Russian Geology and Geophysics © 2019, V.S. Sobolev IGM, Siberian Branch of the RAS
Vol. 60, No. 4, pp. 447–450, 2019 DOI:10.15372/RGG2019043
Geologiya i Geofizika

Stability of Zircon in the System MgO–SiO_2–H_2O at 2.5 GPa

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Received 13 June 2018; received in revised form 12 October 2018; accepted 8 November 2018

Abstract—We report preliminary experimental data on the interaction of zircon with the peridotitic assemblage olivine + serpentine at 2.5 GPa and 1400 °C. In these conditions, zircon is unstable and decomposes with the formation of baddeleyite. Therefore, it is unlikely that zircon could survive in ultramafic rocks for a long time in the presence of a fluid phase at high temperatures. Thus, rigorous constraints on boundary conditions are required for the use of zircon in the dating of high-temperature geologic processes.

Keywords: zircon, baddeleyite, peridotitic mineral assemblage, high pressure, high temperature

INTRODUCTION

Timing the events of magmatism, metamorphism and related metasomatism is a key point of geodynamic modeling. Zircon is a mineral most broadly used for dating high-temperature processes. There is a wealth of published evidence on the formation conditions of zircon and zircon age determination. Judging by its REE patterns (Rubatto and Herman, 2003), zircon in eclogite may form during metamorphism in the presence of an aqueous fluid or during partial melting of felsic gneisses (Liu et al., 2004). Different zones in zircon may record the history of its host rocks, which is especially important for studies of metamorphic complexes.

Nevertheless, there are certain limitations in the use of zircon for dating, especially when mineral reactions responsible for the formation of natural zircon remain unclear. Zircon is assumed to be stable in post-growth processes and to decompose into baddeleyite and quartz in dry conditions at temperatures above 1676 ºC (Godovikov, 1975); decomposition is also possible at lower temperatures in the presence of fluids (Aeyrs et al., 2012). Dating of ultramafic rocks according to the age of the hosted zircon coexisting with olivine may be poorly reliable. The problem can be clarified by studies of zircon stability under experimental conditions in which such mineral assemblages form in nature.

METHODS

The experiments were carried out on a multianvil split-sphere high-pressure apparatus. Details of the instrument and methods of pressure and temperature measurements were described previously (Chepurov et al., 1998; Zhimulev et al., 2012, 2018). The samples were a mixture of serpentine and olivine powders (50:50 in weight) compressed into cylinders with two zircon grains in the center. Serpentine was ground and powdered on a ball mill to >5 μm grain sizes. It was a natural mineral from the East Sayan ophiolites consisting of 41.53 wt.% SiO_2, 0.02 wt.% TiO_2, 0.95 wt.% Al_2O_3, 2.74 wt.% Fe_2O_3, 0.14 wt.% MnO, 42.15 wt.% MgO, 0.05 wt.% CaO, 0.30 wt.% Na_2O, 0.02 wt.% K_2O, 12.42 wt.% LOI, at a total of 100.32 wt.%. Olivine powder had a grain size of >0.25 mm. Zircon (1.5–2 mm), was a natural mineral from the Kuranakh kimberlite (Yakutsk), with a composition of 32.25 wt.% SiO_2, 64.56 wt.% ZrO_2, 1.37 wt.% HfO_2, 1.77 wt.% Nb_2O_5, at a total of 99.95 wt.% (average over 8 analyses).

The experiments were performed using MgO capsules in a pressure cell pre-dried for 10 hours at 120 °C. The assembly was kept for a while at the designed pressure and temperature and then the samples were quenched at a high pressure by current turn-off (quenching time 2–3 s). Decompression was at a rate of 0.2–0.3 GPa/min. The experimental study included two 5-hour runs at 2.5 GPa and 1400 ºC. High *PT*-parameters and pressure, as well as the presence of an aqueous fluid which accelerated reactions, were required to compensate the short run duration compared with the

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Table 1. Mineral chemistry: experimental results at 2.5 GPa and 1400 °C (normalized components)

Mineral	SiO_2	Al_2O_3	FeO	MgO	NiO	ZrO_2	HfO_2	Total, wt.%
Baddeleyite	–	–	–	–	–	98.55	1.45	100
Baddeleyite	–	–	–	–	–	98.66	1.34	100
Olivine	42.07	–	2.15	55.78	–	–	–	100
Olivine	41.68	–	3.82	54.10	0.40	–	–	100
Olivine	41.77	–	4.55	53.37	0.30	–	–	100
Olivine	41.60	–	4.18	53.85	0.37	–	–	100
Olivine	41.62	–	2.09	55.97	0.32	–	–	100
Pyroxene	57.61	2.14	1.83	38.42	–	–	–	100
Pyroxene	57.87	2.08	1.30	38.75	–	–	–	100

characteristic time of geological processes (millions of years). After the runs, the samples were cut and prepared for analysis.

RESULTS AND DISCUSSION

The process reproduced in the experiments began with decomposition of serpentine at 700 °C which led to the formation of olivine and orthopyroxene. Some part of the released water became preserved in minerals enclosed in olivine and orthopyroxene and some part passed into the fluid phase, as confirmed by gas chromatography (Chepurov et al., 2010):

$$2Mg_3(Si_2O_5)(OH)_4 \rightarrow 2Mg_2SiO_4 + 2MgSiO_3 + 4H_2O.$$

The amount of H_2O in the interstitial fluid phase was many times more than inorganic gases (Chepurov et al., 2012). Aqueous fluid released from decomposing serpentine became saturated with MgO upon interaction with olivine and the MgO capsule. During the experiments, all zircon transformed into an assemblage of baddeleyite and olivine ± pyroxene.

Figure 1 shows a zircon grain converted into a mixture of fine aggregated baddeleyite (light) and olivine (dark) grains: olivine segregations among baddeleyites. The groundmass around the zircon grain consists of olivine and some orthopyroxene, as well as minor amounts of chromite and sulfide. The samples have high Mg# (100MgO/(MgO + FeO) = 92–96) and contain 1.34–1.45 wt. % Hf (Table 1). Note that the matrix that accommodates the zircon grains underwent partial melting. Inset in Fig. 1 shows a diffuse boundary of the primary zircon grain at the contact with olivines, with newly formed baddeleyites moved slightly inward the matrix.

The conversion presumably resulted from decomposition of zircon in the presence of a MgO-bearing aqueous fluid

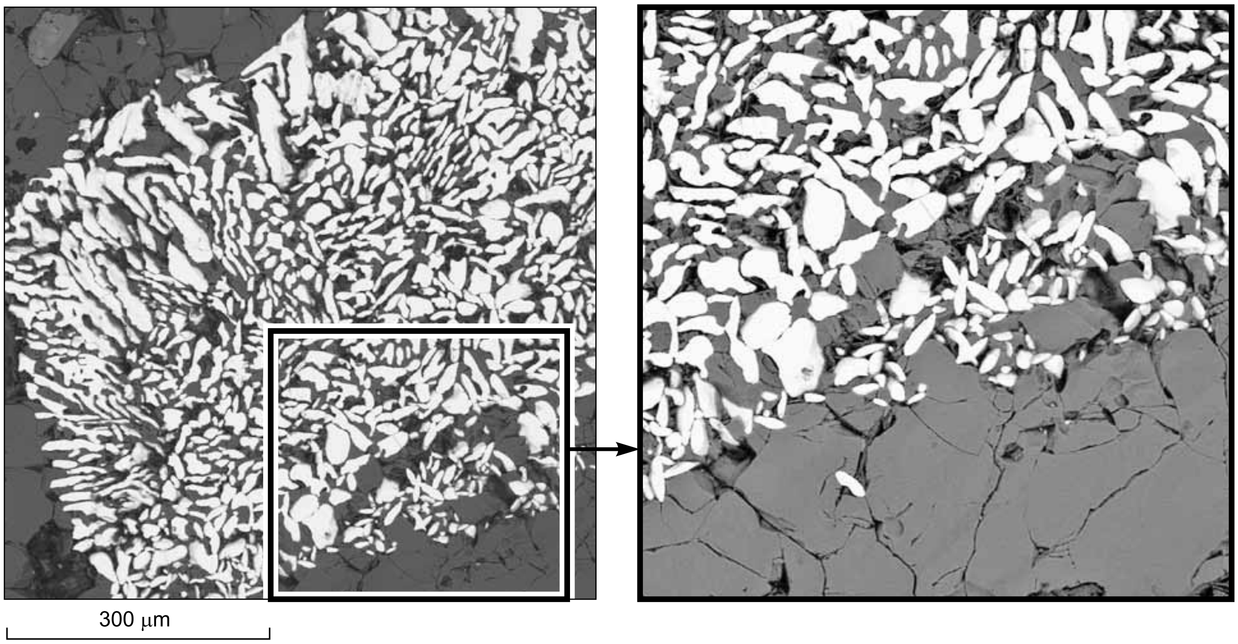

Fig. 1. Photomicrograph of the sample at 2.5 GPa and 1400 °C. Baddeleyite segregations (light) in olivine groundmass (gray). The baddeleyite domain corresponds to the contour of primary zircon.

which produced baddeleyite; then the fluid reacted with SiO_2 to produce olivine:

$$ZrSiO_4 \rightarrow ZrO_2 + SiO_2,$$

$$SiO_2 + 2MgO \rightarrow Mg_2SiO_4.$$

Other possible reactions of zircon-olivine interaction in the presence of a MgO-bearing aqueous fluid might also lead to the formation of orthopyroxene and olivine:

$$ZrSiO_4 + Mg_2SiO_4 \rightarrow ZrO_2 + 2MgSiO_3,$$

$$MgSiO_3 + MgO \rightarrow Mg_2SiO_4.$$

The stability of zircon was modeled under experimental conditions corresponding to natural settings for a peridotitic assemblage: 1400 ºC and a MgO-bearing aqueous fluid. However, zircon in nature can decompose for millions of years at lower temperatures.

Zircon was found out to be unstable in fluids undersaturated with respect to SiO_2 (Aeyrs et al., 2012; Bernini et al., 2013), as well as in carbonate systems (Rizvanova et al., 2000; Gervasoni et al., 2017). The model of Boehnke et al. (2013) is inconsistent with zircon crystallization from MORB-like mafic magmas. According to some other models, zircon may be stable even in peridotitic assemblages. For instance, Anfilogov et al. (2015) suggested that zircon can crystallize and preserve in a refractory ultramafic residue that remains after mantle basalt has molten. The latter inference based on an experimental study of a dunite-zircon assemblage at ambient pressure and temperatures from 1400 to 1550 °C in dry conditions, while baddeleyite appeared at 1400 °C, or below the melting point of dunite (1550 °C). Krasnobaev et al. (2019) presented data on zircon inclusions in plagioclase and spinel peridotite and dunite from the Nurali terrane in the Urals, but the age estimates of rocks they reported may be not very reliable.

The presence of zircon in ophiolites was attributed to interaction of metasomatic and crust-derived fluids with peridotite (Zaccarini et al., 2004; Zheng et al., 2006; Belousova et al., 2015). Nevertheless, our experiments (see above) show that zircon cannot survive in ultramafic rocks containing a fluid phase at high temperatures. In this respect, it is important to properly identify the mineral assemblage that includes zircon and to pay special attention to this subject when handling ultramafic samples. Note that zircons may preserve for a long time as inclusions in solid crystalline rocks or minerals (e.g., as crustal xenoliths in subduction zones (Robinson et al., 2015)), in the absence of fluids, but possible ways of their capture and preservation require explanation. For instance, kimberlites may bear zircons in xenoliths entrained at different depths and transported to short distances. In our case, zircons from ophiolitic peridotite may have fallen into crushed samples of younger and higher-SiO_2 veins where zircon is stable, such as 1–3 mm veins of the Nurali pyroxenite or gabbro-amphibolite.

The manuscript profited from constructive criticism of the reviewers V.S. Shatsky and A.L. Perchuk.

The study was carried out as part of basic project MIG No. 51.2 at the V.S. Sobolev Institute of Geology and Mineralogy, grant No. 0330-2016-0012.

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Editorial responsibility: V.S. Shatsky