Incipient formation of zircon and hafnon during glass alteration at 90°C

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ABSTRACT

Layered zircon and hafnon are observed at the surface of gels resulting from the complete alteration of Zr- or Hf-bearing borosilicate glasses at 90°C and pH 1. The unusually low temperature of formation may arise from the similarity of the local structure around Zr in the gel (from the altered glasses), the leaching solution and the zircon structure, in particular, the majority 8-coordination of Zr and the connectivity of Zr-sites with their surroundings. Similar behavior is expected for Hf, which mimics Zr speciation in solution and hafnon structure. This work expands the known formation methods of zircon and hafnon at low temperature, underlining the importance of amorphous precursors to facilitate crystal growth under unusual conditions.

1. INTRODUCTION

Zirconium and hafnium possess similar electronic structures and ionic radii, which explains the similarity of most structural, physical and chemical properties of Zr–Hf compounds, such

as the orthosilicates, zircon (ZrSiO_4) and hafnon (HfSiO_4).¹ Due to the high thermal stability of these phases, a formation via a direct reaction between oxides by a solid-state reaction, a diffusion-controlled process, requires temperatures in the 1400-1500° C range.² Addition of impurities or sol-gel routes can reduce the synthesis temperature by 500° C or more.² Since the pioneering work of Frondel and Colette,³ zircon has been observed down to 120 °C under pseudo-hydrothermal conditions and 100 °C under refluxing conditions, often after an amorphous precursor.⁴⁻⁸ Overgrowth of porous zircon has been observed around reactive metamict zircon at temperatures evaluated at 100°C in geological formations.⁹ The formation of hafnon is more elusive. Indeed, although predicted by the phase diagram, HfSiO_4 is rarely observed. A sol-gel route results in only small amounts of hafnon and dopants are useful for the formation of hafnon at high temperature.^{2,10} This was interpreted as arising from the instability of aqueous Hf^{4+} complexes, even at low pH, leading to the hydrolysis and polymerization of the $[\text{Hf}(\text{OH}_2)_8]^{4+}$ complexes.¹¹

Zirconium is an important component of nuclear glasses,¹² the alteration of which leads to the formation of Zr-containing gels¹³ that partly govern their long-term behavior.¹⁴ In simplified borosilicate glasses, Zr also plays a key role in dissolution kinetics.¹⁵ The gel that develops at the interface between the glass and the alteration solution shows pH-dependent structural relationships between Zr-sites and the silica network.¹⁶ In particular, acidic conditions favor ^{89}Zr coordination in the gel. It has been shown earlier that Hf has a similar influence on the chemical durability of soda-lime borosilicate glasses.¹⁷ In this study, we show that crystallites develop at the surface of alteration gels obtained at pH 1, reporting the first observation of the incipient formation of zircon and hafnon at temperatures lower than 100°C.

2. MATERIALS AND METHODS

Glasses containing 8 mol % ZrO₂ or HfO₂, previously described,¹⁷ were crushed down to 2 µm and leached until complete alteration at 90 °C and pH 1 in a 0.1M HNO₃ solution. [SiO₂] was around 7.9 mmol.L⁻¹. The composition (Table 1) of the Zr-bearing gels was also already provided¹⁷. For the Hf-bearing gels, it was calculated by the same formalism, i.e. using the mass balance between the mass of the elements added in the form of pristine glass and the quantity of elements found in solution at the end of the alteration. The leaching solution was analyzed by ICP-MS (Thermo-fisher X 7 spectrometer). The composition of the pristine glasses and alteration gels is given on Table 1.

Glass	SiO ₂	B ₂ O ₃	Na ₂ O	CaO	ZrO ₂	HfO ₂	Gel	SiO ₂	CaO	ZrO ₂	HfO ₂
Z8C4	51.7	17.9	18.6	3.8	8.0	-	Z8C4	85,1	0,9	14,0	-
Z8C8	52.5	16.9	14.5	8.0	8.1	-	Z8C8	83,9	2,8	13,3	-
H8C4	53.5	16.1	18.1	3.9	-	8.4	H8C4	84,3	1,6	-	14,1
H8C8	52.8	16.1	14.5	8.3	-	8.3	H8C8	82,0	4,6	-	13,5

Table 1. Composition (mol %) of the starting glasses¹⁷ and the gels obtained after total alteration at 90°C and pH 1.

After leaching, the samples were washed at room temperature in deionized water and dried at 40 °C for 12 h and then at 90 °C for 1 day. Samples were analyzed on a ZEISS Supra 55 Scanning Electron Microscope (SEM) fitted with a Bruker Quantax Energy-Dispersive Spectrometer (EDS). Observations were performed at 5.0 kV with a beam current of 200 nA, and EDS spectra were acquired at 15 kV. X-Ray Diffraction (XRD) was performed with Cu Kα radiation on a Panalytical X'Pert equipped with an X'Celerator detector and operating at 40 kV and 40 mA. Cross - sectional TEM samples were prepared by a Focused Ion Beam dual beam FIB/SEM system (Zeiss CrossBeam Neon50 EsB) using standard *in situ* lift - out

technique. A protective platinum strip with 1 μm thickness was deposited before FIB milling. TEM analyses of 100 nm thick electron-transparent sections were performed using a JEOL 2100F TEM with a 200 kV field emission gun. Both Scanning TEM in High Angle Annular Dark Field (STEM-HAADF) and X-ray Energy Dispersive Spectroscopy (STEM-XEDS) imaging modes were used to characterize the altered surfaces.

3. RESULTS AND DISCUSSION

The alteration of Zr- or Hf-bearing glasses at pH 1 and 90°C results in the formation of gels, at the surface of which crystallites form. The Z8C4 and Z8C8 gels show the presence of disk-shaped crystallites (Figure 1a) of about 200 nm diameter and 80 nm thickness. These particles are homogeneously dispersed at the surface of the Z8C4 gel, where they coexist with rod-shaped particles shorter than 200nm. By contrast, they are unevenly distributed on the surface of the Z8C8 gel, forming agglomerates of lens-shaped particles of about 2 μm or constituting a continuous cover at the surface of some grains (Figure 1b).

Fig. 1. SEM (SE) observations of precipitates forming on the surface of Z8C4 (a), Z8C8 (b) and H8C8 (d) alteration gels after 450 days alteration at $T^\circ = 90^\circ\text{C}$, $\text{pH}_{90^\circ\text{C}} = 1$ and $\text{S/V} = 15 \text{ cm}^{-1}$. The backscattered electron image (ESB) of H8C4 (c) shows the morphology of Hf-rich precipitates.

Despite SEM observations on the Z8C8 gel, the concentration of crystallites or their crystallinity are too low to be detected by XRD. However, the Z8C4 gel gives rise to a faint diffraction peak at 26.89° (d-spacing of $3.316\text{\AA}$) (Figure 2). This peak corresponds to the (200) reflection of zircon ($3.303 \text{ \AA}$: ICDD no. 06-0266), and, being the only diffraction peak, it indicates a preferential crystal growth in the (a,b) plane of the zircon structure. This is in line with the lens-shaped morphology of the nanoparticles observed at the surface of the gel, as shown for zircons synthesized by a low temperature hydrothermal route.⁶⁻⁸ The slightly larger value of the a parameter, $6.632\text{\AA}$ instead of $6.604\text{\AA}$ in the reference zircon, may arise from the incorporation of OH groups in the structure, observed in hydrothermal zircons synthesized at low temperature.⁸ Using the Scherrer relation, the size of coherent domains in

the (*a*, *b*) plane is about 135 Å, close to the size of the lens-shaped crystallites. These observations confirm that the formation of zircon at low-temperature, below 250°C, favors the formation of layered crystallites.^{5,8,18}

Fig. 2. X-ray diffraction pattern of the Z8C4 alteration gel, showing the (200) diffraction peak of zircon that can be extracted using a scan speed of 0.1 °/min (inset).

TEM observation of the FIB thin foil corresponding to the surface of Z8C4 gel grains shows that the particles are located in a 150-200 nm porous outer layer, in which the Pt coating penetrated, hindering the identification of the precipitates by any electron diffraction (Fig. 2a and b). This porous gel covers a dense gel, which confirms that the alteration gel is double-layered.¹⁶ Both gel and particles consist of Zr, Si and O, but the particles are enriched in Zr (Figure 2c). This is consistent with the presence of 100 nm thick particles of zircon on the gel surface, as seen with SEM.

Fig. 3. Cross-sectional FIB plate of a Z8C4 gel grain. (a) STEM- HAADF image showing the external Pt coating overlying surficial precipitates (indicated by an arrow) and the porous gel. The dense gel is at the bottom. (b) STEM- HAADF image at higher magnification showing the precipitates (indicated by an arrow). (c) XEDS profile representing the evolution of Si, O, Zr and Pt concentration along the section represented on b, showing the precipitate enriched in Zr relative to gel.

The surface of the H8C8 and H8C4 gels shows disk-shaped particles of about 350 nm in diameter, i.e. about twice the size of the zircon precipitates at the surface of the Z8C8 and Z8C4 samples. The images recorded with back-scattered electrons (Fig. 1d) are consistent with a higher content of Hf in the particles than in the altered layer. The diffraction pattern (Figure S1) shows the (200) reflection of hafnon HfSiO_4 at 27.18° (d-spacing of $3.277\text{\AA}$, close to $d_{200} = 3.290\text{\AA}$ - ICDD no. 77-1759). Here too, the disk shape indicates a preferential growth orientation, which explains the absence of other diffraction peaks.

The zircon particles found at the surface of the alteration gels, 190 and 75 nm in diameter and thickness, respectively, present a narrow size distribution, as deduced from the analysis of SEM images (Fig. S2). They are smaller by about 50% than the disk-shaped, low temperature, hydrothermal nano-zircons described in the literature, with mean diameter of 300-350 nm and thickness of 60-130 nm, the actual value depending on the synthesis conditions.^{4,6} The smaller size of the nano-zircons here investigated can be related to their unusually low formation temperature.

Acidic conditions favor layered zircon morphology^{8,19} with a preferential radial growth along the crystallographically equivalent *a* and *b* directions, characterized by chains of edge-sharing ZrO₈ dodecahedra. Recently XANES and EXAFS data have shown that the Z8C4 and Z8C8 alteration gels formed at pH 1 consist of SiO₂-ZrO₂ gels with an outer layer showing Zr mostly present as ^[8]Zr.¹⁶ Zircon formation may be described by an interfacial dissolution/precipitation process, according to reaction (1):

After 2 months alteration, the solutions at pH 1 show a high concentration of dissolved SiO₂, 7.9 mmol.L⁻¹ and Zr, 200 μmol.L⁻¹, which will shift reaction (1) to the right. There is a striking similarity between the ^[8]Zr speciation in solutions at pH 1,²⁰ gel¹⁶ and zircon, with the presence of ^[8]Zr sites, short Zr-Si and Zr-Zr distances at 2.99 and 2.95 Å and at 3.62 and 3.7-3.8 Å in the zircon and the alteration gel, respectively.¹⁶ The gel may act as a structural precursor, providing the Si-O-^[8]Zr linkages needed for the crystal growth of zircon. The formation of nano-zircon may be the final result of the multistage alteration process of the initial borosilicate glass. It is speculated that Hf behaves similarly with the formation of nano-hafnon, the concentration of Hf in the alteration solution being the same as for Zr, i.e. 300 μmol.L⁻¹ after 6 months alteration (time needed for the total alteration of the initial glass). Indeed, despite the aqueous chemistry of Zr⁴⁺ and Hf⁴⁺ being characterized by extensive hydrolysis reactions and polymer formation, [Zr(OH₂)₈]⁴⁺ and [Hf(OH₂)₈]⁴⁺ complexes are stable in acidic solutions, where they hydrolyze spontaneously to form a stable cyclic tetramer [M₄(OH)₈(H₂O)₁₆]⁸⁺, with hydroxo bonds M-OH-M.^{20,21} The deprotonation of these bonds at the surface of the alteration gels allows reacting with monomeric Si(OH)₃O⁻ species to create plate-shaped crystallites with M-O-M (M=Zr or Hf) oxobridges along two perpendicular directions, starting a zircon or hafnon crystal structure (Figure 4). This shape explains the

peculiarity of the XRD pattern, the *c* crystallographic axis being perpendicular to the main face of the disk-shaped crystallites.

Fig. 4. (a) Local structure of Zr in the tetramer $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ and in zircon (b). Zr atoms, green; oxygen atoms in OH bridging groups, purple; oxygen atoms, red; Si atoms, blue; Hydrogen atoms omitted for clarity. The presence of $^{[8]}\text{Zr-O-Si}$ bonds in the alteration gel may facilitate the transformation of the Zr local structure from a tetramer structure to crystalline zircon. In both cases, $^{[8]}\text{Zr}$ polyhedra share edges in two perpendicular directions.

4. CONCLUSION

At pH 1, Zr^{4+} and Hf^{4+} occur as polymerized species.²² The formation of aquo/hydroxo complexes in solution at acidic pH gives these cations the possibility of forming secondary phases. This is consistent with geochemical calculations indicating a preferential precipitation of zircon vs. zirconia under these acidic pH conditions.¹⁶ Starting from a single phase gel of intimately mixed Si and Zr atoms has been recognized to be the most important process controlling the formation of hydrothermal zircon,⁵ which is the case of the alteration gels of simplified borosilicate nuclear glasses, which contain Zr-O-Si bonds with $^{[8]}\text{Zr}$ sites. Crystal

chemistry considerations confirm that the crystallization of zircon and hafnon at the expense of these gels results from the similarity of the local structure around Zr in zircon, the alteration gel and the Zr-tetramer in acidic solutions. At low temperature, the formation of edge-sharing ZrO_8 polyhedra generates a preferential growth along two perpendicular directions, already present in the Zr- tetramer complexes and which will form the *a*- and *b*- axes of the zircon/ structure. Due to the structural and chemical similarity between Zr and Hf, the same processes may explain the formation of hafnon at the surface of the gels resulting from the alteration of Hf-bearing borosilicate glasses.

The formation of uranium silicate complexes acting as a precursor of U silicate colloids have been recognized to be a dominant parameter for the stabilization of USiO_4 , coffinite,²³ a mineral isostructural to zircon and hafnon. The external surface layer of the alteration gels of Zr/Hf-bearing glasses may play the role of such precursors in the incipient formation of zircon and hafnon at low temperature.

REFERENCES

1. Cota A, Burton BP, Chaín P, Pavón E, Alba .MD Solution properties of the system $\text{ZrSiO}_4\text{--HfSiO}_4$: a computational and experimental study. J Phys Chem C. 2013;117:10013-10019.
2. Sales TNS, Bosch-Santos B, Saiki M, Burimova A, Pereira LF, Saxena RN, Carbonari AW. Low temperature synthesis of pure and Fe-doped HfSiO_4 : determination of Si and Fe fractions by neutron activation analysis. Rad Phys Chem. 2019;155:287–290.
3. Frondel C, Collette RL. Hydrothermal synthesis of zircon, thorite and huttonite. Am Mineral. 1957;42:759–765.

4. Vilmin G, Komarneni S, Roy R. Lowering crystallization temperature of zircon by nanoheterogeneous sol-gel processing. *J Mater Sci.* 1987;22:3556–60.
5. Kido H, Komarneni S. Hydrothermal processing of zircon. *Trans Mater Res Soc Jpn.* 1990;35:8–69.
6. Mosset A, Baules P, Lecante P, Trombe JC, Ahamdane H, Bensamka F. A new route to silicates, Part 4-Submicron zircon powders. *J Mater Chem.* 1996;6:1527–1532.
7. Veytizou C, Quinson JF, Jorand Y. Preparation of zircon bodies from amorphous precursor powder synthesized by sol-gel processing. *J Eur Ceram Soc.* 2002;22:2901–2909.
8. Lei B, Peng C, Wu J. Controllable synthesis of layered zircons by low-temperature hydrothermal method. *J Am Ceram Soc.* 2012;95:2791–2794.
9. Hay DC, Dempster TJ. Zircon alteration, formation and preservation in sandstones. *Sedimentology.* 2009;56:2175-2191.
10. Kanno Y. Effect of dopants on the formation of hafnon via a sol-gel route. *J Mater Sci Lett.* 1993;12:1807–1809.
11. McGilvery CM, De Gendt S, Payzant EA, MacKenzie M, Craven AJ, McComb DW. Investigation of crystallization processes from hafnium silicate powders prepared from an oxychloride sol-gel. *J Am Ceram Soc.* 2012;95: 3985–3991.
12. Galois L, Pèlerin E, Arrio MA, Ildefonse P, Calas G. Evidence for 6-coordinated zirconium in inactive nuclear waste glasses. *J Am Ceram Soc.* 1999;82:2219–2224.
13. Pèlerin E, Calas G, Ildefonse P, Jollivet P, Galois L. Structural evolution of glass surface during alteration: application to nuclear waste glasses. *J Non - Cryst. Solids.* 2010;356:2497-2508.

14. Poinssot C, Gin S. Long-term Behavior Science: the cornerstone approach for reliably assessing the long-term performance of nuclear waste. *J Nucl Mater.* 2012;420:182–192.
15. Cailleteau C, Angeli F, Devreux F, Gin S, Jestin J, Jollivet P, Spalla O. Insight into silicate - glass corrosion mechanisms. *Nat Mater.* 2008;7:978 - 983.
16. Jollivet P, Galois L, Calas G, Angeli F, Gin S, Ruffoni MP, Trcera N. Zirconium local environment in simplified nuclear glasses altered in basic, neutral or acidic conditions: Evidence of a double-layered gel. *J Non-Cryst Solids.* 2019;503–504: 268-278.
17. Bergeron B, Galois L, Jollivet P, Angeli F., Charpentier T, Calas G, Gin S. First investigations of the influence of IVB elements (Ti, Zr, and Hf) on the chemical durability of soda-lime borosilicate glasses. *J Non-Cryst Solids.* 2010; 356: 2315-2322.
18. Valero R, Durand B, Guth JL, Chopin T. Mechanism of hydrothermal synthesis of zircon in a fluoride medium. *J Sol-Gel Sci Technol.* 1998;13:119– 124.
19. Lei B, Qin W, Kang G, Peng C, Wu J. Desert Rose-shaped zircon synthesized by low-temperature hydrothermolysis. *J Am Ceram Soc.* 2015;98:1626–1633.
20. Messner CB, Hofer TS, Randolph BR, Rode BM. Structure and dynamics of the Zr^{4+} ion in water *Phys Chem Chem Phys.* 2011;13:224-229.
21. Rao N, Holerca MN, Klein ML, Pophristic V. Computational study of the Zr^{4+} tetranuclear polymer, $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$. *J Phys Chem A.* 2007;111:11395–11399.
22. Hagfeldt C, Kessler V, Persson I. Structure of the hydrated, hydrolysed and solvated zirconium (IV) and hafnium (IV) ions in water and aprotic oxygen donor solvents. A crystallographic, EXAFS spectroscopic and large angle X-ray Scattering study. *Dalton Trans.* 2004;14:2142–2151.

259 23. Mesbah A, Szenknect S, Clavier N, Lozano-Rodriguez J, Poinssot C, Den Auwer C,
260 Ewing RC, Dacheux N. Coffinite, USiO_4 , is abundant in nature: so why is it so
261 difficult to synthesize? *Inorg Chem.* 2015;54:6687–6696.

266 Supplementary Materials

268 Figure S1. X-ray powder diffraction indicates the presence of a diffraction peak
269 corresponding to an inter-reticular distance of 3.277 Å for the H8C4 and H8C8 gels formed at
270 pH 1.

276 Figure S2. Diameter and thickness of the particles formed at the surface of the Z8C4 gel
277 formed at pH 1.

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