Appendix

Supporting Information

Table S1. List of the solid phases taken into account in this work for the determination of the (g_i, h_i, s_i) values in *ThermAP* applicable to Jahnsites/Whiteites. Reference thermodynamic data were drawn from the online *Thermoddem* database (except for compounds marked by an asterisk *, see **Table S2**). The two first grey-shaded columns report the 23 phosphate phases out of which the initial *ThermAP* calculations were made (see main text).

Formula	Mineral name	Formula	Mineral name
$CaHPO_4{:}2H_2O$	Brushite	Na_3PO_4	
$Ca_5(PO_4)_3(OH)$	Hydroxyapatite	Na_2HPO_4	
$Ca_3(PO_4)_2$ beta	Whitlockite(low) - βTCP	NaH_2PO_4	
$Mg_3(PO_4)_2 : 8\ H_2O$	Bobbierite	$KH2PO_4$	
$Ca_4H(PO_4)_3 : 2.5H_2O$	Octacalcium phosphate	$Zn_3(PO_4)_2 : 4H_2O$	Hopeite alpha (RT form)
$Ca_4H(PO_4)_3 : 3H_2O$		$ZnAl_6(PO_4)_4(OH)_8 : 4H_2O$	Faustite
$Mg_3(PO_4)_2$	Farringtonite	$ZnFe_4(PO_4)_3(OH)_5$	Rockbridgite (Zn)
$Ca_4O(PO_4)_2$	Hilgenstockite	$CaZn_2(PO_4)_2 : 2H_2O$	Scholzite
$Mg_3(PO_4)_2 : 22H_2O$	Cattiite	$Zn_4(PO_4)_2(OH)_2 : 3H_2O$	Spencerite
$MgHPO_4$ *		$Zn_2(PO_4)OH$	Tarbuttite
$Ca_5(PO_4)_3F$	Fluorapatite	$Zn_3(PO_4)_2$	
$CaHPO_4$	Monetite	$ZnHPO_4$	
$MgHPO_4 : 3H_2O$	Newberyte	$Zn_5(PO_4)_3OH$	
$Fe^{II}_3(PO_4)_2 : 8\ H_2O$ *	Vivianite	$Zn_3(PO_4)_2 : H_2O$	
$Ca_3(PO_4)_2$ alpha	Whitlockite(high) - αTCP	$Zn_3(PO_4)_2 : 2H_2O$	
$AlPO_4$	Berlinite		
$CaAlH(PO_4)_2 : 6H_2O$ *			
$CaAl_3(PO_4)_2(OH)_5 : H_2O$	Crandallite		
$Fe^{III}PO_4 : 2H_2O$	Strengite		

$AlPO_4 : 2H_2O$	Variscite		
$Al_3(PO_4)_2(OH)_3 : 5H_2O$	Wavellite		
$Mn_3(PO_4)_2$			
$MnHPO_4$			

Table S2. Reference ΔGf° data at 298K and 1 bar considered for Vivianite, magnesium hydrogenphosphate and calcium aluminum phosphate from Vieillard and Tardy (1984), and corresponding $\Delta G°_{disso}$ and Log K values calculated by considering the $H_2PO_4^-$ speciation of phosphate ions.

Compounds	**$\Delta G_f°$ (kJ/mol)**	**calculated $\Delta G°_{disso}$ (kJ/mol)**	**calculated Log K ***
$Fe_3(PO_4)_2 : 8\ H_2O$ Vivianite	**-4377.2**	-65.814	11.5
$MgHPO_4$	**-1577.3**	-15.227	2.7
$CaAlH(PO_4)_2 : 6H_2O$	**-4722.2**	-15.390	2.7

* calculated by considering the $H_2PO_4^-$ speciation of phosphate ions.

Table S3. List of reactions for the determination of entropy values using Helgeson's method.

Formula	Mineral name	Reaction* for S° calculation using Helgeson's method	Calculated S° ($J.mol^{-1}.K^{-1}$) this work
$Mg_3(PO_4)_2 : 8\ H_2O$	Bobbierite	$Mg_3(PO_4)_2 + 8Mg(OH)_2 - 8MgO$	480
$Ca_4H(PO_4)_3 : 2.5H_2O$	Octacalcium phosphate	$Ca_3(PO_4)_2 + CaHPO_4 + 2.5Ca(OH)_2 - 2.5CaO$	463
$Ca_4H(PO_4)_3 : 3H_2O$		$Ca_3(PO_4)_2 + CaHPO_4 + 3Ca(OH)_2 - 3CaO$	486
$Ca_4O(PO_4)_2$	Hilgenstockite	$Ca_3(PO_4)_2 + CaO$	277
$Mg_3(PO_4)_2 : 22H_2O$		$Mg_3(PO_4)_2 + 22Mg(OH)_2 - 22\ MgO$	988
$MgHPO_4$		$1/2Mg(OH)_2 + 1/2Mg_3(PO_4)_2 - MgO$	99
$MgHPO_4 : 3H_2O$	Newberyte	$MgHPO_4 + 3Mg(OH)_2 - 3MgO$	208
$Fe^{II}_3(PO_4)_2 : 8\ H_2O$	Vivianite	$Ca_3(PO_4)_2 + 3FeO + 8Ca(OH)_2 - 11CaO$	659
$CaAlH(PO_4)_2 : 6H_2O$		$CaHPO_4 : 2H_2O + AlPO_4 : 2H_2O + 2Ca(OH)_2 - 2CaO$	415
$CaAl_3(PO_4)_2(OH)_5 : H_2O$	Crandallite	$2AlPO_4 + Al(OH)_3 + 2Ca(OH)_2 - CaO$	381
$MnHPO_4$		$1/2Mn(OH)_2 + 1/2Mn_3(PO_4)_2 - MnO$	140

*A negative sign indicates that the corresponding phase was located in the left member of the reaction, therefore its entropy has to be subtracted.

Table S4. Estimations of thermodynamic data (298 K, 1 bar) for some related minerals, based on the present *ThermAP* refinement.

Formula	Compound	$\Delta G_f°$ (kJ/mol) this work	$\Delta H_f°$ (kJ/mol) this work	$S°$ ($J.mol^{-1}.K^{-1}$) this work	Log K *
$CaMgFe^{III}(PO_4)_2OH : 4H_2O$	Segelerite	-4446	-4954	401	6.8
$Ca_{0.75}Mn_{0.75}Mn_{0.75}Fe^{III}_{1.50}(PO_4)_3$	« Alluaudite-(CaMnMnFe^{III}) »	-4220	-4554	351	-4.1
$Ca_{0.75}Mn_{0.75}Mg_{0.75}Fe^{III}_{1.50}(PO_4)_3$	« Alluaudite-(CaMnMgFe^{III}) »	-4366	-4710	321	-0.2

* calculated by considering the $H_2PO_4^-$ speciation of phosphate ions.

Table S5. Estimations of the temperature dependence of C_p for relevant Jahnsites and Alluaudites (see text on the determination of $f(H_2O)$ – T stability curves) from Helgeson's method (Helgeson, 1978) allowing one to estimate the C_p (or entropy) of a solid by considering solid phase reactions with parent phases with known properties, by assuming a negligible variation in C_p (or entropy) between the left and the right member of the reaction scheme. Necessary thermodynamic data were obtained from the database HSC Chemistry for Windows®.

Compound	Estimated C_p temperature coefficients : $C_p(T) = A + BT + C/T^2 + DT^2$			
	A	B	C	D
Jahnsite-(CaMnMn) [a]	821.117	0.3527	$-52.924 \cdot 10^5$	$-2.210 \cdot 10^{-6}$
Jahnsite-(CaMnMg) [b]	853.959	0.3467	$-103.430 \cdot 10^5$	$-2.264 \cdot 10^{-6}$
« Alluaudite-(CaMnMnFe^{III}) » [c] $Ca_{0.75}Mn_{0.75}Mn_{0.75}Fe^{III}_{1.50}(PO_4)_3$	304.106	0.2221	$-54.134 \cdot 10^5$	$-26.961 \cdot 10^{-6}$
« Alluaudite-(CaMnMgFe^{III}) » [d] $Ca_{0.75}Mn_{0.75}Mg_{0.75}Fe^{III}_{1.50}(PO_4)_3$	305.817	0.2665	$-67.557 \cdot 10^5$	$-82.662 \cdot 10^{-6}$

[a]considered reaction : $CaMnMn_2Fe_2(PO_4)_4(OH)_2 : 8H_2O + 2\ MnO + 2\ CaO \rightarrow 2\ FePO_4 : 2H_2O + 2\ Mn(OH)_2 + 3\ Mn(OH)_2 + Ca_3(PO_4)_2$.

[b]considered reaction : $CaMnMg_2Fe_2(PO_4)_4(OH)_2 : 8H_2O + 2\ MnO + 2\ CaO \rightarrow 2\ FePO_4 : 2H_2O + 2\ Mg(OH)_2 + 3\ Mn(OH)_2 + Ca_3(PO_4)_2$.

[c]considered reaction : $Ca_{0.75}Mn(Mn_{0.25}Fe_{0.75})_2(PO_4)_3 \rightarrow 3/2\ FePO_4 + 1/6\ Mn_3(PO_4)_2 + 1/3\ Mn_3(PO_4)_2 + 1/4\ Ca_3(PO_4)_2$. In this case, the $C_p(T)$ function for $FePO_4$ and $Mn_3(PO_4)_2$ not available in the literature was accessed similarly from the reactions :

$FePO_4 + 2\ Mn(OH)_2 \rightarrow Fe(PO_4) : 2H_2O\ +\ 2\ MnO$

$Mn_3(PO_4)_2 + 3\ CaO \rightarrow Ca_3(PO_4)_2\ +\ 3\ MnO$.

[d]considered reaction : $Ca_{0.75}Mn_{0.25}Mg0.75(Mn_{0.25}Fe_{0.75})_2(PO_4)_3 \rightarrow 3/2\ FePO_4 + 1/4\ Mn_3(PO_4)_2 + 1/4\ Mg_3(PO_4)_2 + 1/4\ Ca_3(PO_4)_2$.

Figure S1. Comparison of Log K values as calculated via *ThermAP* with reference data from Janhsite/Whiteite-related phosphate phases (Thermoddem database).

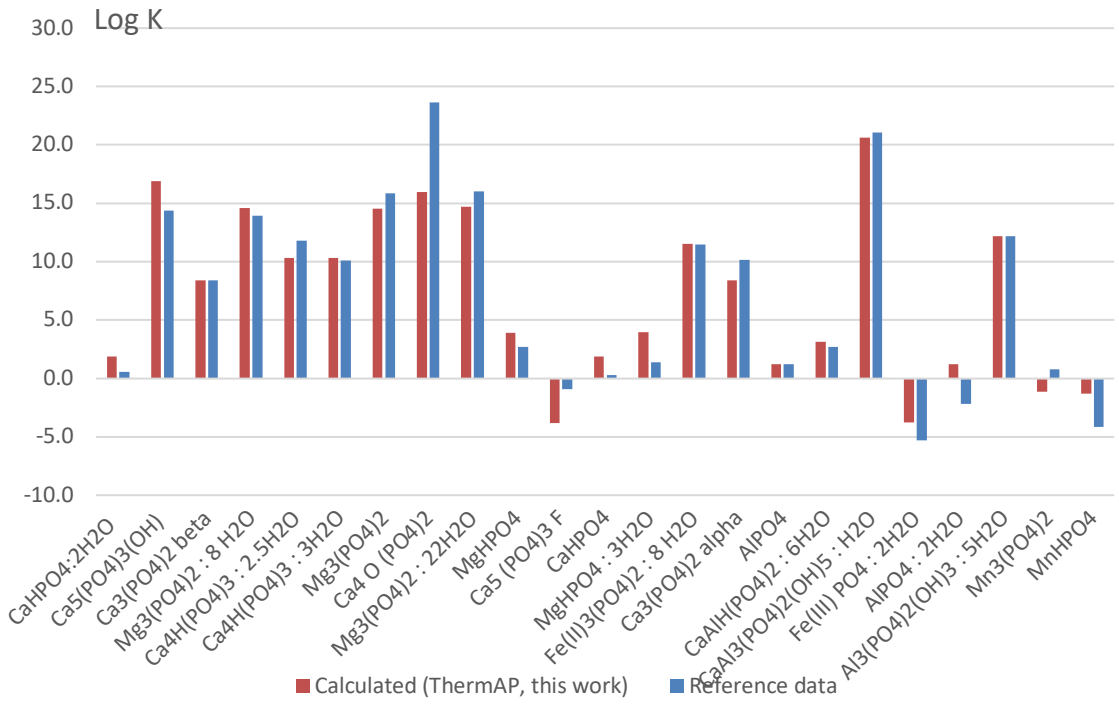


Figure S2. Pictures of the precipitate obtained (100°C, 24 hours) starting from stoichiometric ratios corresponding to the composition of Jahnsite-(CaMnMg). XRD analyses showed (see main text) that this precipitate was essentially composed of $FePO_4 : 2H_2O$ (Strengite/Phosphosiderite).

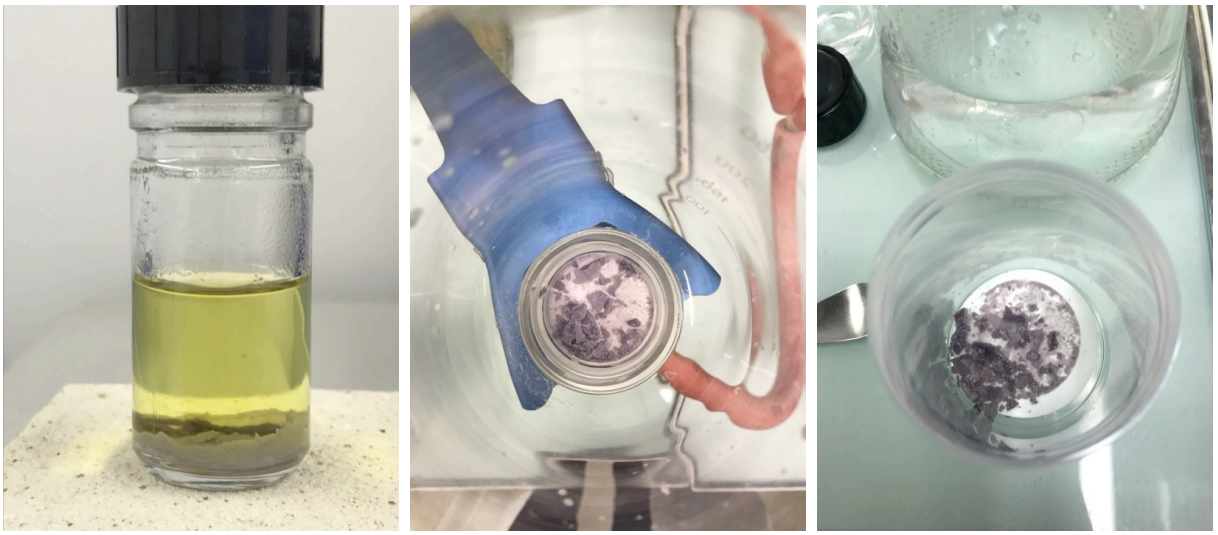
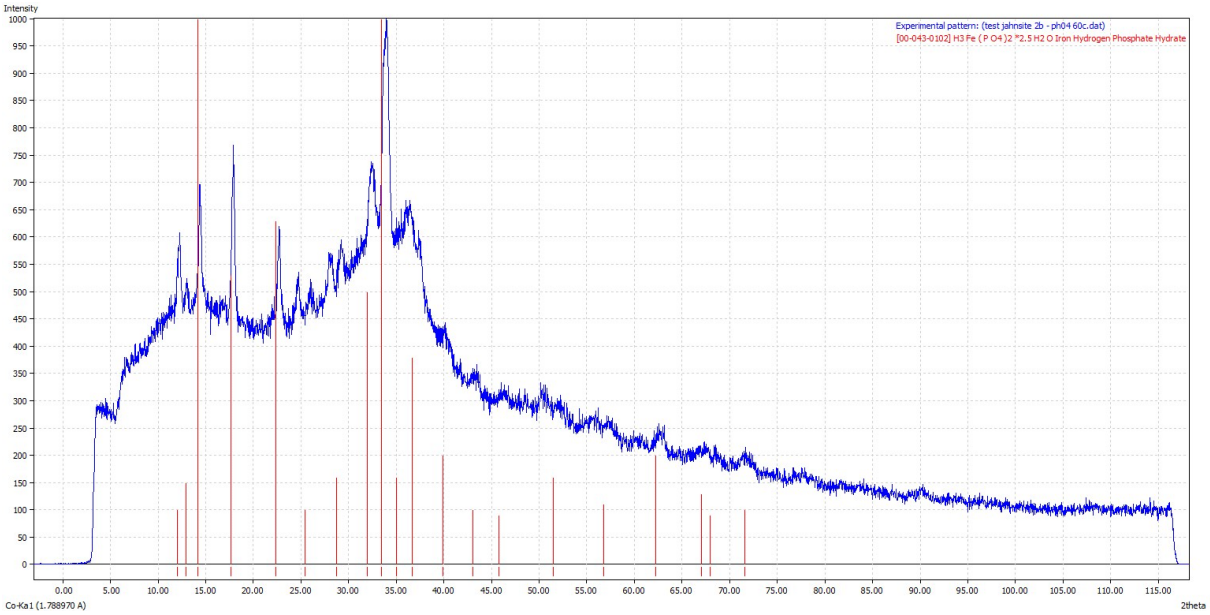


Figure S3. XRD patterns for the experimentally precipitated compounds starting from the initial stoichiometry of Jahnsite-(CaMnMg):

(**a**) Unchanged pH, T = 60 °C



(**b**) Addition of KOH, T = 100 °C