1 of 1

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

**PROGRESS REPORT ON
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. In this report we present preliminary data on the nature and rate of the solution process involving <600,000 year-old zircons being affected by natural fluids in geyser fields of Yellowstone National Park. We also summarize our continuing activity by including in this report articles that have been published or are in press in refereed journals.

Introduction

Polyphase crystalline waste forms, such as the various proposed Synroc assemblages (e.g., Ringwood et al., 1979; 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, 1991). 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. (1984). 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.

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 reactivity of zircon in a hydrothermal environment.

Using the unpolished surfaces we have measured elemental abundances for zircons within, as well as outside geyser fields in Yellowstone National Park. However, no significant differences can be detected, and if either selective depletion or gain of ZrO_2 and SiO_2 and other elements have occurred, microprobe techniques cannot measure these differences.

Response of Zircons to Fluids in Natural Hydrothermal Systems

As part of our ongoing assessment of the stability of zircon in various hydrothermal environments, this preliminary report provides information on zircons in geyser fields. The Yellowstone National Park area is underlain by both Archean age (>2700 m.y.) and very young (<600,000 years) volcanic tuffs and flows of felsic composition. The area is also dominated by hydrothermal activity—a number of rock types act as hosts for the location of hot springs. As part of our research, we are in the process of studying zircons with variable uranium contents within rocks of various ages that have been extensively attacked by hot fluids. This environment provides an unique opportunity to evaluate the response of zircons to a hot fluid over a time period of several tens of thousands of years, and presents an unique opportunity to test the ability of zircon to retain uranium and lead over time intervals envisioned for repository sites.

Preliminary sampling of the young felsic tuffs within a hot spring area (Beryl Springs) and outside the hydrothermal zone has been completed. Zircons extracted from the altered and fresh tuffs are shown in Figure 1. There is a hint of corrosion of the hydrothermally altered zircons, and in this report we provide preliminary microprobe data on (a) chemical changes (alteration) induced by the hot fluids and (b) evidence for

Figure 1. SEM images of zircons extracted from the Lava Creek tuff in Yellowstone National Park. The photograph on the left is of a zircon from a relatively fresh tuff sample, while the one on the right is of a zircon from a portion of the same tuff unit that has been extensively altered by the hydrothermal activity at Beryl Springs. Evidence of hydrothermal interaction with these "young" (<1.0 m.y.) zircons is not manifest as surface features. Our research program will take advantage of this natural hydrothermal environment to more carefully assess the chemical, isotopic and crystal structural response of zircon to near-surface hydrothermal conditions. Microprobe data were acquired from unpolished surfaces of such crystals, as we are interested in variations in surface compositions caused by fluids.

development of surface corrosion features. If we can demonstrate that zircons of varying ages (older ones still to be collected from Archean rocks exposed to hydrothermal activity, e.g., near Trudeau, Montana and Norris, Montana) have acted as relatively stable minerals over tens of thousands of years, then ZrSiO_4 must be considered as a form for RAD waste repository sites.

The analytical data for zircons recovered from both the fresh and hydrothermally altered tuffs is given in Table 1. Although we have a microprobe analytical program specifically designed for zircon analyses, the apparent surface chemistries are not measurably different. We have chosen to utilize unpolished surfaces for compositional studies to permit us to gather information on incongruent versus congruent dissolution processes (e.g., Sinha et al., 1991).

The average element chemistries of the two types of zircons show no significant differences (Table 1), but there is some evidence that Th, Yh and U are higher on the surfaces of the altered zircons. Because of the difficulties in measurements of trace concentrations using microprobe methods, we are not able to more formally highlight significant differences.

We propose to pursue surface analytical schemes using ICP-MS techniques with laser systems, if timely access to such instruments can be acquired at other institutions.

Table 1. Microprobe analyses of fresh and altered zircons from Yellowstone National Park.

Oxide	10 analyses of zircon standard			20 analyses of unaltered zircon			3 analyses of altered zircon					
	Concen.	Std. Dev.	Cations	Concen.	Std. Dev.	Cations	Concen.	Std. Dev.	Cations			
P ₂ O ₅	0.069	0.02752	P	0.00190	0.607	0.94321	P	0.01695	0.813	0.74592	P	0.02233
SiO ₂	32.785	0.20985	Si	1.01020	31.976	1.92684	Si	1.00400	31.841	1.29402	Si	1.00767
ZrO ₂	65.614	0.24785	Zr	0.98590	61.170	4.31009	Zr	0.93615	60.111	3.08830	Zr	0.92733
HfO ₂	0.025	0.01969	Hf	0.00000	0.981	0.11645	Hf	0.00880	0.988	0.05168	Hf	0.00900
ThO ₂	0.028	0.04088	Th	0.00010	0.061	0.05632	Th	0.00030	0.121	0.01929	Th	0.00100
Al ₂ O ₃	0.008	0.00560	Al	0.00010	0.253	0.27009	Al	0.00930	0.049	0.02976	Al	0.00200
Y ₂ O ₃	0.005	0.01280	Y	0.00010	1.200	1.63547	Y -	0.02080	1.412	1.15401	Y	0.02433
Er ₂ O ₃	0.024	0.05105	Er	0.00020	0.168	0.22057	Er	0.00165	0.190	0.17211	Er	0.00167
Yb ₂ O ₃	0.042	0.06102	Yb	0.00040	0.182	0.18447	Yb	0.00275	0.328	0.13219	Yb	0.00300
U ₂ O ₃	0.022	0.02601	U	0.00000	0.037	0.5436	U	0.00025	0.079	0.05076	U	0.00033
CaO	0.008	0.01156	Ca	0.00030	0.033	0.04342	Ca	0.00115	0.058	0.05543	Ca	0.00633
FeO	0.015	0.01721	Fe	0.00040	0.262	0.56020	Fe	0.00695	0.243	0.24923	Fe	0.00633

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