorporated Tl^+ can reach up to 1.40 apfu. The very small quantity of Tl^+ incorporated in kenomicrolite is probably insufficient to produce measurable structural effects such as an increase of the $A-X$ bond distances, as the observation of finer details would require better data quality (which is quite poor for these crystals, especially for KM2). Taddei and Bindi (2025) carried out a study on the kinetics of the Tl^+ incorporation reaction in hydrokenopyrochlore, highlighting an almost linear correlation between the estimated incorporated Tl at A and the $A-X$ distance (Figure 5.6). Given that the $A-X$ bond length of KM2 before the treatment is shorter than that of the hydrokenopyrochlore sample studied by Taddei and Bindi (2025), it was not possible to calculate how long the $A-X$ bond should be after the incorporation of ~ 0.16 Tl pfu at A using directly the equation in Figure 5.6. However, the extent of the lengthening of $A-X$ consequent to the incorporation of the same amount of Tl for hydrokenopyrochlore ($\sim 2\%$) would correspond, considering the starting distance in KM2 ($2.707 \text{ \AA}$), to an expansion up to $2.712 \text{ \AA}$, well within the error on the $A-X$ bond length observed for KM2_Tl (Table 5.8).

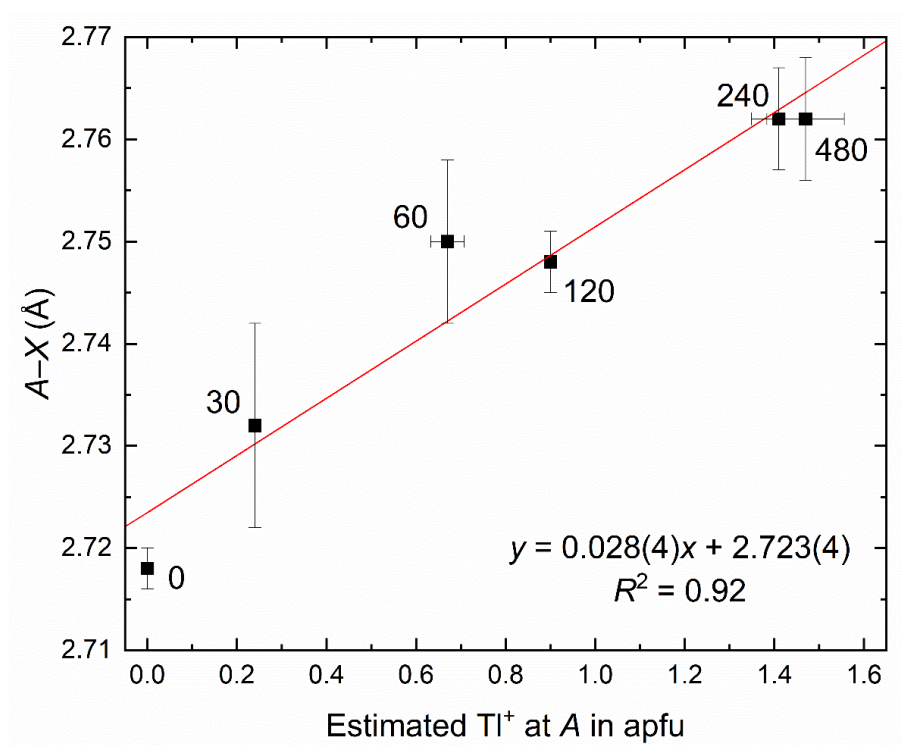


FIGURE 5.6. Linear correlation between the estimated amount of Tl^+ at the A site and the A – X distance, calculated using data from the hydrokenopyrochlore sample Hkpc1 in Taddei and Bindi (2025). The number near the symbols indicate the duration (not cumulative) of the imbibition experiment in minutes; error bars that are not visible are contained within the data symbols.

The hypothesis of a third reaction, based on the deprotonation of hydroxyl groups at X without water loss at Y (${}^A\text{Tl}^+ + {}^X\text{O}^{2-} \rightarrow {}^A\Box + {}^X\text{OH}^-$), cannot be ruled out. In hydropyrochlore, water loss is necessary due to stereochemical constraints; conversely, in kenomicrolite, which has almost-empty tunnel sites, there are no such constraints and water is not required to exit the structure to accommodate Tl^+ . This mechanism appears to be supported by FT-IR data collected on KM2 after the imbibition experiment (Figure 5.7): the H_2O bending mode peak weakens slightly but remains visible, while the broad O – H stretching band decreases more significantly. The peak at 3730 cm^{-1} , possibly attributable to the stretching of OH groups at X , weakens considerably and becomes barely distinguishable from background noise.

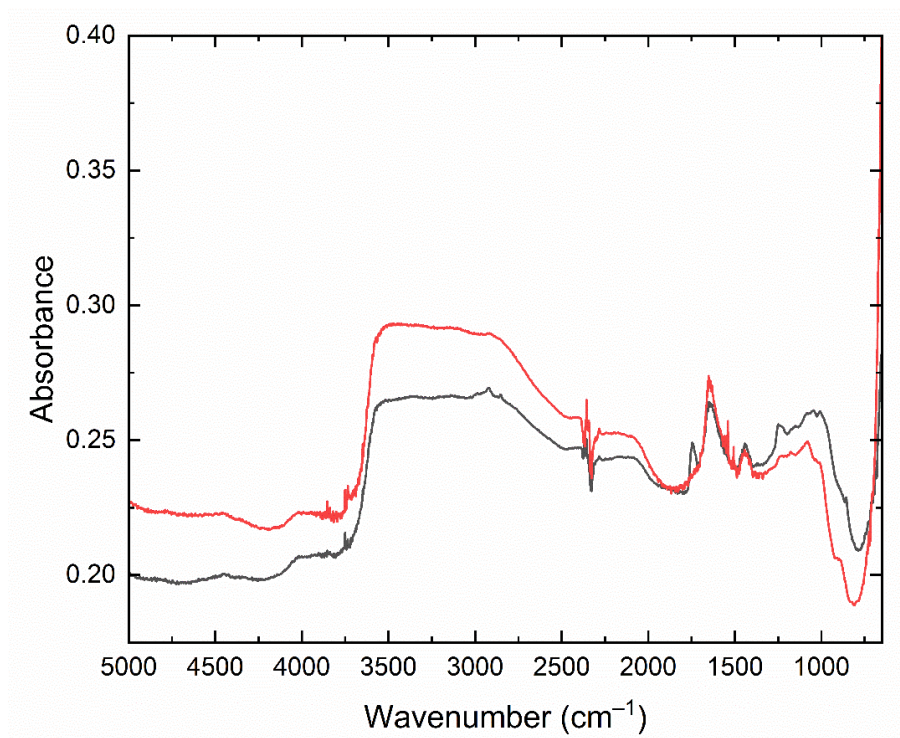


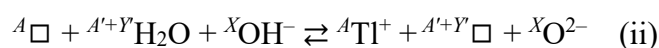
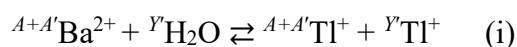
FIGURE 5.7. Comparison between the FT-IR spectra of untreated kenomicrolite (red) and Tl-treated kenomicrolite (black).

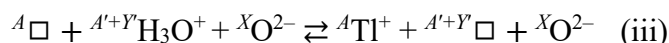
In this scenario, the reaction should not be limited by the amount of OH^- , as it occurs at X in much greater amounts than the Tl^+ incorporated. The limited efficiency of this process, compared to those described in Taddei *et al.* (2024), may be due to other factors such as the pH of the solution, P - T conditions, or even the absence of water, which could facilitate H^+ loss. As for the latter factor, it seems that in pyrochlore-like structures, when hydrogen is present both as tunnel-site water and as OH groups at X , an intra-tunnel reaction may occur with an equilibrium of the type ${}^B\text{M}-{}^X\text{OH} + {}^{A+Y}\text{H}_2\text{O} \rightleftharpoons {}^B\text{M}-\text{O}^- + \text{H}_3\text{O}^+$ (Slade *et al.*, 1996), potentially making H^+ exchange easier in highly hydrated pyrochlore minerals, where both molecular water and hydroxyl groups are largely present.

6. Conclusions

The results presented in this work advance the knowledge of pyrochlore-supergroup minerals by highlighting their crystal-chemical complexity and the mechanisms governing their ion-exchange properties. Their ability to accommodate a wide range of cations, including toxic heavy metals such as Tl^+ , confirms their structural versatility and environmental relevance.

The results of this work clearly indicate that hydrated pyrochlores can incorporate substantial amounts of monovalent thallium within their structures, specifically at the tunnel sites, ordering preferentially at the A site. The uptake process seems to be closely related to the presence of aqueous species at the tunnel sites, as they are loosely bound and act as exchangeable species. These findings provide indirect but convincing evidence for the possible presence of H_3O^+ in the structure of natural pyrochlores, a topic that remains a matter of debate and has implications for mineral systematics. If H_3O^+ actually occurs, a new prefix is needed, and several pyrochlore-supergroup species should be redefined. Comparative analyses among samples from different localities revealed significant variations in ion-exchange capacity and kinetics of the ion-exchange reactions, which are possibly influenced by the specific cationic population and hydration degree. For instance, two varieties of the same mineral species, hydrokenopyrochlore, showed different reaction kinetics based on the exchanged species: samples from Araxá showed slower Tl^+ incorporation, probably at the expenses of Ba^{2+} [reaction (i)], whereas samples from Lueshe displayed much faster exchange rates dominated by exchange reactions involving H^+ [reactions (ii) or (iii)].





In addition to the investigation strictly related to ion-exchange properties, this study also led to the identification and full characterisation of kenomicrolite, a new member of the microlite group, enriching the pyrochlore supergroup with a new species, the first to have the tunnel sites completely vacant, and broadening the understanding of the structural flexibility of these minerals.

Beyond their mineralogical and nomenclatural significance, these results point to promising environmental applications. The remarkable capability of natural, altered pyrochlores to incorporate toxic cations like monovalent thallium makes them ideal candidates for the development of remediation technologies to tackle the issue of heavy metal pollution in aqueous systems. It is important to remark that the presence of microfractures, extremely common in strongly weathered pyrochlores, represents a limitation to the retention of previously incorporated heavy metals, as it may promote leaching of the latter; thus, while natural pyrochlores provide valuable insights into ion-exchange mechanisms, their practical use as sinks for heavy metals should be complemented by the synthesis of pyrochlore-like compounds tailored for enhanced durability. In addition to this, further investigations are required to assess the long-term stability of the sequestration processes under variable conditions of pH, temperature, and competing ions.

This research thus contributes both to the understanding of the crystal-chemistry of pyrochlores and to their potential exploitation as natural or synthetic materials for environmental decontamination, bridging mineralogical and environmental perspectives.

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Appendices

A. Hydropyrochlore and hydrokenopyrochlore from Lueshe (D.R. Congo): additional data

In this appendix are reported additional data for the samples described and discussed in Chapter 3. Single-crystal X-ray diffraction experimental details and crystal data for the samples not included in the Chapter are reported in Table A.1, while Table A.2 contains selected structural parameters for the same samples.

TABLE A.1. SC-XRD experimental details and crystal data for the selected hydropyrochlore and hydrokenopyrochlore crystals from Lueshe.

	L2	L4	L5	L6
a (Å)	10.5699(4)	10.564(2)	10.545(3)	10.5605(8)
V (Å ³)	1180.9(1)	1178.9(8)	1173(1)	1177.8(3)
size (μm)	60×55×50	75×55×45	60×60×60	60×70×35
$\theta_{\max}$ (°; MoK α)	32	32	32	31
R_{int} (%)	4.35	6.08	9.29	8.37
indep. refl.	120	125	124	116
obs. refl.	96	97	91	85
$[F_o > 4\sigma(F_o)]$				
Ref. param.	12	12	13	12
$R1_{\text{all}}$ (%)	4.68	4.61	7.98	6.64
$R1_{\text{obs}}$ (%)	3.45	3.19	5.43	4.29
$\Delta\rho_{\max}$ (e/Å ³)	0.55	0.53	1.10	1.00
$\Delta\rho_{\min}$ (e/Å ³)	−1.10	−0.62	−0.81	−1.16

TABLE A.1 (*continued*)

	L7	L7_Tl	L8_Tl	L10
a (Å)	10.556(1)	10.6514(6)	10.6480(5)	10.5364(6)
V (Å ³)	1176.2(3)	1208.4(2)	1207.3(2)	1169.7(2)
size (μm)	70×50×40	70×50×40	60×60×50	60×50×50
$\theta_{\max}$ (°; MoK α)	32	32	32	32
R_{int} (%)	5.74	6.65	4.66	3.69
indep. refl.	125	128	129	125
obs. refl.	103	94	101	97
$[F_o > 4\sigma(F_o)]$				
Ref. param.	12	14	14	12
$R1_{\text{all}}$ (%)	3.75	5.96	5.39	3.92
$R1_{\text{obs}}$ (%)	2.88	4.36	4.14	2.76
$\Delta\rho_{\max}$ (e/Å ³)	0.46	1.12	1.42	0.49
$\Delta\rho_{\min}$ (e/Å ³)	−0.74	−1.08	−1.07	−0.75
	L12	L12_Tl	L19	L19_Tl
a (Å)	10.5700(3)	10.6477(5)	10.5699(5)	10.6716(6)
V (Å ³)	1180.9(1)	1207.2(2)	1180.9(2)	1215.3(2)
size (μm)	55×50×40	55×50×40	50×60×70	50×60×70
$\theta_{\max}$ (MoK α)	32	32	32	32
R_{int} (%)	3.55	3.63	9.34	5.22
indep. refl.	125	128	125	128
obs. refl.	109	112	89	114
$[F_o > 4\sigma(F_o)]$				
Ref. param.	12	13	13	14
$R1_{\text{all}}$ (%)	2.78	4.18	6.43	3.55
$R1_{\text{obs}}$ (%)	2.29	3.84	3.64	3.26
$\Delta\rho_{\max}$ (e/Å ³)	0.56	1.05	0.70	1.33
$\Delta\rho_{\min}$ (e/Å ³)	−0.67	−1.50	−0.73	−1.06

TABLE A.2. Bond distances and structural parameters for the selected hydropyrochlore and hydrokenopyrochlore crystals from Lueshe.

	L2	L4	L5	L6
n.e ⁻ (A)	4.2	4.2	4.2	4.2
n.e ⁻ (A')	1.3	1.5	5.7	1.6
n.e ⁻ (Y')	9.1	9.1	9.1	9.1
x_{48f} (X)	0.3130(4)	0.3127(4)	0.3134(6)	0.3129(6)
x_{32e} (A')	0.522(4)	0.520(3)	0.5107(16)	0.521(5)
x_{32e} (Y')	0.392(10)	0.392(9)	0.405(2)	0.400(3)
A–X (×6)	2.720(3)	2.720(3)	2.710(4)	2.718(5)
A–Y' (×2)	2.41(8)	2.41(8)	2.52(2)	2.48(3)
<A–O>	2.643	2.643	2.663	2.659
B–X (×6)	1.983(2)	1.982(2)	1.980(2)	1.982(2)
A'–X (×3)	2.81(5)	2.80(4)	2.75(2)	2.80(6)
(×3)	2.69(5)	2.69(4)	2.69(5)	2.69(6)
A'–Y' (×2)	2.81(12)	2.77(11)	2.71(3)	2.86(7)
<A'–O>	2.77	2.75	2.72	2.77
Y'–X (×3)	3.13(9)	3.12(9)	3.00(2)	3.05(3)
(×3)	3.49(7)	3.49(10)	3.63(3)	3.58(4)
<Y'–X>	3.31	3.31	3.32	3.32
X–X (u.)	2.810(6)	2.804(6)	2.810(9)	2.806(9)
X–X (s.)	2.800(2)	2.800(3)	2.792(4)	2.798(3)
<X–X>	2.805	2.802	2.801	2.802
X–B–X (u.)	90.2(2)	90.1(2)	90.4(2)	90.2(3)
X–B–X (s.)	89.8(2)	89.9(2)	89.6(2)	89.8(3)
B–X–B	140.8(2)	140.9(2)	140.5(3)	140.8(4)
B–X–A	104.11(7)	104.08(7)	104.19(9)	104.1(1)
A–X–A	86.8(1)	86.7(1)	86.9(2)	86.8(2)
σ^2 (B)	0.05	0.01	0.15	0.03
	L7	L7_Tl	L8_Tl	L10
n.e ⁻ (A)	4.2	58.9	59.7	4.2
n.e ⁻ (A')	2.0	-	-	5.0
n.e ⁻ (Y')	9.1	4.1	4.8	9.1
x_{48f} (X)	0.3130(3)	0.3107(10)	0.3107(13)	0.3145(3)
x_{32e} (A')	0.519(2)	-	-	0.5134(10)
x_{32e} (Y')	0.398(3)	0.402(9)	0.406(9)	0.4062(13)
A–X (×6)	2.717(3)	2.759(7)	2.758(10)	2.700(2)
A–Y' (×2)	2.46(3)	2.52(8)	2.56(8)	2.528(12)
<A–O>	2.653	2.699	2.709	2.657
B–X (×6)	1.981(1)	1.991(3)	1.990(4)	1.983(1)
A'–X (×3)	2.79(3)	-	-	2.746(11)
(×3)	2.69(3)	-	-	2.675(11)
A'–Y' (×2)	2.80(4)	-	-	2.77(2)

TABLE A.2 (*continued*)

$\langle A'-O \rangle$	2.76	-	-	2.725
$Y'-X (\times 3)$	3.07(3)	3.09(7)	3.05(7)	2.980(11)
$(\times 3)$	3.55(4)	3.66(10)	3.71(10)	3.63(2)
$\langle Y'-X \rangle$	3.31	3.38	3.38	3.305
$X-X$ (u.)	2.807(5)	2.797(16)	2.80(2)	2.824(5)
$X-X$ (s.)	2.797(2)	2.834(6)	2.833(7)	2.784(2)
$\langle X-X \rangle$	2.802	2.816	2.817	2.804
$X-B-X$ (u.)	90.2(1)	89.3(4)	89.2(5)	90.8(1)
$X-B-X$ (s.)	89.8(1)	90.7(4)	90.8(5)	89.2(1)
$B-X-B$	140.8(2)	142.1(6)	142.1(7)	139.9(2)
$B-X-A$	104.12(5)	103.7(2)	103.7(2)	104.37(5)
$A-X-A$	86.8(1)	86.1(3)	86.1(4)	87.2(1)
$\sigma^2 (B)$	0.05	0.59	0.59	0.71
	L12	L12_Tl	L19	L19_Tl
n.e ⁻ (A)	4.2	59.4	4.2	58.2
n.e ⁻ (A')	2.1	-	2.2	-
n.e ⁻ (Y')	9.1	4.7	9.1	4.9
$x_{48f} (X)$	0.3130(3)	0.3105(9)	0.3130(5)	0.3108(5)
$x_{32e} (A')$	0.5187(17)	-	0.514(3)	-
$x_{32e} (Y')$	0.390(11)	0.404(7)	0.396(5)	0.401(6)
$A-X (\times 6)$	2.720(2)	2.760(7)	2.720(3)	2.764(4)
$A-Y' (\times 2)$	2.40(8)	2.54(7)	2.44(4)	2.51(6)
$\langle A-O \rangle$	2.640	2.705	2.650	2.701
$B-X (\times 6)$	1.9836(9)	1.989(3)	1.984(2)	1.995(2)
$A'-X (\times 3)$	2.79(2)	-	2.77(4)	-
$(\times 3)$	2.69(2)	-	2.70(4)	-
$A'-Y' (\times 2)$	2.73(12)	-	2.70(7)	-
$\langle A'-O \rangle$	2.74	-	2.726	-
$Y'-X (\times 3)$	3.14(10)	3.07(6)	3.09(4)	3.10(5)
$(\times 3)$	3.46(12)	3.68(8)	3.53(6)	3.65(7)
$\langle Y'-X \rangle$	3.30	3.38	3.31	3.38
$X-X$ (u.)	2.810(5)	2.793(14)	2.810(8)	2.804(8)
$X-X$ (s.)	2.800(2)	2.834(5)	2.800(3)	2.838(3)
$\langle X-X \rangle$	2.805	2.814	2.805	2.821
$X-B-X$ (u.)	90.2(1)	89.2(4)	90.2(3)	89.3(2)
$X-B-X$ (s.)	89.8(1)	90.8(4)	89.8(3)	90.7(2)
$B-X-B$	140.8(2)	142.2(5)	140.8(3)	142.1(3)
$B-X-A$	104.12(4)	103.7(2)	104.11(8)	103.74(8)
$A-X-A$	86.8(1)	86.0(3)	86.8(1)	86.1(1)
$\sigma^2 (B)$	0.05	0.73	0.05	0.5

Notes: u. = unshared edge of the octahedron; s. = shared edge between *B* and *A* polyhedra.

Bond angle variance (σ^2) was computed according to the formula proposed by Robinson *et al.* (1971).

B. Other pyrochlore samples datasets

In this appendix are reported the chemical data related to samples that were initially investigated but not selected for imbibition experiments. Due to the cationic populations at their tunnel sites, which resulted in a near full occupancy or, even when defective, high in poorly mobile divalent cations, these samples were deemed unsuited for Tl- or Pb-treatments. In some cases, some points of analysis revealed compositions having optimal characteristics, however they were limited to the rims of the grains, which had much larger cores showing the described-above chemistry. The samples are the following (see Table 2.1 for more details):

- “ceriopyrochlore” (Norway), labelled Ce-Pcl;
- kenoplumbomicrolite (Russia), labelled Pb-M;
- “pyrochlore” (Norway), labelled g26838;
- “pyrochlore” (Sweden), labelled g26834;
- “pyrochlore” (Norway), labelled g26870;
- “pyrochlore” (Russia), labelled 0111;
- “uranpyrochlore” (Canada), labelled U-Pcl;
- six “pyrochlores” and “microlites” (Italy), labelled f3706, f4820, f4825, f4827, f4828e, and f4831;
- “plumbopyrochlore” (Russia), labelled Pb-P.

All EMPA data collected from these samples are reported in Table B.1 (wt.%) and Table B.2 (apfu). Counting times for each element were: 30 s (Na, F, Sn, Sb, Ba, Tl, Th, Ca, Mn, Fe, Pb, U, Zr, Si), 20 s (Sr, Ti, Ta), and 15 s (La, Nb, Ce, K, Al).

TABLE B.1. Average microprobe analyses (wt.% oxides) for all the samples that were not chosen for imbibition experiments.

wt.%	Ce-PclA	Ce-PclB	Ce-PclC1	Ce-PclC2	Ce-PclD	Ce-PclE
<i>n</i>	7	4	3	2	5	5
SiO ₂	n.d.	0.68	n.d.	n.d.	0.93	0.38
Al ₂ O ₃	0.02	0.04	0.02	0.02	0.02	0.02
TiO ₂	0.82	0.78	1.76	0.89	1.47	1.66
Fe ₂ O ₃	1.51	2.77	1.41	1.03	2.83	1.86
ZrO ₂	1.57	1.50	1.14	1.25	1.24	1.18
Nb ₂ O ₅	61.89	58.42	64.45	62.00	61.42	61.35
SnO ₂	0.01	0.05	n.d.	n.d.	0.01	0.01
Sb ₂ O ₅	n.d.	0.01	0.01	0.03	0.01	0.02
Ta ₂ O ₅	3.38	2.79	1.14	2.32	2.44	2.20
Na ₂ O	0.31	0.54	0.32	4.62	0.43	0.67
K ₂ O	0.12	0.10	0.15	n.d.	0.10	0.10
CaO	5.05	6.02	6.94	14.88	5.90	6.25
MnO	0.17	0.24	0.16	0.07	0.37	0.15
SrO	0.98	1.00	0.59	0.33	1.19	1.55
BaO	3.89	2.28	2.44	0.06	4.04	4.18
Ce ₂ O ₃	1.02	0.81	0.83	0.54	1.04	0.97
La ₂ O ₃	0.18	0.16	0.04	0.12	0.05	0.15
Tl ₂ O	0.02	n.d.	0.08	n.d.	n.d.	0.01
PbO	0.33	0.24	0.35	0.31	0.21	0.23
ThO ₂	7.93	8.34	6.48	6.92	6.95	5.58
UO ₂	0.55	0.14	0.21	0.22	0.18	0.16
F	0.02	0.37	0.28	2.71	0.15	0.35
= O	−0.01	−0.15	−0.12	−1.14	−0.06	−0.15
Total	89.77	87.08	89.64	97.15	90.89	88.87

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.1 (*continued*)

wt. %	Pb-M_A	Pb-M_B	Pb-M_C	Pb-M_D	Pb-M_E	Pb-M_F
<i>n</i>	5	9	8	7	6	11
SiO ₂	0.46	0.02	0.04	0.03	0.02	0.02
Al ₂ O ₃	0.06	n.d.	0.01	n.d.	n.d.	n.d.
TiO ₂	5.11	4.69	4.64	4.03	4.62	4.60
Fe ₂ O ₃	0.72	0.69	0.60	0.53	0.67	0.65
ZrO ₂	0.01	0.02	n.d.	0.02	0.01	n.d.
Nb ₂ O ₅	20.29	18.79	19.32	19.54	19.36	19.27
SnO ₂	2.16	2.14	2.11	2.23	2.10	2.20
Sb ₂ O ₅	0.12	0.13	0.06	0.10	0.11	0.10
Ta ₂ O ₅	15.32	15.74	15.42	15.58	15.66	15.84
Na ₂ O	0.26	0.15	0.14	0.27	0.20	0.29
K ₂ O	0.01	n.d.	n.d.	n.d.	n.d.	0.01
CaO	0.80	0.05	0.20	0.15	0.03	0.04
MnO	0.20	0.26	0.18	0.19	0.24	0.24
SrO	0.08	n.d.	0.03	0.03	n.d.	0.02
BaO	0.02	0.01	0.01	0.01	n.d.	0.01
Ce ₂ O ₃	0.23	0.14	0.13	0.16	0.18	0.04
La ₂ O ₃	0.11	0.02	0.02	0.04	0.03	0.01
Tl ₂ O	0.01	0.01	n.d.	n.d.	0.01	n.d.
PbO	50.19	54.51	54.68	54.14	54.01	52.65
ThO ₂	n.d.	n.d.	0.07	n.d.	n.d.	n.d.
UO ₂	0.95	0.22	0.17	0.12	0.16	0.35
F	0.01	n.d.	0.01	n.d.	n.d.	n.d.
= O	-0.01	-	-	-	-	-
Total	97.11	97.58	97.82	97.16	97.39	96.36

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.1 (continued)

wt. %	g26838_A	g26838_B1	g26838_B2	g26838_C	g26838_D	g26838_E
<i>n</i>	5	4	2	4	3	3
SiO ₂	n.d.	0.01	n.d.	0.10	n.d.	n.d.
Al ₂ O ₃	0.01	n.d.	0.02	0.01	0.01	n.d.
TiO ₂	9.47	8.83	9.44	9.31	9.72	9.36
Fe ₂ O ₃	1.15	0.20	1.45	1.20	1.49	1.14
ZrO ₂	0.29	0.31	0.39	0.24	0.44	0.32
Nb ₂ O ₅	53.91	50.92	54.10	53.76	53.79	54.62
SnO ₂	0.07	0.05	n.d.	n.d.	0.06	0.06
Sb ₂ O ₅	0.02	0.02	0.06	0.12	n.d.	0.01
Ta ₂ O ₅	4.02	3.76	3.83	3.83	3.65	3.77
Na ₂ O	0.44	5.08	0.49	0.45	0.39	0.45
K ₂ O	0.13	n.d.	0.13	0.12	0.11	0.11
CaO	5.98	17.15	5.07	5.61	4.94	5.62
MnO	1.24	0.08	1.36	1.20	1.32	1.30
SrO	0.34	0.03	0.49	0.42	0.40	0.42
BaO	2.42	n.d.	1.70	1.53	2.21	2.24
Ce ₂ O ₃	2.81	2.49	2.93	2.50	2.87	2.65
La ₂ O ₃	0.76	0.78	0.70	0.69	0.80	0.66
Tl ₂ O	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
PbO	0.31	0.29	0.40	0.33	0.29	0.28
ThO ₂	1.95	1.81	1.93	1.63	2.24	1.66
UO ₂	3.26	3.09	3.22	3.45	2.62	3.31
F	0.26	4.09	0.10	0.18	0.09	0.22
= O	−0.11	−1.72	−0.04	−0.07	−0.04	−0.09
Total	88.71	97.28	87.77	86.66	87.44	88.11

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.1 (continued)

wt. %	g26838_F	g26834_A	g26834_B	g26834_C	g26834_D	g26834_E
<i>n</i>	4	6	5	6	5	6
SiO ₂	n.d.	n.d.	0.13	0.01	0.01	0.07
Al ₂ O ₃	0.02	0.01	n.d.	0.01	0.01	0.01
TiO ₂	9.53	3.10	3.11	3.42	2.87	2.90
Fe ₂ O ₃	1.31	1.16	1.61	1.29	1.36	1.67
ZrO ₂	0.28	1.23	3.16	1.78	2.46	3.20
Nb ₂ O ₅	53.60	61.94	57.57	60.68	59.26	57.92
SnO ₂	0.04	n.d.	0.01	n.d.	0.01	0.02
Sb ₂ O ₅	0.04	0.01	0.02	0.02	0.02	0.04
Ta ₂ O ₅	4.06	0.01	0.13	0.05	0.15	0.15
Na ₂ O	0.44	5.37	4.45	4.85	4.76	4.35
K ₂ O	0.14	0.01	0.07	0.03	0.04	0.07
CaO	5.86	18.07	18.28	18.83	18.04	18.34
MnO	1.24	0.01	0.17	0.07	0.13	0.16
SrO	0.44	0.46	0.20	0.25	0.22	0.22
BaO	1.21	0.01	n.d.	n.d.	n.d.	0.01
Ce ₂ O ₃	2.61	3.68	5.18	3.87	4.65	5.01
La ₂ O ₃	0.86	0.41	0.58	0.42	0.42	0.52
Tl ₂ O	0.03	0.01	0.04	0.01	0.03	0.01
PbO	0.34	0.12	0.15	0.16	0.12	0.11
ThO ₂	2.05	0.02	0.03	0.04	0.01	0.02
UO ₂	3.34	0.02	n.d.	n.d.	n.d.	n.d.
F	0.25	4.00	3.23	3.71	3.54	3.22
= O	−0.10	−1.68	−1.36	−1.56	−1.49	−1.36
Total	87.57	97.97	96.76	97.93	96.60	96.70

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.1 (continued)

wt. %	g26834_F	g26834_G	g26834_H	g26870_A	g26870_B	g26870_C
<i>n</i>	5	6	8	2	1	1
SiO ₂	0.08	0.06	0.02	0.01	n.d.	0.03
Al ₂ O ₃	n.d.	0.01	0.01	0.01	n.d.	n.d.
TiO ₂	3.16	3.15	2.86	9.57	9.05	8.27
Fe ₂ O ₃	1.49	1.45	1.52	1.34	1.82	0.14
ZrO ₂	2.99	3.05	2.32	0.32	0.35	0.33
Nb ₂ O ₅	58.06	57.38	60.20	54.55	57.65	53.31
SnO ₂	0.01	n.d.	0.02	0.03	n.d.	n.d.
Sb ₂ O ₅	0.04	0.02	0.04	0.02	0.53	0.13
Ta ₂ O ₅	0.10	0.15	0.08	3.91	3.52	3.05
Na ₂ O	4.31	4.46	4.74	0.49	0.55	5.29
K ₂ O	0.07	0.04	0.03	0.15	0.21	n.d.
CaO	18.53	18.22	18.47	6.44	4.86	17.89
MnO	0.15	0.14	0.10	1.27	1.55	0.05
SrO	0.22	0.23	0.28	0.20	0.47	0.06
BaO	0.01	0.01	n.d.	0.12	0.70	0.04
Ce ₂ O ₃	5.06	5.17	4.34	2.59	2.18	2.48
La ₂ O ₃	0.52	0.63	0.41	0.90	0.53	0.85
Tl ₂ O	0.04	0.05	n.d.	0.04	0.05	0.06
PbO	0.18	0.11	0.15	0.36	0.26	0.16
ThO ₂	0.02	0.01	0.02	1.61	1.43	1.36
UO ₂	n.d.	0.01	n.d.	3.69	2.42	2.01
F	3.19	3.33	3.54	0.20	n.d.	4.21
= O	-1.34	-1.40	-1.49	-0.09	-	-1.77
Total	96.88	96.27	97.68	87.73	88.13	97.93

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.1 (continued)

wt. %	g26870_D	g26870_E	g26870_F	0111_A	0111_B	0111_C1
<i>n</i>	2	6	5	5	5	4
SiO ₂	n.d.	0.01	n.d.	0.01	n.d.	0.01
Al ₂ O ₃	0.01	n.d.	n.d.	0.01	0.02	0.03
TiO ₂	9.08	8.88	8.74	9.53	9.33	9.50
Fe ₂ O ₃	1.87	0.97	1.73	0.31	0.17	0.09
ZrO ₂	0.29	0.27	0.35	0.10	0.05	0.06
Nb ₂ O ₅	58.65	56.96	59.55	50.76	51.08	50.96
SnO ₂	0.11	n.d.	0.02	0.04	0.02	0.02
Sb ₂ O ₅	0.02	0.02	0.03	n.d.	0.01	n.d.
Ta ₂ O ₅	3.53	3.39	3.08	2.08	1.85	1.91
Na ₂ O	0.37	0.52	0.46	5.39	5.48	5.94
K ₂ O	0.21	0.15	0.18	n.d.	n.d.	n.d.
CaO	4.37	8.28	5.03	15.37	15.18	13.94
MnO	1.72	0.81	1.50	0.26	0.26	0.22
SrO	0.61	0.07	0.50	0.08	0.04	0.01
BaO	1.05	0.01	1.20	n.d.	0.01	0.03
Ce ₂ O ₃	2.73	2.55	2.51	3.31	3.28	3.39
La ₂ O ₃	0.81	0.79	0.71	1.00	1.08	0.98
Tl ₂ O	n.d.	0.02	0.01	n.d.	n.d.	n.d.
PbO	0.20	0.33	0.20	0.23	0.18	0.21
ThO ₂	1.47	1.45	1.39	7.19	6.78	7.00
UO ₂	2.00	2.38	1.49	0.16	0.22	0.20
F	n.d.	0.48	0.04	4.04	4.09	4.66
= O	-	-0.20	-0.02	-1.70	-1.72	-1.96
Total	89.06	88.12	88.72	98.17	97.40	97.20

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.1 (*continued*)

wt. %	0111_C2	0111_D	0111_E	0111_F	0111_G	0111_H
<i>n</i>	3	4	5	3	4	6
SiO ₂	0.59	n.d.	0.01	n.d.	n.d.	0.04
Al ₂ O ₃	0.05	0.03	0.02	0.03	0.02	0.01
TiO ₂	9.00	9.38	9.42	9.49	9.28	9.32
Fe ₂ O ₃	0.17	0.15	0.23	0.18	0.14	0.12
ZrO ₂	0.04	0.06	0.07	0.05	0.08	0.03
Nb ₂ O ₅	48.40	50.23	50.53	51.07	51.06	51.20
SnO ₂	0.07	n.d.	0.02	0.02	n.d.	0.05
Sb ₂ O ₅	n.d.	0.02	0.02	0.01	0.02	0.02
Ta ₂ O ₅	2.03	1.94	1.98	1.93	2.37	2.05
Na ₂ O	1.50	5.62	5.45	5.60	5.90	5.86
K ₂ O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CaO	12.96	14.27	15.16	14.91	14.47	13.92
MnO	0.25	0.23	0.25	0.26	0.19	0.21
SrO	0.50	0.04	0.03	0.06	0.05	0.07
BaO	0.06	0.04	0.02	0.03	0.02	0.03
Ce ₂ O ₃	3.09	3.51	3.40	3.45	3.30	3.12
La ₂ O ₃	0.76	1.15	1.03	1.10	1.03	0.98
Tl ₂ O	n.d.	n.d.	0.06	0.08	0.04	n.d.
PbO	0.32	0.20	0.26	0.25	0.20	0.26
ThO ₂	7.09	7.03	6.85	7.04	6.93	7.29
UO ₂	0.16	0.21	0.23	0.25	0.24	0.19
F	2.78	4.33	4.16	4.24	4.46	4.70
= O	−1.17	−1.82	−1.75	−1.79	−1.88	−1.98
Total	88.64	96.38	97.42	98.26	97.94	97.50

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.1 (continued)

wt. %	U-Pcl	f3706_A	f3706_B	f3706_C	f3706_D	f3706_E
<i>n</i>	9	5	3	5	6	5
SiO ₂	3.43	0.01	0.44	0.64	n.d.	n.d.
Al ₂ O ₃	0.19	0.01	0.02	0.01	0.01	n.d.
TiO ₂	10.36	2.32	2.87	2.61	2.28	2.98
Fe ₂ O ₃	3.22	0.54	1.06	0.39	0.53	0.48
ZrO ₂	0.02	0.96	0.28	0.93	0.72	0.59
Nb ₂ O ₅	34.75	61.75	65.22	62.05	62.73	63.68
SnO ₂	0.04	0.03	0.02	n.d.	0.01	0.01
Sb ₂ O ₅	0.01	0.02	0.01	0.02	0.01	0.01
Ta ₂ O ₅	1.68	1.86	1.02	1.99	2.45	1.14
Na ₂ O	n.d.	5.36	2.54	2.64	3.64	5.67
K ₂ O	0.02	n.d.	0.09	0.06	0.01	n.d.
CaO	15.39	15.24	12.41	11.30	14.32	15.31
MnO	0.20	0.03	0.13	0.03	0.03	0.01
SrO	1.19	0.33	1.62	0.54	0.51	0.45
BaO	0.21	0.02	0.71	2.14	0.28	0.49
Ce ₂ O ₃	0.24	0.62	0.90	0.85	0.68	0.68
La ₂ O ₃	0.03	0.10	0.13	0.14	0.16	0.09
Tl ₂ O	0.04	0.08	n.d.	0.01	0.05	0.07
PbO	1.02	0.37	0.33	0.29	0.26	0.28
ThO ₂	0.15	4.89	3.05	4.91	4.65	4.15
UO ₂	17.34	0.04	0.09	0.03	0.15	0.06
F	0.20	4.36	2.70	2.39	3.60	4.19
= O	−0.09	−1.84	−1.14	−1.00	−1.52	−1.76
Total	89.65	97.09	94.51	92.94	95.57	98.58

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.1 (continued)

wt. %	f3706_F	f3706_G	f4820_A	f4820_B	f4825_A	f4825_B
<i>n</i>	5	5	6	5	4	5
SiO ₂	n.d.	n.d.	n.d.	0.34	2.83	1.90
Al ₂ O ₃	0.01	0.01	n.d.	0.02	0.25	0.20
TiO ₂	2.37	2.33	2.06	0.11	0.02	0.05
Fe ₂ O ₃	0.25	0.16	0.47	0.02	0.01	0.01
ZrO ₂	1.05	0.92	0.70	n.d.	0.03	0.03
Nb ₂ O ₅	61.32	61.55	62.96	11.82	4.92	5.05
SnO ₂	0.01	0.01	0.01	0.10	0.34	0.29
Sb ₂ O ₅	0.03	0.02	0.02	0.09	0.10	0.11
Ta ₂ O ₅	3.41	2.92	3.64	67.93	75.00	75.23
Na ₂ O	5.44	5.73	6.06	5.33	4.87	5.06
K ₂ O	0.01	n.d.	0.01	0.01	0.03	0.01
CaO	15.07	15.15	15.23	9.80	10.94	10.84
MnO	0.03	n.d.	0.02	n.d.	0.03	0.03
SrO	0.36	0.38	0.36	0.02	n.d.	0.04
BaO	0.02	0.03	0.03	0.02	n.d.	n.d.
Ce ₂ O ₃	0.76	0.63	0.60	0.25	0.32	0.33
La ₂ O ₃	0.10	0.08	0.10	0.04	0.05	0.03
Tl ₂ O	0.05	0.05	0.03	n.d.	0.03	0.03
PbO	0.31	0.30	0.33	0.14	0.03	0.10
ThO ₂	4.90	4.26	4.11	0.09	0.01	0.01
UO ₂	0.22	0.13	0.13	3.97	n.d.	0.83
F	3.93	4.32	4.36	3.04	3.37	3.36
= O	-1.65	-1.82	-1.84	-1.28	-1.42	-1.41
Total	97.99	97.17	99.40	101.87	101.75	102.13

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.1 (continued)

wt. %	f4825_C	f4825_D	f4825_E	f4825_F	f4825_G	f4827_A
<i>n</i>	5	5	3	5	5	5
SiO ₂	1.98	1.58	1.65	1.77	0.52	2.39
Al ₂ O ₃	0.22	0.12	0.14	0.17	0.12	0.24
TiO ₂	0.04	0.02	0.04	0.03	0.08	0.04
Fe ₂ O ₃	0.03	0.01	n.d.	0.04	n.d.	0.01
ZrO ₂	0.02	0.01	0.01	0.03	n.d.	0.07
Nb ₂ O ₅	4.73	5.09	4.89	5.01	7.40	4.88
SnO ₂	0.25	0.29	0.30	0.25	0.30	0.29
Sb ₂ O ₅	0.13	0.07	0.08	0.10	0.12	0.12
Ta ₂ O ₅	76.09	76.29	75.92	75.39	72.29	75.20
Na ₂ O	4.88	5.11	5.04	5.18	5.24	4.96
K ₂ O	0.03	0.01	0.02	0.02	0.01	0.02
CaO	11.07	11.18	11.06	10.96	10.39	11.09
MnO	0.02	0.01	0.01	0.01	0.02	0.05
SrO	n.d.	n.d.	0.01	0.04	0.05	0.04
BaO	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Ce ₂ O ₃	0.32	0.29	0.32	0.39	0.34	0.23
La ₂ O ₃	0.08	0.01	0.08	0.06	0.05	0.02
Tl ₂ O	0.02	n.d.	0.01	n.d.	0.01	n.d.
PbO	0.05	0.08	0.08	0.06	0.11	0.03
ThO ₂	n.d.	0.04	n.d.	0.02	0.02	n.d.
UO ₂	0.16	0.03	n.d.	0.15	2.40	0.01
F	3.40	3.52	3.42	3.51	3.30	3.40
= O	-1.43	-1.48	-1.44	-1.48	-1.39	-1.43
Total	102.11	102.28	101.66	101.70	101.39	101.65

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.1 (continued)

wt. %	f4827_B	f4828e_A1	f4828e_A2	f4828e_B	f4828e_C1	f4828e_C2
<i>n</i>	3	4	2	4	4	2
SiO ₂	2.79	1.46	0.27	1.77	1.38	0.24
Al ₂ O ₃	0.28	0.39	0.06	0.36	0.35	0.05
TiO ₂	0.03	0.03	0.16	0.02	0.05	0.19
Fe ₂ O ₃	0.01	0.01	n.d.	0.02	0.02	0.03
ZrO ₂	0.02	0.02	n.d.	0.01	0.02	0.01
Nb ₂ O ₅	4.23	13.04	21.59	12.85	12.22	21.47
SnO ₂	0.19	0.43	0.71	0.37	0.38	0.53
Sb ₂ O ₅	0.08	0.09	0.06	0.09	0.09	n.d.
Ta ₂ O ₅	76.41	64.41	46.39	65.70	66.72	48.10
Na ₂ O	4.95	5.56	4.14	5.42	5.46	3.17
K ₂ O	0.02	0.02	0.02	0.06	0.02	0.03
CaO	10.79	11.23	3.05	11.25	11.51	3.38
MnO	0.03	0.01	0.02	n.d.	0.01	0.01
SrO	n.d.	0.04	0.01	n.d.	0.02	0.02
BaO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ce ₂ O ₃	0.21	0.29	0.19	0.31	0.29	0.18
La ₂ O ₃	0.04	0.02	n.d.	0.06	0.03	0.13
Tl ₂ O	0.01	0.01	n.d.	0.02	0.03	n.d.
PbO	0.11	0.16	0.36	0.07	0.10	0.67
ThO ₂	n.d.	0.02	n.d.	n.d.	n.d.	n.d.
UO ₂	0.09	0.83	20.43	0.07	0.03	19.71
F	3.44	3.59	1.01	3.63	3.63	1.01
= O	−1.45	−1.51	−0.43	−1.53	−1.53	−0.43
Total	102.26	100.12	98.04	100.56	100.84	98.52

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.1 (continued)

wt. %	f4831_A	f4831_B	Pb-P_A	Pb-P_B
<i>n</i>	4	3	5	8
SiO ₂	1.27	1.33	0.03	0.02
Al ₂ O ₃	0.31	0.39	0.01	n.d.
TiO ₂	0.06	0.05	4.81	5.28
Fe ₂ O ₃	0.02	0.02	0.79	0.64
ZrO ₂	0.01	n.d.	0.02	0.01
Nb ₂ O ₅	12.53	13.13	17.77	18.21
SnO ₂	0.46	0.45	2.77	2.64
Sb ₂ O ₅	0.08	0.10	0.02	0.01
Ta ₂ O ₅	66.09	65.24	12.24	11.21
Na ₂ O	5.76	5.63	0.03	0.02
K ₂ O	0.01	0.02	n.d.	n.d.
CaO	11.45	11.65	0.01	n.d.
MnO	0.02	0.02	0.13	0.06
SrO	0.02	n.d.	0.01	0.03
BaO	n.d.	n.d.	0.03	0.02
Ce ₂ O ₃	0.30	0.36	0.11	0.11
La ₂ O ₃	0.04	0.01	0.05	0.03
Tl ₂ O	0.01	0.01	0.13	n.d.
PbO	0.07	0.11	60.65	61.04
ThO ₂	0.03	0.02	n.d.	n.d.
UO ₂	0.08	0.07	0.02	n.d.
F	3.78	3.81	n.d.	n.d.
= O	-1.59	-1.60	-	-
Total	100.80	100.81	99.61	99.31

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.2. Microprobe data normalised to $\Sigma B = 2$ apfu for all the samples that were not chosen for imbibition experiments.

	Ce-PclA	Ce-PclB	Ce-PclC1	Ce-PclC2	Ce-PclD	Ce-PclE
Si	-	0.03	-	-	0.06	0.02
Al	-	-	-	-	-	-
Ti	0.04	0.04	0.08	0.04	0.07	0.08
Fe ³⁺	0.07	0.13	0.06	0.05	0.12	0.09
Zr	0.05	0.05	0.03	0.04	0.04	0.04
Nb	1.78	1.71	1.78	1.83	1.68	1.73
Sn	-	-	-	-	-	-
Sb ⁵⁺	-	-	-	-	-	-
Ta	0.06	0.05	0.04	0.04	0.04	0.04
Na	0.04	0.07	0.04	0.59	0.05	0.08
Ca	0.34	0.42	0.45	1.04	0.38	0.42
Mn ²⁺	0.01	0.02	0.01	0.01	0.02	0.01
Sr	0.04	0.04	0.02	0.02	0.04	0.06
Ba	0.10	0.06	0.06	-	0.10	0.11
Ce	0.02	0.02	0.02	0.02	0.02	0.02
La	-	-	-	-	-	-
Tl ⁺	-	-	-	-	-	-
Pb	0.01	0.01	0.01	0.01	-	-
Th	0.12	0.13	0.09	0.10	0.10	0.08
U	0.01	-	-	-	-	-
ΣA	0.69	0.77	0.70	1.79	0.71	0.78
K	0.01	0.01	0.01	-	0.01	0.01
F	-	0.08	0.05	0.57	0.03	0.07
ΣY	0.01	0.09	0.06	0.57	0.04	0.08

TABLE B.2 (*continued*)

	Pb-M_A	Pb-M_B	Pb-M_C	Pb-M_D	Pb-M_E	Pb-M_F
Si	-	-	-	-	-	-
Al	-	-	-	-	-	-
Ti	0.39	0.39	0.39	0.39	0.39	0.39
Fe ³⁺	0.06	0.06	0.05	0.05	0.06	0.05
Zr	-	-	-	-	-	-
Nb	0.99	0.99	0.98	0.98	0.98	0.97
Sn	0.10	0.10	0.10	0.10	0.09	0.10
Sb ⁵⁺	-	-	-	-	0.01	-
Ta	0.46	0.46	0.47	0.47	0.48	0.48
Na	0.06	0.06	0.03	0.06	0.04	0.06
Ca	-	-	0.03	0.02	-	0.01
Mn ²⁺	0.03	0.03	0.02	0.02	0.02	0.02
Sr	-	-	-	-	-	-
Ba	-	-	-	-	-	-
Ce	-	-	0.01	0.01	0.01	-
La	-	-	-	-	-	-
Tl ⁺	-	-	-	-	-	-
Pb	1.62	1.62	1.66	1.62	1.63	1.58
Th	-	-	-	-	-	-
U	0.02	0.02	-	-	-	0.01
ΣA	1.73	1.73	1.75	1.73	1.70	1.68
K	-	-	-	-	-	-
F	-	-	-	-	-	-
ΣY	-	-	-	-	-	-

TABLE B.2 (*continued*)

	g26838_A	g26838_B1	g26838_B2	g26838_C	g26838_D	g26838_E
Si	-	-	-	0.01	-	-
Al	-	-	-	-	-	-
Ti	0.42	0.43	0.42	0.42	0.43	0.42
Fe ³⁺	0.05	0.01	0.06	0.05	0.07	0.05
Zr	0.01	0.01	0.01	0.01	0.01	0.01
Nb	1.45	1.48	1.44	1.45	1.43	1.46
Sn	-	-	-	-	-	-
Sb ⁵⁺	-	-	-	-	-	-
Ta	0.06	0.07	0.06	0.06	0.06	0.06
Na	0.05	0.63	0.06	0.05	0.04	0.05
Ca	0.38	1.18	0.32	0.36	0.31	0.36
Mn ²⁺	0.06	-	0.07	0.06	0.07	0.07
Sr	0.01	-	0.02	0.01	0.01	0.01
Ba	0.06	-	0.04	0.04	0.05	0.05
Ce	0.06	0.06	0.06	0.05	0.06	0.06
La	0.02	0.02	0.02	0.02	0.02	0.01
Tl ⁺	-	-	-	-	-	-
Pb	-	0.01	0.01	0.01	-	-
Th	0.03	0.03	0.03	0.02	0.03	0.02
U	0.04	0.04	0.04	0.05	0.03	0.04
ΣA	0.71	1.97	0.67	0.67	0.62	0.67
K	0.01	-	0.01	0.01	0.01	0.01
F	0.05	0.83	0.02	0.03	0.02	0.04
ΣY	0.06	0.83	0.03	0.04	0.03	0.05

TABLE B.2 (*continued*)

	g26838_F	g26834_A	g26834_B	g26834_C	g26834_D	g26834_E
Si	-	-	0.01	-	-	-
Al	-	-	-	-	-	-
Ti	0.43	0.15	0.15	0.16	0.14	0.14
Fe ³⁺	0.06	0.06	0.08	0.06	0.07	0.08
Zr	0.01	0.04	0.10	0.05	0.08	0.10
Nb	1.44	1.76	1.66	1.72	1.72	1.67
Sn	-	-	-	-	-	-
Sb ⁵⁺	-	-	-	-	-	-
Ta	0.07	-	-	-	-	-
Na	0.05	0.65	0.55	0.59	0.59	0.54
Ca	0.37	1.22	1.25	1.27	1.24	1.25
Mn ²⁺	0.06	-	0.01	-	0.01	0.01
Sr	0.02	0.02	0.01	0.01	0.01	0.01
Ba	0.03	-	-	-	-	-
Ce	0.06	0.08	0.12	0.09	0.11	0.12
La	0.02	0.01	0.01	0.01	0.01	0.01
Tl ⁺	-	-	-	-	-	-
Pb	0.01	-	-	-	-	-
Th	0.03	-	-	-	-	-
U	0.04	-	-	-	-	-
ΣA	0.69	1.98	1.95	1.97	1.97	1.94
K	0.01	-	0.01	-	-	0.01
F	0.05	0.80	0.65	0.74	0.72	0.65
ΣY	0.06	0.80	0.66	0.74	0.72	0.66

TABLE B.2 (*continued*)

	g26834_F	g26834_G	g26834_H	g26870_A	g26870_B	g26870_C
Si	0.01	-	-	-	-	-
Al	-	-	-	-	-	-
Ti	0.15	0.15	0.14	0.42	0.38	0.39
Fe ³⁺	0.07	0.07	0.07	0.06	0.08	0.01
Zr	0.09	0.10	0.07	0.01	0.01	0.01
Nb	1.68	1.67	1.72	1.45	1.47	1.53
Sn	-	-	-	-	-	-
Sb ⁵⁺	-	-	-	-	0.01	-
Ta	-	-	-	0.06	0.05	0.05
Na	0.53	0.56	0.58	0.06	0.06	0.65
Ca	1.27	1.26	1.25	0.40	0.29	1.22
Mn ²⁺	0.01	0.01	0.01	0.06	0.07	-
Sr	0.01	0.01	0.01	0.01	0.02	-
Ba	-	-	-	-	0.02	-
Ce	0.12	0.12	0.10	0.06	0.04	0.06
La	0.01	0.02	0.01	0.02	0.01	0.02
Tl ⁺	-	-	-	-	-	-
Pb	-	-	-	0.01	-	-
Th	-	-	-	0.02	0.02	0.02
U	-	-	-	0.05	0.03	0.03
ΣA	1.95	1.98	1.96	0.69	0.56	2.00
K	0.01	-	-	0.01	0.02	-
F	0.64	0.68	0.71	0.04	-	0.85
ΣY	0.65	0.68	0.71	0.05	0.02	0.85

TABLE B.2 (*continued*)

	g26870_D	g26870_E	g26870_F	0111_A	0111_B	0111_C1
Si	-	-	-	-	-	-
Al	-	-	-	-	-	-
Ti	0.38	0.39	0.37	0.46	0.46	0.46
Fe ³⁺	0.08	0.04	0.07	0.02	0.01	-
Zr	0.01	0.01	0.01	-	-	-
Nb	1.48	1.50	1.50	1.48	1.50	1.49
Sn	-	-	-	-	-	-
Sb ⁵⁺	-	-	-	-	-	-
Ta	0.05	0.05	0.05	0.04	0.03	0.03
Na	0.04	0.06	0.05	0.68	0.69	0.75
Ca	0.26	0.52	0.30	1.06	1.06	0.97
Mn ²⁺	0.08	0.04	0.07	0.01	0.01	0.01
Sr	0.02	-	0.02	-	-	-
Ba	0.02	-	0.03	-	-	-
Ce	0.06	0.05	0.05	0.08	0.08	0.08
La	0.02	0.02	0.01	0.02	0.03	0.02
Tl ⁺	-	-	-	-	-	-
Pb	-	0.01	-	-	-	-
Th	0.02	0.02	0.02	0.10	0.10	0.10
U	0.02	0.03	0.02	-	-	-
ΣA	0.54	0.75	0.57	1.95	1.97	1.93
K	0.01	0.01	0.01	-	-	-
F	-	0.09	0.01	0.82	0.84	0.96
ΣY	0.01	0.10	0.02	0.82	0.84	0.96

TABLE B.2 (*continued*)

	0111_C2	0111_D	0111_E	0111_F	0111_G	0111_H
Si	0.04	-	-	-	-	-
Al	-	-	-	-	-	-
Ti	0.45	0.46	0.46	0.46	0.45	0.45
Fe ³⁺	0.01	0.01	0.01	0.01	0.01	0.01
Zr	-	-	-	-	-	-
Nb	1.46	1.49	1.49	1.49	1.49	1.50
Sn	-	-	-	-	-	-
Sb ⁵⁺	-	-	-	-	-	-
Ta	0.04	0.03	0.04	0.03	0.04	0.04
Na	0.19	0.71	0.69	0.70	0.74	0.74
Ca	0.92	1.00	1.06	1.03	1.00	0.97
Mn ²⁺	0.01	0.01	0.01	0.01	0.01	0.01
Sr	0.02	-	-	-	-	-
Ba	-	-	-	-	-	-
Ce	0.08	0.08	0.08	0.08	0.08	0.07
La	0.02	0.03	0.02	0.03	0.02	0.02
Tl ⁺	-	-	-	-	-	-
Pb	0.01	-	-	-	-	-
Th	0.11	0.10	0.10	0.10	0.10	0.11
U	-	-	-	-	-	-
ΣA	1.36	1.93	1.97	1.95	1.95	1.92
K	-	-	-	-	-	-
F	0.59	0.90	0.86	0.87	0.91	0.96
ΣY	0.59	0.90	0.86	0.87	0.91	0.96

TABLE B.2 (*continued*)

	U-Pcl	f3706_A	f3706_B	f3706_C	f3706_D	f3706_E
Si	0.23	-	0.03	0.04	-	-
Al	0.02	-	-	-	-	-
Ti	0.52	0.11	0.13	0.12	0.11	0.14
Fe ³⁺	0.16	0.03	0.05	0.02	0.03	0.02
Zr	-	0.03	0.01	0.03	0.02	0.02
Nb	1.05	1.80	1.77	1.76	1.80	1.80
Sn	-	-	-	-	-	-
Sb ⁵⁺	-	-	-	-	-	-
Ta	0.03	0.03	0.02	0.03	0.04	0.02
Na	-	0.67	0.30	0.33	0.45	0.69
Ca	1.10	1.05	0.80	0.76	0.97	1.03
Mn ²⁺	0.01	-	0.01	-	-	-
Sr	0.05	0.01	0.06	0.02	0.02	0.02
Ba	0.01	-	0.02	0.05	0.01	0.01
Ce	0.01	0.01	0.02	0.02	0.02	0.02
La	-	-	-	-	-	-
Tl ⁺	-	-	-	-	-	-
Pb	0.02	0.01	0.01	-	-	-
Th	-	0.07	0.04	0.07	0.07	0.06
U	0.26	-	-	-	-	-
ΣA	1.46	1.82	1.26	1.25	1.54	1.83
K	-	-	0.01	-	-	-
F	0.04	0.89	0.52	0.48	0.73	0.83
ΣY	0.04	0.89	0.53	0.48	0.73	0.83

TABLE B.2 (*continued*)

	f3706_F	f3706_G	f4820_A	f4820_B	f4825_A	f4825_B
Si	-	0.04	-	0.03	0.22	0.15
Al	-	-	-	-	0.02	0.02
Ti	0.11	0.12	0.10	0.01	-	-
Fe ³⁺	0.01	0.02	0.02	-	-	-
Zr	0.03	0.03	0.02	-	-	-
Nb	1.78	1.76	1.79	0.44	0.17	0.18
Sn	-	-	-	-	0.01	0.01
Sb ⁵⁺	-	-	-	-	-	-
Ta	0.06	0.03	0.06	1.52	1.57	1.63
Na	0.80	0.48	0.74	0.85	0.73	0.78
Ca	1.04	0.76	1.03	0.86	0.90	0.93
Mn ²⁺	-	-	-	-	-	-
Sr	0.01	0.02	0.01	-	-	-
Ba	-	0.05	-	-	-	-
Ce	0.02	0.02	0.01	0.01	0.01	0.01
La	-	-	-	-	-	-
Tl ⁺	-	-	-	-	-	-
Pb	0.01	-	0.01	-	-	-
Th	0.07	0.07	0.06	-	-	-
U	-	-	-	0.07	-	0.02
ΣA	1.95	1.40	1.86	1.79	1.64	1.74
K	-	-	-	-	-	-
F	0.80	0.48	0.87	0.79	0.82	0.85
ΣY	0.80	0.48	0.87	0.79	0.82	0.85

TABLE B.2 (*continued*)

	f4825_C	f4825_D	f4825_E	f4825_F	f4825_G	f4827_A
Si	0.16	0.13	0.13	0.14	0.04	0.19
Al	0.02	0.01	0.01	0.02	0.01	0.02
Ti	-	-	-	-	0.01	-
Fe ³⁺	-	-	-	-	-	-
Zr	-	-	-	-	-	-
Nb	0.17	0.18	0.18	0.18	0.28	0.17
Sn	0.01	0.01	0.01	0.01	0.01	0.01
Sb ⁵⁺	-	-	-	-	-	-
Ta	1.64	1.66	1.66	1.65	1.65	1.60
Na	0.75	0.80	0.79	0.81	0.85	0.75
Ca	0.94	0.96	0.95	0.94	0.93	0.93
Mn ²⁺	-	-	-	-	-	-
Sr	-	-	-	-	-	-
Ba	-	-	-	-	-	-
Ce	0.01	0.01	0.01	0.01	0.01	0.01
La	-	-	-	-	-	-
Tl ⁺	-	-	-	-	-	-
Pb	-	-	-	-	-	-
Th	-	-	-	-	-	-
U	-	-	-	-	0.05	-
ΣA	1.70	1.77	1.75	1.76	1.84	1.69
K	-	-	-	-	-	-
F	0.75	0.80	0.79	0.81	0.85	0.84
ΣY	0.75	0.80	0.79	0.81	0.85	0.84

TABLE B.2 (*continued*)

	f4827_B	f4828e_A1	f4828e_A2	f4828e_B	f4828e_C1	f4828e_C2
Si	0.21	0.11	0.02	0.14	0.11	0.02
Al	0.02	0.04	0.01	0.03	0.03	-
Ti	-	-	0.01	-	-	0.01
Fe ³⁺	-	-	-	-	-	-
Zr	-	-	-	-	-	-
Nb	0.15	0.46	0.84	0.45	0.43	0.83
Sn	0.01	0.01	0.02	0.01	0.01	0.02
Sb ⁵⁺	-	-	-	-	-	-
Ta	1.60	1.37	1.09	1.37	1.41	1.11
Na	0.74	0.84	0.69	0.81	0.82	0.52
Ca	0.89	0.94	0.28	0.92	0.96	0.31
Mn ²⁺	-	-	-	-	-	-
Sr	-	-	-	-	-	-
Ba	-	-	-	-	-	-
Ce	0.01	0.01	0.01	0.01	0.01	0.01
La	-	-	-	-	-	-
Tl ⁺	-	-	-	-	-	-
Pb	-	-	0.01	-	-	0.02
Th	-	-	-	-	-	-
U	-	0.01	0.39	-	-	0.37
ΣA	1.64	1.80	1.38	1.74	1.79	1.23
K	-	-	-	0.01	-	-
F	0.84	0.89	0.28	0.88	0.89	0.27
ΣY	0.84	0.89	0.28	0.89	0.89	0.27

TABLE B.2 (continued)

	f4831_A	f4831_B	Pb-P_A	Pb-P_B
Si	0.10	0.10	-	-
Al	0.03	0.04	-	-
Ti	-	-	0.44	0.47
Fe ³⁺	-	-	0.07	0.06
Zr	-	-	-	-
Nb	0.44	0.46	0.96	0.98
Sn	0.01	0.01	0.14	0.12
Sb ⁵⁺	-	-	-	-
Ta	1.41	1.38	0.40	0.37
Na	0.88	0.85	0.01	0.01
Ca	0.96	0.97	-	-
Mn ²⁺	-	-	0.01	0.01
Sr	-	-	-	-
Ba	-	-	-	-
Ce	0.01	0.01	0.01	0.01
La	-	-	-	-
Tl ⁺	-	-	0.01	-
Pb	-	-	1.96	1.94
Th	-	-	-	-
U	-	-	-	-
ΣA	1.85	1.83	2.00	1.97
K	-	-	-	-
F	0.94	0.94	-	-
ΣY	0.94	0.94	-	-

These data allow to infer the species of these samples; in some instances, however, it is not possible to assign the *A*- and *Y*-prefixes due to the lack of structural information (e.g., presence of structural vacancies and/or water), and only the root name can be assigned.

Sample Ce-Pcl is a defective, hydrated pyrochlore (~12 wt.% H₂O, Table B.1); despite the label, the Ce-enrichment is not actually pronounced. Given that the dominant species at *A* and *Y* is clearly a zero-valent species, it is not possible to assign any prefixes without collecting additional data. The grain Ce-Pcl_C2 revealed, instead, a composition compatible with fluorcalciopyrochlore. Pb-M, initially labelled as “kenoplumbomicrolite”, is, in fact, a pyrochlore-group mineral, due to the dominance of Nb at *B*. While the *A*-prefix “plumbo” was correctly assigned, it is not possible to discern the dominant species at *Y*, which could be either OH[−] (hydroxy-) or vacancy (keno-), based on charge-balance considerations; the slightly low analytical totals (~97 wt.%) suggest the presence of hydroxyl groups at *Y*, although further investigations are required to quantify their exact amount and thus conclude whether it is OH or structural vacancy to dominate the site. Similarly to Ce-Pcl, both samples g26838 and g26870 are defective, hydrated pyrochlores, and only one grain each yielded a fluorcalciopyrochlore composition (g26838_B1; g26870_C). Samples g26834 and 0111 are fluorcalciopyrochlores (the latter presenting a hydrothermally altered rim; 0111_C2), while samples f4825, f4827, and f4831 are fluorcalciomicrolite. The same compositions were observed for sample f4828e, although in two out of the three investigated grains a rim composed of an altered microlite (f4828e_A2 and _C2). Once again, it is not possible to assign any prefixes for these two points of analysis. Sample f4820 is quite interesting as it consists of two grains, a fluorcalciomicrolite (grain B) and a fluorcalciopyrochlore (grain A); these two species were thus associated in this specimen. Lastly, Pb-P is a pyrochlore having Pb largely dominant at *A*; due to the high positive charge carried by Pb, the only two possible species that could dominate at *Y* would be O^{2−} or OH[−]. The high analytical totals, in this case, point to an anhydrous mineral, making the occurrence of O^{2−} at *Y* more likely – the mineral would thus be an oxyplumbopyrochlore.

B.1 Hydrokenoelsmoreite from Devon (United Kingdom)

An additional sample, hydrokenoelsmoreite [labelled HKE; ideal formula □₂W₂O₆(H₂O)], was also investigated through EMPA: it was initially considered

suitable for the imbibition experiments, but the extremely low diffraction quality of the crystals prevented SC-XRD data collection. Even so, a grain extracted from the sample was treated directly from within the epoxy mount with a 1M Ti^+ -rich solution to assess the chemical variations following the imbibition experiment. In these crystals, F, Si, Ba, and Ta were sought but found below detection limit. Chemical data are listed in Table B.3 (wt.%) and Table B.4 (apfu). Counting times for each element are the same as those listed in Appendix B, plus W, As = 15 s.

TABLE B.3. Average microprobe analyses (wt.% oxides) for treated and untreated HKE.

wt.%	HKE_A	HKE_B	HKE_C	HKE_D	HKE_E	HKE_TI
<i>n</i>	6	5	4	4	5	10
Al_2O_3	0.05	0.30	0.17	0.15	0.24	0.32
TiO_2	0.01	n.d.	n.d.	n.d.	n.d.	n.d.
Fe_2O_3	8.86	9.80	8.59	9.48	8.77	7.78
As_2O_5	0.04	0.21	0.08	0.12	0.10	0.19
ZrO_2	0.30	0.35	0.35	0.33	0.30	0.38
Nb_2O_5	0.01	0.01	0.01	n.d.	n.d.	n.d.
SnO_2	0.01	n.d.	n.d.	n.d.	n.d.	n.d.
Sb_2O_5	0.01	0.03	0.02	0.01	0.01	n.d.
WO_3	77.47	74.24	74.59	74.96	75.51	61.35
Na_2O	2.05	1.08	1.39	1.27	1.37	0.52
K_2O	0.63	0.52	0.44	0.51	0.45	0.19
CaO	0.46	0.65	0.72	0.66	0.60	0.45
MnO	0.01	0.01	n.d.	0.01	0.02	n.d.
SrO	0.17	0.25	0.08	0.25	0.18	0.10
Ce_2O_3	1.60	1.66	1.79	1.58	1.66	1.50
La_2O_3	0.05	0.16	0.11	0.09	0.07	0.13
Tl_2O	0.02	0.04	0.01	0.02	0.03	19.56
PbO	0.06	0.13	0.03	0.04	0.02	n.d.
ThO_2	0.01	0.02	n.d.	0.01	0.01	n.d.
UO_2	n.d.	0.37	0.11	0.11	0.22	0.36
Total	91.81	89.81	88.51	89.62	89.54	92.83

Notes: *n* = number of analytical points; n.d. = not detected.

TABLE B.4. Microprobe data normalised to $\Sigma B = 2$ apfu collected from treated and untreated HKE.

	HKE_A	HKE_B	HKE_C	HKE_D	HKE_E	HKE_TI
Al	-	0.03	0.02	0.01	0.02	0.03
Ti	-	-	-	-	-	-
Fe ³⁺	0.49	0.54	0.49	0.53	0.50	0.52
As ⁵⁺	-	0.01	-	-	-	0.01
Zr	0.01	0.01	0.01	0.01	0.01	0.02
Nb	-	-	-	-	-	-
Sn	-	-	-	-	-	-
Sb ⁵⁺	-	-	-	-	-	-
W	1.49	1.41	1.47	1.44	1.47	1.42
Na	0.29	0.15	0.21	0.18	0.20	0.09
Ca	0.04	0.05	0.06	0.05	0.05	0.04
Mn ²⁺	-	-	-	-	-	-
Sr	0.01	0.01	-	0.01	0.01	0.01
Ce	0.04	0.04	0.05	0.04	0.05	0.05
La	-	-	-	-	-	0.01
Tl ⁺	-	-	-	-	-	0.50
Pb	-	-	-	-	-	-
Th	-	-	-	-	-	-
U	-	0.01	-	-	-	0.01
ΣA	0.38	0.26	0.32	0.28	0.31	0.71
K	0.06	0.05	0.04	0.05	0.04	0.02
ΣY	0.06	0.05	0.04	0.05	0.04	0.02

Hydroknoelsmoreite shows a poor-to-decent Tl-incorporation capacity, although the 0.50 Tl⁺ pfu detected by the microprobe might be overestimated. Indeed, considering the analytical totals before and after the imbibition experiments, only a slight increase (1–3 wt.%) is observed, indicating a limited involvement of H₃O⁺ or (H₂O+OH⁻). A plausible exchanger is sodium, which decreases by about 50% after the treatment; however, this amount only accounts for 0.10–0.20 apfu of entered

thallium. The remaining 0.30–0.40 apfu could have been exchanged with an aqueous species or could have been not incorporated at all but only adsorbed on the crystal surface.