Immobilization and removal of hazardous elements by geomaterials: the harder and the softer solutions

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Water and soil pollution by heavy metals and other hazardous compounds is a global problem threatening the entire biosphere and affecting the life of many millions of people around the world. For instance, approximately two million tons of industrial, sewage and agriculture waste are discharged every day into water, causing serious health problems and the death of many thousands of people every day on a worldwide basis [1]. Design and assessment of technologies for immobilization and removal of hazardous elements (HEs) is one of the highest priorities for environmental protection both in the industrialized and the developing countries [2].

The incorporation of HEs into crystalline and glassy silicate ceramics (the "harder" geomaterials) provides a perfect example to show that modelling the preferential distribution and the efficiency of immobilization of HEs in the crystal lattice and vitreous phase requires a detailed crystallographic knowledge at both the long- (XRD) and the short- (XAS) range (see Fig. 1) [3].

celsian/ paracelsian (s.g. 2/c)	orthoclase (s.g. R/c, C2/m ^{Maxi} (X) ^{MADV} SbOs B ^{ph} in (Bau Kushau)/Feu Al-oSou(C		mullite (s.g. Pbam) (^{(V,VI} AL ^{MI} M)+a2 ^(V) SbaD10+ O th In AbaQodSbaDow [13]		Elem.	Valence state	Oxygen coordination	Metal-oxygen distance (Å)	Complexes or oxyanions	Notes
Bath In PBathMA/PSiLOs [1] (Ba-O) = 2.902 Å; Viscal = 40.55 Å? D.1 = 0.0547; EColN = 7.80	(8a-0) = 2.999 Å; V _{beth} = 41.91 Å ² D.1 = 0.0359; ECoN = 7.78 Pb ⁽²⁾ in PbA(₂ Si ₂ O ₂ [15]		(Cr-O) = 1.935 Å; Voce = 9.54 Å ³ O.Q.E. = 1.0087; O.A.V. = 28.55* ³ D.I. = 0.0170; ECoN = 5.53	the of	Sb	Sb ³⁺ predominant Sb ⁵⁺ minor	Sb ³⁺ [3] Sb ⁵⁺ [6]	Sb ³⁺ -O 1.938 Sb ⁵⁺ -O 1.964	[:Sb ³⁺ O ₃] likely in 4[:Sb ³⁺ O ₃] rings	Sb ⁵⁺ increasing with fO ₂ , CaO and glass basicity
	(7b-0) = 2.808 A; V _{PCR} = 38, 15 A ² D.1. = 0.0751; ECoN = 6.13				As	As ³⁺ predominant As ⁵⁺ minor	As ³⁺ [3] As ⁵⁺ [4]	As ³⁺ -O 1.78	[:As ³⁺ O ₃]	As ⁵⁺ increasing with fO ₂ and glass basicity
			12		Ba	Ba ²⁺	Ba ²⁺ [12]	Ba ²⁺ -O 2.75-3.5	[Al ³⁺ O ₄]-Ba ²⁺ -[Al ³⁺ O ₄]	charge compensator of Al3+ in tetrahedral coordination
melilite (s.g. P.42/m) I ^{mi} (X)p ^{Mi} (T) ^{Mi} SigOr Bi th in BaMgSigOr, 7] Bith-0 = 2730 K hum = 3028 Å	melilite (s.g. C2/c) vit(X)g ¹⁰ (17) ⁰⁴ SigOr Ba ²⁻ in Ba ₂ MgSiO ₂ (10) (Sa-O) - 2.1818 Å V _{baas} = 33.32 Å		Clinopyroxene (s.g. [Mil](M2) ^{(al} (M1) ^{(bl} ()) ₂ O ₆ O th In NaCS;O ₈ [2] (O-O) = 1.998 k V ₁₀₀ = 10.51 k ³		Cr	Cr ³⁺ predominant Cr ⁴⁺ minor Cr ⁶⁺ minor	Cr ³⁺ [6] Cr ⁴⁺ [4] Cr ⁶⁺ [4]	Cr ³⁺ –O 1.96 Cr ⁶⁺ –O 1.72	$Cr^{3+}-Cr^{3+}$ dimers dominant for $Cr_2O_3>0.25\%$ $[Cr^{6+}O_4]^{2-}$	Cr ⁶⁺ increasing with fO ₂ and glass basicity. Cr ⁴⁺ prevailing with glass modifiers >60%
0.1 = 0.0002; EC.M = 7.45 Ch ⁺ In BluCuB(c-); M Ch-O): 1500; K Ling = 1.86 År T GE = 15001; T AV, = 910; AP	D1 = 0.0330; ECoN = 7.49 Cu th in Ba ₂ CuBi ₂ O ₇ [11] (Cu-O) = 1.973 Å; V _{DDN} = 3.86 Å ¹ T.Q.E. = 1.0158; T.A.V. = 63.88 ¹⁰ D1 = 0.0074; ECoN = 3.99		0.Q.E. = 1.0080; O.A.V. = 28.71* D. = 8.0173; ECAN = 5.91 Ou ¹ ~ In CaCuCe ₂ O ₄ [5] (Ou-O) = 2.116 Å; Vocce = 11.98 Å? 0.Q.E. = 1.0447; O.A.V. = 96.9671 D. = 8.0794; ECAN = 4.47		Cu	Cu ⁺ predominant Cu ²⁺ minor	Cu+ [2] Cu+ [3] minor Cu+ [4] minor	Cu+-O 1.84 [2] Cu+-O 1.88 [3] Cu+-O 1.91 [4]		Cu ²⁺ increasing with fO ₂ and glass basicity. Coordination number grows with Cu ⁺ %
2H ² In Ca ₂ 2rdis,O ₁ [9] (2h-O) = 1520 A, Yala = 342, A ²	Zn ² in Ba ₂ 275i ₀ O ₇ [12] (2n-O) = 1.960 Å V _{MIN} = 3.78 Å ³ TOE = 1.040 TAV = 40.647		NP- in CaNSI;Or [4] (96-0) = 2.058 Å; Voux = 11.70 Å ¹ 0.02. = 1.0053; O.A.V. = 17.58 ¹² D.I. = 0.0500; E.O.M. = 5.97	00 0000	Pb	Pb ²⁺	Pb ²⁺ [3] Pb ²⁺ [4] minor	Pb2+-O [3] 2.24		PbO ₃ and PbO ₄ pyramidal units in lead silicate glasses
D.). = 0; ECuN = 4	D.1 = 0.0059; ECoN = 4.00	·	V ^{III} in NaVS ₂ O ₄ [S] (V-O) = 2.022 Å; V ₄₀₈ = 10.90 Å ³ (0.Q.E. = 1.0085; O.A.V. = 25.96 ⁴) (D.I. = 0.0254; ECoN = 5.81	$\begin{array}{l} Zr^{(2)} & \mbox{in Ca2nGEQ}_r[6] \\ (2n\!\!-\!\!0) = 2 102 \mbox{\widehat{A}} $	Mo	Mo ⁶⁺ predominant Mo ⁴⁺ minor	Mo ⁶⁺ [4] Mo ⁴⁺ [6]	Mo ⁶ *-O 1.75-1.78 Mo ⁴ *-O 2.01-2.02	[Mo ⁶⁺ O ₄] ²⁻ [Mo ⁴⁺ O ₆] ⁶⁻ molybdenyl Mo ⁴⁺ O ²⁺	Mo oxyanions are not connected with the glass tetrahedral network
T.(O.)Q.E. = Tetrahedral (Octahedral) Quadratic Elongation, and T.(O.)A.V. = Tetrahedral (Octahedral) Angle Variance (Robinson et al., 1971); D. L. = Distortion Index (Baur, 1974).	spinel (s.g. <i>Fd</i> -3 <i>m</i>) ^[v] (<i>A</i>) ^[v] (<i>B</i>) ₀ O ₄	Cu ⁽⁺ in CuMh ₂ O ₄ [19] (Cu-O) + 2,006 Å; V _{CuC4} = 4,14 Å ³ Mo ⁽⁺ in MoNa ₂ O ₄ [20]	V* in VMg:Ov [24] (V-O) = 1.979 Å: Vvice = 3.98 Å ³ V* in Mg:V. aMg: aOv [25]	Mar Mar	Ni	Ni ² *	Ni ²⁺ [4] Ni ²⁺ [5] minor	Ni ²⁺ O 1.95 [4] Ni ²⁺ O 2.00 [5]		Ni ²⁺ [4] stabilized by K Ni ²⁺ [5] by Na, Ca, Mg
ECoN = Effective Coordination Number (Hoppe, 1979). Note: T.Q.E. and T.A.V. for spinel structure are 1 and 0 ¹¹ , respectively, by sile summeric constraints.	Cd="in SIC6;Cb[16] (Cd=O) = 2.307 Å; V _{DDD} = 16.09 Å ⁰ O.Q.E. = 1.0120; O.A.V. = 39.38 ⁿ	$(Mo-O) = 1.772 \text{ Å} V_{MOR} = 2.85 \text{ Å}^3$ NP- in NFe ₂ O ₄ [21] $(36-O) = 1.848 \text{ Å} V_{MOR} = 3.23 \text{ Å}^3$	(V-O) = 2.018 Å V _{cm} = 10.84 Å ³ 0.Q.E. = 1.0072; O.A.V. = 27.18 ⁴¹ 2m ² in (2numOtic)(2numOtics)Ov (28)		Se	Se ⁶⁺	Se ⁶⁺ [3]	Se ⁶⁺ -O 1.69 Å		fully inserted in the glass network but in Zn glasses
	(Ci=C) = 1.994 Å; V _{DOE} = 10.44 Å ³ 0.Q.E. = 1.0067; O.A.V. = 32.88 ^{ng}	NP* in SINI ₇ O ₄ [22] (Ni-O) = 2.062 Å; V _{MOT} = 11.64 Å ³ O.Q.E. = 1.0023; O.A.V. = 7.92* ³	(2h-O) = 1.970 Å; V _{2hON} = 3.92 Å)		۷	V ⁵⁺ predominant V ⁴⁺ minor	V ⁵ + [4] V ⁴ + [5]	V ⁵⁺ -O 1.69-1.70 V ⁴⁺ -O 1.90	[V ⁵⁺ O ₄] ^{3.}	V3+ scarce
	(Ca-O) = 2.087 Å; V _{CDM} = 4.06 Å ³ (Ca-O) = 2.087 Å; V _{CDM} = 4.06 Å ³ Ca ^{-D} in Ca(Ca _D -MH ₁ -m)Ce [18] (Ca-O) = 1.936 Å; V _{CDM} = 9.31 Å ³ O, Q, E = 1.0278; O, AV, = 108.13 ⁴⁷	$ \begin{array}{l} NP^{\rm in} \mbox{ in } FeN_{\rm F}O_{\rm H}\left[228\right] \\ (16-O) = 2.008 \ \mbox{k} \ \ \mbox{$V_{\rm MOI}$} = 10.72 \ \mbox{k}^{\rm J} \\ O, Q, E. = 1.0042, O, A, V. = 16, 13^{\rm eq} \end{array} $	2n ⁻ⁱⁿ (2n ₁₀ G ₁₀)(2n ₁₀ G ₁₀)(2 ₁₀ G (2n-O) = 1.990 Å; V _{2n0} = 10.36 Å ² 0.Q.E. = 1.0004; O.A.V. = 35.37 ⁺¹		Zn	Zn ²⁺	Zn ²⁺ [4]	Zn ²⁺ -O 1.95-1.96		glass network former

Figure 1. On the left: main crystalline phases that can form during firing of silicate ceramics with structural parameters of sites that can accommodate HEs. On the right: HEs hosted in natural and synthetic aluminosilicate melts and glasses [3].

Concerning the application of "softer" geomaterials, crystallographic knowledge of the zeolite structures proved successful for removal of heavy metals and VOCs from contaminated water [4] and for the clean-up of water polluted with antibiotics [5]. Simultaneous toxic metal uptake and bacteria disinfection from aqueous solution was achieved using well characterized nanocomposites of both the softer (zeolite) and the harder (e.g. Fe_3O_4) geomaterials [6].

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