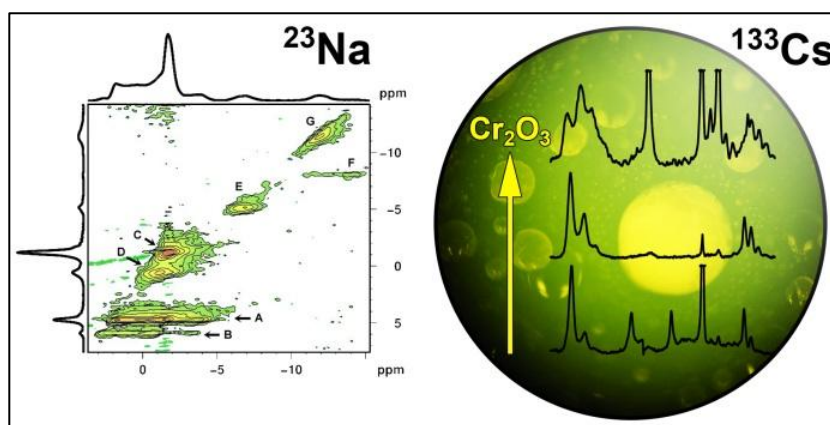# Supplementary Material for:

Characterisation of heterogeneous molybdate and chromate phase assemblages in model nuclear waste glasses by multinuclear magnetic resonance spectroscopy

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Predicting Yellow Phase Composition by EMPA

The mol% composition determined by EMPA can be normalised to SiO_2 to show how the quantity of components that are present in both glassy and crystalline phases (i.e., Na_2O, MoO_3, Cs_2O, Cr_2O_3) have changed (compared to the nominal composition) upon heating. Table S1 shows a comparison between the nominal and EMPA (SiO_2-normalised) values, and how their difference can be used to obtain an estimate of yellow phase composition that is comparable to that determined through the direct measurement.

Table S1. Calculation of YP4 Composition Based on its Parent Glass (Cr-4)

	B_2O_3	Na_2O	MoO_3	Cs_2O	Cr_2O_3	SiO_2	Sum
Cr-4 Nominal	17.26	15.50	2.56	3.71	0.52	60.44	100
Cr-4 EMPA (normSiO2)	17.92	14.21	0.60	2.31	0.32	60.44	95.8
Difference[a]	(-0.65)	1.29	1.96	1.40	0.20	0.00	4.2
		↓	↓	↓	↓		
YP4 calc[b]	-	26.63	40.30	28.86	4.20	-	100
YP4 calc (25% Cs vol)[c]	-	**32.92**	**49.82**	**12.06**	**5.19**	-	100
		± 0.72	± 4.98	± 0.31	± 0.97		
YP4 EMPA	-	**38.88**	**44.99**	**11.34**	**4.79**	-	100
		± 4.84	± 2.16	± 4.11	± 0.99		

a: "Difference" = "Cr-4 Nominal" – "Cr-4 EMPA (normSiO2)".

b: "YP4calc" = Values from the "Difference" composition normalised to 100%, excluding B_2O_3.

c: 25% Cs_2O volatilisation was applied to nominal value, and a new difference was taken and normalised.

Statistics of Chromium Substitution – Three-Cation Model

The expected intensity (as a percentage) for each Cs site in $Cs_3NaMo_2O_8$ is given according to the product of the combinations ("n choose r") of the corresponding probabilities of occurrence for Mo and Cr atoms. For a three-cation model, the distribution is given by the general formula:

$$p(3-yMo, yCr) \; = \; (^n_r C) \, (p(Mo))^{3-y} \, (p(Cr))^y, \text{ where } y = 0, 1, 2, \text{ or } 3 \text{ Cr atoms} \tag{1}$$

$$\text{and } _nC_r = n!/(r!(n\text{-}r)!), \;\; n = \text{number of atoms, r = positions taken by Cr} \tag{2}$$

In equation 1, the quantities p(Mo) and p(Cr) refer to the probabilities of encountering a molybdenum or chromium atom, respectively.. If the crystalline phase is defined by $Cs_3Na(Mo_{1-x}Cr_xO_4)_2$, Eq. (1) can be written as:

$$p(3-yMo, yCr) \; = \; (^n_r C) \, (1-x)^{3-y} \, (x)^y \tag{3}$$

It should be noted that this model assumes a completely random substitution, and that Cs sites (1) and (2) behave similarly and have equal second-sphere occupancy. The four-cation model follows similar notation, however using '**4-y**' and '**y**' as coefficients.
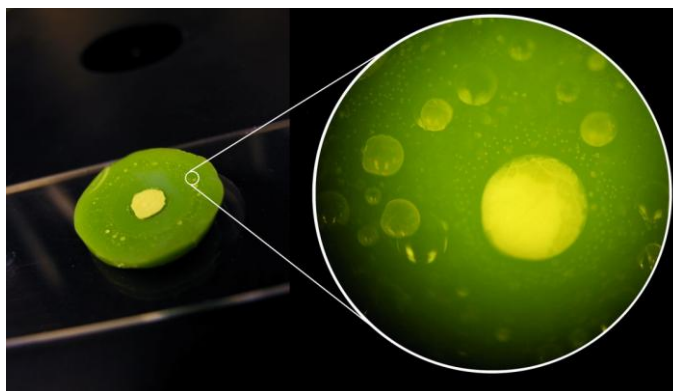
Other Supplementary Figures and Tables

Figure S1. Glass Cr-3 showing a large collection of yellow phase congregated in the center. The crystalline phase (YP3) was separated by hand. The glassy regions are green while the crystal phase is yellow in colour, suggesting the presence of Cr^{3+} in the glass and Cr^{6+} in the crystalline portions.
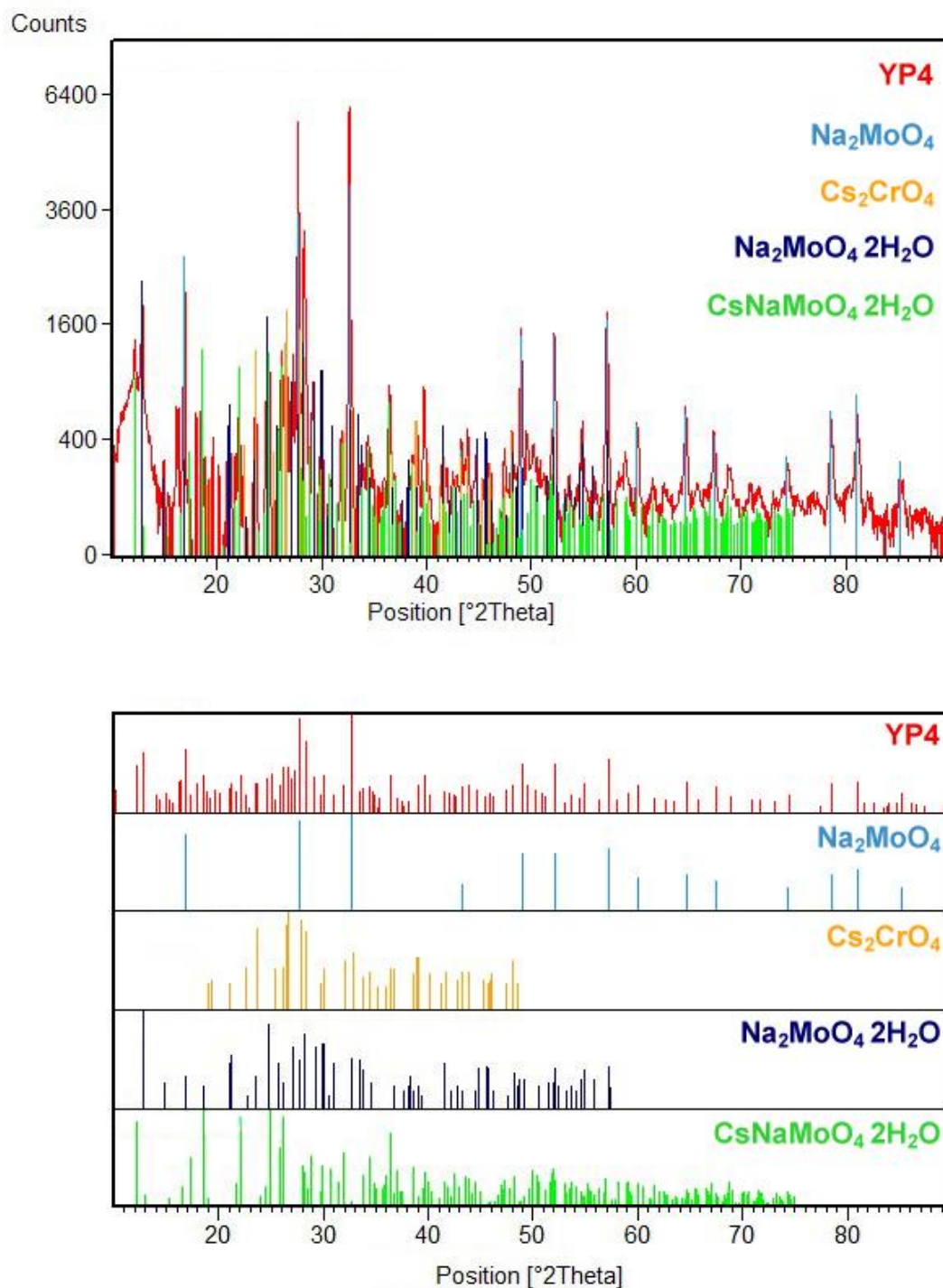
Figure S2. Powder x-ray diffraction pattern (upper) and peak pattern (lower) of the crystalline composite YP4, with database matches confirming the presence of Na_2MoO_4, Cs_2CrO_4, $Na_2MoO_4 \cdot 2H_2O$, and $CsNaMoO_4 \cdot 2H_2O$.
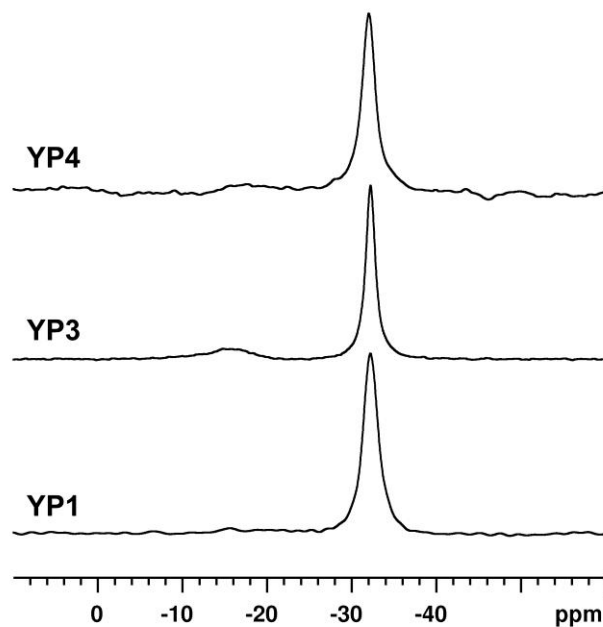
Figure S3. ^{95}Mo MAS NMR of crystalline yellow phase samples at 14.1 T. The spectral patterns of Na$_2$MoO$_4$ and CsNaMoO$_4$·2H$_2$O overlap at 33 ppm, while Cs$_3$NaMo$_2$O$_8$ appears at -15 ppm.
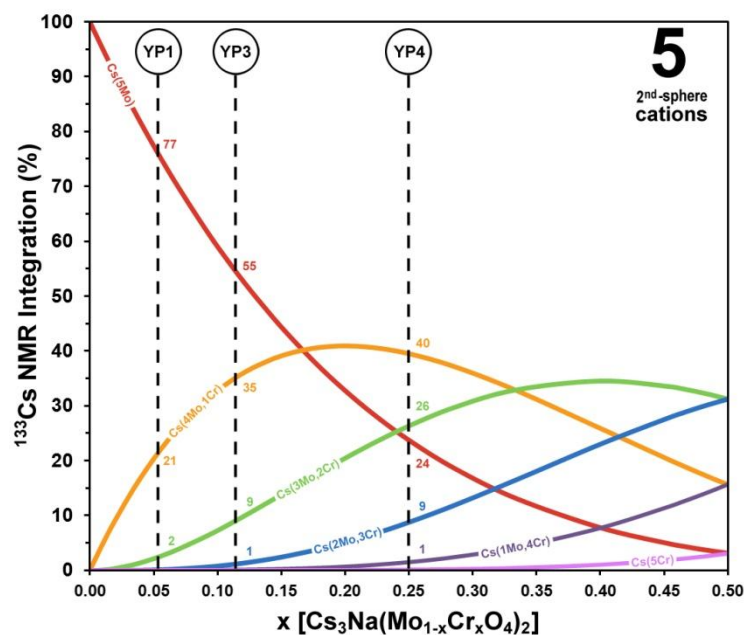

Figure S4. Theoretical ^{133}Cs NMR integration of the Cs$_3$NaMo$_2$O$_8$ site a function of chromium substitution assuming cesium surrounded by five cations. Each line represents a particular substitution, with the local cations indicated in brackets. In the notation introduced by the ^{133}Cs NMR spectra: 0 (red), 1 (orange), 2(green), 3 (blue), and the final peaks: 4 (purple) and 5 (pink) were not observed in our NMR. The dashed lines indicate the best theoretical match for the experimental ^{133}Cs NMR data of YP1, YP3, and YP4. Under this model, the phase compositions are: Cs$_3$Na(Mo$_{1.95}$Cr$_{0.05}$)O$_8$ (YP1), Cs$_3$Na(Mo$_{0.88}$Cr$_{0.12}$)O$_8$ (YP3), and Cs$_3$Na(Mo$_{0.75}$Cr$_{0.25}$)O$_8$ (YP4).

Table S2. ^{23}Na NMR Parameters and Integrations of YP1 and YP3

Site	Label in MQMAS	C_Q (MHz)	η	δ_{iso} (ppm)	YP1 Integration, 14.1 T (%)	YP3 Integration, 14.1 T (%)	Integration, 21.1 T (%)	ref
Na$_2$MoO$_4$	A	2.59	0	3.2	86	85	77	Skibsted 1994
Na$_2$MoO$_4$·2H$_2$O								
Na(1)	B	0.875	0.23	-1.4	-	-	-	Skibsted 1994
Na(2)	C	2.69	0.09	4.0	-	-	-	
CsNaMoO$_4$·2H$_2$O	D	1.33	1	-0.4	9	-	11	Kroeker 2010
Unknown 1	E	1.0	1	-6.0	-	5	4	this work
Unknown 2	F	2.6	0	-9.5	2	6	5	this work
Cs$_3$NaMo$_2$O$_8$	G	0.7	1	-11.8	3	4	3	Kroeker 2010