Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

—Supporting Information—

Fluoride Frameworks as Potential Calcium Battery Cathodes

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Projector Augmented Wave potentials

Table S1: Projector augmented wave potentials used to describe the core electrons in our calculations.

Element	Potential
Ca	Ca_sv 06Sep2000
Ti	Ti_pv 07Sep2000
V	V_pv 07Sep2000
Cr	Cr_pv 02Aug2007
Mn	Mn_pv 02Aug2007
Fe	Fe_pv 02Aug2007
Co	Co_pv 23Apr2009
Ni	Ni_pv 06Sep2000
F	F 08Apr2002

Na coordination in weberites

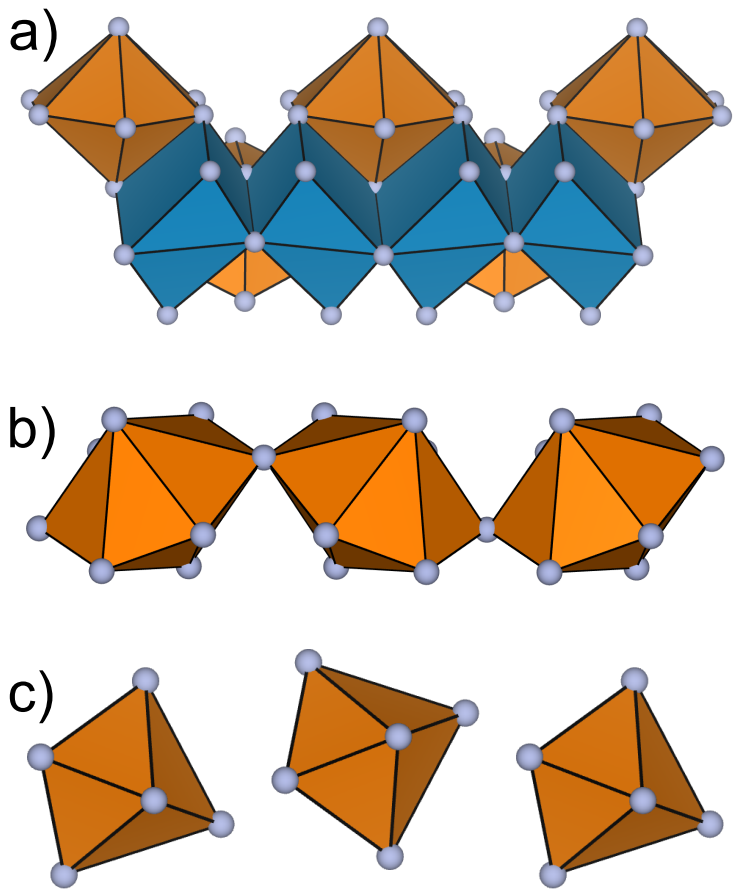

Figure S1: Coordination environment of Na in orthorhombic weberite. (a) Na2 cations represented as a distorted cubic-type (or square prism) polyhedra (blue polyhedra) that interconnect through shared edges with Na2 and Na1 (orange polyhedra). (b) Na1 cations indicated by hexagonal bipyramids (orange polyhedra) that interconnect through corner-sharing. (c) Na1 cations in *Pmnb* symmetry exhibiting distorted pentagonal bipyramid coordination with each polyhedra not being interconnected via common edges or corners.

Kagome network in weberites

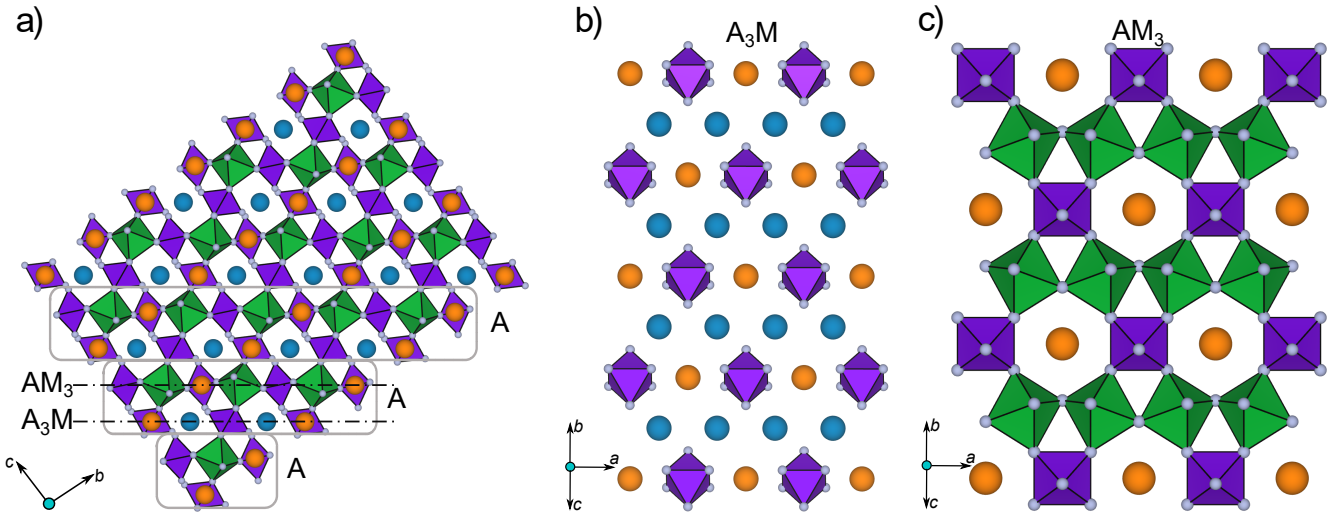

Figure S2: (a) Layers of A_3M (A/Na-rich layer) and AM_3 (redox-metal-rich layer) forming an 'AA' stacking sequence (marked by grey dotted boxes) in orthorhombic-weberite. Kagome-type network for A_3M (panel b) and AM_3 (panel c) layers. Notations in the figure are identical to **Figure 1a-b** of the main text.

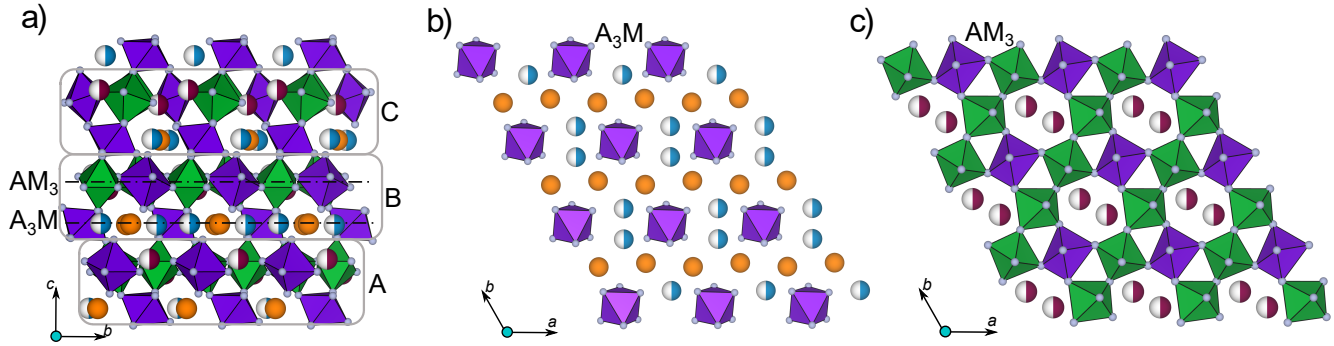

Figure S3: (a) Layers of A_3M (A/Na-rich layer) and AM_3 (redox-metal-rich layer) forming an 'ABCABC' stacking sequence (marked by grey boxes) in trigonal-weberite. Kagome-type network for A_3M (panel b) and AM_3 (panel c) layer. Notations in the figure are identical to **Figure 1c** of the main text.

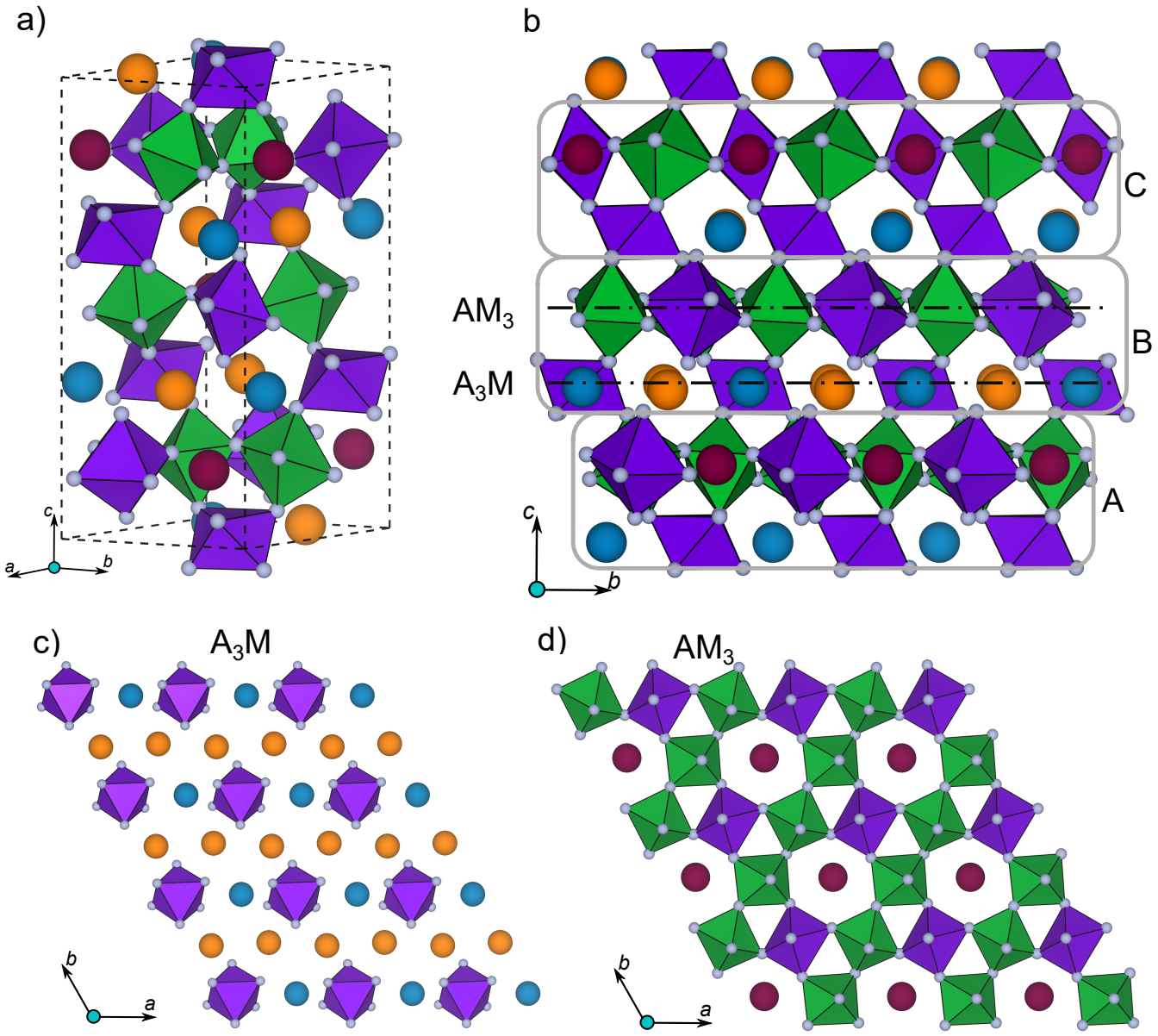

Figure S4: (a) Crystal structure of trigonal-weberite with full Na site occupancy (i.e., 2 Na per formula unit). (b) Layers of A_3M (A/Na-rich layer) and AM_3 (redox-metal-rich layer) forming an 'ABCABC' stacking sequence (marked by grey boxes) in trigonal-weberite with full Na site occupancy. Kagome-type network for A_3M (panel c) and AM_3 (panel d) layer for trigonal-weberite with full Na site occupancy. Notations in the figure are identical to **Figure 1c** of the main text, with the exception of select Na2 and Na3 sites being represented by full light blue and maroon spheres to indicate full occupancy of the select Na sites.

Ground state Ca-vacancy configuration of weberites and perovskites

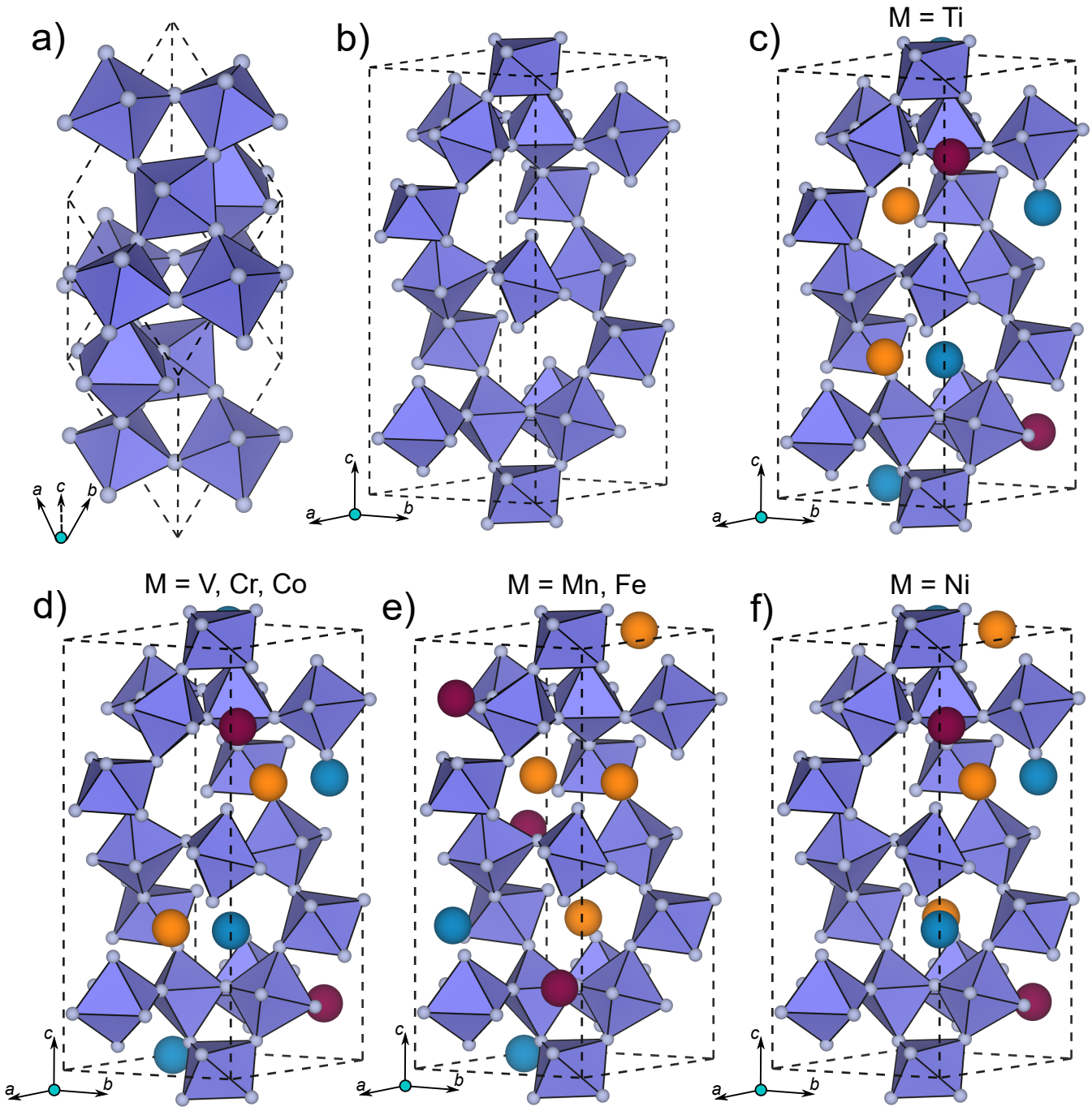

Figure S5: The ground state Ca-vacancy configuration of charged (a) orthorhombic and (b) trigonal weberite (M_2F_7, M = Ti, V, Cr, Mn, Fe, Co, or Ni), and discharged trigonal weberite with compositions, (c) $Ca_{1.5}Ti_2F_7$, (d) $Ca_{1.5}M_2F_7$, M = V, Cr, or Co, (e) $Ca_{1.5}M_2F_7$, M = Mn or Fe and (f) $Ca_{1.5}Ni_2F_7$. Purple polyhedra indicate MF_6 units, where F atoms are represented by grey spheres. Ca at Ca1, Ca2, and Ca3 sites are indicated by orange, blue and maroon spheres, respectively. Dashed black lines signify the extent of the unit cell.

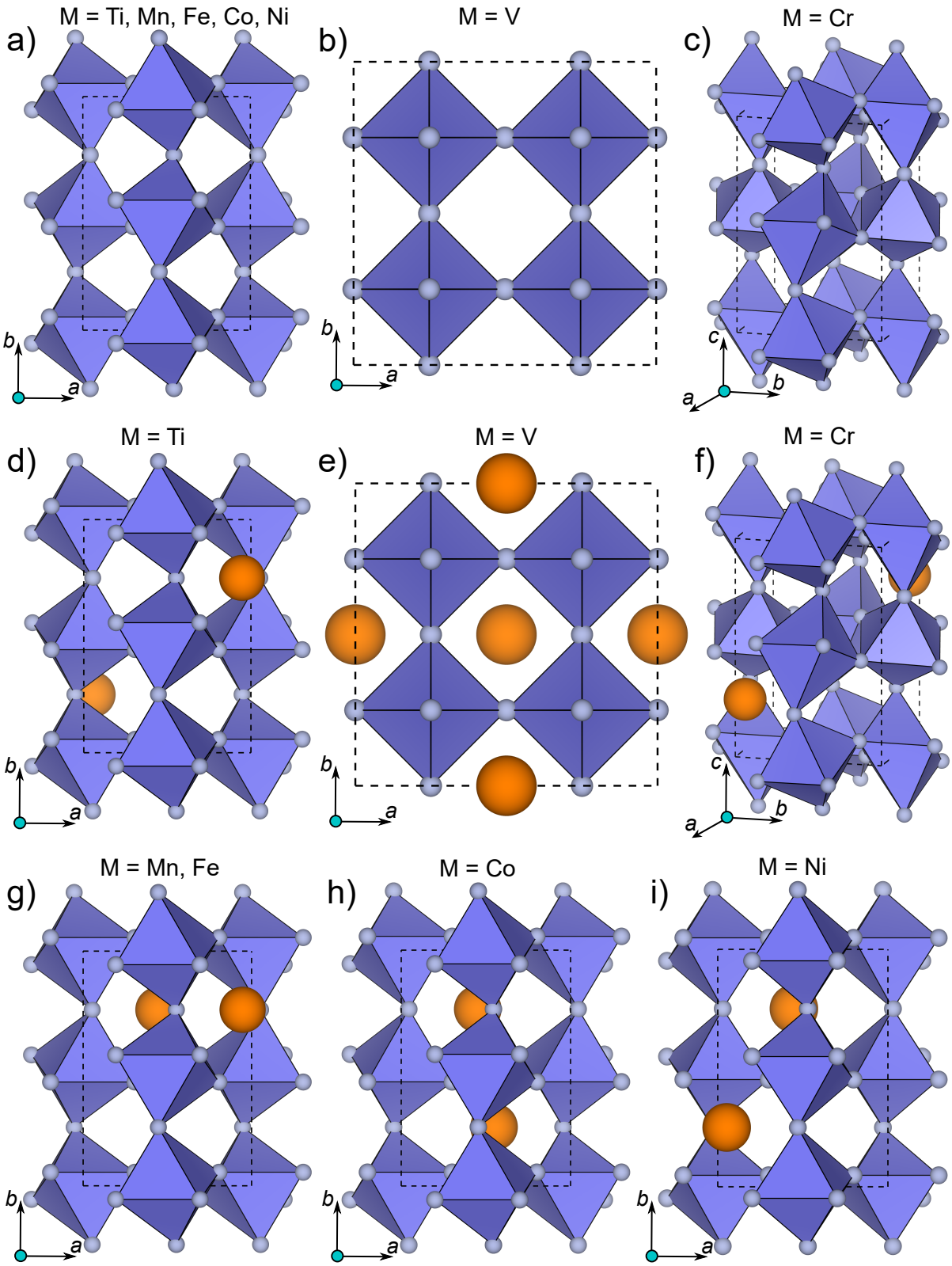

Figure S6: The ground state Ca-vacancy configuration of charged (a) orthorhombic (MF_3, M = Ti, Mn, Fe, Co, or Ni), (b) cubic-VF_3 and (c) triclinic-CrF_3 perovskites. Ground state structures of discharged perovskites, namely (d) orthorhombic-$Ca_{0.5}TiF_3$, (e) cubic-$Ca_{0.5}VF_3$, (f) triclinic-$Ca_{0.5}CrF_3$ (g) orthorhombic-$Ca_{0.5}MF_3$, M = Mn, Fe, (h) orthorhombic-$Ca_{0.5}CoF_3$ and (i) -$Ca_{0.5}NiF_3$. Notations in the figure are identical to **Figure S4**.

Table S2: Relative energy of orthorhombic weberites with respect to the corresponding trigonal weberites at discharged ($Ca_{1.5}M_2F_7$) and charged (M_2F_7) compositions. M represents a $3d$ transition metal. Positive (negative) energy indicates trigonal (orthorhombic) weberite being energetically favored.

M	Relative energies (meV/atom)	
	Discharged	Charged
Ti	39	8
V	11	-8
Cr	17	8
Mn	17	53
Fe	10	-9
Co	15	-29
Ni	3	9

0 K phase diagrams

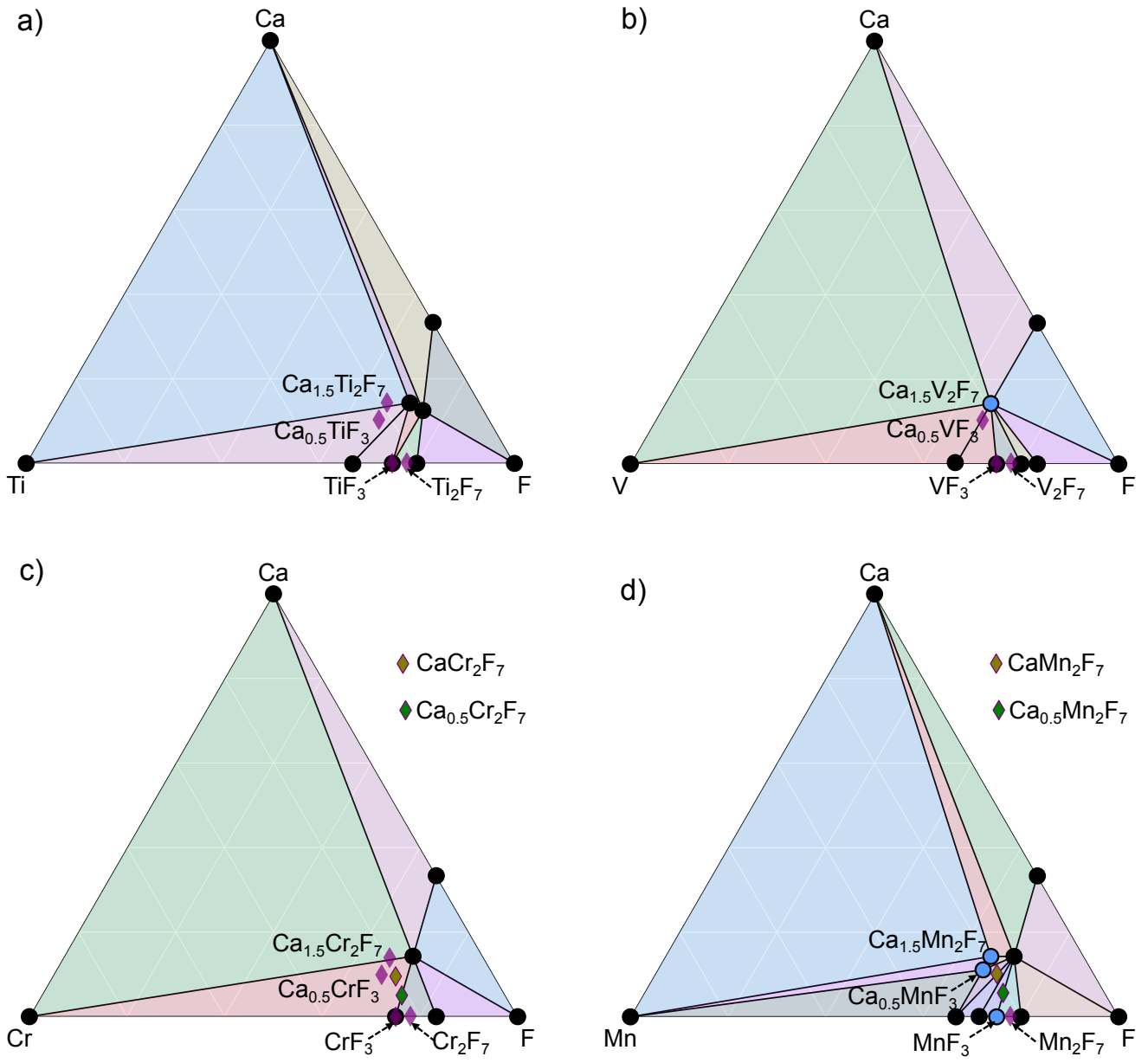

Figure S7: Ternary Ca-M-F phase diagrams, where M = Ti (panel a), V (b), Cr (c), and Mn (d). Stable entities within each phase diagram are indicated by solid black circles. Stable charged or discharged weberite and perovskite phases are represented by blue circles with black outlines. Black lines connecting different compositions are tie-lines. Unstable/metastable weberite and perovskite phases are indicated by purple diamonds. Weberites with intermediate Ca compositions, such as $Ca_{0.5}M_2F_7$ and CaM_2F_7, are indicated by green and light green diamonds, respectively, where M = Cr, Mn.

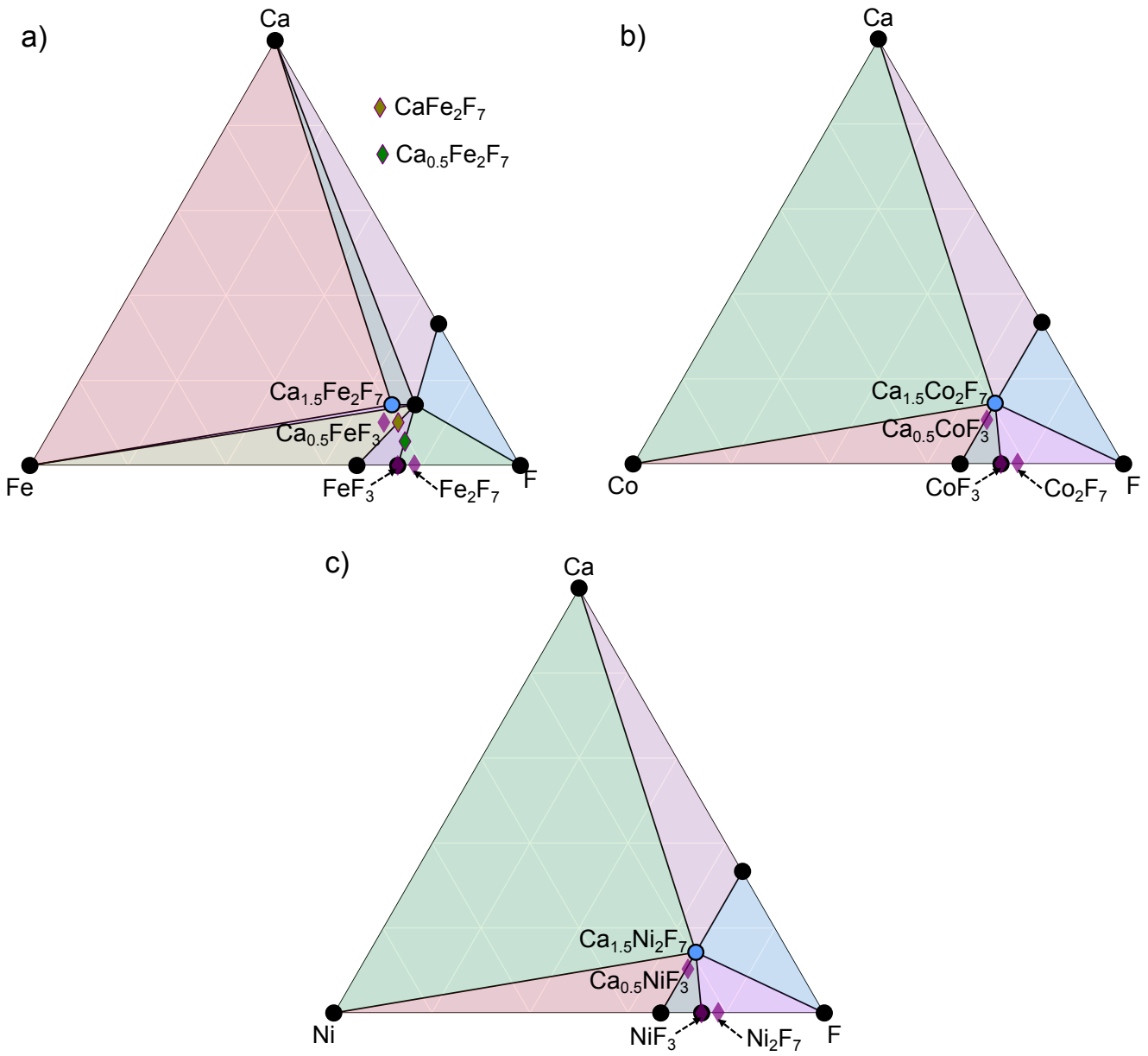

Figure S8: Ternary Ca-M-F phase diagrams, where M = Fe (panel a), Co (b), and Ni (c). Notations in the figure are identical to **Figure S7**.

Table S3: The predicted adjacent phases (or decomposition products) for all stable (metastable/unstable) weberite and perovskite fluorides are presented. Note that for all stable (metastable/unstable) entities on a phase diagram, energy below (above) the convex hull represents the formation energy (decomposition energy) of the stable (metastable/unstable) phase with respect to the adjacent stable phases (decomposition products) on the convex hull. Energy above the convex hull values for select weberites with intermediate Ca compositions are presented in parentheses.

Stable weberites	**Adjacent phases**
$Ca_{1.5}V_2F_7$	CaF_2, $Ca_{0.5}VF_3$
$Ca_{1.5}Mn_2F_7$	Ca, $CaMnF_5$, $Ca_{0.5}MnF_3$
$Ca_{1.5}Fe_2F_7$	Ca, Fe, $CaFeF_5$
$Ca_{1.5}Co_2F_7$	CaF_2, $Ca_{0.5}CoF_3$
$Ca_{1.5}Ni_2F_7$	CaF_2, $Ca_{0.5}NiF_3$
Metastable/unstable weberites	**Decomposition products**
Ti_2F_7	TiF_3, TiF_4
$Ca_{1.5}Ti_2F_7$	Ca, Ti, $CaTiF_5$
V_2F_7	VF_3, VF_4
Cr_2F_7	CrF_3, CrF_5
$Ca_{0.5}Cr_2F_7$ (57 meV/atom)	CrF_3, $CaCrF_5$
$CaCr_2F_7$ (65 meV/atom)	Ca, Cr, $CaCrF_5$
$Ca_{1.5}Cr_2F_7$	Cr, CrF_3, $CaCrF_5$
Mn_2F_7	MnF_3, MnF_4
$Ca_{0.5}Mn_2F_7$ (52 meV/atom)	MnF_3, $CaMnF_5$
$CaMn_2F_7$ (54 meV/atom)	MnF_2, $CaMnF_5$
Fe_2F_7	F_2, FeF_3
$Ca_{0.5}Fe_2F_7$ (71 meV/atom)	FeF_3, $CaFeF_5$
$CaFe_2F_7$ (57 meV/atom)	FeF_2, $CaFeF_5$
Co_2F_7	F_2, CoF_3
Ni_2F_7	F_2, NiF_3
Stable perovskites	**Adjacent phases**
MnF_3	MnF_3 ($R\bar{3}cR$)
$Ca_{0.5}MnF_3$	MnF_2, $Ca_{1.5}Mn_2F_7$
Metastable/unstable perovskites	**Decomposition products**
TiF_3	TiF_3 ($R\bar{3}cR$)
$Ca_{0.5}TiF_3$	TiF_2, Ti, $CaTiF_5$
VF_3	VF_3 ($R\bar{3}cR$)
$Ca_{0.5}VF_3$	VF_2, V, $Ca_{1.5}V_2F_7$
CrF_3	CrF_3 ($R\bar{3}cR$)
$Ca_{0.5}CrF_3$	CrF_3 ($R\bar{3}cR$), Cr, $CaCrF_5$
FeF_3	FeF_3 ($R\bar{3}cR$)
$Ca_{0.5}FeF_3$	FeF_2, Fe, $CaFeF_5$
CoF_3	CoF_3 ($R\bar{3}cR$)
$Ca_{0.5}CoF_3$	CoF_2, $Ca_{1.5}Co_2F_7$
NiF_3	NiF_3 ($R\bar{3}cR$)
$Ca_{0.5}NiF_3$	NiF_2, $Ca_{1.5}Ni_2F_7$

Minimum energy pathways (MEPs) in select weberites and perovskites

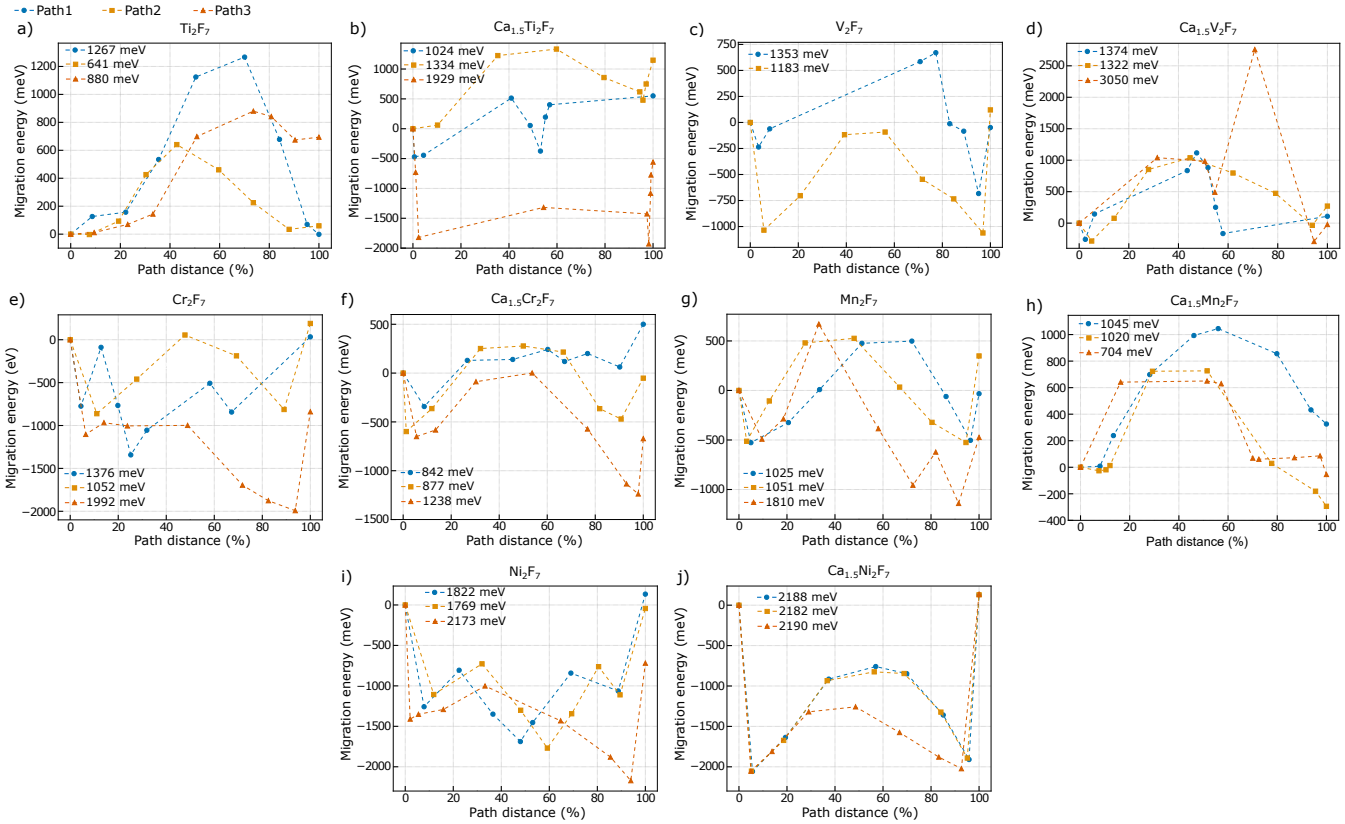

Figure S9: The calculated MEPs of Ca^{2+} migration in select weberite fluorides at charged and discharged compositions, namely (a, b) $Ca_xTi_2F_7$, (c, d) $Ca_xV_2F_7$, (e, f) $Ca_xCr_2F_7$, (g, h) $Ca_xMn_2F_7$, and (i, j) $Ca_xNi_2F_7$. The MEPs across Path1, Path2, and Path3 are represented by blue circles, yellow squares and orange triangles, respectively, and the corresponding E_m values are listed as legends within each panel.

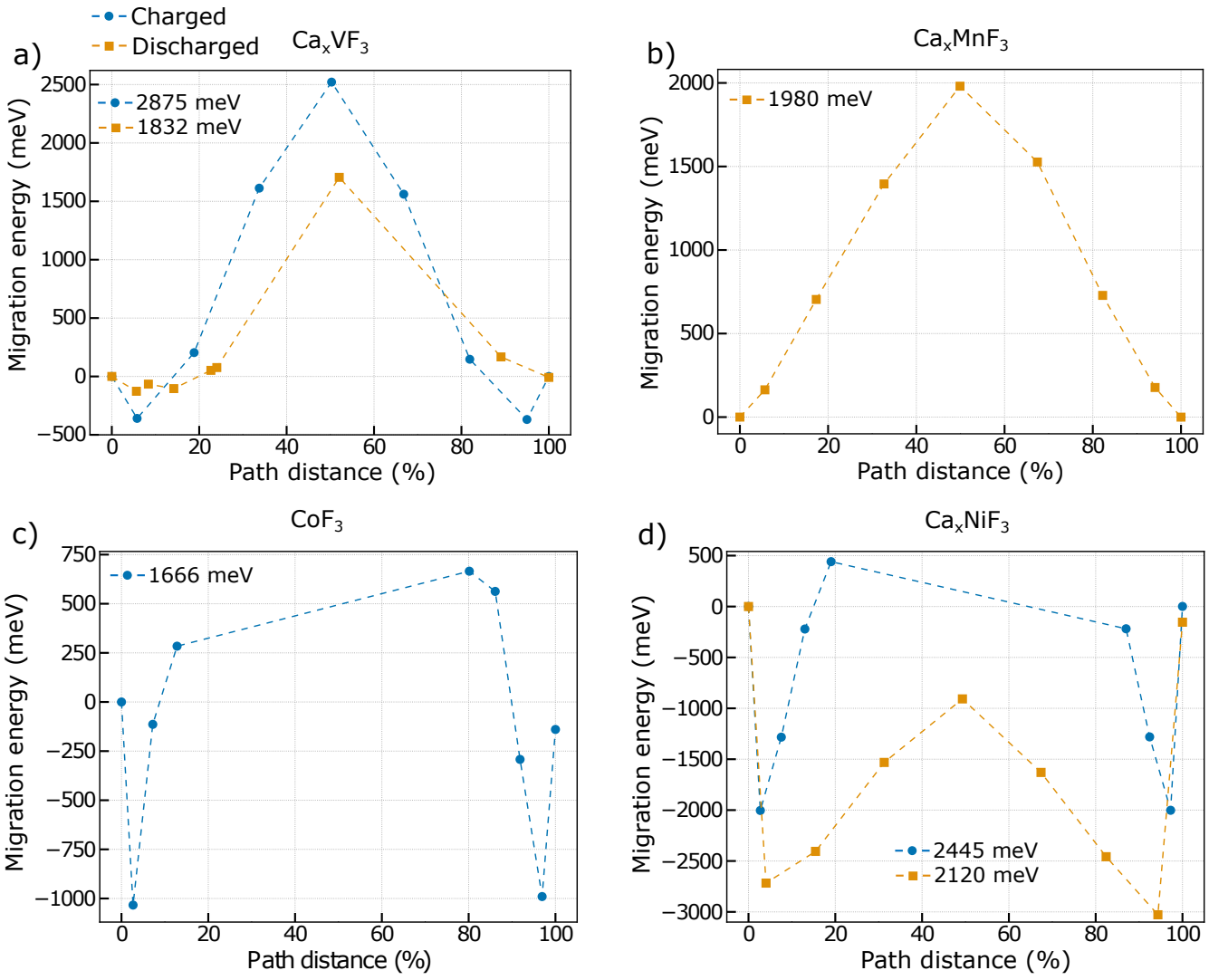

Figure S10: The calculated MEPs of Ca^{2+} migration in select perovskites fluorides at charged and discharged compositions, namely (a) Ca_xVF_3, (b) Ca_xMnF_3, (c) Ca_xCoF_3, and (d) Ca_xNiF_3. The charged and discharged MEPs are represented by blue circles and yellow squares, respectively, and the corresponding E_m values are listed as legends within each panel.

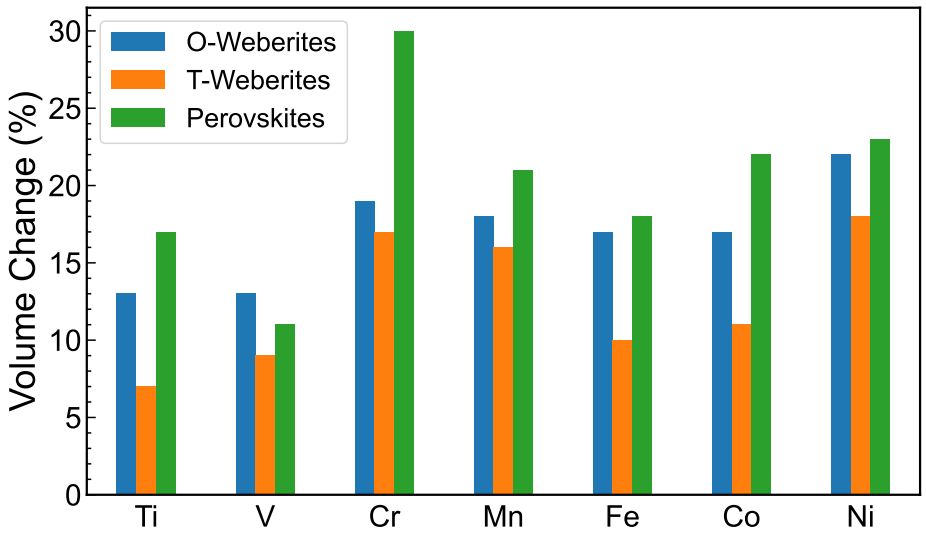

Figure S11: Computed volume change as a function of transition metal, between the fully charged and the fully discharged orthorhombic weberite (O-Weberite, represented by blue bar), trigonal weberite (T-Weberite, orange) and perovskite (green) fluorides.

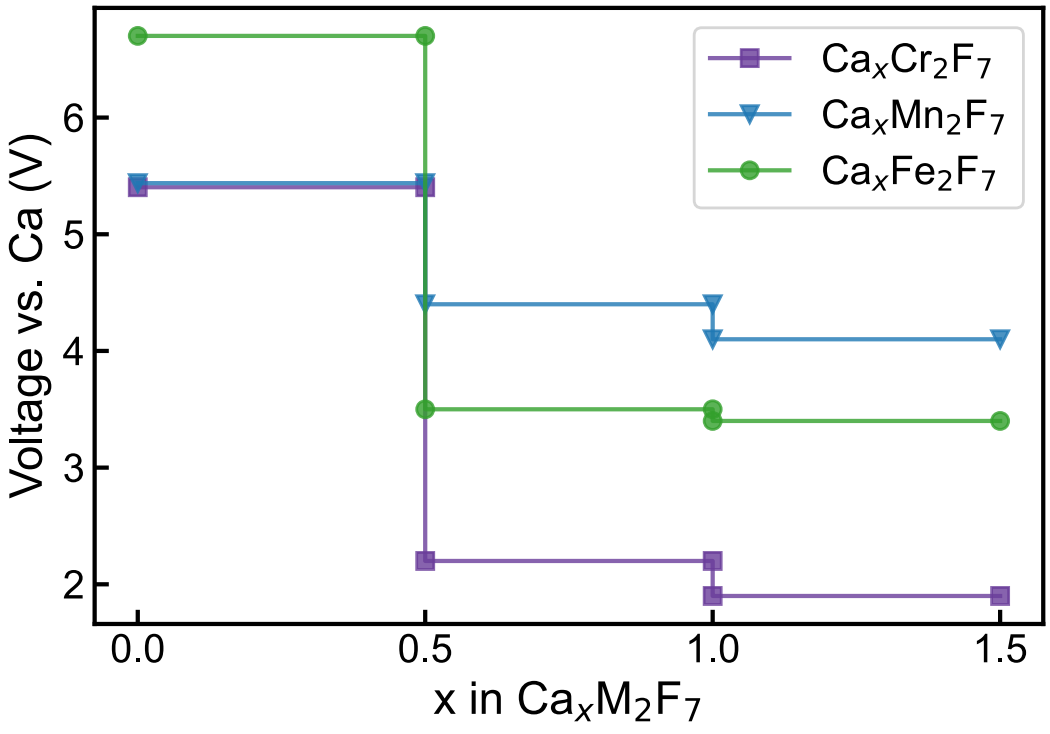

Figure S12: Computed voltage-composition profiles for $Ca_xCr_2F_7$ (purple squares), $Ca_xMn_2F_7$ (blue triangles), and $Ca_xFe_2F_7$ (green circles).