# Alteration of zircon in alkaline fluids: Nature and experiment

D.E. HARLOV[1*], A. LEWERENTZ[2], A. SCHERSTEN[2]

[1]GeoForschungsZentrum, Telegrafenberg, 14473 Potsdam, Germany, dharlov@gfz-potsdam.de (* presenting author)
[2]Dept Earth Sciences, Lund University, 22362 Lund, Sweden, alexander.lewerentz@gmail.com, anders.schersten@geol.lu.se

Natural alteration of zircon can take place either via partial dissolution coupled with partial overgrowth or via fluid-aided coupled dissolution-reprecipitation or both processes in tandem [1][2]. Coupled dissolution-reprecipitation results in the zircon being partially to totally replaced by compositionally re-equilibrated zircon, a new mineral phase, or both.

In this study, fragments (50 to 200 µm) from an inclusion-free, relatively non-metamict euhedral zircon (nepheline syenite pegmatite, Seiland magmatic province, northern Norway) were experimentally reacted in 20 mg batches with Ca-bearing fluids (1 mg $Ca(OH)_2$ + 5 mg $H_2O$) plus 5 mg ($ThO_2$ + $ThSiO_2$ + $SiO_2$) in sealed Pt capsules at 900 °C and 1000 MPa for 6 to 11 days (piston cylinder press, $CaF_2$ setup, cylindrical graphite oven). In the experiment, the fluid reacted with the zircon. This took the form of partial replacement of the zircon with compositionally altered zircon via coupled dissolution-reprecipitation. The reacted zircon is characterized by a sharp compositional boundary between the altered and original zircon. The altered zircon generally contains a micro-porosity. Inclusions of baddelyite ($ZrO_2$) are seen outlining the reaction front between the altered and unaltered zircon. SIMS analysis of the altered zircon indicates that it is strongly enriched in Th + Si, heavily depleted in U, and heavily to moderately depleted in (Y+REE). In all experiments radiogenic $^{206}$Pb (3 to 5 ppm in the unaltered zircon) is strongly depleted in the altered zircon. Hf concentrations in the altered zircon retain the same approximate value as in the original zircon. The results from these experiments indicate that zircon can be compositionally altered via Ca-bearing fluids via coupled dissolution-reprecipitation processes under high-grade conditions and that their internal geochronometer can be reset due to the massive loss of U and radiogenic Pb and the additon of Th.

The baddelyite-zircon textures from these experiments replicate similar, highly-localized zircon-baddelyite textures seen in albitised, 2.9 to 2.7 Ga, amphibolite- and granulite-facies granitoid rocks from SW Greenland [3]. Here Ca was released into the fluid during the albitisation of plagioclase. Baddelyite should not be stable in the presence of $SiO_2$ (present in both the experiments and in the granitoid rocks) but rather react with $SiO_2$ to form zircon. However, if sufficient Ca is present in the fluid, it appears to complex with the $SiO_2$ as $CaSiO_3$ thereby lowering the $SiO_2$ activity such that baddelyite is stable with co-existing zircon and quartz. The experiments also demonstrated that, with sufficiently high enough concentrations of $SiO_2$ in the fluid, not all of the $SiO_2$ will complex with Ca allowing for the activity of $SiO_2$ to remain at 1. In this case baddelyite did not form in or with the altered zircon.

[1] Geisler et al., 2007 **Elements** 3, 43-50 [2] Putnis, 2009 **Rev Mineral Geochem**, vol 70, 87-124. [3] Windley and Garde (2009) Earth Sci Rev 93, 1-30

---

# Multiple sulfur isotope model of temperature dependent isotope fraction in *Archaeoglobus fulgidus*

BRIAN HARMS[1*], KRISTEN MITCHELL[2], KIRSTEN HABICHT[3], JOOST HOEK[1], JAMES FARQUHAR[1]

[1]Department of Geology and ESSIC, University of Maryland, College Park, Maryland, USA
(*Correspondence: bharms@umd.edu)
[2]Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Ontario, Canada
[3]Institute of Biology, Nordic Center for Earth Evolution (NordCEE), University of Southern Denmark, Odense, Denmark

Dissimilatory sulfate reduction (DSR) has a central role in the global sulfur cycle. Understanding how environmental factors and physiological variables influence DSR-mediated sulfur isotope fractionation is therefore crucial for interpting the sedimentary sulfide record. The hyperthermophile *Archaeoglobus fulgidus* grows over a wide range of temperature conditions (54°-92°C [1]), making it an ideal test subject for investigating how aspects of the DSR pathway respond to temperature extremes. A previous study of *A. fulgidus* [1] found that fractionations between sulfate and sulfide were greatest at intermediate temperatures. An inverse correlation between cell specific sulfate reduction rate and fractionation was found in the intermediate temperature range, but this correlation broke down at the extreme hot and cold limits of growth. A potential solution to a flow network model [2] was proposed, one in which sulfate exchange across the cell membrane controlled fractionation at high and low temperatures, and internal sulfur transformations were the dominant influence at intermediate temperatures [1].

Here we present multiple sulfur isotope results from the same culture experiments in [1]. Our calculated flow parameters ($f_3$ and $f_5$) give a markedly different trend from that predicted in [1], and our observed $\Delta^{33}$S values also implicate a DSR flow network in which large fractionations (as in e.g. [3]) are permitted. The mismatch between predictions and results suggests a different physiological response to temperature change than expected. Several possibilities are investigated. Following the framework of [4], we also investigate solutions in which the fractionation factor associated with the reduction of sulfite to sulfide is not a fixed quantity.

[1] Mitchell et al. (2009) *Environ Microbiol* **11**, 2998-3006.
[2] Canfield et al. (2006) *Geochim, Cosmochim. Acta* **70** 548-561.
[3] Brunner and Bernasconi (2005) *Geochim. Cosmochim. Acta* **69** 4759 – 4771. [4] Bradley et al. (2011) *Geobiology* **9** 446-457.