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Yttrium speciation in subduction-zone fluids from ab initio molecular dynamics simulations

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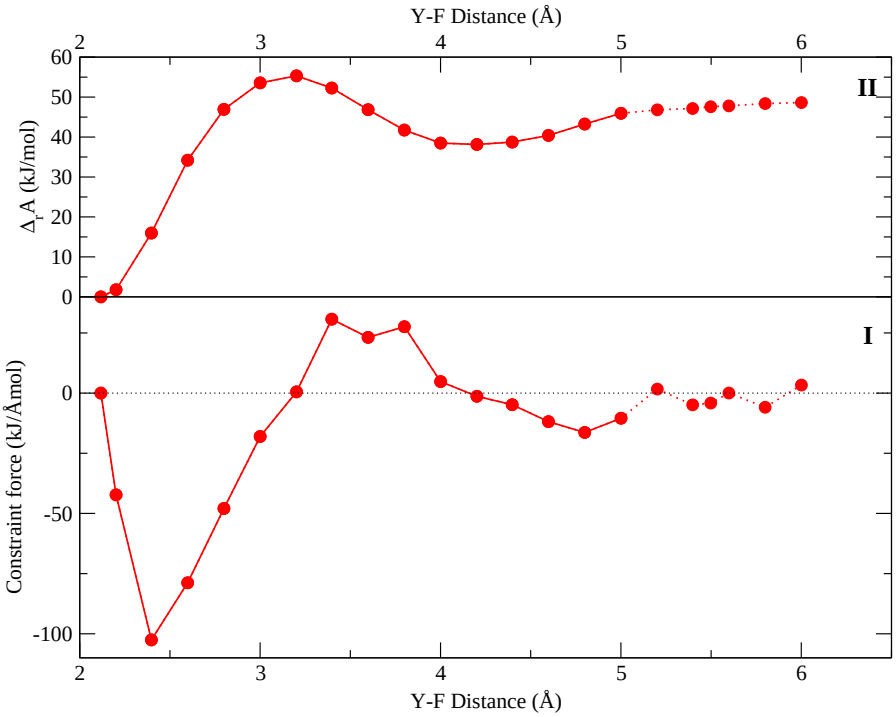

Figure S1: (I) potential of mean force of the dissociation reaction of YF^{2+} to Y^{3+} and F^- at 4.5 GPa and 800 °C for a integration length of 5.0 Å and 6.0 Å, (II) resulting Helmholtz free energy along the integration path.

Table S1: List of atomic distances and coordination numbers. The cutoff distance to compute the Na-Cl/YCl-Na coordination numbers was set to 3.8-4.0 Å and to 3.0-3.5 Å for Na-F/YF-Na.

		distances (Å)			coordination numbers			NaCl species distribution (in %)		
Run ID	Cell	Y-OH_2	Y-OH^-	Y-O (2^{nd})	YCl-Na†	YF-Na†	Na-Cl*	NaCl	$NaCl_2$	$NaCl_3$
#1	A1	2.35	2.13	4.7	0.1	0.0	0.6	89	8	2
#2	A1	2.37	2.11	4.8	0.5	0.0	0.7	78	22	0
#3	A1	2.37	-	5	0.4	0.0	0.6	79	20	1
#4	A1	2.35	-	5.1	0.8	0.0	0.9	66	25	10
#5	A1	2.41	-	5.2	1.2	0.0	0.8	55	39	6
#6	A2	2.42	2.10	4.5	0.0	0.0	0.7	91	9	0
#7	A3	2.39	-	4.4	0.0	0.1	0.6	84	16	0
#8	A4	2.43	-	4.5	0.0	0.1	0.3	98	2	0
#9	A2	2.39	2.13	4.4	0.2	0.3	0.6	76	24	0
#10	A2	2.39	2.12	4.5	0.3	0.7	0.7	74	24	2
#11	A3	2.4	-	4.5	0.0	0.7	0.6	74	26	0
#12	A1	2.37	2.08	4.6	0.0	0.0	1.0	62	34	4
#13	B1	2.37	2.13	4.5	0.1	0.0	1.2	69	20	10
#14	B1	2.35	2.14	4.5	0.3	0.0	0.5	82	17	1
#15	B1	2.36	2.13	4.4	0.4	0.0	0.9	79	17	4
#16	B2	2.34	2.19	4.5	0.0	0.1	0.4	100	0	0
#17	B2	2.38	2.17	4.6	0.0	0.4	0.3	91	9	0
#18	B2	2.39	2.16	4.3	0.0	0.8	0.4	94	6	0
#19	B2	2.37	2.19	4.5	0.3	0.1	0.5	69	31	0
#20	B2	2.39	2.15	4.4	0.1	0.5	0.2	100	0	0
#21	B2	2.35	2.14	4.5	0.1	0.5	0.3	93	7	0
#22	B1	2.32	2.16	4.4	0.0	0.0	0.9	81	17	2

† Total number of sodium ions that are associated with the halide of the yttrium complex over the simulation run.

* Mean coordination of sodium by chloride over the simulation run.

Table S2: Hydration number of halide ions for associated (Y)Cl and (Y)F complexes and dissociated halide ions (Cl^- and F^-). For the Y chloride complexes, only those are considered that persist for at least 10 ps in the AIMD simulations. Δ refers to the number of H_2O molecules that are released during association of the halide ion with Y.

run ID	initial	$\rho\,(\frac{kg}{m^3})$	time (ps)	cell	(Y)Cl-H_2O	Cl^--H_2O	Δ_{Cl}	(Y)F-H_2O	F^--H_2O	Δ_F
#1	$[YCl(H_2O)_5]^{2+}$	1072	25	A1	3	4	1	-	-	-
#2	$[YCl_2(H_2O)_4]^{+}$	1072	23	A1	2	4	2	-	-	-
#3	$[YCl_3(H_2O)_3]_{aq}$	1072	24	A1	2	4	2	-	-	-
#4	$[YCl_4(H_2O)_2]^{-}$	1072	26	A1	2	4	2	-	-	-
#5	$[YCl_5(H_2O)]^{2-}$	1072	26	A1	2	4	2	-	-	-
#6	$[YF(OH)(H_2O)_5]^{+}$	1072	25	A2	-	-	-	1	-	-
#7	$[YF_2(H_2O)_5]^{+}$,	1072	29	A3	-	-	-	1	-	-
#8	$[YF_3(H_2O)_4]_{aq}$	1072	29	A4	-	-	-	1	-	-
#9	$[YClF(H_2O)_5]^{+}$	1072	29	A2	2	4	2	1	-	-
#10	$[YCl_2F(H_2O)_4]_{aq}$	1072	29	A2	2	4	2	1	-	-
#11	$[YClF_2(H_2O)_4]_{aq}$	1072	27	A3	3	4	1	1	-	-
#12	$[Y(H_2O)_7]^{3+}$	1072	29	A1	-	-	-	-	-	-
#13	$[YCl(H_2O)_6]^{2+}$	1447	27	B1	3	5	2	-	-	-
#14	$[YCl_2(H_2O)_5]^{+}$	1447	27	B1	3	5	2	-	-	-
#15	$[YCl_3(H_2O)_4]_{aq}$	1447	27	B1	-	-	-	-	-	-
#16	$[YF(H_2O)_7]^{2+}$	1447	24	B2	-	-	-	2	4	2
#17	$[YF_2(H_2O)_5]^{+}$	1447	27	B2	-	-	-	2	4	2
#18	$[YF_3(H_2O)_4]_{aq}$	1447	25	B2	-	-	-	2	4	2
#19	$[YClF(H_2O)_5]^{+}$	1447	25	B2	3	5	2	2	4	2
#20	$[YCl_2F(H_2O)_5]_{aq}$	1447	25	B2	-	-	-	2	4	2
#21	$[YClF_2(H_2O)_5]_{aq}$	1447	27	B2	-	-	-	2	4	2
#22	$[Y(H_2O)_8]^{3+}$	1447	27	B1	-	-	-	-	-	-

Table S3: List of the simulation runs with their initial coordination complexes and complexes observed for at least 3 ps during the simulation. For runs where multiple complexes appear the observed complexes are listed in order of decreasing abundance.

ID	Cell	initial	formed
#1	A1	$[YCl(H_2O)_5]^{2+}$	$[YClOH(H_2O)_5]^{+}$, $[YCl(H_2O)_6]^{2+}$
#2	A1	$[YCl_2(H_2O)_4]^{+}$	$[YCl_2(H_2O)_5]^{+} \cdot Na^{+}$, $[YCl_2(H_2O)_5]^{+}$, $[YCl_2OH(H_2O)_4]_{aq}$
#3	A1	$[YCl_3(H_2O)_3]_{aq}$	$[YCl_3(H_2O)_4]_{aq}$, $[YCl_3(H_2O)_4]_{aq} \cdot Na^{+}$
#4	A1	$[YCl_4(H_2O)_2]^{-}$	$[YCl_4(H_2O)_2]^{-}$, $[YCl_4(H_2O)_2]^{-} \cdot Na^{+}$, $[YCl_3(H_2O)_3]_{aq} \cdot Na^{+}$, $[YCl_2(H_2O)_5]^{+} \cdot Na^{+}$
#5	A1	$[YCl_5(H_2O)]^{2-}$	$[YCl_5(H_2O)]^{2-} \cdot Na^{+}$, $[YCl_5(H_2O)]^{2-}$, $[YCl_4(H_2O)_2]^{-} \cdot Na^{+}$
#6	A2	$[YF(OH)(H_2O)_5]^{+}$	$[YFOH(H_2O)_5]^{+}$
#7	A3	$[YF_2(H_2O)_5]^{+}$,	$[YF_2(H_2O)_5]^{+}$
#8	A4	$[YF_3(H_2O)_4]_{aq}$	$[YF_3(H_2O)_4]_{aq}$
#9	A2	$[YClF(H_2O)_5]^{+}$	$[YClF(H_2O)_5]^{+}$, $[YClF(H_2O)_5]^{+} \cdot Na^{+}$
#10	A2	$[YCl_2F(H_2O)_4]_{aq}$	$[YCl_2F(H_2O)_4]_{aq} \cdot Na^{+}$, $[YClF(H_2O)_5]^{+}$, $[YClFOH(H_2O)_4]_{aq} \cdot Na^{+}$
#11	A3	$[YClF_2(H_2O)_4]_{aq}$	$[YF_2(H_2O)_5]^{+} \cdot Na^{+}$, $[YClF_2(H_2O)_4]_{aq}$, $[YClF_2(H_2O)_4]_{aq} \cdot Na^{+}$
#12	A1	$[Y(H_2O)_7]^{3+}$	$[YOH(H_2O)_6]^{2+}$, $[Y(H_2O)_7]^{3+}$
#13	B1	$[YCl(H_2O)_6]^{2+}$	$[YCl(H_2O)_7]^{2+}$, $[YOH(H_2O)_7]^{2+}$
#14	B1	$[YCl_2(H_2O)_5]^{+}$	$[YCl_2(H_2O)_6]^{+}$, $[YCl_2(H_2O)_6]^{+} \cdot Na^{+}$
#15	B1	$[YCl_3(H_2O)_4]_{aq}$	$[YCl(H_2O)_7]^{2+}$, $[YOH(H_2O)_7]^{2+}$
#16	B2	$[YF(H_2O)_7]^{2+}$	$[YF(H_2O)_7]^{2+}$,$[YFOH(H_2O)_6]^{+}$
#17	B2	$[YF_2(H_2O)_5]^{+}$	$[YF_2(H_2O)_6]^{+}$, $[YF_2OH(H_2O)_5]_{aq}$
#18	B2	$[YF_3(H_2O)_4]_{aq}$	$[YF_3(H_2O)_5]_{aq} \cdot Na^{+}$, $[YF_2(H_2O)_6]^{+} \cdot Na^{+}$, $[YF_2OH(H_2O)_5]_{aq} \cdot Na^{+}$
#19	B2	$[YClF(H_2O)_5]^{+}$	$[YF(H_2O)_7]^{2+}$, $[YClF(H_2O)_6]^{+} \cdot Na^{+}$,
#20	B2	$[YCl_2F(H_2O)_5]_{aq}$	$[YFCl(H_2O)_6]^{+}$, $[YFCl(H_2O)_6]^{+} \cdot Na^{+}$, $[YF(H_2O)_5]^{+} \cdot Na^{+}$, $[YFOH(H_2O)_6]^{+}$
#21	B2	$[YClF_2(H_2O)_5]_{aq}$	$[YF_2(H_2O)_6]^{+} \cdot Na^{+}$, $[YClF_2(H_2O)_5]_{aq}Na^{+}$, $[YF_2(H_2O)_5]^{+}$
#22	B1	$[Y(H_2O)_8]^{3+}$	$[YOH(H_2O)_7]^{2+}$, $[Y(H_2O)_8]^{3+}$