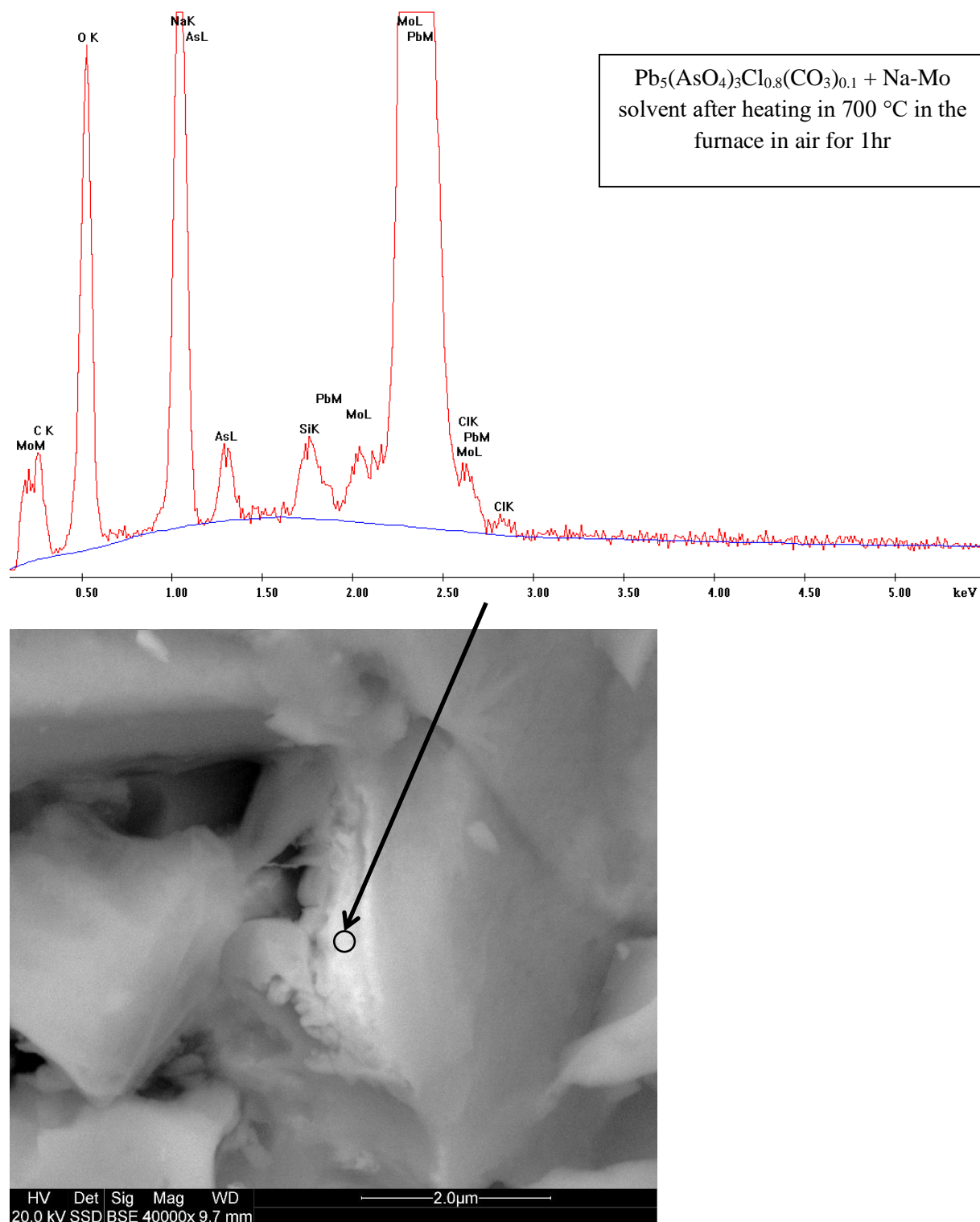**Supplemental Information**

Thermodynamic characterization of synthetic lead-arsenate apatites with different halogen substitutions

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Pb$_5$(AsO$_4$)$_3$Cl$_{0.8}$(CO$_3$)$_{0.1}$ + Na-Mo solvent after heating in 700 °C in the furnace in air for 1hr

Supplemental Figure S1a. BSE image and EDS spectrum of the quenched mixture of Na-Mo solvent with Mim-Cl after heating in furnace in air at 700 °C for 1hr.
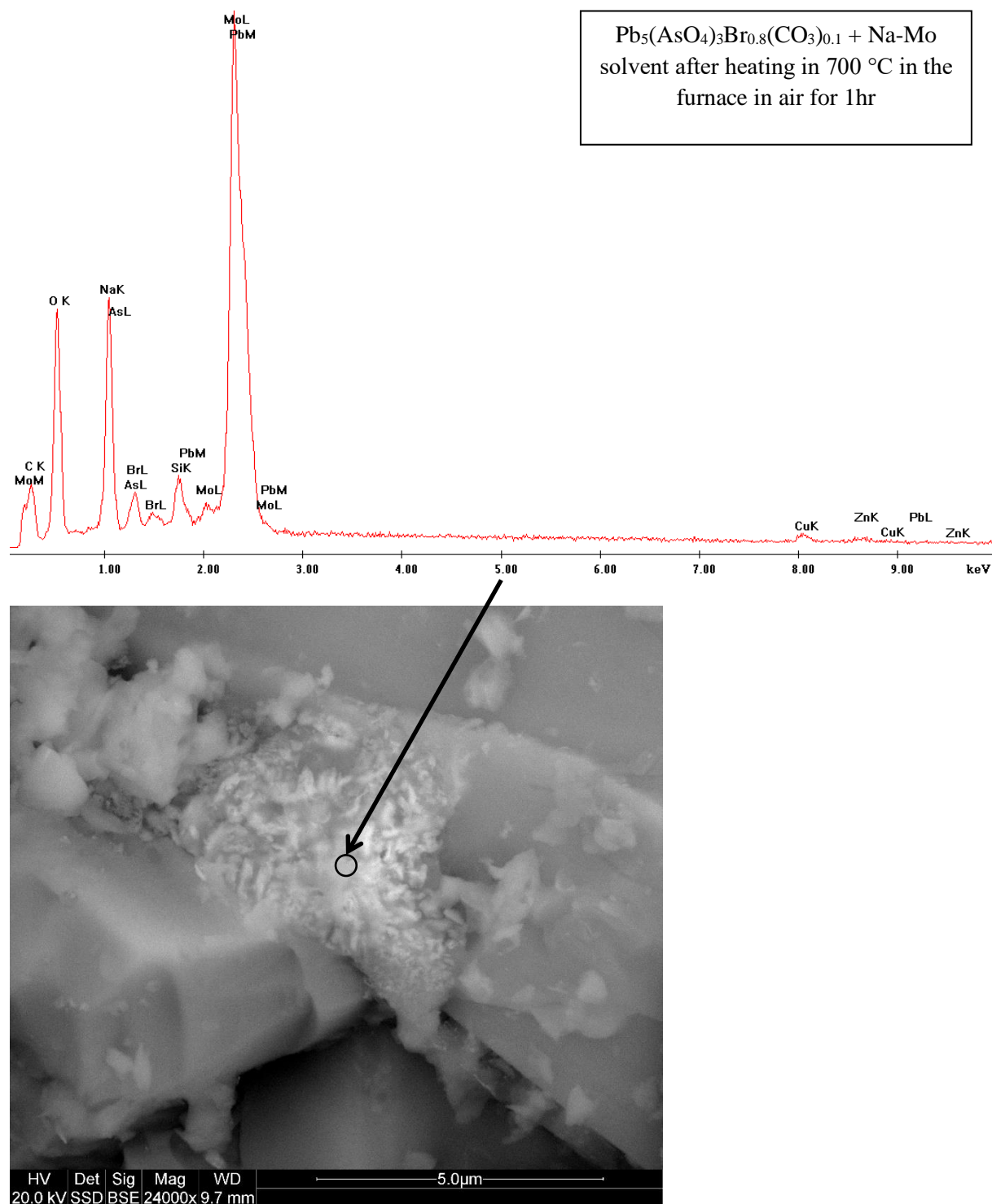
Supplemental Figure S1b. BSE image and EDS spectrum of the quenched mixture of Na-Mo solvent with Mim-Br after heating in furnace in air at 700 °C for 1hr.

Pb$_5$(AsO$_4$)$_3$I$_{0.45}$OH$_{0.35}$(CO$_3$)$_{0.1}$ + Na-Mo solvent after heating in 700 °C in the furnace in air for 1hr
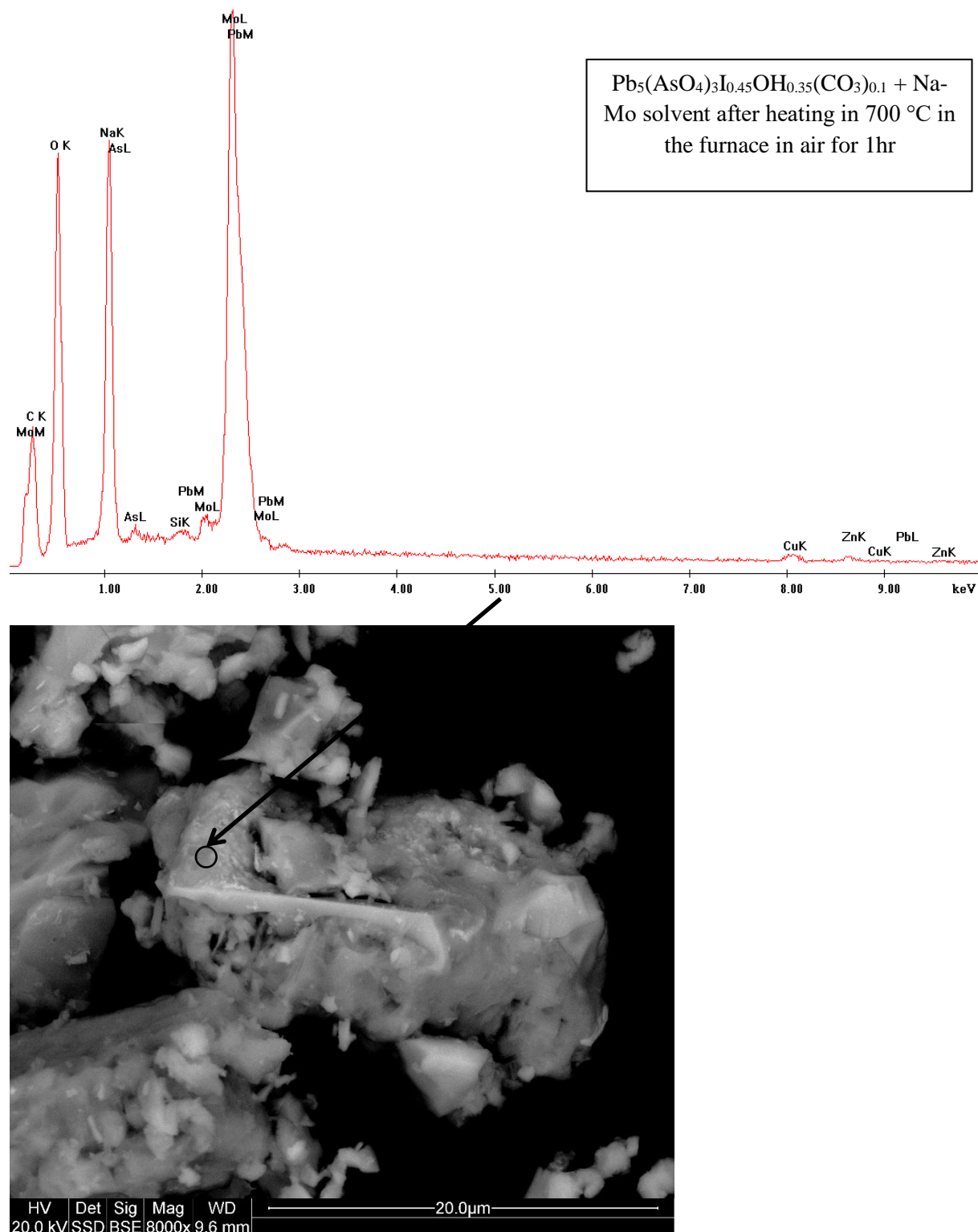
Supplemental Figure S1c. BSE image and EDS spectrum of the quenched mixture of Na-Mo solvent with Mim-Br after heating in furnace in air at 700 °C for 1hr.

Supplemental Table S1. The measured drop solution enthalpies, ΔH_{DS}, at T = 700 °C and p = 0.1 MPa (atmospheric pressure) for $Pb_{5.00}(AsO_4)_{3.00}OH_{0.86}(CO_3)_{0.07}$.

Experiment number	m/mg	ΔH_{DS} (kJ/mol)
1	5.25	492.60
2	5.51	463.87
3	5.4	458.17
4	5.24	451.36
5	4.74	467.78
6	5.59	492.80
7	5.13	482.79
8	5.91	464.57
9	5.39	479.79
10	5.96	492.90
Mean		474.66 ± 9.79

Note: The associated error represents two standard errors ($2\sigma_M$) of the mean.

Supplemental Table S2. The measured drop solution enthalpies, ΔH_{DS}, at T = 700 °C and p =

0.1 MPa (atmospheric pressure) for $Pb_{5.00}(AsO_4)_{3.00}Cl_{0.80}(CO_3)_{0.10}$.

Experiment number	m/mg	ΔH_{DS} (kJ/mol)
1	5.31	516.92
2	5.31	558.58
3	5.59	565.79
4	5.41	528.31
5	4.96	503.82
6	5.14	501.83
7	5.24	513.12
8	5.58	545.39
9	5.12	561.48
10	5.55	520.02
11	5.37	551.89
Mean		533.38 ± 13.75

Note: The associated error represents two standard errors ($2\sigma_M$) of the mean.

Supplemental Table S3. The measured drop solution enthalpies, ΔH_{DS}, at T = 700 °C and p = 0.1 MPa (atmospheric pressure) for $Pb_{5.00}(AsO_4)_{3.00}Br_{0.80}(CO_3)_{0.10}$.

Experiment number	m/mg	ΔH_{DS} (kJ/mol)
1	5.33	540.35
2	5.16	485.21
3	5.33	564.40
4	5.46	543.04
5	5.65	473.59
6	5.45	552.58
7	5.38	515.91
8	5.23	531.01
9	5.49	466.25
10	5.06	469.91
Mean		514.23 ± 22.40

Note: The associated error represents two standard errors ($2\sigma_M$) of the mean.

Supplemental Table S4. The measured drop solution enthalpies, ΔH_{DS}, at T = 700 °C and p = 0.1 MPa (atmospheric pressure) for $Pb_{5.00}(AsO_4)_{3.00}I_{0.45}OH_{0.35}(CO_3)_{0.10}$.

Experiment number	m/mg	ΔH_{DS} (kJ/mol)
1	5.88	486.31
2	5.18	516.28
3	5.68	506.63
4	4.95	500.47
5	5.65	483.71
6	5.11	492.67
7	5.68	506.63
Mean		498.96 ± 8.34

Note: The associated error represents two standard errors ($2\sigma_M$) of the mean.

Supplemental Table S5. The measured drop solution enthalpies, ΔH_{DS}, at T = 700 °C and p = 0.1 MPa (atmospheric pressure) for KCl.

Experiment number	m/mg	ΔH_{DS} (kJ/mol)
1	5.21	73.29
2	5.65	71.24
3	5.47	70.90
4	5.37	67.13
5	5.72	70.65
6	5.55	72.82
7	5.52	72.78
8	5.73	71.74
Mean		71.32 ± 1.38

Note: The associated error represents two standard errors ($2\sigma_M$) of the mean.

Supplemental Table S6. The measured drop solution enthalpies, ΔH_{DS}, at T = 700 °C and p = 0.1 MPa (atmospheric pressure) for KBr.

Experiment number	m/mg	ΔH_{DS} (kJ/mol)
1	5.31	76.01
2	5.62	83.25
3	5.56	78.06
4	5.22	75.28
5	5.32	78.26
6	5.15	82.00
7	5.40	76.34
8	4.98	78.11
Mean		78.41 ± 2.01

Note: The associated error represents two standard errors ($2\sigma_M$) of the mean.

Supplemental Table S7. Reactions and thermodynamic cycles used for

$Pb_{5.00}(AsO_4)_{3.00}Br_{0.80}(CO_3)_{0.10}$ to calculate the enthalpies of formation from the elements at 25

°C according to the reaction: $5PbO + 1.5As_2O_5 + 0.4Br_2 + 0.1CO_2 =$

$Pb_{5.00}(AsO_4)_{3.00}Br_{0.80}(CO_3)_{0.10} + 0.2O_2$. Assuming that Br from the mimetite during the

measurement in the calorimeter at 700 °C released as a gas phase and do not remain in the

solvent. The enthalpy of formation from the elements calculated using thermochemical cycle

below is equal to $\Delta H°_{f, el}$ [$Pb_{5.00}(AsO_4)_{3.00}Br_{0.80}(CO_3)_{0.10}$] = -2969.7 ± 25.04 (kJ/mol).

No	Reaction	ΔH (kJ/mol)
(1)	$Pb_{5.00}(AsO_4)_{3.00}Br_{0.80}(CO_3)_{0.10(c, 25\,°C)} +$ $0.2O_{2(g, 25\,°C)} \rightarrow 5PbO_{(sln, 700\,°C)} +$ $1.5As_2O_{5(sln, 700\,°C)} + 0.4Br_{2(g, 700\,°C)} +$ $0.1CO_{2(g, 700°C)}$	$\Delta H_{(1)} =$ $\Delta H_{DS}[Pb_{5.00}(AsO_4)_{3.00}Br_{0.80}(CO_3)_{0.10}] +$ $0.2\Delta H_{hc}(O_2)$
(2)	$PbO_{(c, 25\,°C)} \rightarrow PbO_{(sln, 700\,°C)}$	$\Delta H_{(2)} = \Delta H_{DS}(PbO)^a$
(3)	$As_2O_{5(c, 25\,°C)} \rightarrow As_2O_{5(sln, 700\,°C)}$	$\Delta H_{(3)} = \Delta H_{DS}(As_2O_5)^b$
(4)	$Br_{2(l, 25\,°C)} \rightarrow Br_{2(g, 700\,°C)}$	$\Delta H_{(4)} = \Delta H_{hc}(Br_2)^c$
(5)	$CO_{2(g, 25\,°C)} \rightarrow CO_{2(g, 700\,°C)}$	$\Delta H_{(5)} = \Delta H_{hc}(CO_2)^c$
(6)	$O_{2(g, 25\,°C)} \rightarrow O_{2(g, 700\,°C)}$	$\Delta H_{(6)} = \Delta H_{hc}(O_2)^d$
(7)	$Pb_{(c, 25\,°C)} + 0.5O_{2(g, 25\,°C)} \rightarrow PbO_{(c, 25\,°C)}$	$\Delta H_{(7)} = \Delta H_{f, el}(PbO)^d$
(8)	$2As_{(c, 25\,°C)} + 2.5O_{2(g, 25\,°C)} \rightarrow As_2O_{5(c, 25\,°C)}$	$\Delta H_{(8)} = \Delta H_{f, el}(As_2O_5)^e$
(9)	$C_{(c, 25\,°C)} + O_{2(g, 25\,°C)} \rightarrow CO_{2(g, 25\,°C)}$	$\Delta H_{(9)} = \Delta H_{f, el}(CO_2)^d$
(10)	$5Pb_{(c, 25\,°C)} + 3As_{(c, 25\,°C)} + 0.4Br_{2(l, 25\,°C)} +$ $0.1C_{(c, 25\,°C)} + 6.15O_{2(g, 25\,°C)} \rightarrow$ $Pb_{5.00}(AsO_4)_{3.00}Br_{0.80}(CO_3)_{0.10\ (c, 25\,°C)}$	$\Delta H_{(10)} = \Delta H_{f,}$ $_{el}[Pb_{5.00}(AsO_4)_{3.00}Br_{0.80}(CO_3)_{0.10}] = -$ $\Delta H_{(1)} + 5\Delta H_{(2)} + 1.5\Delta H_{(3)} + 0.4\Delta H_{(4)} +$ $0.1\Delta H_{(5)} + 5\Delta H_{(7)} + 1.5\Delta H_{(8)} + 0.1\Delta H_{(9)}$

Note: c-crystal; g-gas state; sln-solution; l-liquid; [a] – Majzlan et al. (2002); [b] - Forray et al. (2014); [c] – calculated from JANAF; [d] - Robie and Hemingway (1995); [e] - Dinsdale (1991).

Supplemental Table S8. Overview of experimental-based literature data available for Pb and Ca phosphate-bearing apatite end-members as well as Pb and Ca arsenate-bearing, at T = 25°C and 1 atm.

Chemical formula	$\Delta H^\circ_{f, el}$ (kJ/mol)	Reference
$Pb_5(AsO_4)_3F$	-	-
$Pb_5(AsO_4)_3OH$	-	-
$Pb_5(AsO_4)_3Cl$	-2965.9	Bajda (2010)
$Pb_5(AsO_4)_3Br$	-	-
$Pb_5(AsO_4)_3I$	-	-
$Ca_5(AsO_4)_3F$	-5629.4	(calculated from Zhu et al. 2011)
$Ca_5(AsO_4)_3OH$	-5604.0	(Puzio et al. 2018)
$Ca_5(AsO_4)_3Cl$	-	-
$Ca_5(AsO_4)_3Br$	-	-
$Ca_5(AsO_4)_3I$	-	-
$Pb_5(PO_4)_3F$	-4264.5	(Jemal et al. 1995)
	-4233.0	(Ntahomvukiye et al. 1997)
	-4261.5	(calculated from Yan et al. 2020)
$Pb_5(PO_4)_3OH$	-4077.3	(calculated from Zhu et al. 2015)
	-4130.5	(Jemal et al. 1995)
$Pb_5(PO_4)_3Cl$	-4110.0	(Flora et al. 2004)

	-4102.0	(Jemal et al. 2004)
	-4108.4	(Topolska et al. 2016)
	-4124.0	(Bisengalieva et al. 2010)
$Pb_5(PO_4)_3Br$	-4090.0	(Flora et al. 2004)
$Pb_5(PO_4)_3I$	**-**	**-**
$Ca_5(PO_4)_3F$	-6779.0	(Flora et al. 2004)
	-6772.5	(Jemal et al. 1995)
	-6859.4	Kelley and King (1961)
	-6827.4	Gottschall (1958)
	-6775.0	(Ntahomvukiye et al. 1997)
	-6838.3	Farr and Elmore (1962)
	-6898.6	Jacques (1963)
	-6828.6	(Valyashko et al. 1968)
	-6774.0	Cherifa and Jemal (2004)
	-6767.9	(Cherifa et al. 1991)
	-6842.0	(Smirnova et al. 1962)
	-6872.2	Smith (1997)
	-6872.0	Robie and Hemingway (1995)
	-6826.7	Zhu and Sverjensky (1991)
$Ca_5(PO_4)_3OH$	-6652.5	(Jemal et al. 1995)
	-6699.5	(Cruz et al. 2005)
	-6722.7	(Smirnova et al. 1962)
	-6715.5	(Rollin-Martinet et al. 2013)
	-6710.8	(Valyashko et al. 1968)
	-6758.3	Jacques (1963)

	-6762.5	Gottschall (1958)
	-6657.0	(Flora et al. 2004)
	-6754.0	(Krivtsov et al. 1997)
	-6646.0	(Cherifa et al. 1991)
	-6721.6	Smith (1997)
	-6697.9	Zhu and Sverjensky (1991)
	-6738.5	Vieillard and Tardy (1984)
	-6855.0	(Puzio et al. 2018)
$Ca_5(PO_4)_3Cl$	-6590.0	(Flora et al. 2004)
	-6615.5	(Cruz et al. 2005)
	-6559.5	Cherifa and Jemal (2004)
	-6569.5	Khattech and Jemal (1997)
	-6548.1	Tacker and Stormer (1989)
	-6589.5	Cherifa and Jemal (2004)
	-6600.4	Zhu and Sverjensky (1991)
	-6639.0	Gottschall (1958)
	-6580.4	(Cherifa et al. 1991)
$Ca_5(PO_4)_3Br$	-6531.5	(Cruz et al. 2005)
$Ca_5(PO_4)_3I$	-6474.5	(Cruz et al. 2005)

Supplemental Table S9. Enthalpies of formation $\Delta H°_{f,\ el}$ for Pb – P and Ca – P of synthetic

apatite-like phases extracted from Supplemental Table S8 and calculated lattice energies U_{POT}

taken from Table 2 in Flora et al. 2004.

Chemical formula of apatite-like phase:	$\Delta H°_{f,\ el}$ of apatite (kJ/mol)	Error (kJ/mol)	Calculated U_{POT} (kJ) single cell	References
$Pb_5(PO_4)_3OH$	-4130.5	-	16639	Jemal et al. 1995
$Pb_5(PO_4)_3F$	-4233	31.5	16792	Ntahomvukiye et al. 1997
$Pb_5(PO_4)_3Cl$	-4124	20	16328	Bisengalieva et al. 2010
$Pb_5(PO_4)_3Br$	-4090	-	16152	calculated by Flora et al. (2004) from Nriagu (1974)
$Pb_5(PO_4)_3I$	*-4021*	*148*	15858	This work
$Ca_5(PO_4)_3OH$	-6697.9	-	16868	Zhu and Sverjensky 1991
$Ca_5(PO_4)_3F$	-6772.5	-	17030	Jemal et al. 1995
$Ca_5(PO_4)_3Cl$	-6600.4	53	16540	Zhu and Sverjensky 1991
$Ca_5(PO_4)_3Br$	-6531.5	40.5	16355	Cruz et al. 2005
$Ca_5(PO_4)_3I$	*-6423*	*76*	16046	This work

Note: $\Delta H°_{f,\ el}$ for $Pb_5(PO_4)_3I$ and $Ca_5(PO_4)_3I$ (italic) are extrapolated from trend lines presented

in Supplemental Figure S1.
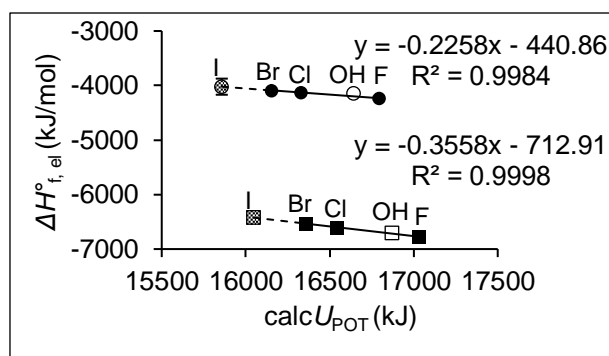
Supplemental Figure S2. Strong linear correlation of calculated (calc) U_{POT} and $\Delta H^{\circ}_{f,\,el}$ for $Pb_5(PO_4)_3X$ (circles) and $Ca_5(PO_4)_3X$ (squares) synthetic apatite-like phases (where X = I, Br, Cl, OH, I) from Supplemental Table S9 used for prediction of $\Delta H^{\circ}_{f,\,el}$ for $Pb_5(PO_4)_3I$ and $Ca_5(PO_4)_3I$. Empty markers ($\Delta H^{\circ}_{f,\,el}$ for OH-apatites) are not included to the trend lines.

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