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Reaction kinetics of the microwave enhanced digestion of zircon with ammonium acid fluoride

J.T. Nel [a,*], W. du Plessis [a], T.N. Nhlabathi [a], C.J. Pretorius [a], A.A. Jansen [a], P.L. Crouse [b]

[a] The South African Nuclear Energy Corporation Ltd. (Necsa), P.O. Box 582, Pretoria 0001, South Africa
[b] The Department of Chemical Engineering, University of Pretoria, Pretoria 0002, South Africa

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ABSTRACT

Zircon is notorious for its chemical inertness. Extreme processing conditions such as alkaline fusion (NaOH at 600 °C or Na_2CO_3 at 1200 °C) are used to extract the zirconium values from the mineral. In this study zircon was treated with ammonium acid fluoride ($NH_4F\cdot1.5HF$) by means of microwave assisted digestion. Reaction times ranged from 15 to 260 min at temperatures between 120 °C and 240 °C. Successive microwave digestion steps, interrupted by an aqueous wash procedure, resulted in a >99% conversion of zircon to the water soluble intermediates $(NH_4)_3ZrF_7$ and $(NH_4)_2SiF_6$. Arrhenius rate laws are derived for both reaction control (progressively shrinking particle) and diffusion control by the product layer. Both models show reasonably good agreement with the experimental data. The derived diffusion coefficient corresponds to a solid–liquid case.

1. Introduction

South Africa is the second largest producer of zircon ($ZrSiO_4$) in the world, Australia being the largest [1]. In 2009 South Africa supplied about 400,000 tonnes (29% of the global demand). Zircon concentrate is separated from ilmenite ($FeTiO_3$) and rutile (TiO_2) in beach sand dredgings [2,3]. The main heavy mineral sand industries in South Africa are located on the KwaZulu Natal coast at Richards Bay, and on the west coast at Namakwa Sands [4].

Zircon is mainly used as an opacifier in the ceramic tile industry and this accounts for more than 80% of all zircon mined. Zircon must be milled to an average particle size of <5 μm to be suitable for opacifier applications. The different opacifier grades of zircon depend mainly on the particle size and particle size distribution. Purity also plays a role and prime grade zircon is usually used in these applications [5,6]. Chemicals such as acid zirconium sulphate tetrahydrate (AZST), zirconium oxychloride (ZOC), zirconium acetate, zirconium basic sulphate (ZBS), and zirconium metal are usually manufactured from zircon [7]. In 2009 the global market for zirconium chemicals was about 10,000 tonnes and for zirconium metal between 5,000 and 10,000 tonnes [2,8]. Zirconium metal is almost exclusively used as a cladding material for nuclear fuel in nuclear reactors [8]. Hafnium, which is always present in zircon in concentrations of 1–3%, has to be removed from zirconium intended for nuclear applications [9].

Zircon is notorious for its chemical inertness [10]. In order to extract the zirconium values from the mineral, extreme processes like alkaline smelting with NaOH at 600 °C or with Na_2CO_3 at 1200 °C have to be applied. These reactions proceed according to Eqs. (1) and (2):

$$ZrSiO_4 + 4NaOH \xrightarrow{600\,^{\circ}C} Na_2ZrO_3 + Na_2SiO_3 + 2H_2O \tag{1}$$

$$ZrSiO_4 + 2Na_2CO_3 \xrightarrow{1200\,^{\circ}C} Na_2ZrO_3 + Na_2SiO_3 + 2CO_2 \tag{2}$$

Separation of the sodium zirconate from the sodium silicate is achieved by dissolution in water, filtration and precipitation.

Zirconium tetrachloride is produced by carbo-chlorination of zircon at >800 °C according to Eq. (3):

$$ZrSiO_4 + 4Cl_2 + 2C \xrightarrow{>800\,^{\circ}C} ZrCl_4 + SiCl_4 + 2CO_2 \tag{3}$$

The $ZrCl_4$ and $SiCl_4$ are separated by distillation. $ZrCl_4$ serves as a starting material for the manufacture of several zirconium chemicals as well as the metal.

Zircon can also be made chemically more tractable by dissociation in a plasma flame at >1700 °C. This product is called plasma dissociated zircon (PDZ, $ZrO_2\cdot SiO_2$). Compared to zircon, PDZ is chemically very reactive. The amorphous silica can be dissolved selectively with concentrated NaOH solutions, or reacted with anhydrous HF [11–15]. The processes are represented by Eqs. (4)–(6):

$$ZrSiO_4 \xrightarrow{>1700\,^{\circ}C} ZrO_2 \cdot SiO_2 \tag{4}$$

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[*] Corresponding author. Tel.: +27 12 305 3134; fax: +27 12 305 3197.
E-mail address: johann.nel@necsa.co.za (J.T. Nel).

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$$ZrO_2{\cdot}SiO_2 + 2NaOH(aq) \rightarrow ZrO_2 + Na_2SiO_3 + H_2O \quad (5)$$

$$ZrO_2{\cdot}SiO_2 + 4HF(g) \rightarrow ZrO_2(s) + SiF_4 + 2H_2O \quad (6)$$

PDZ can also be fully dissolved in 40% HF as follows [16]:

$$ZrO_2{\cdot}SiO_2 + 12HF(aq) \rightarrow H_2ZrF_6 + H_2SiF_6 + 4H_2O \quad (7)$$

The H_2ZrF_6 and H_2SiF_6 are separated by evaporative crystallization. The crystallization also serves as a purification step for the H_2ZrF_6. Pure ZrO_2 can be produced from H_2ZrF_6 by steam pyrolysis at 600–800 °C, according to Eq. (8).

$$H_2ZrF_6 + 2H_2O \xrightarrow{600-800\,^{\circ}C} ZrO_2 + 6HF \quad (8)$$

The present work investigates the reaction of zircon with ammonium acid fluoride (AAF) under microwave assisted digestion conditions. The reaction kinetics under these conditions is reported.

2. Results and discussion

It is assumed that the reaction between zircon and $NH_4F{\cdot}1.5HF$ proceeds according to Eq. (9):

$$3ZrSiO_4 + 16NH_4F\cdot 1.5HF \rightarrow 3(NH_4)_3ZrF_7 + 3(NH_4)_2SiF_6 + 12H_2O + NH_4F \quad (9)$$

The AAF and ammonium fluoride, as well as the two ammonium fluorometallates, $(NH_4)_3ZrF_7$ and $(NH_4)_2SiF_6$, are totally soluble in water [17,18]. The fractional conversion, α, is thus readily obtained by washing, filtering, and drying the zircon residue after time t. The fractional residue α is defined as

$$\alpha = \frac{m_{\text{residue}}}{m_0} \quad (10)$$

with m_{residue} and m_0 the mass of the residue and starting mass respectively.

After completion of each run, and after the vessel had been cooled to room temperature, uncapped, the reaction was terminated by the addition of a boric acid (H_3BO_3) solution to neutralise the remaining free and bound HF. The reaction proceeds according to Eqs. (11) and (12) below, with the formation of water-soluble HBF_4 and NH_4BF_4:

$$4HF + H_3BO_3 \rightarrow HBF_4 + 3H_2O \quad (11)$$

$$2NH_4F\cdot 1.5HF + H_3BO_3 \rightarrow NH_4F + NH_4BF_4 + 3H_2O \quad (12)$$

The fact that digestion takes place during heating to temperature and during cooling complicates the extraction of kinetic data. Temperature ramp-up time (t_h) and ramp-down time (t_c) were 10 and 15 min respectively. The following simplifying assumptions were made in processing the experimental data. A linear contribution to the total reaction time was assumed for these periods and added to the isothermal reaction times, t_r, at the preset temperature (T). The total reaction time was then calculated using the time-temperature integral (surface under the heating curve), *viz.*

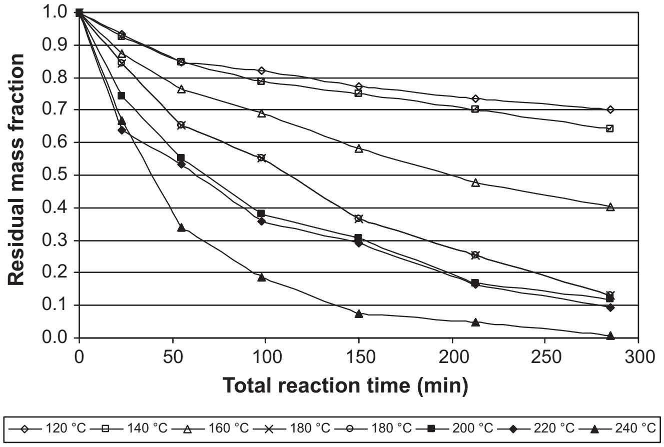

Fig. 1. The effect of temperature and repeated addition of NH_4F 1.5HF on the conversion of zircon.

$$Tt_{\text{total}} = Tt_r + \frac{Tt_h}{2} + \frac{Tt_c}{2} \quad (13)$$

Division by T simplifies Eq. (13) to:

$$t_{\text{total}} = t_r + \frac{t_h}{2} + \frac{t_c}{2} \quad (14)$$

The raw (nominal) and corrected time data are displayed in Table 1. The experimental fractional residues as function of time and temperature are given numerically and graphically in Table 2 and Fig. 1 respectively. An increase in temperature clearly increases the rate of conversion of zircon. After 285 min about 30% (α = 0.70) of the zircon was converted at 120 °C, while >99% (α = 0.007) conversion was achieved at 240 °C, the highest temperature investigated.

Raman spectroscopy and XRD (Figs. 2 and 3) confirm that zircon remained the major phase present in the residue after washing. A close examination of the XRD pattern shows some mismatch between the zircon reference and experimental spectra, as well as unindexed reflections at 16, 24, 25, and 29° 2θ.

A number of kinetic models are possible for fluid-solid reactions [19]. For this work the two most likely models were considered to be (1) a progressively shrinking particle and (2) reaction rate control by diffusion through the product layer. For simplicity the particles are assumed to be spherical.

The expression for the progressive conversion model is

$$\alpha^{1/3} = 1 - \frac{t}{\tau} \quad (15)$$

with

$$\tau = \frac{\rho_s r_0}{bM_s kc} \quad (16)$$

Table 1
Nominal and corrected reaction times.

Isothermal reaction time (t_r) (min)	Ramp-up time (t_h) (min)	Ramp-down time (t_c) (min)	Ramp time contribution factor	Adjusted reaction time (min)	Cumulative reaction time (min)
10	10	15	0.56	22.5	22.5
20	10	15	0.38	32.5	55.0
30	10	15	0.29	42.5	97.5
40	10	15	0.24	52.5	150.0
50	10	15	0.20	62.5	212.5
60	10	15	0.17	72.5	285.0

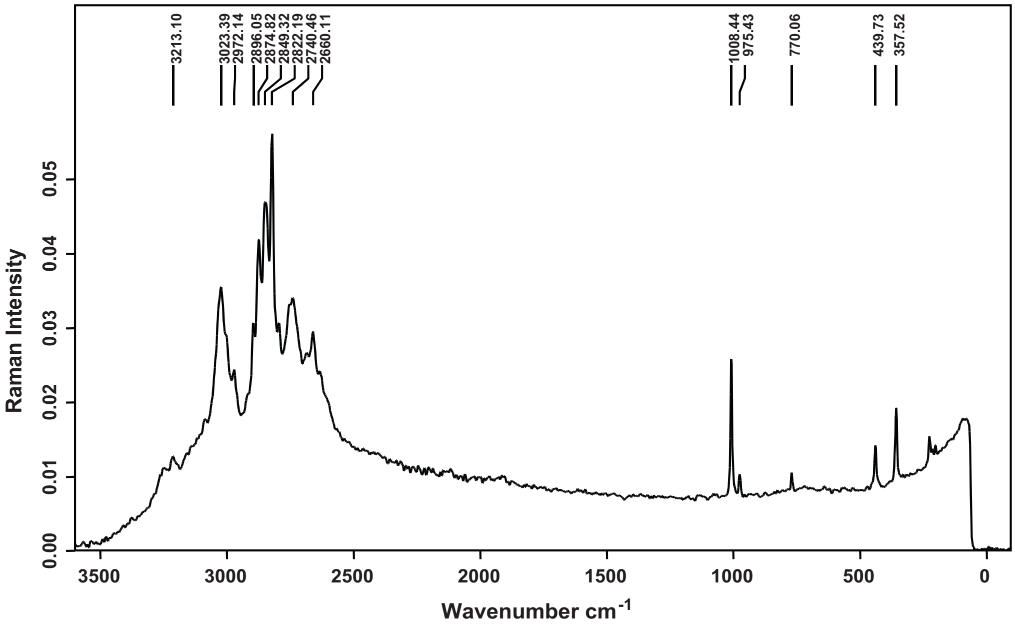

Fig. 2. A Raman spectrum of zircon after leaching in $NH_4F{\cdot}1.5HF$ for 285 min.

Here τ is the full time for complete conversion, M_s and ρ_s are the molecular weight (183.3 g mol^{-1}) and density (4.65 g cm^{-3}) of the solid zircon respectively, r_0 is the initial radius of the zircon particles (63 μm), t is the reaction time, b and c are the stoichiometric coefficient and the concentration of the active species (taken to be HF) in the melt, and k is the rate constant in m s^{-1}.

For the diffusion controlled model the rate expression is

$$3\alpha^{2/3} - 2\alpha = 1 - \frac{t}{\tau} \qquad (17)$$

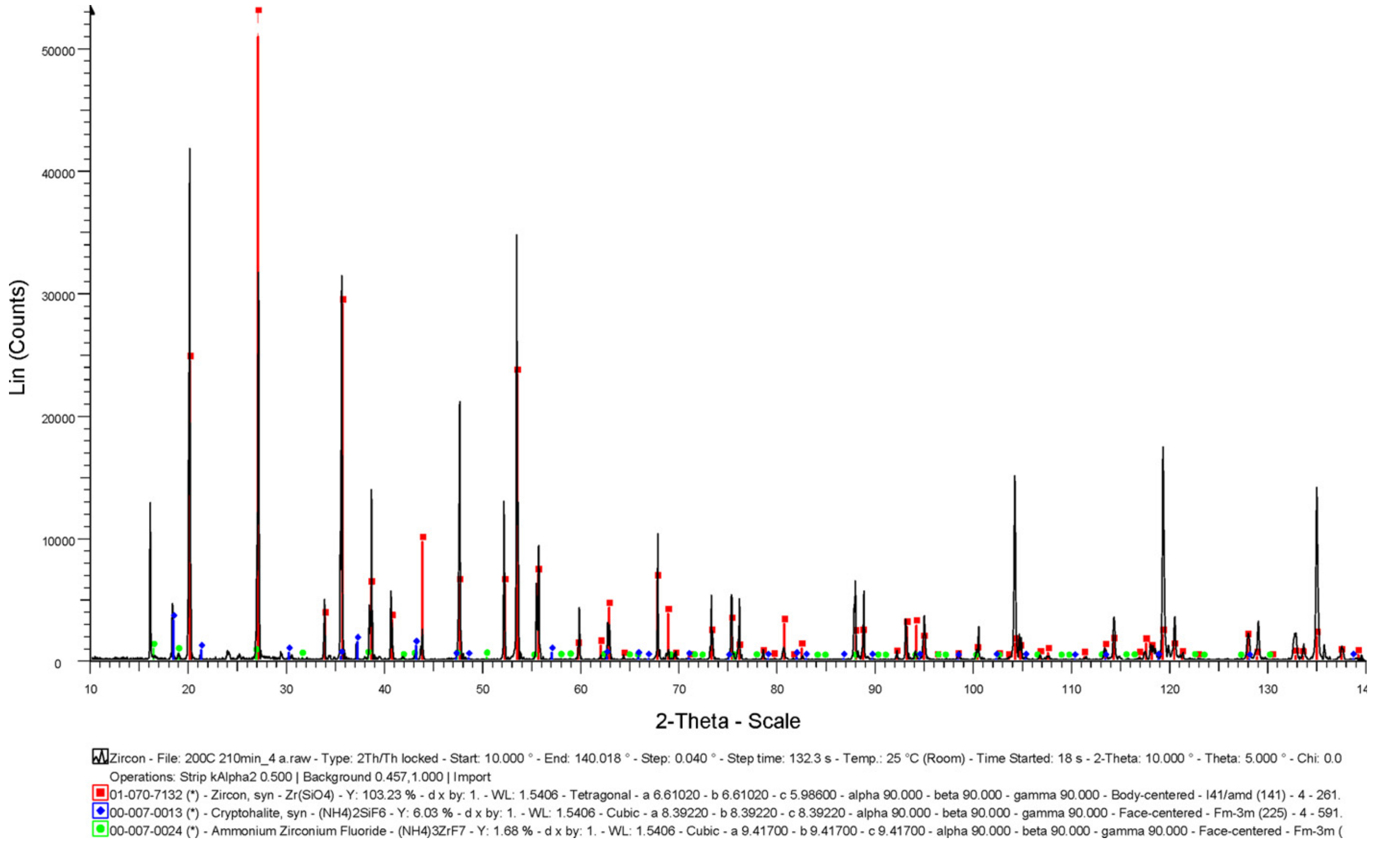

Fig. 3. X-ray diffraction pattern of zircon leached in $NH_4F{\cdot}1.5HF$ and re-digested for 285 min at 200 °C overlaid with the proposed stick pattern from the ICDD database.

Table 2
The effect of temperature and repeated addition of $NH_4F{\cdot}1.5HF$ on the conversion of zircon.

Sample	Cumulative digestion time (min)	120 °C	140 °C	160 °C	180 °C	200 °C	220 °C	240 °C
		α	α	α	α	α	α	α
	0	1	1	1	1	1	1	1
Original	22.5	0.933	0.927	0.873	0.843	0.743	0.637	0.667
Residue 1	55.0	0.847	0.847	0.767	0.653	0.553	0.533	0.340
Residue 2	97.5	0.820	0.787	0.690	0.553	0.380	0.360	0.187
Residue 3	150.0	0.773	0.750	0.583	0.367	0.307	0.290	0.073
Residue 4	212.5	0.733	0.703	0.477	0.253	0.167	0.163	0.047
Residue 5	285.0	0.700	0.640	0.403	0.130	0.120	0.093	0.007

with

$$\tau = \frac{\rho r_0^2}{6bD_e c} \tag{18}$$

Here D_e is the effective diffusion coefficient of the active species in the fluid through the product layer. In order to obtain the appropriate descriptive constant for either model, k or D_e, the left hand side of either Eq. (16) or (18) is generally plotted against time, τ is obtained from the slope, and the relevant constant is calculated from τ. To decide between the two models, the linear curve fits of the data plots are then compared. The better fit suggests the more correct model.

For this case, because of the experimental procedure followed, this method is not strictly correct. The particles were washed with water after each successive digestion step, effectively destroying the processing history of the material. The use of the cumulative processing time is thus not valid and r_0 in Eqs. (17) and (19) should be replaced by the initial particle radius for each step, obtained after washing the product of the previous step. For the progressive conversion model, this can be expressed explicitly as

$$\alpha_{i+1}^{1/3} - \alpha_i^{1/3} = \frac{bM_s kc}{\rho_s r_{0,i}}[t_{i+1} - t_i] \tag{19}$$

For the diffusion controlled model the expression is

$$3\alpha_{i+1}^{2/3} - 2\alpha_{i+1} - \alpha_i^{2/3} + 2\alpha_i = \frac{bM_s D_e c}{\rho_s r_{0,i}^2}[t_{i+1} - t_i] \tag{20}$$

For both Eqs. (19) and (20) per definition $\alpha_i = 1$, t_{i+1} = zero, and $r_{0,i}$ is the initial particle radius for each digestion step. Each digestion step at a given temperature thus yields either a k or a D_e value. For each temperature series an average value is calculated, and the average values for the different temperature ranges are used in Arrhenius plots to obtain the usual constants for deriving temperature-dependent values, as illustrated in Figs. 4 and 5.

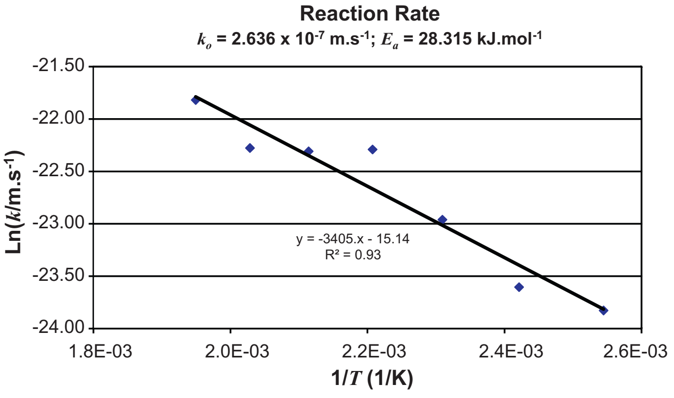

Fig. 4. Arrhenius plot for a progressive conversion model.

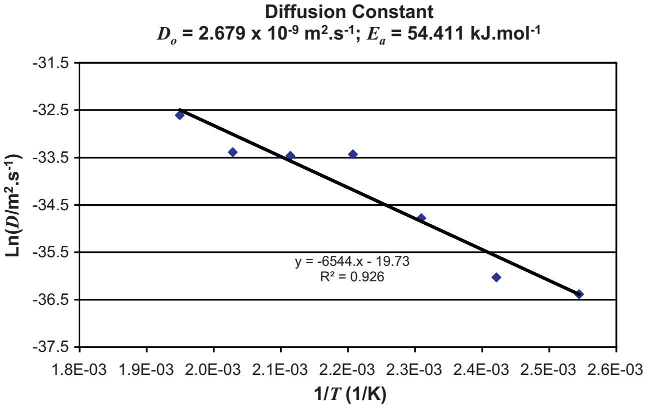

Fig. 5. Arrhenius plot for a diffusion control model.

Both plots (Figs. 4 and 5) display reasonable linearity, with very similar R^2 values. A pre-exponential factor $k_0 = 2.636 \times 10^{-7}$ m s^{-1} and activation energy E_a = 28.315 kJ mol^{-1} are obtained from Fig. 4 for the reaction constant for a progressively shrinking particle. If we assume that the effective diffusion coefficient can also be expressed as an exponential function of temperature, *i.e.* $D_e = D_0 e^{-(E_a/RT)}$, the corresponding values $D_0 = 2.679 \times 10^{-9}$ m^2 s^{-1} and E_a = 54.411 kJ mol^{-1} are obtained from Fig. 5. The magnitude of the effective diffusion constant for this case lies between 10^{-15} and 10^{-17} m^2 s^{-1}, depending on temperature. This is several orders of magnitude lower than for molecular diffusion through liquids, and typical for molecular diffusion through solids [20,21] as reproduced in Table 3. This, coupled to the fact that the process has to be interupted by washing steps to go to completion, suggests that diffusion control is the more realistic model. A reasonable interpretation is thus that an adhesive layer of ammonium fluorosilicate-zirconate forms around each particle, thereby inhibiting access by the diffusing HF/HF_2^-, and controlling the process kinetics.

Table 3
Typical diffusivity values for various compounds (after [20,21]).

System	T (°C)	D (m^2 s^{-1})
Gas phase		
CO_2 in N_2	25	1.65×10^{-5}
Ar in O_2	20	2.00×10^{-5}
Air in H_2	0	6.11×10^{-5}
Liquid phase		
Ethanol (50 mass %) in water	25	9.00×10^{-1}
Water (50 mass %) in n-butanol	25	2.67×10^{-1}
Acetone in water	25	1.28×10^{-9}
Solid state		
He in Pyrex®	20	4.5×10^{-15}
	500	2.0×10^{-12}
Hg in Pb	20	2.5×10^{-19}

3. Conclusions

Zircon can be converted practically quantitatively to water soluble products by microwave assisted digestion with $NH_4F{\cdot}1.5HF$ coupled with repeated removal of the product layer and addition of fresh reagent. This was achieved in 4 h at a temperature of 240 °C. The kinetics is mathematically equally well explained by both a progressively shrinking particle model and a product layer diffusion control model. The order of magnitude value of the diffusion constant calculated from this work corresponds to that for diffusion in solids. Because of this, and the fact that the process requires intermittent wash steps, the diffusion model is preferred and regarded as being physically more realistic.

4. Experimental

Prime grade zircon (d_{50} particle size 125 μm) obtained from Namakwa Sands was used for all work reported here. The hafnium content was 1.5%. Ammonium acid fluoride (AAF, $NH_4F{\cdot}1.5HF$) was obtained from Pelchem (Pty) Ltd. HF (40%) and H_3BO_3 were Merck analytical grade. All chemicals had a purity of >99%.

A CEM Mars 5 programmable microwave unit was used for digestion experiments. The system is capable of delivering a maximum power of 1600 W at a frequency of 2450 MHz. The sample carousel allows for up to 12 digestion vessels to be mounted simultaneously, one of which is a control vessel for monitoring of pressure and temperature. These data are used for feedback control of the reaction conditions. The carousel rotates through 360° during processing. CEM XP-1500 PFA lined digestion vessels (100 ml) and caps were used in these experiments. The maximum recommended working pressure and temperature of the vessels are 5.5 MPa and 240 °C respectively.

A starting mass of 0.5 g of zircon was used for each set of experiments. This was mixed with 5 g of $NH_4F{\cdot}1.5HF$ in the microwave vessel. Assuming that the reaction proceeds according to Eq. (9), this represents a roughly 5:1 excess based on AAF. The vessel was capped and placed in the microwave system for the desired time at a selected temperature setting. After completion, the vessel was cooled to room temperature, uncapped, and the reaction stopped by addition of 50 ml of a 3% boric acid (H_3BO_3) solution to neutralise the remaining free and bound HF.

The reaction mixture was centrifuged and the supernatant liquid decanted. The solid residue was washed with propanol, dried at 80 °C for 3 h and weighed. This material was then again digested with 5 g of $NH_4F{\cdot}1.5HF$ under identical conditions. The digestion time was increased by 10 min for each subsequent cycle up to a maximum of 60 min (total digestion time per series 260 min).

The digestion cycles were done at 120, 140, 160, 180, 200 220 and 240 °C. All experiments were conducted in triplicate and the averaged values are reported here. The residue was analysed by FT-Raman spectrometry (Bruker Ram II) and XRD (Bruker A-D8 Advance).

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