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Formation of hydrothermal zircon by replacement of metamict $ZrSiO_4$

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Hydrothermal zircon may form by precipitation from hydrothermal fluids to form new zircon or by replacement of preexisting zircon. In both cases a spatial gradient in zircon solubility resulting from gradients in pressure, temperature, or fluid composition is required. During replacement Zr from zircon dissolution under high solubility conditions is transported to conditions of low solubility where zircon precipitates. Without these spatial gradients in solubility there is no driving force for coupled dissolution/precipitation of crystalline zircon.

Alternatively, hydrothermal zircon may form by replacement of amorphous (metamict) $ZrSiO_4$ without spatial gradients in zircon solubility or transport. Metamict $ZrSiO_4$ has a higher Gibbs Free Energy and higher aqueous solubility than crystalline $ZrSiO_4$. As a result, dissolution of metamict $ZrSiO_4$ in hydrothermal fluids results in supersaturation of crystalline zircon. The coupled dissolution of metamict $ZrSiO_4$ and precipitation of crystalline zircon causes the replacement of the former by the latter. Because metamict $ZrSiO_4$ is less dense than zircon, replacement will create an assemblage of zircon and pores, which would explain the commonly observed porosity in hydrothermal zircon.

We performed cold-seal pressure vessel experiments at 600-800°C and 0.2 GPa using zircon with varying degrees of crystallinity and either H_2O, 1m NaF, or 1m HCl fluid compositions. Results show that crystalline zircon is insoluble and not prone to recrystallization, while metamict $ZrSiO_4$ is partially or completely replaced by hydrothermal zircon. Thermodynamic modeling using the Supcrt database shows that hydrolysis of NaF can create fluid with high pH, and that $ZrSiO_4$ solubility is enhanced at high pH, which results in more rapid replacement of metamict zircon. Run products show zircon with pores like those observed in hydrothermal zircon reported in the literature. We propose that in cases where $ZrSiO_4$ is present in a rock that aqueous fluids infiltrate, metamict $ZrSiO_4$ will be replaced to form hydrothermal zircon, but crystalline zircon will not recrystallize.