

U-Pb ISOTOPIC SYSTEMATICS OF EXPERIMENTALLY SHOCKED BADDELEYITE. T. Niihara¹, H. Kaiden^{1,2}, K. Misawa^{1,2}, and T. Sekine³, ¹Dept. of Polar Science, The Graduate University for Advanced Studies, 1-9-10 Kaga, Itabashi, Tokyo 173-8515, Japan (niihara@nipr.ac.jp), ²Antarctic Meteorite Research Center, National Institute of Polar Research, Itabashi, Tokyo 173-8515, Japan, ³National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan.

Introduction: The age significance of isotope chronometers in shocked, but not totally molten, extraterrestrial materials is still a matter of debate [1–3]. Numerous isotopic data from different isotopic systems have been obtained for meteorites, but most meteorites with apparent shock ages do not show petrographic evidence of strong shock metamorphic overprint.

Deutsh and Schärer [4] carried out comparative isotope investigation on experimentally shocked zircon. In that case, lead isotope fractionation was not observed in experimentally shocked samples despite equilibrium shock pressures up to 59 GPa.

Baddeleyite (ZrO₂) is an important and useful mineral for U-Pb dating of lunar and Martian meteorites. ZrO₂ crystallizes in baddeleyite structure (monoclinic) under pressure of ~4 GPa and temperature of ~1000 °C [5], and transforms to a tetragonal and then to a cubic fluorite structure at high temperatures. Baddeleyite is stable at ~4 GPa in the phase diagram, and, by compression, monoclinic baddeleyite shows sequential transition to two orthorhombic phases up to 70 GPa [5].

We performed shock recovery experiments on baddeleyite at the shock pressures of 24, 34, and 47 GPa, to understand the shock effects on U-Pb isotopic systematics of baddeleyite. Here we report the results of SEM-CL observation, Raman spectroscopy, and U-Th-Pb isotope analysis of experimentally shocked baddeleyite.

Samples and Techniques: The shock recovery experiments were performed using a single stage 30 mm-bore propellant gun at the National Institute for Materials Science, Japan [6]. We used coarse-grained baddeleyite (200–250 μm in size) from Phalaborwa, South Africa, (2059.8 Ma) for a starting material. The baddeleyite is mixed with a coarse-grained terrestrial basalt sample, S690-7a, from North Kona, Hawaii [7] with a weight ratio of 1:2. The mixture was encapsulated in a cylindrical container made of SUS304 stainless steel and pressed at 29 MPa. We performed three experiments under different shock pressure conditions at 24, 34, and 47 GPa. Porosity of the samples before the shock experiments was 26–30 %.

Textures of the run products were examined by a scanning electron microscope with a cathode luminescence detector (SEM-CL; JEOL JSM-5900LV). We analyzed Raman spectra with a Micro Raman spectrometer (JASCO NRS-1000) operated with a focused

green laser beam of a wavelength of 531.91 nm and an intensity of 11 mW.

In situ U-Th-Pb isotopic analysis was carried out using a polished section with the SHRIMP II ion microprobe at National Institute of Polar Research, Japan [8]. An oxygen primary beam (O₂⁻) of ~2 nA current was focused on a spot with a diameter of ~10 μm. Standard baddeleyite samples, Phalaborwa and FC1 (1099.1 Ma) from Duluth Complex, Minnesota, and SL13 zircon were used for age references, for elemental concentrations, respectively.

Results and Discussion:

SEM-CL observation and Raman spectroscopy

A starting material, S690-7a [7], showed an interstitial texture with olivine phenocrysts (~400 μm in size) and a finer-grained matrix of pyroxene, plagioclase and glasses. Textures of the matrices of shocked samples at 24, 34, and 47 GPa did not change from those of the unshocked basalt. Olivine phenocrysts and baddeleyite grains in each shocked samples were irregularly fractured. The matrices were partly melted at the shock pressures of 34 and 47 GPa. Numerous vesicles (~10–40 μm in diameter) were observed in the 47 GPa sample.

A correlation between the brightness of CL and the shock pressures was observed (Fig. 1). We could not observe luminescence in unshocked Phalaborwa baddeleyite. Luminescence appeared at the rim of baddeleyite grains and along the fractures in the 24 GPa sample. In addition to the features, luminescence at the inner part of baddeleyite grains was weakly produced in the 34 GPa sample. In the 47 GPa sample, the whole baddeleyite grains emit luminescence.

The Raman spectra of unshocked baddeleyite include peaks at 177, 333, 477, 616, and 636 cm⁻¹ (Fig. 1). There is no measurable Raman peak shift in the 24 GPa baddeleyite sample. Raman peak shifts of 2 cm⁻¹ and 4 cm⁻¹ from unshocked baddeleyite were observed in the 34 and 47 GPa samples, respectively.

There is no evidence on phase transformation from baddeleyite to two orthorhombic phases in the Raman spectra. Similar to the result of Bouvier et al. [9], the main Raman peaks were shifted under the effect of pressure. CL images and Raman spectra are now useful tools for characterizing the shock metamorphism on baddeleyite as previously suggested for zircon [10].

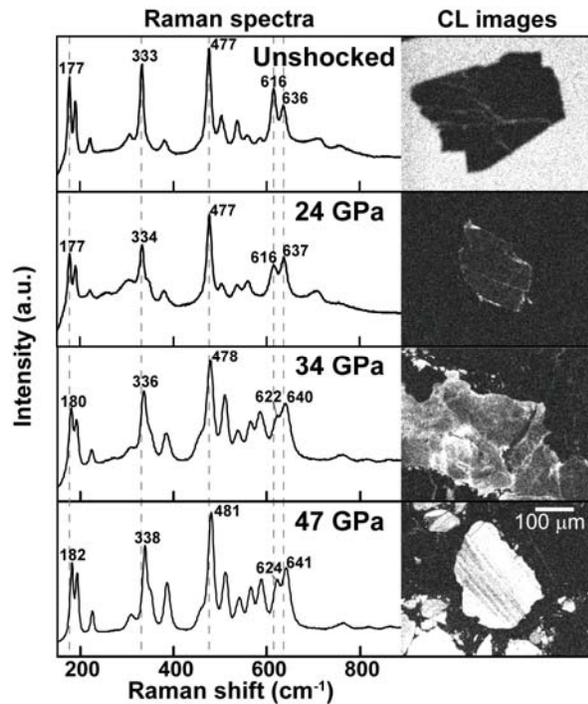


Fig. 1. Raman spectra of experimentally shocked baddeleyite. CL images are also shown.

U-Pb isotopic systematics

The U-Pb data on shocked baddeleyite along with starting baddeleyite are shown in modified concordia diagrams (Fig. 2). There is no correlation between shock pressures and degrees of discordancy. Lead loss from baddeleyite was observed for none of the experimentally shocked samples. In addition, the ^{206}Pb - ^{207}Pb ages of shocked baddeleyites are indistinguishable from those of unshocked baddeleyite within error (Fig. 3), suggesting that the shock pressures up to 47 GPa do not measurably affect U-Pb isotopic systems.

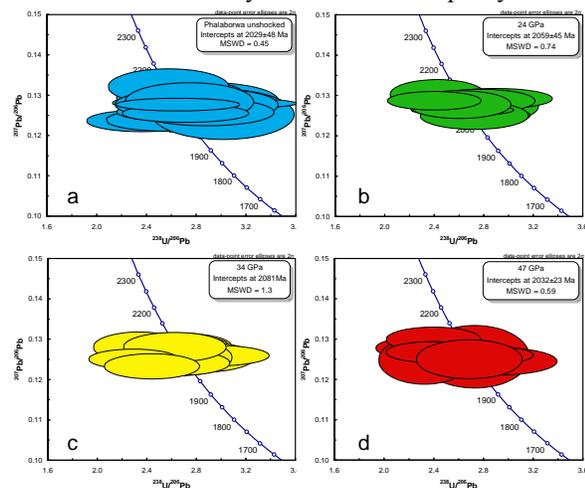


Fig. 2. Modified Tera-Wasserburg concordia diagrams for Phalaborwa baddeleyites.

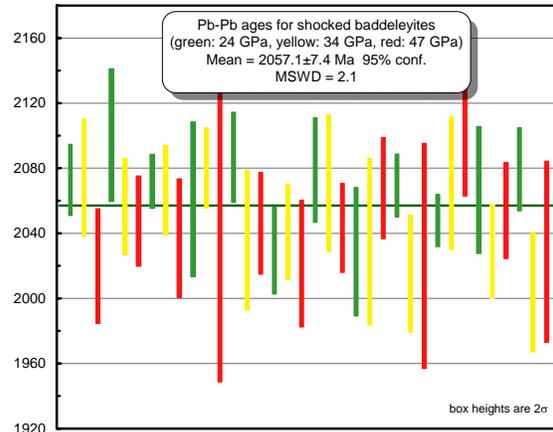


Fig. 3. The averaged ^{206}Pb - ^{207}Pb baddeleyite age of 2057 ± 7 Ma for three run products with different shock pressures is indistinguishable from the age of starting baddeleyite (2059.8 Ma).

Summary: Distinct differences in brightness of CL exist between the unshocked and the shocked samples. In Raman spectra, the peak positions of shocked baddeleyite are shifted from those of unshocked baddeleyite. These are potentially useful tools for characterizing the shock stage of baddeleyite. The data on U-Pb isotope and corresponding ages for experimentally shocked baddeleyite are indistinguishable from those of unshocked baddeleyite.

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