Project Title:

**Zircons and Fluids: An Experimental Investigation with Applications for
Radioactive Waste Storage**

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Final Report

The project objective was to develop a relationship between the stability of zircons (both natural and synthetic) with variable levels of radiation damage to fluids because of the clear relationship between enhanced solubility (leachability) and α - damage, our research was able to quantify this process. We also analyzed the mechanics of fractures induced due to both radiation and temperature enhanced stresses. Both objective were successfully carried out, and although details are available in progress reports and referred publications, a brief summary is presented here.

1. The study of physical properties including fractures produced by volume expansion and associated with amorphitization.

Natural zircons from different localities show a considerable range of physical properties such as density, refractive index and birefringence that may be correlated to internal nuclear refraction induced structural damage. Our research program generated fundamental new data on dynamic elastic constants through ultrasonic wave velocity measurements of single crystals obtained from the Smithsonian Museum. We demonstrated that both longitudinal and transverse wave velocities showed measurable decrease with increasing radiation damage. Utilizing 5.07% maximum volume change associated with the development of a totally metamict zircon, we were able to develop a relationship between stress and increase in volume within zircons. Our calculations, utilizing a spherical model for isotropic media and 5.07% volume change predicted a pressure gradient of 450 megapascals between metamict and non-metamict domains. These physical models predict that zircon as a nuclear waste form with "uneven" loading of radionuclides is liable to suffer self-induced fractures.

2. Solubility of zircon - low temperature

The measurements of the solubility constants for zircons is hampered by the low abundance of zirconium (<ppb) in various analytical fluids, and the uncertain nature of zirconium aqueous species. Assuming congruent dissolution of zircon, dissolution activation energy of 12-8 kcal/mole has been reported (Tole,1985). We completed batch dissolution experiments, where zirconium concentrations were detectable in the analytical fluids, but the data was inconclusive regarding the role of baddelyite formation to zircon

dissolution. Our calculated dissolution activation energy of ~30 kcal/mole suggests that surface detachment processes were likely to be the dominant rate limiting mechanism. Through careful compilation of known zircon dissolution experiments, together with theoretical saturations for zircon, baddelyite and silica at 25°C, we can suggest that zircon stability, even when metamict, is greater than silica. However, it appears that over time silica saturation could be the controlling mechanism limiting zircon dissolution. In summary, our current understanding of zircon solubility suggests:

- (a) enhanced solubility related to alpha damage
- (b) possible incongruent dissolution ($\text{pH} = -0.5$, ZrO_2 soluble field) where Zr:Si atomic ratio
- (c) calculated value of dissolution activation energy ($\Delta E_a \cong 30$ kcal)
- (d) surface detachment reactions are likely to be rate limiting

3. High pressure - temperature (4-6kb, 400-600°C) hydrothermal studies

We conducted numerous experiments utilizing both 2MNaCl and 2% HNO_3 solutions to derive a relationship between loss of lead versus uranium from both metamict and non-metamict zircons. We clearly demonstrated that the severity of uranium loss, and, to a lesser extent lead loss varied with solution composition. Scanning electron microscopy of the run products revealed a range of corrosion related surface features, which suggests that some of the observed trends in Pb and U loss must be attributed to zircon dissolution. Backscattered electron imaging of the run products suggested that partial homogenization of chemical zoning patterns occurred during the experiments and may be the result of annealing of lattice defects.

4. Stability of zircons in high fluid/rock environments

We have conducted extensive studies of the physical, chemical and isotopic studies of zircons in high fluid (shear zone) environments. We have been able to demonstrate the enhanced solubility of zircon with varying levels of alpha damage to both temperature and fluid composition. New growth of zircon during metamorphism suggests mobility of zirconium, and the dissolution and reprecipitation of zircon is controlled by $\text{H}_2\text{O}/\text{Hf}$ ratio of the fluid. Our data suggest that if zircon is to be used as a host for nuclear waste, the fluorine activity of the groundwater must be a criterion in site selection.

5. Production of synthetic zircon

We successfully conducted experiments for producing synthetic zircons doped with trace elements as analogs for nuclear waste. Although no solubility experiments were performed, our results demonstrate distinct growth patterns for zircons as a function of element substitution. It is likely that the energetics of dissolution may vary across different crystal faces (energy of formation) and should be considered as a factor in utilization of zircon as a host for nuclear waste of varying compositions.

Product Output

Journal Articles and Reports:

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