**ZIRCONS AND FLUIDS: AN EXPERIMENTAL INVESTIGATION
WITH APPLICATIONS FOR RADIOACTIVE WASTE DISPOSAL**

**PROGRESS REPORT ON
HYDROTHERMAL STABILITY OF ZIRCONS**

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Abstract

The long-term stability of nuclear waste forms or barriers is related to changes in physical properties of the material induced through radiation damage and subsequent changes in solubility. Investigations conducted by us on natural zircons (ZrSiO_4) supports a positive correlation between level of alpha damage and fluid composition to enhanced levels of corrosion. New data are presented on the nature and rate of the solution process. We also present data on our continuing efforts to synthesize and characterize both pure ZrSiO_4 and doped with U, Th, Hf, Dy and P.

Introduction

Polyphase crystalline waste forms, such as the various proposed Synroc assemblages (e.g., Ringwood et al., 1970; Ringwood, 1985) are thought to be superior to noncrystalline waste forms because the latter are highly susceptible to hydrothermal alteration by aqueous brines at elevated temperatures, resulting in the release and transport of potentially dangerous waste constituents (McCarthy et al., 1978). However, questions have been raised as to the ability of crystalline waste forms to resist chemical alteration as radiation damage accumulates. Studies by Ewing and Headley (1983) and Lumpkin and Ewing (1985) have shown that zirconolite and pyrochlore, both natural analogues to the proposed Synroc constituents, may undergo complete amorphitization and subsequently suffer hydration and loss of A-site cations (Ca, Na) as the result of long-term weathering processes. Other major constituents of Synroc (e.g., Ba-Ti hollandite) are not found in nature; thus, their resistance to natural leaching processes cannot be ascertained. Furthermore, experimental evidence (Nesbitt et al., 1980) has indicated that Synroc constituent minerals, such as perovskite, may be thermodynamically unstable in a silica-rich environment.

Naturally-occurring refractory phases, such as monazite, sphene and zircon, are known by geoscientists to be stable in a wide range of geologic environments (both silica

saturated and silica undersaturated) and have been proposed as constituents of crystalline, ceramic and composite waste forms (e.g., Harker and Flintoff, 1984; Ewing and Haaker, 1980; Hayward et al., 1983, Sinha et al., 1989, 1990). The long-term stability of natural monazite, sphene and zircon samples has been discussed in terms of their resistance to U-Th-Pb isotopic loss throughout geologic time, their relative insolubility, refractory nature, and in the case of monazite, an apparent resistance to radiation damage.

Of all the aforementioned minerals, the most thoroughly investigated mineral with regards to isotopic systematics, crystal chemistry and radiation damage is zircon. Furthermore, a vast amount of data on the behavior of the zircon U-Pb isotopic system in a wide variety of rock types has been obtained. The chemical and isotopic response of zircons to fluids is poorly understood, but there is a general consensus that radiation-damaged crystals are more likely to be isotopically discordant and act as an open system to cation transport (Krogh, 1982; Wayne and Sinha, 1988). Although it has been proposed that the retentivity of Pb in zircons is indicative of the stability of the mineral at below -300°C (Gentry et al., 1982), strong arguments against such a model have been presented by Ludwig et al. (1983). These disagreements are clear indications of the lack of a data base in which relationships among crystal chemistry, age, and radiation damage may be clarified.

OBJECTIVES

Our current research is aimed at providing a new physical, chemical and isotopic data base for zircons (ZrSiO_4), using both natural and synthetic crystals. Because of the clear relationship between enhanced solubility (leachability) and α -damage, we are now in a position to attempt to quantify this process through: (1) long-term calibrated studies on the reactivity of ZrSiO_4 in fluids at repository conditions (1000 bars and lower pressures and up to 400°C) and (2) studies of the mechanics of fractures induced due to both radiation and temperature-enhanced stresses. Both objectives are clearly and uniquely

related to the DOE mission of careful documentation and characterization of possible waste form containment materials. In this progress report we present new analytical data on the first objective listed earlier, and attempts are underway to further refine our predictive capabilities. We ultimately wish to draw a relationship between degree of metamictization due to incorporation of radioactive waste and changes in solubility.

References

- Ewing, R.C. and R.F. Haaker (1980) The metamict state: Implications for radiation damage in crystalline waste forms. *Nucl. Chem. Waste Management*, 1, 51-57.
- Ewing, R.C. and T.J. Headley (1983) Alpha-recoil damage in natural zirconolite ($\text{CaZrTi}_2\text{O}_7$). *J. Nucl. Mat.*, 199, 102-109.
- Gentry, R.V., T.J. Sworski, H.S. McKown, D.H. Smith, R.E. Eby and W.H. Christie (1982) Differential lead retention in zircons: Implications for nuclear waste containment. *Science*, 216, 296-298.
- Harker, A.B. and J.F. Flintoff (1984) Polyphase ceramic and glass-ceramic forms for immobilizing ICPP high-level nuclear waste. In G.L. McVay, ed., *Scientific Basis for Nuclear Waste management—VII*, p. 513-520.
- Hayward, P.J., F.E. Doern, E.V. Cecchetto and S.L. Mitchell (1983) Leaching studies of natural and synthetic titanite, a potential host for wastes from the reprocessing of Canadian nuclear fuel. *Can. Mineral.*, 21, 611-623.
- Krogh, T.E. (1982) Improved accuracy of U-Pb zircon ages by the creation of more concordant systems using an air abrasion technique. *Geochim. Cosmochim. Acta*, 46, 637-649.
- Lumpkin, G.R. and R.C. Ewing (1985) Natural pyrochlores: Analogues for actinide host phases in radioactive waste forms. In C.M. Jantzen et al., eds., *Materials Research Society Symposium, Proceedings v. 44*, 647-654. Materials Research Society, Pittsburgh, Pennsylvania.
- Ludwig, R.E., R.E. Zartman and S.S. Goldich (1984) Lead retention in zircons. *Science*, 223, 835.
- McCarthy, G.J., S. Komarneni, B.E. Scheetz and W.B. White (1978) Hydrothermal reactivity of simulated nuclear waste forms and water-catalysed waste forms and water-catalysed waste-rock interactions. In G.J. McCarthy, ed., *Scientific Basis for Nuclear Waste Management*, p. 329-340.
- Nesbitt, H.W., G.M. Bancroft, W.S. Fyfe, S. Karkhanis, P. Melling and A. Nishimjima (1980) On the thermodynamic and kinetic stability of perovskite in natural waters. In *Workshop on Alternate Nuclear Waste Forms and Interactions in Geologic Media*, Gatlinburg, Tennessee.
- Ringwood, A.E. (1985) Disposal of high-level nuclear wastes: A geological perspective. *Mineral. Mag.*, 49, 159-176.
- Ringwood, A.E., S.E. Kesson, N.G. Ware, W. Hibberson and A. Major (1979) Immobilization of high-level nuclear wastes in Synroc. *Nature*, 178-219.
- Sinha, A.K., D.A. Hewitt, P.H. Ribbe and D. Wayne (1989) Zircons and fluids. Progress Report VPI & SU 13951-1 for Dept of Energy Contract No. DE-FG05-88ER13951.

Sinha, A.K., D.A. Hewitt, P.H. Ribbe and D. Wayne (1990) Zircons and fluids. Progress Report VPI & SU 13951-1 for Dept. of Energy Contract No. DE-FG05-88ER13951-2.

Wayne, D.M. and A.K. Sinha (1988) Physical and chemical response of zircons to deformation. Contrib. Mineral. Petrol., 98. 109-121.

THE CURRENT STATUS OF ZIRCON DISSOLUTION AND RELATED ZIRCONIUM PHASES: MODERN DISSOLUTION RATE LAW KINETICS AND THERMODYNAMIC CONSTRAINTS.

Introduction

The solubility of a mineral is controlled by fluid composition, mechanical mixing of the solvent, temperature, pressure, crystalline integrity of the solid phase (degree of metamictization or amorphous state), chemical composition of the mineral due to limited ionic substitution, and the chemical stability of secondary phases produced by dissolution. Properties of fluid composition which effect solubility include pH, Eh, and ionic strength. Fluid flow and mixing related to diffusion and dispersion of ionic species dissociated from a solid compound will control the kinetic rate of dissolution. Open and closed systems with regards to fluid migration and flux can effect the net dissolution of a mineral and control the kinetic rate of dissolution (Langmuir, 1971; Berner, 1978), and chemical reactions can have their kinetic rates doubled or trebled by a 10° C rise in temperature (Krauskopf, 1967). The slope of P-T boundaries in relationship to phase transitions will determine the effect of pressure on phase stability. Growth defects, crystal size, surface area, and crystalline status of a phase will determine the instantaneous rate of dissolution and overall solubility. Crystal surface reactions with a solvent can also be rate limiting. Meta-stable complexes and secondary alteration products may control kinetic rate and overall solubility of mineral. Specific surface reactions could armor the mineral from the chemical effects of the solvent. Variation in dissolution rate due to solid solution substitution in a mineral series is known in specimens with different compositions (Casey et.al, 1991). A simple system can have numerous factors which effect the overall solubility of a mineral phase. It is the hope of the experimentalist to limit the number of contributing factors controlling

solubility while extrapolating the data to natural environments.

Mineral dissolution can change the eH and pH properties of the solvent in a chemically closed system, so dissolution of a mineral in fixed Eh-pH fluid compositions can be controlled through the open system addition of acid or base. HCl and NH_4OH can be used for pH control (Topley, 1985). The addition of acid or base can effect experimental results by introducing cations which could form complex ions or dissolved species containing the major oxide components of zircon. An example of this effect would be the addition of NaOH in zircon stability studies. In this case, Na^+ becomes available in solution and a zirconium silicates could precipitate, such as $\text{Na}_2\text{O} \cdot \text{ZrO}_2 \cdot 1.5\text{SiO}_2$ (Maurice, 1949). Saturation of a solution with more than one zirconium solid phase would complicate any quantitative determination of zircon stability. The A/V (surface area of reacting material/ volume of solvent) is increased by periodic sampling and evaporation (Topley, 1982). A correction factor for the change in A/V during the experimental run can be calculated for a time integrated evaluation of thermodynamic and kinetic data. The standardization of $\Delta A/V$ is needed to integrate data from batch reaction experiments for sound interpretation of concentration verses time diagrams (Topley, 1982).

The heat of reaction in endothermic dissolution reactions is such that thermal energy is needed for the reaction to proceed, so the temperature of a closed system would be decreased from dissolution. In thermally controlled dissolution experiments, thermal energy is added or removed to maintain a constant temperature in the chemically closed system. Thermal gradients within a reaction vessel are rarely monitored due to constraints imposed by apparatus design. Manipulation of the thermal energy budget complicates the open system nature of a controlled dissolution experiment. In a natural ground water system, additional thermal energy may not be available, so extrapolation of experimental kinetic rates could be erroneous with regards to thermal budget controls.

Solubility in water is typically calculated in terms of equilibrium constant (K_{eq}) using the activity of ionic species in solution. The solubility product (K_{sp}) is equivalent to K_{eq} and dissociation constant (K_d) with all terms being dimensionless.

$$K_d = \frac{[(\alpha C)^c (\alpha D)^d]}{[(\alpha A)^a (\alpha B)^b]}$$

α = activity

$$\alpha = \lambda * m_i$$

λ = activity coefficient

m_i = molar concentration of species i

$$\alpha_i \rightarrow m_i \text{ as } m_i \rightarrow 0$$

$$\Delta G^\circ_r = \sum G^\circ_{f(\text{products})} - \sum G^\circ_{f(\text{reactants})}$$

$$\Delta G^\circ_r = [G^\circ_{f\text{Zr(OH)}_4} + G^\circ_{f\text{H}_4\text{SiO}_4}] - [G^\circ_{f\text{ZrSiO}_4} + 4 * G^\circ_{f\text{H}_2\text{O}}]$$

$$\log K_d = - \frac{\Delta G^\circ}{1.364} \quad \Delta G^\circ \text{ at } 25^\circ\text{C in kcal/mol}$$

With zircon solubility studies it is assumed that $m_i \rightarrow \alpha$ due to the low concentrations of Zr species in solution. Uncertainty in the thermodynamic Gibb's free energy constants along with the relationship between ionic species concentration, activity coefficient, and activity can lead to the calculation of erroneous solubility products based on theoretical models. While the analytically detection limit of apparatus may hinder well designed experiments, the theoretical determination of solubility products can help to model experimental results under extremely low solubility conditions.

In the case of several zircon studies, the below detection limit of Zr ions in solution or the assumption of congruent dissolution limited interpretation of experimental data (Tole, 1982; Ewing et al., 1982). Due to a lack of conclusive data the theoretical determination of zircon solubility based on Gibb's free energy data from varied sources was needed to interpret experimental results (Tole, 1982). Uncertainties from experimental results due to the extrapolation of mixed thermodynamic data sets will increase when results are compared to natural systems. With waste forms, material durability is typically expressed in units of g/cm²/day which is known as the normalized leach rate (Brookins, 1984). Standards for a dissolution experiment are lacking, so comparison of mineral dissolution rates in which minerals have been subjected to dissimilar physical conditions may hide important correlations or lead to weak comparisons.

The numerical value of a dissolution rate determined under experimental conditions may be difficult to interpret in light of the complexities found in natural systems. Actual dissolution rates cannot be extrapolated from experimental data, because experiments fail to reproduce the composition and structure of natural mineral surfaces and fluid compositions in regards to biologic effects and undetermined adsorbed inhibitors (Berner, 1978). Data for the composition of natural fluids modified by the breakdown of solid phase nuclear waste is necessary for a complete evaluation of the stability of any host phase used for radioactive waste disposal or containment. Over extended periods, the heat generated by radioactive decay could reach super critical temperatures if the thermal conductivity of the surrounding site is low. As the temperature increases the solubility of most minerals will increase. Results from Walther and Helgeson, 1977 established the effects of temperature change for silica solubility in H₂O from both experimental determined and theoretically calculated solubility versus pressure (Figure 1). The question must be asked, "What is the purpose of the experiment?". Clearly the approach here is to determine the stability-solubility-dissolution kinetics of ZrSiO₄ under defined conditions.

PRESSURE AND TEMPERATURE EFFECTS ON QUARTZ SOLUBILITY

Figure 1. Log of aqueous SiO_2 molal concentration at saturation versus pressure in kbar at 25° C, 100° C, and 300° C. Quartz solubility increases from 6ppm(25° C, 0 kbar) to 600ppm(300° C, 0 kbar). Pressure effects on quartz solubility are minimal compared to temperature effects. Note the variation between theoretical and measured solubilities. Diagram adapted from Nordstrom & Munoz, 1985 with data from Walther & Helgeson, 1977.

An account of possible zirconium aqueous phases in a simple solution such as H_2O can be examined using the system $Zr-O-H$. Brookins (1988) compiled an Eh-pH diagram for the system (Figure 2), which shows that the stability field for $Zr(OH)_4$ decreases with a decrease in Zr activity. It is important to keep in mind that natural waters fall within a limited range on the diagram. The Eh and pH range of natural waters was compiled from the data of Becking et al, (1960) and it can be seen that only in extreme environments do pH values fall below 2 (Figure 3). Recently, in underground mine waters associated with iron sulfide ores, - pH values have been sampled from waters (Nordstrom, K.D., 1991). Baes and Mesmer (1976) calculated the distribution of zirconium hydrolysis products related to the stability of baddeleyite in pH space. K_d (dissociation constant) for ZrO_2 hydrolysis products were determined from a variety of experimentally determined and theoretical values. The distribution of zirconium hydrolysis products from ZrO_2 can be determined from figure 4. Distribution diagrams for hydrolysis species in simple systems related to zircon dissolution can be used for a comprehensive analysis of saturation limitations. Detailed hydrolysis distribution diagrams at 25° C include: quartz and amorphous silica (figure 5); PbO (figure 6); zircon (figure 7). Figure 8 provides hydrolysis product concentration at 25° C for materials closely associated with zircon dissolution, including baddeleyite, zircon, quartz, amorphous silica, and lead oxide. The minimum solubility of baddeleyite is approximately $10^{-11.6}$ near Ph 5.5. based on K_d values from Baes and Mezmer, 1976. Determination of baddeleyite solubility based on K_d determined from Gibb's free energy of formation; $Zr(OH)_4$ from Naumov, 1974; ZrO_2 from Robie, 1979; and H_2O from Helgeson, 1978; give baddeleyite solubility at $10^{-9.168}$ (Tol, 1982).

The drastic difference in baddeleyite solubility from 10^{-12} to $10^{-9.168}$ further shows the contrasting effects of experimental versus theoretically determined values (figure 8).

**Eh-pH DISTRIBUTION OF Zr-O-H
SPECIATION IN SOLUTION**

Figure 2. Eh-pH diagram from zirconium hydrolysis products in the system Zr-O-H with an assumed Zr activity of 10^{-6} and 10^{-8} at 25° C and 1 bar. As the concentration of Zr species decrease, the stability field for $Zr(OH)_4$ decreases. The stability field of $Zr(OH)_4$ was based on G° for crystalline instead of aqueous species. From Brookins, D.G., Eh-pH Diagrams for Geochemistry, Springer-Verlag 1987, p.117.

GENERIC Eh-pH DIAGRAM

FOR H_2O

Figure 3. The Eh-pH range from measurements of natural water are contained within the dotted line (measurements from Becking et al., 1960). The upper and lower stability limits for water at 25° C occur at P_{O_2} and $P_{H_2} = 1 \text{ bar}$. Numbers refer to specific environments include: 1 mine waters; 2 rain; 3 streams; 4 normal ocean water; 5 aerated saline water residues; 6 ground waters; 7 bog waters; 8 water-logged soils; 9 euxenic marine waters; 10 organic-rich saline waters. Sulfide-sulfate boundary and carbon-carbonate boundary separate oxidizing from reducing environments buffered by sulfur and carbon species. Adapted from Brookins, D.G., Eh-pH Diagrams for Geochemistry, Springer-Verlag 1987, p11.

DISTRIBUTION OF ZIRCONIUM HYDROLYSIS PRODUCTS
FROM ZrO_2 DISSOLUTION

Figure 4. Log molal concentration of Zr hydrolysis products at 25° C versus pH. Total Zr saturation concentration is represented by the heavy line. The species Zr(OH)_4^0 is represented by the horizontal line at $\log [] = -11.6$, which is the lowest saturation value for ZrO_2 . Other species are represented by the dashed and light lines. Numbers in the diagram represent x,y values for Zr hydrolysis species (3,5 = $\text{Zr}_3(\text{OH})_5^{7+}$) distribution lines. The speciation for Zr hydrolysis is not clearly defined and species may be meta-stable. Adapted from Baes & Mesmer, *The Hydrolysis of Cations*, John Wiley & Sons, 1976, p.159.

**DISTRIBUTION OF SILICA HYDROLYSIS PRODUCTS
FROM QUARTZ AND AMORPHOUS SILICA DISSOLUTION**

Figure 5. Log activity of dissolved silica hydrolysis products at 25° C versus pH. Dashed line represents activities of total dissolved products with respect to amorphous silica, and heavy line represents total saturation with respect to quartz. Saturation with respect to both phases is independent from pH at values pH < 8.5. Adapted from Drever, *The Geochemistry of Natural Waters*, Prentice Hall, Inc, 1988, p.100.

DISTRIBUTION OF LEAD HYDROLYSIS PRODUCTS
FROM PbO DISSOLUTION

Figure 6. Log molal concentration of Pb hydrolysis products at 25° C versus pH. Total Pb saturation concentration is represented by the heavy curve. Numbers in the diagram represent x,y values for Pb hydrolysis species(1,3 = $\text{Pb}(\text{OH})_3^-$) distribution lines. PbO is extremely soluble in acidic solutions. Species may be meta-stable. Pb produced by U decay could be highly soluble in most natural solutions unless the Pb is confined within a stable phase. Adapted from Baes & Mesmer, The Hydrolysis of Cations, John Wiley & Sons, 1976, p.364.

DISTRIBUTION OF ZIRCONIUM HYDROLYSIS PRODUCTS
FROM ZIRCON DISSOLUTION

1	Zr^{4+}
2	ZrOH^{3+}
3	$\text{Zr}(\text{OH})_2^{2+}$
4	$\text{Zr}(\text{OH})_3^+$
5	$\text{Zr}(\text{OH})_4$

Figure 7. Activity of Zr hydrolysis products at 25° C verses pH. Calculated from thermodynamic data of Naumov 1971. Zircon stability is not effected by pH in the range pH 0.8 to pH 11.

HYDROLYSIS PRODUCT DISTRIBUTION DIAGRAM for ZrO_2 , ZrSiO_4 , PbO , and Silica

Figure 8. Distribution of hydrolysis products at 25°C for ZrO_2 & PbO (Baes & Mesmer, 1976), $\text{ZrO}_{2(l)}$ & ZrSiO_4 (Tole, 1982), quartz ($\text{SiO}_{2(c)}$) and amorphous silica ($\text{SiO}_{2(amp)}$), (Drever, 1988). value for $\log$ hydrolysis species concentration ($\log [M_x(OH)_y]$) is given at left margin and pH at lower margin. Curves represent $\log$ concentration of total hydrolyzed species at saturated conditions. At pH 3, ZrO_2 becomes more soluble than zircon. For a more detailed range description of individual hydrolysis species see figures 4, 5, 6, and 7 for ZrO_2 , silica, PbO , and zircon, respectively.

The exact nature of the hydrolysis species from zirconium phase dissolution is clearly debatable. Erlank (1978) reviews contrasting views on Zr speciation in solutions from seven sources. Hydrolysis products from Brookins EH-pH diagram (figure 2) does not include the species $\text{Zr}(\text{OH})_3^+$, $\text{Zr}(\text{OH})_2^{+2}$, and $\text{Zr}(\text{OH})^{+3}$ while Baes and Mezmers clearly show the distribution of these products in their ZrO_2 hydrolysis distribution diagram (figure 4). The uncertain nature of Zr aqueous species clearly complicates any interpretation related to zircon dissolution. A complete kinetic and thermodynamic understanding of baddeleyite and silica in natural solutions is necessary to interpret the behavior and solubility of zircon in nature. The major difficulty in zircon dissolution rate studies is the extremely low solubility of zirconium silicate and zirconium oxide phases in a natural aqueous solution. Saturation of phases in solution may take extended periods of time. With respect to the low solubility of Zr, laboratory experiments increase temperatures and ionic strength of solution to increase solubility, but these conditions may be unrealistic in most natural systems.

Solubility of Zircon and Zirconolite

Numerous studies have examined the chemical behavior of zircon based on a geochronologic perspective. Other studies have looked at the saturation of zircon in various igneous melt systems (Watson & Harrison, 1983). REE distribution in zircons has also been examined in igneous systems (Fujimaki, 1986). Studies dealing with zircon stability include: Maurice, 1949; solubility and leachability: Bouyoucos, 1921, Ewing et al, 1982; and kinetics related to zircon dissolution mechanisms: Tole, 1982. These studies have been unable to document the precise mechanism of zircon dissolution under hydrothermal conditions in the laboratory or natural systems. Bouyoucos (1921) determined zircon dissolution based on freezing point depression, and a qualitative determination of Zr in solution was not performed.

Maurice (1949) looked at the stability of zirconium phases in three hydrothermal systems at 400° C. Using the starting materials sodium hydroxide, silicic acid, water, and zirconium oxide, these systems include $\text{ZrO}_2\text{-SiO}_2\text{-H}_2\text{O}$, $\text{ZrO}_2\text{-Na}_2\text{O-H}_2\text{O}$, $\text{ZrO}_2\text{-HCl-H}_2\text{O}$. The zirconium oxide was converted into ZrO(OH)_2 for each experiment. This study also included a measurement of the stability field of quartz in the systems $\text{SiO}_2\text{-Na}_2\text{O-H}_2\text{O}$ and $\text{SiO}_2\text{-HCl-H}_2\text{O}$. The phase relationships at 400° C in the system $\text{ZrO}_2\text{-SiO}_2$ in solutions of HCl and Na_2O can be delineated (Figure 9). The association of baddeleyite and zircon in solutions of natural composition is limited to liquids in which the ratio of SiO_2 to ZrO_2 is near or less than 1. Under extremely low acidic conditions ($\text{pH} < .42$) baddeleyite is no longer stable, and under highly alkaline conditions ($\text{pH} > 13.45$) zircon becomes unstable.

Tole (1982) examined the solubility of zircon and cyrtolite (totally metamict zircon) in aqueous solutions at several pH and temperature conditions using approximately 1 gram of sample per run in a 1 liter starting volume of solutions. Samples were withdrawn periodically and pH was controlled by the addition of HCl or NH_4OH (Tole, 1982). The crystalline zircon solubility measurements were conducted at $\text{pH}=0$ at 80° C, and at pH 5.0, 7.0, and 9.0 at 60° C. Solubility of crystalline zircon were also studied in .1m and 5.0m NaCl at 60° C. In the crystalline zircon runs, no Si or Zr was detected using Plasma Emission Spectrometry (PES) which has a minimum detection limit of 50ppb for both Si and Zr. Cyrtolite runs were conducted at pH 5.0 for the temperatures of 25°, 60°, and 80° C. Si was detected in the analyzed solution but no Zr was detected. These data were used to calculate the dissolution activation energy for cyrtolite (based on congruent dissolution with Si from the 60° and 80° C runs as 12.8 Kcal/mole (Tole, 1982). The solubility of zircon and baddeleyite in H_2O at 25° C using thermodynamic data of Naumov 1974 was calculated. Assuming congruent dissolution of zircon and no baddeleyite precipitation, baddeleyite reaches saturation at .06ppb Zr(OH)_4^+ while zircon will not reach saturation until Zr(OH)_4^+ reaches concentrations of .45ppb. With

$\text{ZrO}_2\text{-SiO}_2\text{-H}_2\text{O-HCl-NaO}_2$
PHASE STABILITY FIELDS at 400°C

Figure 9. Phase relationships in the system $\text{ZrO}_2\text{-SiO}_2\text{-H}_2\text{O-HCl-NaO}_2$ at 400°C (modified from Maurice, 1949). The ratio $\text{SiO}_2\text{:ZrO}_2$ verses solvent concentration (normality HCl or NaOH) is presented for determination of zirconium phase stability fields under hydrothermal conditions (400°C). The equivalent pH values is given on the upper margin. Stippled area indicates pH range of natural groundwaters (Baas et al., 1960: see fig. 2). Under conditions of $\text{SiO}_2\text{:ZrO}_2 > 1$, saturated zircon and quartz are stable in acidic solutions. Zircono-silicates include $\text{Na}_2\text{ZrO}_2\cdot 1.5\text{SiO}_2$ and three unidentified Zr species.

baddelyite precipitation, H_4SiO_4^0 would need to reach concentrations of 1.0ppb(at .06ppb $\text{Zr}(\text{OH})_4^0$) before zircon would precipitate(Tole, 1982). Based on the thermodynamic calculations it is possible to explain why Zr was below detection limits in Tole's crytolite solubility experiments, as Zr detection limit from PES analysis is 50 ppb, and baddeleyite saturation is calculated to be only .06ppb.

Ewing, Haaker, and Lutze in 1982 conducted studies on the "Leachability of zircon as a function of Alpha Dose". With an increase in the metamictization of natural zircon the bulk leach rate and wt % of zircon dissolved in the experiments increased. The detailed description of eleven zircons included U/Pb, Pb/Pb and Th/Pb age determinations and density measurements. Ten 3-20mg samples were placed in .5ml solutions of 5% KHCO_3 sealed in fused quartz ampoules except for sample #C1. Sample #C1 weighed 978mg and was placed in 5ml of 5% KHCO_3 solution. The use of fused quartz ampoules limited analysis to determination of Zr concentration, so all leach rate determinations were based on congruent dissolution from Zr. The minimum detection limit for Zr in the induced coupled plasma analysis was 11ppb. Zircon(#77-215) with a calculated alpha dose of 6.02×10^{16} alphas/gm reached Zr concentrations in solution after 9.9 days of .270ppm while zircon(#4b) with an alpha dose of 1×10^{19} in similar conditions reached Zr concentrations in solution of 27ppm(Ewing et al, 1982). Alpha dose was determined from isotopic data and ages, x-ray diffraction patterns, and density. Table 1 provides U, Th, and Pb concentrations, density, and alpha dose(alpha/gram), Zr concentration of leachate after dissolution, and sample identification # in order of Zr concentration in leachate(data from Ewing, 1982). Figure 10 plots density and log of leach rate verses log of alpha dose(Ewing, 1982). The study indicates that radioactive waste leach rates will increase as a result of radiation effects(Ewing, 1982).

Table 1. Data on zircon leaching experiments of Ewing et al. (1982).

ZIRCON LEACHING DATA AND RESULTS

Sample No. and Mesh Size	Alpha Dose (alphas/gm)	ISaturation ($\frac{100 \times \text{Dose}}{1 \times 10^{19}}$)	Surface ^a area (cm ²)
77-215 (-200+270)	6.02×10^{16}	0.8	1.91
M-83-NH (-200+270)	9.44×10^{18}	85.0	2.76
DB-10 (-200+270)	6.49×10^{18}	59.0	2.56
RSD-9 (-200+270)	3.30×10^{17}	3.0	5.68
#3 (-140+300)	$\leq 2 \times 10^{18}$ (est.)	≤ 20.0	1.76
#4a (-200+270)	$\geq 1 \times 10^{19}$ (est.)	≥ 100.0	0.61
#4b (-140+300)	$\geq 1 \times 10^{19}$ (est.)	≥ 100.0	2.31
#17 (-140+300)	$\leq 2 \times 10^{18}$ (est.)	≤ 20.0	2.82
#C1 (-140+300)	$\geq 1 \times 10^{19}$ (est.)	≥ 100.0	124.0
5b (-140+300)	0	0.0	0.60
7 (-140+300)	0	0.0	1.45

Sample No.	Zr in solution ^b (ppm)	ZrSiO ₄ dissolved (wt. %)	Bulk Leach Rate ^c (gm/cm ² day)
77-215	0.027	2.42×10^{-3}	2.9×10^{-8}
M-83-NH	0.315	2.00×10^{-2}	2.3×10^{-7}
DB-10	0.116	7.88×10^{-3}	9.2×10^{-8}
RSD-9	0.0425	1.57×10^{-3}	1.9×10^{-8}
#3	0.193	1.63×10^{-2}	2.2×10^{-7}
#4a	0.54	1.50×10^{-1}	1.8×10^{-6}
#4b	2.70	1.12×10^{-1}	2.4×10^{-7}
#17	0.21	$.99 \times 10^{-3}$	1.5×10^{-7}
#C1	12.79	1.30×10^{-1}	2.1×10^{-6}
5b	0.095	1.94×10^{-2}	3.2×10^{-8}
7	0.243	1.03×10^{-2}	3.4×10^{-7}

a Surface areas were estimated using the assumption of spherical particles of 0.75 mm diameter for (-200+270) and 0.104 mm for (-140+300) mesh.

b Zr concentrations in the leachate after the 10 fold dilution was made.

c The bulk leach rates were calculated on the basis of Zr and the assumption of congruent dissolution.

AGES AND ALPHA DOSES FOR THE ZIRCON SPECIMENS

Sample No.	Concentration (ppm)			Age (millions years)			
	U	Th	Pb	$\frac{206\text{Pb}}{238\text{U}}$	$\frac{207\text{Pb}}{235\text{U}}$	$\frac{207\text{Pb}}{206\text{Pb}}$	$\frac{208\text{Pb}}{232\text{Th}}$
77-215	163.3	48.9	3.85	148	149	169	144
M-83-NH	556.6	188.3	396.9	3,009	3,210	3,340	3,359
DB-10	1,081	740	299	1,417	1,422	1,433	1,316
RSD-9	1,407.7	-	76.8	1,431	1,433	1,438	1,393

TABLE 1 Continued

Sample No.	Density (gm/cm ³)	Alpha Dose (alphas/gm)	Reference, Source or Locality
77-215	-	6.02×10^{16}	21, Zartman
M-83-NH	-	9.44×10^{18}	22, Zartman
DB-10	-	6.49×10^{18}	23, Zartman
RSD-9	-	3.30×10^{17}	24, Zartman
#3	4.61	$\leq 2 \times 10^{18}$ (est.)	Thailand
#4a	3.81	$\geq 1 \times 10^{19}$ (est.)	Southwestern Mineral Co.
#4b	3.81	$\geq 1 \times 10^{19}$ (est.)	Southwestern Mineral Co.
#17	4.64	$\leq 2 \times 10^{18}$ (est.)	Southwestern Mineral Co.
#C1	3.45	$\geq 1 \times 10^{19}$ (est.)	Raleigh Peak, Jefferson County Colorado
5b		0	flux grown zircon
7		0	sol-gel zircon

ALPHA DOSE VERSES LEACH RATE

Figure 10. A negative correlation between log alpha dose and zircon density exists with respect to log leach rate. $\blacktriangle$ represent alpha dose calculated from radiometric age and U-Th concentration where $\bullet$ represents alpha dose estimated from density-alpha dose relationship. Leach rate increases with an increase in alpha dose. Complete metamictization has been observed in zircon with alpha dose $> 1.1 \times 10^{19}$ (Headley et al., 1982). Adapted from Ewing et al., Scientific Basis For Radioactive Waste Management-5, Elsevier, 1982, p.395.

New Studies on Solubility

Studies conducted at VPI & SU include both batch and mixed flow reactor experiments. A batch reaction experiment can be used to determine dissolution kinetics at constant temperature conditions in a chosen solvent solution. A rate of dissolution can be calculated by concentration versus time analysis of data. In our batch reaction experiments, separate reaction vessels were used for each sampling, so a homogeneous sample material and a precise measurement of sample size and solution volume must be duplicated for each sampling time. This technique neglects the pH change of solution due to mineral dissolution, while a near constant A/V parameter could be maintained. Tole (1982) sampled his zircon dissolution experimental runs out of the same reaction bottle thus reducing solution volume during sampling. In ideal terms, data from an experimental batch run series will have a high initial dissolution rate due to the increased rate of dissolution from crystal defects and minute crystals fragments including thin edges. The dissolution rate should decrease with time until saturation is reached, but depending on the kinetic effects saturation may not occur for long periods of time.

In mixed flow reaction experiments, solution is constantly mixed by external mechanical means while a constant flow rate of solution through a reaction vessel is maintained. Pressure can be controlled as well as temperature. To minimize variability, temperature, pressure, mixing rate, and flow rate are maintained at a constant value. Initial sampling may have elevated concentrations of dissolved material due to defect dissolution, but over time, a decreased steady state value for dissolved material should be reached. After steady state is reached, a new temperature value can be selected. This temperature change should result in a change in the steady state concentration value. With two steady state values of concentration at two given temperatures, activation energies for dissolution can be calculated. Steady state rates for zircon dissolution in 2M NaCl and 2% HNO₃ at 210° C have recently been conducted. Activation energies can be

accurately determined by duplicating experiments at lower temperatures, and are currently in progress.

Mixed Flow Reactor Experiments

Physical Description

Tanzanian placer zircon was purchased from Graystone Inc.. The zircon pebbles are rounded and range from 7-13mm in maximum dimension. Two color fractions, red-yellow and red were dominant in polished samples, and may be attributed to very slight variations in iron impurities. Perfect optic axis figures were obtained from slices cut perpendicular to the c-axis in both color fractions indicating crystalline integrity. Distinct and sharp peaks were obtained from XRD analysis patterns on a Scintag XRD unit also indicating crystalline integrity(Figure 11). The Tanzanian zircon was crushed in an agate mortar and sieved into a size fraction of 270 μ m - 425 μ m. This crushed size fraction was used in XRD, SEM, mass spectrometry, dissolution experiments, and composition analysis. Backscattered electron images of whole crystals indicate no visible zonation of Z-contrast within the zircon. The presence of Hf was detected on EDS analysis(Figure 12). Isotope dilution analysis on the VG-54 mass spectrometer at VPI & SU was used to determine U and Pb concentrations in the Tanzanian zircon. Total U in the Tanzanian zircon is 63ppm and total lead is .233ppm. Relatively young U/Pb ages of 20.7 and 22.6Ma for Pb²⁰⁶/U²³⁸ and Pb²⁰⁷/U²³⁵ respectively, together with the low U content of the zircon is additional evidence for the crystalline integrity of the Tanzanian zircon. The older Pb²⁰⁷/Pb²⁰⁶ age of 228Ma is the result of error introduced by extremely low levels of Pb in the zircon relative to the blank and spike, and the poor sensitivity of Pb²⁰⁷/U²³⁸ for young zircons. Isotope data was calculated using PBDAT version 1.07 by Ludwig 1990 (Table 2). Unreacted Tanzanian zircon was photographed with an SEM for determining the surface morphology before dissolution(figure 13).

TANZANIAN ZIRCON XRD

ANALYSIS

Figure 11. XRD analysis for Tanzanian Zircon with matching JCPDL card 06-0266 Zircon. Sharp peaks indicate crystalline integrity of the Tanzanian zircon material

EDS SPECTRUM OF TANZANIAN ZIRCON

Sample ID: Allocated 10-Aug-91 at 10:09:56

Energy Range: 0 - 20 keV 10 eV bin

Preset: Off

Real Time: 122.28 Sec. Live Time: 64.56 Sec.

31% Deadtime 5435 Counts/Second

Acquisition date: 10-Aug-91 Acquisition time: 10:21:51

Cfs 10K Log

Figure 12. EDS spectrum of Tanzanian zircon showing detectable Hf content. EDS surface chemistry scan of crushed Tanzanian zircon fragment. Both L α and L β emission are present for Hf. Hf in natural zircon is common, but no data is available to establish Hf-Zr solid substitution effects on stability and solubility.

SEM PHOTOGRAPH OF UNREACTED
TANZANIAN ZIRCON GRAIN

Figure 13. Right photograph shows general morphology of crushed Tanzanian zircon fragment displaying sharp edges and parting planes due to crushing. Scale bar indicates size of fragments used in dissolution experiments. Left inset at 600x shows close-up details of smooth cleavage and parting planes. Micro fragments on surface are the result of carbon coating used for beam emission.

Experimental Techniques

Details of the flow reactor

A hydrothermal stirred flow system was used to determine leachability of zircon in a 2% HNO_3 and a 2mNaCl solution. Coretest Systems Inc. built the control panel and dual vessel stirred flow system(Figure 14a). The panel controls temperature, mixing rate, total bleed pressure, and sampling port. Maximum temperature and pressure of the reactor vessel is 250° C and 1800psi. Variable flow is controlled by an Isco Model 2350 HPLC(high pressure liquid chromatography) pump with a flow rate control ranging in pressure from 0 - 2500psi and a flow rate from 0 or .01 - 10ml/min. Fluid within the system contacts only inert materials such as teflon, Peek, Viton and Hastelloy C-276. The reaction vessels are of a modified Parr acid digestion design (Figure 14b). Mixing in the reaction vessel is accomplished with a teflon coated magnetic bar placed within the vessel controlled by a stirrer mechanism built into the hot plate. Heat for the system is generated by a modified hot plate which directly heats and insulates the dissolution vessel. J-type thermocouples monitor both the hot plate and the vessel temperature. The reaction vessel will hold 7ml of solvent while the pump bladder holds 250ml of solvent. The reaction vessel contains a detachable powder sample holder with replaceable teflon filter screens of 60 μm mesh.

Experimental Procedure

The 2mNaCl and 2% HNO_3 mixed flow experimental runs contained .4986 and .4994 grams of Tanzanian zircon respectively. The zircon was placed in the powder sample holder. The pressure, temperature, flow rate and sampling of the two mixed flow runs were similar with minor variations. Mixing in the vessel began at the initiation of both runs. Both the 2NaCl and 2% HNO_3 runs were allowed to reach run conditions of 1000 $\pm$ 50psi and 210 $\pm$ 4° C in 27 and 24hrs respectively. At this time the line volume was

STIRRED FLOW SYSTEM

Figure 14a. Coretest hydrothermal stirred flow system control panel and heating unit with Isco 2350 HCPL pump on right.

Figure 14b. Modified Parr dissolution vessels for stirred flow system

flushed out(.5ml) and the first 7ml samples were removed(A NaCl and A HNO₃). Removal of the sample was accomplished using 10cc disposable Nalgene syringes from a port on the BPR valve(bleed, pressure, relief). Additional samples for each run were collected at 24 hour intervals. The flow rate was set at the minimum for remainder of both the 2NaCl and 2%HNO₃ runs. This setting produced a .0142ml/min flow rate average in the 2mNaCl experiment, and a .0136ml/min flow rate average in the 2%HNO₃ experiment. All additional analysis reflect 7ml samples which represent the bulk composition of fluid released from the BPR valve over 24hr intervals. Fluid volume released during the 24hr flow interval from 18-21ml.

Analytical Data

Both Si and Zr bearing solutions were analyzed with induced coupled plasma(ICP) by XRAL Assay Laboratories(with a detection limit of 0.1ppm for Si and Zr). Data from the 2mNaCl and 2%HNO₃ stirred flow reaction experiments is presented in tables 2 and 3 respectively. Zirconium concentration was below detection limit by ICP analysis in all the mixed flow reaction samples. Silica was detected in all samples except for D NaCl. The data can be interpreted for the 2mNaCl and 2%HNO₃ experiments in figure 15 and 16 respectively. It is clear from the lack of measurable Zr in solution, that the precise mechanism of zircon dissolution is still undeterminable(congruent verses incongruent dissolution of Zr and Si). It can be shown in both experiments that the solution was less reactive as time progressed. After 170 hrs both systems reached a steady state. With the extremely low solubility of crystalline zircon it could be expected that the common defects that accelerate dissolution in the beginning of solubility experiments(such as thin edges and crystal lattice defects) may take an extended amount of time to dissolve. This could be the primary cause for not reaching steady state in a shorter period of time. Dissolution features of the Tanzanian zircon surface in 2mNaCl is shown in SEM images (figures 17 & 18). An unsuccessful

Table 2, 3. Concentration data for Si and Zr for two differing solutions
(Table 2 for 2 molal NaCl, Table 3 for 2% HNO₃).

2 molal NaCl Flow Reactor

Sample #	Time hours	Si ppm	Zr ppm
ANaCl	26.75	2.3	<0.10
BNaCl	50.75	1.5	<0.10
CNaCl	74.75	0.2	<0.10
DNaCl	98.75	0.1	<0.10
ENaCl	122.75	1.3	<0.10
FNaCl	146.75	0.6	<0.10
GNaCl	170.75	0.3	<0.10
HNaCl	194.75	0.3	<0.10
INaCl	242.75	0.4	<0.10

2% HNO₃ Flow Reactor

AHNO ₃	24	0.8	<0.10
BHNO ₃	48	2.0	<0.10
CHNO ₃	72	1.1	<0.10
DHNO ₃	96	1.0	<0.10
EHNO ₃	120	0.7	<0.10
FHNO ₃	144	0.7	<0.10
GHNO ₃	168	0.8	<0.10
HHNO ₃	192	0.6	<0.10
IHNO ₃	240	0.5	<0.10
JHNO ₃	266	0.5	<0.10
KHNO ₃	266	0.5	0.10

ZIRCON DISSOLUTION FLOW REACTOR 2 Molal NaCl

Figure 15. Zr was not detected in the reacted fluids, but silica concentrations display steady state saturation after 170 hours. Silica steady state saturation is .3ppm. Rapid rise in Si dissolution reflects dissolution of crystal defects and thin edges. Based on congruent dissolution of Zr and Si, zirconium dissolution at steady state could be as high as .97ppm, but precipitation of ZrO_2 or other zirconium phases precludes detection. Discongruent dissolution could imply dissolution of silica at greater rate than zirconium dissolution.

ZIRCON DISSOLUTION FLOW REACTOR 2% HNO₃

Figure 16. Zr was not detected in the reacted fluids, but silica concentrations display steady state saturation after 170 hours. Silica steady state saturation is .5ppm. Rapid rise in Si dissolution reflects dissolution of crystal defects and thin edges. Based on congruent dissolution of Zr and Si, zirconium dissolution at steady state could be as high as 1.62ppm, but precipitation of ZrO₂ or other zirconium phases precludes detection. Discongruent dissolution could imply removing of silica at greater rate than zirconium dissolution. The zircon is slightly more reactive in the 2% HNO₃ solution compared to the 2m NaCl (compare with figure 15).

DISSOLUTION SURFACE OF ZIRCON
FROM 2 m NaCl FLOW REACTOR EXPERIMENT

Figure 17. SEM photograph of Tanzanian zircon from the 2 m NaCl flow reactor experiment. Distinct dissolution pits are visible on upper left edge of grain . Cleavage planes on right appear free of dissolution effects. Preferred dissolution on grain edges reflects surface energy differences between flat surface and intersecting faces.

CLOSE-UP OF ZIRCON DISSOLUTION SURFACE

2 m NaCl FLOW REACTOR

Figure 18. Close-up of upper left hand edge of zircon grain from figure 17. Note the scalely surface due to dissolution along cleavage planes and deep dissolution pits. This deep etching appears to have an orthogonal geometry indicating preferred dissolution directions. Precipitate from the dissolution reaction could be present in lower right hand corner of photograph.

21 day 2mNaCl(250° C) batch run lost H₂O producing a solution saturated in NaCl. In figure 19, the highly eroded zircon surface displays the extreme corrosion of zircon induced by saturated NaCl solutions. EDS analysis confirm the formation of a Zr, Na, Si precipitate(Figure 20). The Hastelloy C-276 metallic inlet tube to the teflon dissolution sleeve reacted with the HNO₃ solution, and the final zircon product in the HNO₃ flow reactor had a distinct brown color when removed from the sample holder. A precipitate containing Fe, Cr, and Ni was found growing in thin tabular rosettes sometimes cementing zircon grains together(Figure 21). This same material could be coating all zircon grains removed from the run, yet EDS analysis was unable to detect any coating. Dissolution of the Tanzanian zircon surface in 2%HNO₃ is shown in figure 22. The effects of Fe oxides and hydroxides is unknown in the overall determination of zircon solubility, yet in natural acidic solutions iron would be expected. Simple Fe oxide or hydroxide staining could armor zircon from a solution especially if zircon acts as a primary nucleation site. The steady state dissolution concentration with flow at .014ml/min was slightly greater in the 2%HNO₃ at .5ppm verses .3ppm in the 2mNaCl.

Discussion

Both the VPI(NaCl) and Tole experiments added two drops of 48% HF to keep zirconium complexes in solution during shipping and to compensate for reduction in temperature at run end. Complex zirconium halides exist such as Na₃ZrF₇(Harris, 1959) and Na₇Zr₆F₃₁(Burns, Ellison, Levy, 1968) which might precipitate during shipping and become undetectable to analytical techniques. The detection of Zr in a 3.1NHCl batch run(Table 4) and in Ewing et al, (1982) indicates that detectable amounts of Zr go into simple chemical solutions, but the data is inconclusive regarding the role of baddelyite formation related to zircon dissolution. Maurice's (1949) work indicates that zircon and baddelyite can

PRECIPITATE FROM ZIRCON DISSOLUTION
EXPERIMENT

Figure 19. SEM photograph of Tanzanian zircon from a 21 day, 250° C batch dissolution experiment. An Na, Si, Zr, precipitate has been confirmed by EDS analysis. Zircon grain in center is highly corroded on all surfaces with deep dissolution crevices parallel of crystallographic axis.

**EDS SPECTRUM OF PRECIPITATE FROM
21 BATCH REACTION AT 250°**

Energy Range: 0 - 20 keV 10 eV/ch
Preset: Live Time 120 Seconds
Real Time: 134.17 Sec. Live Time: 120.00 Sec.
12% Deadtime 1679 Counts/Second
Acquisition date: 13-Aug-91 Acquisition time: 10:58:15
Cfs 10K Lsc

Figure 20. EDS spectrum of a Na, Zr, Si, precipitate from 21 day NaCl saturated Tanzanian dissolution batch reaction experiment at 250° C. Note the difference in intensity for the Si and Zr peaks of the precipitate and zircon from figure 12.

PRECIPITATE FROM 2% HNO_3 FLOW REACTION EXPERIMENT

Figure 21. SEM photograph of Tanzanian zircon from the 2% HNO_3 stirred flow reaction. Note the iron oxide precipitate from the dissolution of Hastelloy tubing entering the dissolution vessel. Precipitate has cemented two Tanzanian zircon grains together and appears to grow from the smooth cleavage surface. The near left face of front grain has undergone dissolution.

DISSOLUTION EFFECTS OF ZIRCON FROM
2 % HNO_3 FLOW REACTION EXPERIMENT

Figure 22. Close-up SEM photograph of Tanzanian zircon from figure 21. The mottled surface is the result of dissolution effects. Compare mottled surface to figure 13 of unreacted zircon.

Table 4. Zr and Si concentrations in 3.1N HCl solution as a function of time. Data are shown in Figure 23.

3.1NHCl Batch Reaction Experiment

Sample	Time hours	Si micromoles	Zr micromoles
AHCl	48	3.47	1.44
BHCl	96	3.31	1.81
CHCl	168	4.09	1.85
DHCl	192	5.95	4.34
EHCl	312	4.88	2.52

coexist under normal solution conditions, but under equilibrium with high silica in solution the relative amounts of each phase should be investigated. At 25° C figure 8 indicates that zircon will be less soluble than baddelyite in solutions with pH<3. Based on the thermodynamic data of Naumov (1974) and the calculations of Tole 1982, Tole's interpretation seems quit adequate for describing the basic processes of solution chemistry involving zircon dissolution at pH>3. Tole's interpretation suggests that upon ZrSiO_4 dissolution(Eq 1), baddeleyite will precipitate once Zr reaches .06ppb(Eq 2). Zircon will continue to dissolve till H_4SiO_4 reaches 1.0ppb when zircon will begin to precipitate(Eq 1). Baddelyite could be a surface reaction product in zircon dissolution producing an armoring effect. Microfractures and alpha damage tracks related to radioactive decay could be sealed and the net dissolution to the zircon would be reduced. Depending on the kinetic rate of crystallization, zircon could crystallize at a faster rate than baddeleyite when both minerals are saturated and competing for $\text{Zr}(\text{OH})_4$. In highly acidic solutions(pH<3), baddelyite should not be considered a stable phase. At a pH of 0.8, ZrO^2 in HCl should be highly soluble, and if no complex Zr chlorides precipitate Zr concentrations in solution could reach 1 Mole/liter at saturation(Figure 4). A review in Erlank et al (1978) provides Zr contents of common natural waters, ocean .026ppb, lake water 2.61ppb, Saratoga spring water 255ppb. The concentrations of Zr in natural waters is above the thermodynamic saturation level for both zircon and baddeleyite. It is likely that based on the thermodynamic evidence most Zr analysis should be suspect. At this time the thermodynamic calculations would also be open to reinterpretation. Tole predicted a baddeleyite saturation at 25° C when the activity of $\text{Zr}(\text{OH})_4 = 10^{-9.168}$ were as Baes and Mesmer calculate 10^{-12} (.062ppb vs .09ppt). Figure 23 compile the available data on zircon dissolution concentrations together with data from silica and theoretical saturations for zircon, baddelyite and silica at 25° C. Figure 23 indicates that zircon stabilty even when metamict is greater than silica at temperatures below 300° C, but it appears

Figure 23. Known zircon dissolution data is plotted for solvent concentration of Zr or Si versus time. Data includes Bouyoucos (1921); Degenhardt (1957); Ewing et al., (1982); Tole (1982); quartz solubility from Walther & Helgeson (1977), ocean water Zr concentration Brewer (1975); and present study. All data plots below quartz saturation data for a equivalent temperature except for Bouyoucos (1921) whose zircon material integrity is unknown.

that over time silica saturation could be the controlling mechanism limiting zircon dissolution. There is not enough available thermodynamic data to constrain Zr in solution at higher temperatures. The actual solubility of zircon versus baddelyite is unknown. It is clear from hydrolysis activity diagrams that the mechanisms for baddelyite and zircon dissolution are pH controlled.

APPLICATION OF DATA TO ZIRCON STABILITY

Studies that have examined the stability of zircon, test the stability in conditions which may be unrealistic in terms of a natural analog. The stability of crystalline zircon as a waste host can be increased under any thermal condition if amorphous ZrO_2 phases or zirconium hydroxides are incorporated into the waste. The less stable phases will dissolve at a higher rate and saturate the solution in $Zr(OH)_4$ before the waste host phase can be effected. The dissolution of preferred material would need to be designed in such a way as to not create porous barrier material. The diffusion of the actinide elements out of the waste host is of primary concern, yet under zirconium saturated conditions U and Th may remain relatively immobile as absorbed by precipitating zircon or baddelyite in ZrO_2 saturated conditions. Low flow rates can be modeled as infiltration of undersaturated groundwater into radioactive waste disposal sites. Under constant seepage conditions steady state leach rate should occur. Our mixed flow reaction test on zircon solubility may be the best approach available to test zircon as a radioactive waste barrier. As saturation concentrations are approached the kinetic rate of dissolution is greatly reduced. In natural environment this high level of saturation may not be reached due to replenishment of the local groundwater supply. With extremely under-saturated fluids, kinetic rates of dissolution would be relatively high compared to kinetic rates of dissolution at saturated conditions. Mixed flow reaction experiments are able to maintain

undersaturated fluid compositions while monitoring dissolution effects due to large volumes of flux. Experiments underway in our laboratory are continuing to investigate these complex relationships.

References

- Baes, C.F.Jr., Mesmer, R.E., 1976, The hydrolysis of cations, John Wiley & Sons, Inc., New York, 489pp.
- Baas Becking LGM, Kaplin, I.R., Moore, D., 1960, Limits of the natural environments in terms of pH and oxidation-reduction potential. *J Geol* v 68 p.243-284.
- Berner, R.A., 1978, Rate control of mineral dissolution under earth surface conditions: *Am. Jour. Sci.*, v.278, p.1235-1252.
- Bouyoucos, G.J., 1921, Rate and extent of solubility of minerals and rocks under different treatments and conditions: Michigan Agricultural College Experiment Station, Technical Bulletin No. 50, 32pp.
- Brewer, P.G., 1975: Minor elements in sea water. In: Riley, J. D., Skirrow, G. (eds): *Chemical Oceanography*. (2nd.) Vol. I London : Academic Press
- Brookins, D.G., 1984, Geochemical aspects of radioactive waste disposal. Springer, Berlin, Heidelberg New York Tokyo , 347 pp.
- Brookins D.G., 1988, Eh-pH Diagrams for geochemistry, Springer, Berlin, Heidelberg, New York, Tokyo , 176 pp.
- Burns, J.H., Ellison, R.D., Levy, H.A., : The crystal structure of $\text{Na}_7\text{Zr}_6\text{F}_{31}$. *Acta Cryst. B* 24, p230.
- Casey, W.H., Westrich, H.R., Holdren, G.R., 1991, Dissolution rates of plagioclase at pH = 2 and 3: *Am. Min.*, v. 76, 211-217.
- Degenhardt, H., 1957: Untersuchungen zur geochemischen Verteilung des Zirkoniums in der Lithosphäre. *Geochem. Cosmochim. Acta.*, v. 11, p 279.
- Drever, J.I., 1982, The geochemistry of natural waters, Prentice Hall. Englewood Cliffs, 437pp.
- Erlank, A.J., 1978, Zirconium in: *Handbook of geochemistry*, v II-4. Springer, Berlin, Heidelberg, New York, Tokyo , ref 40B-O.
- Ewing, R.C., Haaker, R.F., Werner, L., Leachability of zircon as a function of alpha dose: *Scientific basis for radioactive waste management- V*, v.11, p.389-397.
- Fujimaki, H., 1986, Partition coefficients for Hf, Zr, and REE between zircon, apatite, and liquid. *Contr. Min. Pet.*, v. 94, p. 42-45.
- Krauskopf, K.B., 1979, *Introduction to Geochemistry*: New York, McGraw-Hill, 617 pp.
- Headley, T.J., Arnold, G.W., Northrup, C.J.M., 1982, Dose-dependence of Pb-ion implantation damage in zirconolite, Hollandite, and zircon: *Scientific basis for radioactive waste management- V*, v.11, p.379-388.
- Hill, C.G., Jr., 1977, *An introduction to Chemical Engineering Kinetics & Reactor Design*: New York, John Wiley & Sons, 594pp.
- Langmuir, D., 1971, The geochemistry of some carbonate ground

- waters in central Pennsylvania: *Geochim. et Cosmochim. Acta*, v. 35, p. 1023-1046.
- Ludwig, K.R., 1990, PBDat for MS-DOS: a computer program for IBM-PC compatibles for processing Pb, U, Th isotope data, USGS open file report 88-542.
- Maurice, O.D., 1949, Transport and deposition of the non-sulphide vein minerals. v. zirconium minerals.
- Norstrom, D.K., 1991, measurement of negative pH values and high metal concentrations in extremely acidic mine waters from Iron Mountain, California, GSA abstracts 1991 annual meeting.
- Norstrom, D.K., Munoz, J.L., *Geochemical Thermodynamics*, Benjamin/Cummings Pub. Co., Inc. Menlo Park, 477pp.
- Tole, M.P., 1982, Factors controlling the kinetics of silicate water interaction. Ph.D. Thesis, The Pennsylvania State University 220 pp.
- Tole, M.P., 1985, The kinetics of dissolution of zircon (ZrSiO_4): *Geochim. Cosmochim. Acta.*, v. 49, 453-458.
- Walther J.V., Helgeson, H.C., 1977, Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressures and temperatures. *Am. Mineral.* v 68 p.731-741.
- Watson, B.E., Harrison M.T., 1983, Zircon saturation revisited: temperature and composition effects in a variety of crustal magma types. *Earth and Planetary Science Letters*, v.64 p. 295-304.

TABLE OF THERMODYNAMIC DATA
FOR ZIRCON DISSOLUTION REACTIONS

SPECIES	G°f kcal/mole	REFERENCE
$\text{Zr}^{4+}_{(\text{aq})}$	-125.35	Naumov, 1974
	-141.0	Latimer, 1952
	-142.0	Garrels & Christ, 1965
$\text{Zr}(\text{OH})^{3+}$	-182.1	Naumov, 1974
$\text{Zr}(\text{OH})_2^{2+}$	-238.4	Naumov, 1974
$\text{Zr}(\text{OH})_3^+$	-294.5	Naumov, 1974
$\text{Zr}(\text{OH})_4^{0(aq)}$	-350.1	Naumov, 1974
$\text{Zr}(\text{OH})_{4(c)}$	-370.1	Garrels & Christ, 1965
$\text{Zr}(\text{OH})_5^-$	-394.86	Cal. from k_d value of Beas & Mesmer, 1976
HZrO_3^-	-287.7	Latimer, 1952
$\text{ZrO}_{2(c)}$	-249.7	Robie et al., 1979
$\text{ZrSiO}_{4(c)}$	-458.62	Robie et al., 1979
$\text{SiO}_{2(c)}$	-204.7	Weast et al., 1986
$\text{SiO}_{2(am)}$	-203.3	Weast et al., 1986
H_4SiO_4^0	-312.66	Lindsay, 1979
H_3SiO_4^-	-295.53	Brookins, 1988
	-299.5	Woods & Garrels, 1987
	-299.1	Drever, 1982
$\text{H}_2\text{SiO}_4^{2-}$	-283.1	Drever, 1982
$\text{H}_2\text{O}_{(l)}$	-56.684	Woods and Garrels, 1987

SYNTHETIC ZIRCONS: MORPHOLOGY AND COMPOSITION

INTRODUCTION

Zircons crystals (ZrSiO_4) have been synthesized in an effort to produce a high purity starting material for hydrothermal solubility experiments. The synthetic zircon will be used to determine zircon dissolution rates and to test for solubility differences that may result from cation substitutions in the zircon structure. Similarly, the solubility of zircons containing radioactive cations but having essentially no radiation damage will be determined. Pure synthetic zircon as well as hafnium, thorium, uranium, cerium, and dysprosium-phosphorus doped synthetic zircon have been produced. A lithium tungstate flux method similar to that used by Wayne (1989) has been utilized with minor variations in preparation procedure and run durations.

PROCEDURE

Zircons were synthesized in platinum crucibles at 1atm by a simple lithium tungstate flux method. The platinum crucibles and covers were cleaned by being immersed in a beaker filled with 5N NaOH, and placed in an ultrasonic cleaner until all visible foreign material was removed. The crucibles and covers were then rinsed with deionized water and placed in a bath of 3N HCl. This bath was also placed in an ultrasonic cleaner for one to two hours. Once clean, the crucibles were rinsed with deionized water and dried. This procedure was also used to remove fused run products from the crucibles.

Synthetic zircon charges were prepared by weighing equal molar fractions of high purity SiO_2 and ZrO_2 powders. These powders were placed in clean glass sample bottles and a Li_2WO_4 - WO_3 flux was added to the silicon and zirconium oxide powders. The molar proportion of flux to Si and Zr oxides was approximately 10:1. The molar quantity

of dopant added to the doped charges was compensated by an equivalent reduction in the quantity of Si and/or Zr in the charge. All of the chemicals used in this procedure were weighed to within $\pm .1$ mg of the reported weights (table 2) on a Mettler balance (model # H31). The powder mixtures were homogenized by vigorous shaking for 2 to 3 minutes. After mixing the charges were incrementally added to crucibles and fused over a Bunsen burner to avoid overflow that may occur as trapped air and volatiles escape during heating. A complete listing of chemical specifications and charge weights are provided in tables 1 and 2 respectively.

Chemical	Brand Name	Batch#/ Lot #	Purity
ZrO ₂	Aldrich	EM01711CM	99.99%
	Johnson Matthey	S20122	99.9%
SiO ₂	Apache Chemicals Inc.	L2096	99.99%
	Johnson Matthey	C31G	99.995%
Li ₂ WO ₄	Alfa Products	092784	98%
	Johnson Matthey	19985	99.9%
WO ₃	Alfa Products	041085	99.7%
	Johnson Matthey	S94725	99%
HfO ₂	Apache Chemicals Inc.	11167	99.99%
ThO ₂	Johnson Matthey	B28A25	99.99%
UO ₃	Johnson Matthey	K12A13	99.9%
CeO ₂	Apache Chemicals Inc.	07074	99.9%
Dy ₂ O ₃	Apache Chemicals Inc.	D0612D	99.9%
CaHPO ₄	Fisher Scientific Co.	752207	99.95%

Table 1. Chemicals used in zircon synthesis and purity specifications

Once fused the charges were placed into a Blue M Carborundum-rod furnace (model RB-2090A-1). The furnace was brought up to a temperature of 1300°C in 2 1/2 hours. This temperature was maintained for 100 hours after which the temperature was reduced linearly to 1000°C over a period of 300 hours. At the end of the 300 hour cooling period power to the furnace was terminated and the charges were allowed to cool to room temperature inside the furnace (usually within 4 hours). The temperature of the furnace was monitored by a Pt - Pt⁹⁰Rh¹⁰ thermocouple attached to a digital display (Omega). The temperature, run time, and cooling rate of the furnace were controlled by a programmable temperature control

system (Omega 'Digicator'). The accuracy of the Omega controller is dictated by the accuracy of the thermocouple which is accepted to be $\pm 10^{\circ}\text{C}$.

After the charges were removed from the crucible (see above) all crystalline phases and remaining flux were poured into a bath of 5N NaOH which was placed in an ultrasonic cleaner. Within half a day all remaining flux was either dissolved or in suspension and could be poured off. The remaining crystalline phases were rinsed in deionized water, then rinsed in dilute HCl, rinsed repeatedly in deionized water again, and dried with acetone.

Run #	ZrO2	SiO2	Li2WO4	WO3	dopant A	dopant B
A1	0.2700g	0.2734g	15.7047g	13.9140g		
A2	1.2195g	0.5998g	52.3504g	46.3761g		
A3	1.2203g	0.6011g	26.1751g	23.1871g		
A4	1.2200g	0.6008g	26.1749g	23.1883g		
A5	1.2103g	0.5955g	26.2502g	23.2190g		
A6	0.4062g	0.2003g	08.7249g	07.7275g		
A7	0.2440g	0.1200g	05.2350g	04.6351g		
A8	1.2200g	0.6002g	26.1747g	23.1882g		
A9	0.4067g	0.2000g	08.7250g	07.7249g		
A10	1.2199g	0.6004g	26.1750g	23.1855g		
A11	0.4080g	0.2019g	08.7258g	07.7298g		
A12	1.2200g	0.6011g	26.1763g	23.1854g		
A13	1.2200g	0.6009g	26.1758g	23.1887g		
A14	1.2200g	0.6003g	26.1738g	23.1781g		
HfO2						
C1	0.4943g	0.2438g	10.4760g	09.2700g	0.0124g	
C2	0.2465g	0.1217g	05.2385g	04.6353g	0.0061g	
C3	0.2472g	0.1213g	05.2375g	04.6413g	0.0061g	
C4	0.2468g	0.1221g	05.2387g	04.6395g	0.0064g	
UO3						
D1	0.4928g	0.2465g	10.8288g	9.5051g	0.0270g	
D2	0.4938g	0.2471g	10.7293g	9.4928g	0.0180g	
D3	0.4835g	0.2484g	10.7321g	9.5077g	0.0270g	
D4	0.4924g	0.2445g	10.7348g	9.5005g	0.0300g	
ThO2						
E1	0.5040g	0.2433g	10.4619g	09.2743g	0.0578g	
E2	0.4937g	0.2435g	10.4639g	09.2728g	0.0578g	
CeO2						
F1	0.2468g	0.1212g	05.2334g	04.6400g	0.0176g	
F2	0.2468g	0.1215g	05.2332g	04.6384g	0.0173g	
Dy2O3 CaHPO4						
I1	0.2499g	0.1241g	05.2705g	04.6788g	0.1546g	0.3353g
I2	0.5003g	0.2490g	10.5420g	09.3569g	0.3091g	0.6709g

Table 2. Synthetic zircon run numbers and charge weights

RESULTS

Twenty eight synthetic zircon charges have been completed. The presence of synthetic zircon in the run products of the charges was confirmed by petrographic examination and compositional determinations using a HNU Model 5000 X-ray spectrometer (EDS).

Of the twenty eight synthetic zircon charges fourteen are undoped or "pure" charges. Of these, only two charges (A1, A2) did not yield zircon due to low concentrations of silicon and/or zirconium oxides (table 2). Synthetic zircons from the twelve successful charges are euhedral, generally colorless and ranged from .12mm to 2mm in size. A percentage of zircons from all pure, Hf, U, and Th doped charges have a yellow-brown discoloration but are identical to the colorless zircons in all other respects (**Fig.1A**). Wayne (1989) observed inclusions within larger zircons produced by the $\text{LiWO}_4\text{-WO}_3$ flux method. Wayne (1989) also observed a surface dusting of an unknown residue. Both of these features have also been observed here. Analysis with the EDS showed that the surface residue on one pure synthetic zircon is 50 atomic% Si and 50 atomic% Zr. Since the EDS does not analyse for O this residue is probably zircon as well. Growth zoning in many of the larger zircons has also been observed (**Fig. 1B**).

CRYSTAL MORPHOLOGY

The habit or morphology of a crystalline substance results from the interaction of crystal structure, chemical composition, environment of formation, and surface energy effects. Therefore, careful consideration of crystal morphology is invaluable for characterizing the physical properties of a crystalline substance.

Undoped Zircon:

The Crystal habit of the pure synthetic zircons is represented by a gradation of morphologies between two end member (**fig. 2A,2B**). At all size fractions ($>590\mu\text{m}$; $<590\mu\text{m}$ - $>250\mu\text{m}$; $<250\mu\text{m}$) the dominant crystal morphology is a tabular form that could easily be mistaken for a monoclinic crystal form. This morphology is a distorted tetragonal

Figure 1

A

B

Fig. 1 A) Hf doped zircon with faintly discolored center B) undoped zircon possessing a distorted (101) dipyrarnidal morphology; note concentric growth zones

Figure 2

Fig. 2 End member morphologies of pure and Hf doped synthetic zircon a) distorted (110) dipyrmaid b) (100) prism with pyramidal terminations.

dipyramid produced by a (101) face that is highly exaggerated at the expense of the other pyramidal faces. The second distinct crystal morphology is a stubby (100) prism with simple pyramidal terminations. More complex forms are present but these are generally minor variations of one end member morphology or transitional forms between end members. For example, a commonly observed morphology is a (100) prism with pyramidal terminations that have exaggerated (101) faces reminiscent of the distorted (101) dipyramids. Random intergrowths of crystals and crystal truncated due to nucleation on the crucible surface are rare.

Hf Doped Zircon:

All four hafnium doped charges produced zircon. EDS analyses confirmed that Hf is present in the synthetic zircon. The morphology, size range, and color of the Hf doped zircons are essentially the same as pure zircons (**Fig. 3A,3B**).

Th Doped Zircon:

Two thorium doped charges produced colorless zircons of similar shape and size to the pure synthetic zircons (**Fig. 4A,4B**). Preliminary EDS analyses confirm the presence of Th and surprisingly show the presence of W in the synthetic zircon. Back scatter imaging shows that W is concentrated in irregular blotchy zones within Th doped crystals (**Fig. 4C**). In zones of high concentration, W is present in excess of 2% atomic. These zones also have high Th concentrations (> 1.5% atomic). The depleted zones have no detectable W and less than 1/2% atomic Th.

U Doped Zircon:

Four uranium doped charges have been completed. These charges produced the same stubby (100) prisms and distorted (101) dipyramids that characterize zircon crystals in the pure, Hf, and Th doped charges. Discolored zircons were observed in the products of all runs. The presence of U in the synthetic zircon has not yet been confirmed.

REE Doped Zircon:

To date four rare earth element (REE) doped charges have been completed. Two of

Figure 3

Fig. 3 two morphologies of Hf doped synthetic zircon **A)** (100) prisms; note crystal truncated due to nucleation on crucible surface
B) distorted (101) dipyramid

Figure 4

A

└── .5mm

B

└── .2mm

Fig. 4 Th doped zircon **A)** distorted (101) dipyrmaid **B)** perfect tetragonal dipyrmaid **C)** Back scatter SEM image showing Th and W zoning, Bright white areas are high in W and Th, darker areas are less concentrated in Th and have W below EDS detection limit, black areas are graphite paint

these charges were doped with the light REE cerium and two were doped with the heavy REE dysprosium. The cerium doped charges produced zircons with same color and size range as the undoped charges but slightly different morphologies (**Fig. 5A**). Although the distorted (101) dipramids and the stubby (100) prisms are the most common morphologies, random intergrowths of zircons are more frequent in Ce doped charges than in the undoped charges. One of the two synthetic zircons analyzed with the EDS did not show the presence of Ce nor did back scatter imaging show any zoning. However, a second crystal from the same charge did show W zoning reminiscent of the Th doped zircons (**Fig. 5B**). Only the zones with high W concentration (1% atomic) had Ce (.2% atomic) present in concentration great enough to be detected by the EDS.

The dysprosium doped charges were also doped with phosphorus to produce a coupled cation substitution in the zircon structure. Both Dy-P doped charges produced zircons that range in size from .1mm to 1mm and have very distinctive morphologies. The dominant morphology of the Dy-P doped zircons is a well formed acicular (100) prisms with pyramidal terminations. These crystals occur mainly as radiating aggregates of crystals (**Fig.6 and 7A**). Within a single aggregate the length to width ratio of different crystals may vary from 3 to greater than 20. A less common morphology consists of small (.1mm) well formed (100) prisms that are randomly intergrown (**Fig. 7B**). The length to width ratio of the crystals in these aggregates are a relatively uniform 4-5. Analyses with the EDS confirmed the presence of Dy in both zircon morphologies with the zircon of the acicular radiating bundles containing over 3.5% atomic Dy and the zircon of the randomly oriented bundles having less than 1% atomic Dy. P concentration could not be determined with the HNU EDS (see discussion).

Accessory Phases:

Two crystalline phases in addition to zircon have formed in all charges (**Fig. 8**). Both phases have densities well below that of zircon, are anhedral to subhedral, and are rarely above 250 μ m in size. Optical examination and analysis with the EDS suggest that the

Figure 5

A

0.2mm

Fig.5 Ce doped zircon A) distorted (101) dipyrarnid note intergrown crystal at bottom left, striations on crystal surface B) back scatter SEM image showing W and Ce zoning; bright areas have relatively high W and Ce concentrations, darker area Ce and W are below EDS detection limit

Figure 6

Fig. 6. Morphology of dysprosium-phosphorus doped zircon

Figure 7

A

B

Fig. 7 Dy-P doped zircon morphologies A) radiating acicular (100) prisms B) *left* radiating (100) prisms; *right* randomly intergrown (100) prisms

Figure 8

Fig.8 SEM photograph of accessory silicate phases; anhedral crystals are cristobalite, crystals with blocky morphology are lithium disilicate

phases observed here are cristobalite and lithium disilicate. Since these phases are both silicates it can be concluded that some percentage of the zirconium oxide in the charges is not being incorporated into zircon. This may result from the kinetics of zircon growth or zirconium solubility in the flux. It should be noted that the accessory phases examined with the EDS did contain up to 5% atomic Zr, but this only accounts for a portion of the excess Zr.

DISCUSSION

In the run products of the pure charges and the Th, U, and Hf doped charges a few discolored zircons (yellow-brown) were observed. The discoloration of these zircons did not occur in a systematic way. No charge was completely devoid of discolored zircons nor were any charges dominated by discolored crystals. However, these zircons do tend to be greater than .5mm in size and have a stubby prismatic morphology (**fig. 1A**). EDS studies could not identify any contaminants in the discolored crystals. Although W contamination does occur (see above) it is unlikely that this element is responsible for the observed coloration, due to the fact that zircons containing W in excess of .5 wt% are colorless. This coloration is probably due to contamination of these zircons by trace (i.e. ppm) amounts of a transition metal (Nassau 1978). What effect this contamination has on the size and morphology of the synthetic zircons is unclear since large size and prismatic morphology are by no means restricted to discolored zircon nor are all discolored zircons large and prismatic.

All of the successful synthetic zircon runs with the exception of the Dy-P doped charges produced crystals with a distorted (101) dipyramidal morphology. It has been well documented that the morphology of zircon is controlled by many factors including temperature, melt composition, elemental contaminants, and rate of crystallization (Pupin 1980). Because distorted (101) dipyramids were common in Hf, Th, U, and Ce doped zircons as well as undoped zircons elemental contamination can be ruled out as the major

cause for the distorted crystal morphology. It is probable that a combination of a high melt temperature, an artificial growth medium, and rapid growth rate contributed to the production of this unusual crystal morphology. This hypothesis is supported by the observation that when a cooled charge is removed from the furnace the dominant (101) face is often oriented parallel to the solidified surface.

Different orientations of the zircon unit cell have differing bond strengths and surface energies. Because crystal morphology is a macroscopic expression of internal structure nucleation on one crystal face may be energetically "easier" than nucleation on another (Klein and Hurlbutt 1985). As the crystal faces on which nucleation is most easily accomplished build outward the surface area of the less stable faces increases due to concentric deposition of material on the surrounding crystal faces. If this process is taken to an extreme the result could be the distorted (101) dipyrramids observed here.

Thorium and tungsten zoning was observed in synthetic zircon crystals produced in the Th doped runs. If the W and Th detected by the EDS are part of the zircon crystal structure they must occupy the triangular dodecahedral site normally occupied by Zr (ionic radius .79 Å). The large ionic radii of W ($W^{6+}=.62\text{ Å}$, $W^{4+}=.70\text{ Å}$) and Th (1.02 Å) preclude them from substituting into the site occupied by the much smaller Si (.42 Å) (Pauling 1960). A 1:1 substitution of Th for Zr is not precluded by charge imbalance. Both cations have a 4+ valence state. W can also have a 4+ valence but the W added to the charges here is in the oxidized 6+ valence state. Possible inclusions of tungsten oxide (WO_6) or of thorite ($ThSiO_4$ which is isostructural with zircon, Speer 1980) can not be ruled out without further analyses.

The ratio of a cation ionic radius to the ionic radius of the anions that surround it, is termed the 'ionic radius ratio'. The ionic radius ratio strongly influences the number of anions that can be coordinated with a cation in a stable crystal structure. The ionic radius ratio of W to O is 0.44. This is well below the stability range for the 8 fold coordination of O around Zr in the zircon structure (Klein and Hurlbutt 1985). Therefore a cation

substitution of W for Zr is not likely. However, crystal lattice distortions produced by large cations, such as Th, substituting in the zircon crystal structure may cause enough change in coordination geometry to make W substitution less energetically unfavorable. This may explain the sympathetic relationship of Th and W in zoned crystals. W and Ce in a zoned Ce doped zircon display a similar sympathetic relationship.

The relatively unsuccessful cerium doping of synthetic zircon is difficult to explain. Cerium has two valence states 3^+ and 4^+ . $\text{Ce}(4^+)$ has an ionic radius of $94 \text{ \AA}$ and $\text{Ce}(3^+)$ has an ionic radius of $1.07 \text{ \AA}$ (Pauling 1960). The dopant used for these experiments was in the oxidized state (CeO_2) and should have been readily incorporated into the zircon structure. Given the chemical constituents of the zircon charges (ZrO_2 , SiO_2 , CeO_2 , WO_3 , and Li_2WO_4) it is clear that a reducing reaction is very unlikely. The ionic radius of $\text{Ce}(4^+)$ is larger than $\text{Zr}(4^+)$ and may have inhibited its substitution for Zr, but not to the point of almost complete exclusion. As already noted, $\text{Th}(4^+)$ with an ionic radius even greater than Ce, was incorporated into zircon in amounts great enough to be detected with the EDS.

Dysprosium has a smaller ionic radius ($.92 \text{ \AA}$) than cerium but only has a 3^+ valence state (Pauling 1960). To compensate for the charge imbalance that would result from $\text{Dy}(3^+)$ doping of zircon $\text{P}(5^+)$ was added as a second dopant. The process by which the Dy and P are incorporated into the zircon structure is a coupled substitution. For this coupled substitution the Dy (3^+) ion occupies the triangular dodecahedral site normally occupied by the $\text{Zr}(4^+)$ ion. To compensate for the charge difference a $\text{P}(5^+)$ ion occupies the tetrahedral site normally occupied by a $\text{Si}(4^+)$ ion thus maintaining overall electrical neutrality.

Although EDS analysis demonstrated that Dy doping was clearly successful an inherent problem with HNU EDS system emerges when analyzing for P in zircon. Phosphorus and

zirconium have emission spectra that overlap to a great extent. So when an emission spectrum is analyzed for P any Zr present will be reported as P by the software of the HNU system . Similarly if the emission spectra is analyzed for all elements but P any of the P present will be reported as Zr. Despite this limitation the success of the Dy doping and the consistently low ϵ' values for the analyses of doped zircon are strong indications that P doping was successful.

SUMMARY

Sufficient quantities of pure and doped synthetic zircon is now available to begin hydrothermal solubility studies (**Table 3**). The zircon to be used for dissolution studies has been carefully examined and characterized to insure the consistency of the starting

Dopant	Size	Fraction	Weight
undoped	>30	mesh	2.59g
	<30, >60	mesh	0.21g
Hf doped	>30	mesh	0.52g
Th doped	>30	mesh	0.34g
U doped	>30	mesh	0.39g
Ce doped	all		?
Dy-P doped	all		?

Table 3. Quantities of synthetic zircon produced to date; smaller size fractions of Hf, Th, and U doped zircon have not yet been separated from accessory silicates and amount to less than 50 mg for all dopants; Ce and Dy-P doped zircons have not been separated due to the small quantities of run product (<.25g uncleaned)

materials. Because composition, surface energy, and crystal structure have a considerable influence on both crystal morphology and solubility the morphologies of the synthetic zircons have been examined in detail. These solubility studies will aid in assessing the possibility of using zircon as a host for or a barrier around radioactive waste.

REFERENCES

- Klein, C., Hurlbut, C.S. Jr., 1985, *Manual of Mineralogy after James D. Dana*, John Wiley & Sons, New York, 596 pp.
- Nassau, K., 1978, The Origins of Color in Minerals, *American Mineralogist*, 63: 219-229.
- Pauling, L., 1960, *The Nature of the Chemical Bond*, Third Edition, Cornell University Press, Ithica, 644 pp.
- Speer, J.A., 1980, Zircon, in *Reviews in Mineralogy: Orthosilicates*, Ribbe P.H. ed., Mineralogical Society of America., Washington D.C.
- Wayne, D. 1989, Synthetic Zircons: Crystal Form and Composition, *in Zircons and Fluids: An Investigation With Applications For Radioactive Waste Disposal*, Sinha, A.K., Hewitt, D.A., Ribbe, P.H., Wayne, D., Virginia Polytechnic Institute and State University, Blacksburg, Va., Progress Report for U.S. Dept. of Energy.

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