Zircon uses baddeleyite nanoparticles as fundamental building blocks

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Numerous experiments have been performed in the past to determine the crystallization temperature of zircon from silicate melts (Watson & Harrison 1983; Boehnke et al. 2013; Gervasoni et al. 2016; Borisov & Aranovich 2019; Marxer & Ulmer 2019). In designing those experiments, the implicit assumption was that zircon is a primary magmatic phase that crystallizes directly from the melt. Factors that determine the saturation of zircon are the Zr^{4+} (or ZrO_2) content of the melt, its silica activity ($aSiO_2$), and the cation ratio M = (Na + K + 2Ca) / (AI * Si) (Watson & Harrison 1983). The latter parameter roughly reflects the polymerization degree of a melt.

Our experiments give a somewhat different picture. We performed experiments with a phonolite composition that is modeled on a ne-normative pumice of the Laacher See, Eifel. The composition contains 60.6 SiO_2, 20.1 Al_2O_3, 2.5 FeO and CaO each, MgO 0.5, and total alkalies of 12.5 (all in wt.%). It is just corundum-normative. To prevent the introduction of zircon seeds, a synthetic aliquot of oxides and carbonates (Ca, alkalies) was synthesized. After the sample was sintered at 950 °C and CO_2 was expelled, Zr was added as $ZrCl_2O$ ICP standard solution. The mixture was then equilibrated at 1200 °C and 300 MPa in a piston cylinder press for 2 to 24 hours. After completion of the experiments, the Zr contents of the glasses were 1300 ± 160 ppm (average ± 1σ of 20 EPMA analyses).

Liquidus phases at 1200 °C were silicate melt and corundum (crn). Zircon did not crystallize because the composition is undersaturated with respect to zircon by factor of 10 (Fig. 1). Four Focussed Ion Beam (FIB) sections cut from experimental glasses showed that all charges crystallized at 1200 °C crystalline (and possibly amorphous) ZrO_2 nanophases (baddeleyite) (Fig. 2). The smallest and earliest ZrO_2 nanoparticles are found as inclusions in crn. These nanophases are as small as 3 to 4 nm and comprise perhaps 500 unit cells. They are so small because their growth was arrested after they were trapped by crn.
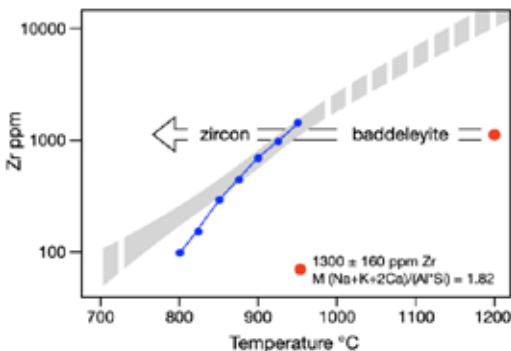

Figure 1. Starting mix with 1300 ± 160 ppm Zr - red circle. Grey - region in Zr-temperature space where magmatic zircon is stabilised (Watson & Harrison 1983; Boehnke et al. 2013; Gervasoni et al. 2016; Borisov & Aranovich, 2019). Blue symbols - zircon satutation experiments by Marxer & Ulmer (2019). For our composition zircon is expected to become stable at ~ 900 °C.

The results imply that zircon uses nanometer-sized ZrO_2 particles as building blocks when it nucleates from silicate melt. Zircon is stabilized by the reaction ZrO_2 (nanoparticle) + SiO_2 (melt) $\rightarrow$ $ZrSiO_4$ (crystal). We think that in nature this reaction is a solution-precipitation reaction. Direct crystallization of zircon from Zr^{4+} and SiO_2, if it indeed occurs, may be the exception rather than the rule. We assume that the ZrO_2 nanoparticles illustrated in Fig. 2 are stable, that they nucleated in local ΔG minima.

Many igneous rocks undersaturated with zircon may carry baddeleyite (e.g., Heaman & LeCheminant 1993). However, because baddeleyite tends to be extremely small, its presence is easily overlooked.
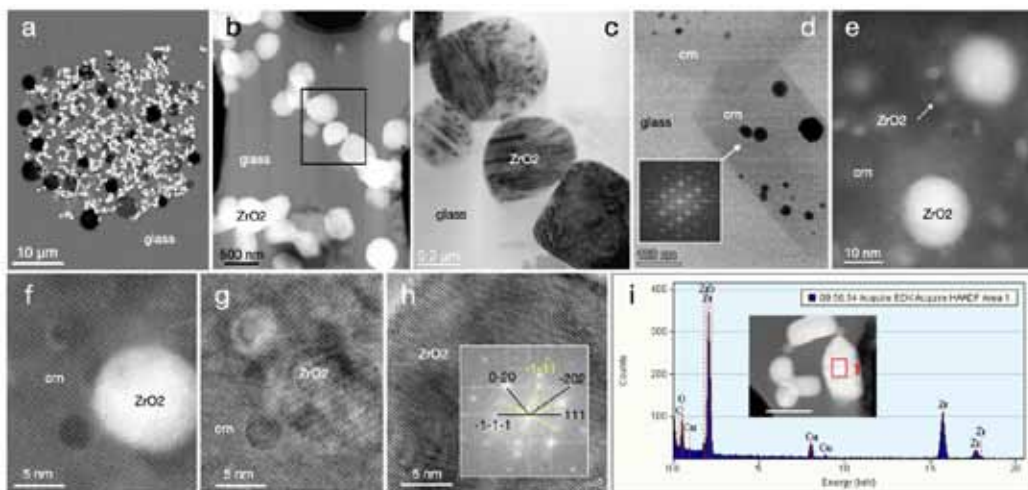

Fig. 2. ZrO_2 nanoparticles. (a) Baddeleyite (bdy) cluster in glass, after 10 hours at 1200 °C, in (b) TEM image at higher magnification; note tendency of bdy to attach and align to clusters and chains. (c) Brightfield (BF) image of twinned bdy in glass. (d) ZrO_2 nanoparticles trapped by liquidus corundum (crn). (e) HAADF image of ZrO_2 nanoparticles < 4 nm, in crn. (f) and (g) HAADF images, ZrO_2 nanoparticles in crn. (h) FFT of HREM, ZrO_2 in crn (crn in yellow). (i) Energy-dispersive spectrum to illustrate composition of bdy.

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