Appendix

Endmember formula calculation using the site total charge (STC) approach for zero-valent-dominant pyrochlores:

All empirical formulae are calculated based on 2 *B*-site cations (Nb+W+P+Ta+Ti+Si+Zr+Al+Fe3+ = 2)

1. *Kalipyrochlore*

A(□0.46H2O1.41Na0.05Ca0.06Ba0.01U4+0.01)B(Nb1.80Ti0.14Al0.03Fe3+0.02P5+0.03)X(O4.05OH1.93)Y(K0.45H2O0.55) representing the *kalipyrochlore* from Lushe carbonatite, Zaire (Wall *et al*. 1996). STC(A) = +0.26 (0); STC(B)= +9.80 (+10); STC(X)= -10.52 (-11) STC(Y) = -0.45 (0).

Endmember STC: (*A*)2Σ0(*B*)2Σ10+(*X*)6Σ10-(*Y*)Σ0; Dominant endmember charge arrangement *A*(R02)Σ0 *B*(R5+2)Σ10+ *X*(R2-4R-2­)Σ10- *Y*(R0). Therefore, the endmember formula is (H2O)2Nb2(O4OH2)(H2O)for the species name *K-bearing hydropyrochlore*

1. *Strontiopyrochlore*

These pyrochlores occur aslate-stageveinsin granitoids and marble of Sierra de Sumampa, Santiago del Estero, Argentina (Franchini et al. 2005).

A(□0.75Na0.30Ca0.31Fe2+0.06Sr0.58)B(Nb1.93Ti0.04Si4+0.03)X(O5.70F0.30)Y(F0.43□0.57)

STC(A) = 2.20 (+2); STC(B) = 9.93 (+10); STC(X,Y) = -12.13 out of which F is -0.73 and rest is O2- anions.

Endmember STC: (*A*2) Σ2+(*B*2) Σ10+(*X*6)Σ12-(*Y*)Σ0; The most dominant atomic arrangement of the dominant endmember charge arrangement, *A*(R0R2+)Σ2+ *B*(R5+2)Σ10+ *X*(R2-6­)Σ12- *Y*(R0), is [(Sr□)Nb2O6□]0.75 = 8.25 *apfu* (limited by vacancy contents). Therefore, the species name is *kenostrontiopyrochlore* (R2+ > vacancy at *A*-site)

1. *Oxybariopyrochlore* in dolomite carbonatite, from Sevattur carbonatite complex (Table 2 composition 11 of Dey *et al*. 2021b). A(□0.60Na0.05Ca0.17Fe2+0.12Pb0.04Sr0.08Ba0.45U0.48)B(Nb1.49Ta0.13Si4+0.11Ti0.25Al0.02)X(O6)Y(O0.65□0.36); STC(A) = 3.69 (+4); STC(B) = 9.6 (+10); STC(X) = -12; STC(Y) = -1.29 (-1)

Possible groups of total site charges: (*A*2)Σ4+(*B*2)Σ10+(*X*6)Σ12-(*Y*)Σ2- and (*A*2)Σ3+(*B*2) Σ10+(*X*6)Σ12-(*Y*)Σ1-. The latter is discarded due to the absence of any monovalent anion at *Y*-site.The endmember charge arrangements and atomic arrangements for (*A*2)Σ4+(*B*2)Σ10+(*X*6)Σ12-(*Y*)Σ2- are as follows:

*- A*(R2+2)Σ4+ *B*(R5+2)Σ12+ *X*(R2-6­)Σ12- *Y*(R)Σ2- → [Ba2Nb2O6O]0.43 = 4.73 *apfu* (limited by Ba, Sr, Fe, Pb, and Ca contents)

- *A*(R0R4+)Σ4+ *B*(R5+2)Σ12+ *X*(R2-6­)Σ12- *Y*(R)Σ2- →[(□U4+)Nb2O6O]0.48 = 5.28 *apfu* (limited by U+4 contents). The most dominant atomic arrangement of the dominant endmember charge arrangement, is [(□U4+)Nb2O6O] for the species name *Ba-bearing, U-rich* *oxykenopyrochlore*.

1. *Plumbopyrochlore*

A(□0.08Ca0.04Fe2+0.50Pb0.81Gd3+0.03Dy3+0.01Tm3+0.01Yb3+0.03Y3+0.24Ce3+0.06Th4+0.06 U4+0.13)B(W6+0.07P5+0.01Nb1.41Ta0.10Ti0.03Si4+0.38)X(O6)Y(O0.935F0.39)Σ1.325 from Xihuashan granitic complex, China (Table 9; composition 1 of Wang et al. 2003); STC(A) = +4.6 (+5); STC(B) = +9.66 (+10); STC(X) = -11.61; STC (Y) = -2.26 (-2). Note that the formula calculation leads to an over estimation of Y-site cations (1.325 pfu).

Endmember site total charges: (*A*2)Σ4+(*B*2) Σ10+(*X*6)Σ12-(*Y*)Σ2-

The most abundant atomic charge arrangement following the dominant endmember charge arrangement [*A*(R2+2)Σ4+ *B*(R5+2)Σ12+ *X*(R2-6­)Σ12- *Y*(R)Σ2] is [Pb2­Nb2O6O]0.75 = 8.36 *apfu* (limited by R5+ contents). Therefore, the species name is *oxyplumbopyrochlore.*

Similarly, plumbopyrochlore from Borborema Pegmatite Province, Northeast Brazil (Table 1; composition 4 of Beurlen et al. 2005) has a composition: A(□0.32K0.07Na0.12Mg0.02Ca0.09Fe2+0.82Pb0.38U4+0.18)B(P0.28Nb1.04Ta0.28Ti0.15Si4+0.05Zr0.01Al0.19)X(O6)Y(O0.47□0.53); STC(A) = +3.53(+4); STC(B) = -9.41(-9); STC(X) = -12; STC(Y) = -0.94(-1). Endmember STC: (*A*2)Σ2+(*B*2)Σ10+(*X*6)Σ12-(*Y*)Σ0- . Dominant endmember formula following this site charge constraints is (Fe□)Nb2O6□.

1. *Ceriopyrochlore*

A(□1.22K0.07Na0.11Ca0.04Fe2+0.01Pb0.01Sr0.07Ba0.09Nd3+0.01La3+0.15Y3+0.01Ce3+0.24)B(Nb1.82Ti0.16Si4+0.02)X(O5.61OH0.39)Y(□) representing the *ceriopyrochlores* from calciocarbonatite in South Morocco (Benaouda *et* *al*. 2020)

STC(*A*) = +1.79 (+2); STC(*B*)= +9.81(+10); STC(*X*)= -11.61(-12)

(□4/3R3+2/3)2+ 🡪 (□4/3Ce3+2/3)0.615 = 1.23 *apfu* (limited by R3+ contents)

(□R2+)2+ 🡪 (□Sr2+)0.105 = 0.21 *apfu* (limited by R2+ contents)

(R+2)2+ 🡪 (K+2)2+0.09 = 0.18 *apfu*

Nb2 and O6 are consistent with the site charge at *A* and *X*-site, respectively. Therefore, the endmember formula is (□4/3Ce3+2/3)Nb2O6(□) for the species name *Ce-rich kenopyrochlore*.

1. *Bismutopyrochlore*

A(□0.84Ca0.15Sr0.02Pb0.07Bi3+0.55Yb3+0.01Dy3+0.02Gd3+0.01Sm3+0.01Ce3+0.05Pr3+0.01La3+0.01U4+0.07 Th4+0.16)B(Nb0.52Ta0.24Ti0.12Si0.88Zr0.02Al3+0.21Fe3+0.07)X(O5.01 OH0.99)Y(□) representing the zero-valent-dominated *bismutopyrochlore* from granitic pegmatite of the O’ Grady batholith, NWT, Canada (Ercit *et al*. 2003).

STC(*A*)= +3.48 (+2); STC(*B*)= +8.53 (+10); STC(*X*)= -12.01(-12).

Considering R4+2 at *B*-site, the endmember site total charges are (*A*2)4+(*B*2)8+­(*X*6)12-(Y)0 corresponding to the atomic arrangement [(Bi3+4/3□2/3)Si2O6□]0.5025 = 5.025 *apfu*

Considering R5+2 at *B*-site, the endmember site total charges are (*A*2)2+(*B*2)10+­(X6)12-(Y)0 corresponding to the atomic arrangement[(□4/3 Bi3+2/3)Nb2O6□]0.38 = 3.8 *apfu*. Although (Bi3+4/3□2/3)Si2O6□ > (□4/3 Bi3+2/3)Nb2O6□ in terms of *apfu*, but a pyrochlore group with Si dominant at *B*-site is not feasible at the moment (see the section on R4+-pyrochlores). Therefore, the endmember formula is (□4/3Bi3+2/3)Nb2O6□.

1. *Hydrokenopyrochlore*

A(□1.32Sb3+0.35Na0.26Ca0.07)Σ2B(Nb1.47Ta0.28W0.16Sb5+0.05Si0.04)Σ2X(O5.12OH0.88)Y[(H2O)0.55Cs0.45] represents the *Hydrokenopyrochlore* from Sahatany Pegmatite field, Madagascar (Biagioni *et al.* 2018) STC(A) = +1.45 (+1); STC(B) = +10.12 (+10); STC(X) = -11.12(+12); STC(Y) = -0.45(0)

Endmember site total charges: (*A*2)Σ2+(*B*2)Σ10+(*X*6)Σ12-(*Y*)Σ0- [∆A+∆X = 2.43]. Dominant endmember charge arrangement is A(R01.33R3+0.67)Σ2+ *B*(R5+2)Σ10+ *X*(R2-6­)Σ12- *Y*(R0). The most abundant atomic arrangement according to the endmember charge arrangement is [(□1.33Sb0.67)Nb2O6(H2O)]0.522 = 5.75 *apfu* (limited by Sb3+ contents).

Endmember site charges: (*A*2)Σ0(*B*2)Σ10+(*X*6)Σ10-(*Y*)Σ0- [∆A+∆Y = 1.57]; dominant endmember charge arrangement: *A*(R02)Σ0 *B*(R5+2)Σ10+ *X*(R2-4R-2­)Σ10- *Y*(R0). The most abundant atomic arrangement according to the endmember charge arrangement is [(□2)Nb2(O4OH2)(H2O)]0.66 = 7.26 *apfu* (limited by vacancy contents). Therefore the endmember formula is (□2)Nb2(O4OH2)(H2O) for a species name Sb3+-bearing *hydrokenopyrochlore*

8*. Yttropyrochlore*

A(□0.97Ca0.46Pb0.09Gd3+0.02Nd3+0.02La3+0.01Y3+0.27Ce3+0.02Th4+0.02U4+0.10)B(Nb1.10Ta0.39Ti0.06Si0.35Al0.05Fe0.06)x(O5.04OH0.96)Y(□) representing the *yttropyrochlor*e from granitic pegmatite of the O’ Grady batholith, NWT, Canada (Ercit *et al*. 2003).

STC(A)= +2.65 (+2); STC(B)= +9.39 (+10); STC(X)= -12.04 (-12)

For a charge constraint of +2; +10 and -12 at *A-*, *B*-, and X-sites respectively. The possible atomic arrangements at *A*-site are: (□Ca)0.55 = 1.1 *apfu*; (□4/3Y3+2/3)0.51 = 1.02 *apfu*; (□1.5U0.5)0.24 = 0.48 *apfu*. Therefore the endmember formula is (□Ca)Nb2O6(□) for the species name *Y-bearing,* *Ca-rich kenopyrochlore*.

9. *Uranoan pyrochlore*

A(□0.272Na0.725Ca0.418Sr0.124Ce3+0.132U4+0.329)B(Nb1.479Ta0.038Ti0.483)X(O6)Y(O0.52□0.46) uranoan pyrochlore (Chakhmouradian & Mitchell 2002).

STC(A) = +3.521(-4); STC(B) = +9.517(-10); STC(X) = -12; STC(*Y*) = -1.04

Endmember STC: (*A*2)Σ4+(*B*2)Σ10+(*X*6)Σ12-(*Y*)Σ2-

(R2+2)4+ → (Ca2)4+0.271 = 0.542 *apfu* (limited by Ca and Sr contents)

(R+1.33 R4+0.67)4+ → (Na+1.33U4+0.67)4+0.491 = 0.982 *apfu* (limited by U contents)

(R0 R4+)4+  → (□U)4+0.272 = 0.544 *apfu* (limited by vacancy contents)

(R00.67 R3+1.33) → (□0.67Ce3+1.33)4+0.099 = 0.198 *apfu* (limited by Ce contents)

Therefore, the dominant atomic arrangement at *A*-site is (Na+1.33U4+0.67). Thus, the endmember formula is (Na1.33U0.67)Nb2O6O for the species name *Ce-, Sr- bearing* *U-rich oxynatropyrochlore*.