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Formation of ultrafine particles from impact-generated supercritical water

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Abstract

Shock-recovery experiments were performed targeting an olivine, iron, and water mixture to simulate a low-velocity ocean impact event. The maximum pressure in the sample container reached 20 GPa during the experiments. Ultrafine particles (UPs) of olivine and metal oxides were newly formed, even at pressures less than their vaporization pressure (150–200 GPa). Impedance-match and thermodynamic calculations suggest that supercritical water formed during the shock wave traversal. Such supercritical water dissolves impacted materials and precipitates UPs. Results of our experiments further suggest that many extraterrestrial objects that have impacted on oceans might have been converted to large masses of UPs and probably influenced the climate and UV shielding, especially during the late Hadean and early Archean eras.

Keywords: ultrafine particle; supercritical water; impact; ocean

1. Introduction

The Earth has undergone repeated bombardments by extraterrestrial objects since its origin. Such extraterrestrial objects might melt or vaporize along with shock heating that occurs during hypervelocity impacts [1]. Considered thermodynamically, the heat depends on increased internal energy through shock compression. Results of theoretical studies suggest that impact-induced vaporization requires extremely high pressures, e.g., 150–200 GPa for iron, and ca. 180 for dunite [2–4]. These impact pressures correspond respectively to impact velocities of about 4.9–5.9 km/s and 9.6 km/s.

On the other hand, our recent experiments have indicated the possible formation of ultrafine particles (UPs) of metallic Cu in low-velocity impact experiments under the presence of liquid water [5]. Those experiments further indicate that the formation of such UPs was probably attributable not only to vaporization of objects by shock heating but also by dissolution into supercritical water. If such were the case, extraterrestrial objects that impacted to oceans in ancient geological ages might have generated larger masses of UPs than previously supposed. However, no experimental data exist to indicate if any geological materials could have

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been converted into UPs by such a shock event. It is therefore necessary to examine whether UPs can be formed from components of common meteorites.

The most common extraterrestrial object is ordinary chondrite, which is a constituent of more than 85% of collected meteorites [6–8]. Major constituents of ordinary chondrite are olivine and iron. Therefore, we performed shock-recovery experiments targeting a mixture of olivine, iron, and water. The experimental system simulates a specific velocity (low-velocity) impact of a meteorite to the ocean in terms of a shock-induced chemical reaction.

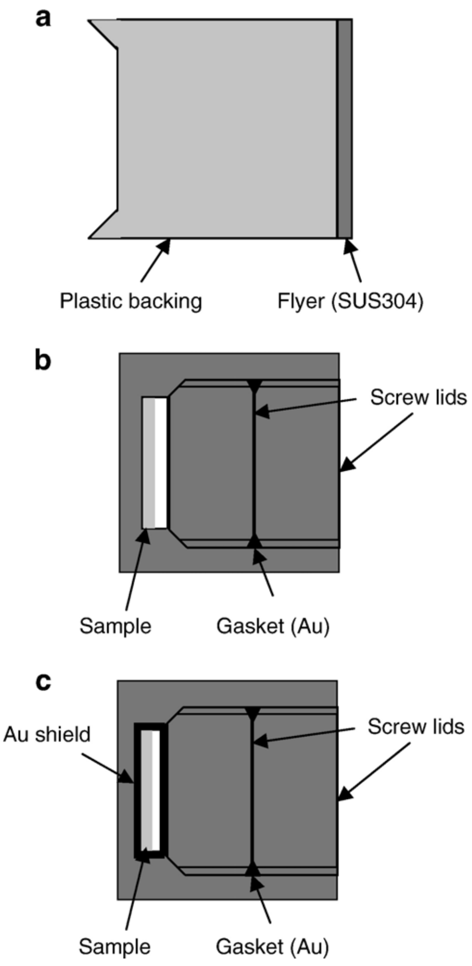

Fig. 1. Schematic illustration of the flyer and sample container used for the present study. a) Flyer with plastic backing. The flyer is a metal plate (SUS304; 29-mm diameter, 2-mm thick) with a plastic backing. b) Sample containers (SUS304; 30-mm diameter, 30-mm height) used for the experiments #1005 and #1010, having a sample cavity of 18 mm diameter and 3.5 mm depth. The sample cavity is closed with double screw lids. Samples are pasted on the inner wall. Air in the free space is not evacuated. The gold gasket was interleaved and pressed between the double screw lids. An impact aspect of the sample cavity is 3 mm thick. c) Sample containers used for #1011, #1012, and #1013. The Au shields are entirely attached to the inner wall.

2. Experimental

2.1. Shock-recovery experiment

The experiments were performed using a conventional single-stage propellant gun [5,9]. A metallic flyer plate (29-mm diameter, 2-mm thick) with a plastic backing (Fig. 1a) was accelerated and then impacted onto the sample container. The flyer velocity was measured by the travel time between a series of pick-up coils with a given distance (100 mm). Both the flyer plate and the sample container are made of SUS304 (Fe: 74%, Cr: 18% and Ni: 8%).

The sample container has a sample cavity (18-mm diameter, 3.5-mm depth) in which to place a sample (Fig. 1b). The cavity is closed using a double screw lid. Samples used for the present experiments are a mixture of water (distilled water for HPLC; Wako Pure Chemical Industries Ltd.) and natural olivine powder ($(Mg_{0.9}, Fe_{0.1})_2SiO_4$, ca. 10–100 μm grain size; San Carlos, USA) of which the chemical compositions and grain sizes are the similar to those of individual olivine grains in chondrules and the chondrite matrix. The olivine powder was adhered with water on the cavity's inner wall (Fig. 1b and c).

The experimental conditions and results are listed in Table 1. The inner surface of a metal container is known to eject small fragments of metal by the traversing shock wave. Those small amounts of metal will react with samples and behave as reductants in the impact-induced chemical reactions. Sample cavities were coated entirely by thin (0.1-mm-thick) gold shields in three runs (#1011, #1012, and #1013, also Fig. 1c) to minimize such effects.

In the case of high-velocity impacts greater than 1.14 km/s, the metal container burst because the inner pressure was greater than the SUS304 tensile strength. By conducting various pilot studies on the impact velocity and on sample weights, we found an optimum range of impact velocities, as listed in Table 1, to achieve the purposes of the present study.

2.2. Analysis and observation

Reaction products after impact were recovered from the sample cavities and lyophilized under low pressure. Portions of the recovered samples were analyzed using X-ray powder diffraction (XRD, PW3050; Philips Co.) and scanning electron microscopy (SEM, JSM-6500F; JEOL). A fraction of the sample was dispersed in ethanol

Table 1
Types of samples, impact conditions and products

Shot No.	Sample		Gold-shield	Impact		UP in products	
	Olivine (mg)	H_2O (μL)		Velocity (km/s)	Pressure (GPa)	Olivine	Hematite
#1005	151	130	–	0.97	20.4	+++	+++
#1010	50	130	–	0.91	18.9	+	+++
#1011	150	0	○	0.91	18.9	ND	+
#1012	150	130	○	0.90	18.7	+	+++
#1013	150	65	○	0.88	18.1	ND	++

Relative amounts of products are indicated by the symbol +: +++ = large amounts; ++ = small amounts; + = trace amounts; ND = not detected. The symbols – and ○ respectively indicate sample cavities with and without the gold shield.

after gentle grinding to concentrate the grains suitably for further analyses. They were then observed using transmission electron microscopy (TEM, JEM-2010; JEOL) after drying on a micro-grid. Electron diffraction (ED) and energy dispersive X-ray spectrometry of TEM (EDS-TEM) were also used for mineral identification.

3. Results

The appearance of recovered products was somewhat darkened and wetted compared to the appearance of the starting materials. Subsequent XRD analyses of the products indicated that olivine remained the major constituent in all samples after shock experiments. On the other hand, newly produced fine particles were identified through SEM and TEM observations (Fig. 2). The grain sizes of new fine products were 0.1–10 μm diameter. ED and EDS-TEM analyses indicated that the new fine particles were olivine and metal oxide crystals. Those particles were much smaller than the particles in the starting material and showed characteristic morphologies of UPs (see Section 4.1). Detailed observations using TEM also indicated that the surfaces of the *original* olivine grains were covered thinly by feather-like materials, which were most likely serpentines.

The UPs of olivine had formed clusters (Fig. 2a and b) or were found as single crystals (Fig. 2c) of less than 300 nm diameter. The composition of the ultrafine olivine was $(Mg_{0.7}, Fe_{0.3})_2SiO_4$, as determined through EDS-TEM analyses. That composition differs from that of the starting olivine, $(Mg_{0.9}, Fe_{0.1})_2SiO_4$, indicating Fe enrichment. Other UPs found in run products were hematite (Fig. 2d and e), magnesiochromite $(Mg_{0.8}, Fe_{0.2})(Cr_{1.2}, Fe_{0.8})O_4$ (Fig. 2f) and oxides of iron–chromium and nickel (unidentified minerals). The most abundant size of those UPs is some hundreds of nanometers in diameter.

Table 1 shows the relative abundance of UPs produced through a series of experiments. The UPs were found in all run products. Their amounts and mineral types depended either on water contents or the presence of the gold shield. Runs #1005 and #1010 were experiments performed without the gold shield. The UPs of olivine and hematite were most abundant in run #1005. Olivine UPs became less abundant in run #1010 when the amount of starting olivine was reduced to 50 mg.

Runs #1011, 1012 and 1013 were performed using the gold shield. Olivine UPs were not found in products of runs #1011 and 1013, for which water contents were set to zero and 65 ml respectively, suggesting that olivine UPs can not be formed in the absence of water. Only small amounts of olivine UPs were formed in runs #1012, although experimental conditions were identical to those of run #1005, except for the presence of the gold shield, which suggests that the presence of gold shield also affects to prevent the formation of olivine UPs. In the case of run #1012, the gold shield might, however, not completely be successful to prevent the olivine UPs formation.

UPs of hematite were also found in all runs. Hematite UPs became abundant when the gold shields were absent (runs #1005 and #1010; Table 1). When the gold shields were present (runs #1011, 1012 and 1013), apparent amounts of hematite UPs were correlated with amounts of water, suggesting the water-enhanced formation of hematite UPs.

4. Discussion

4.1. Supercritical water generated by impact

The state of water under the present shock conditions can be constrained as follows. The Hugoniots for water and stainless steel are known [10] and the impedance-match method and thermodynamic calculation are used [4] for pressure and temperature calculations, respectively. The calculated pressure and temperature changes

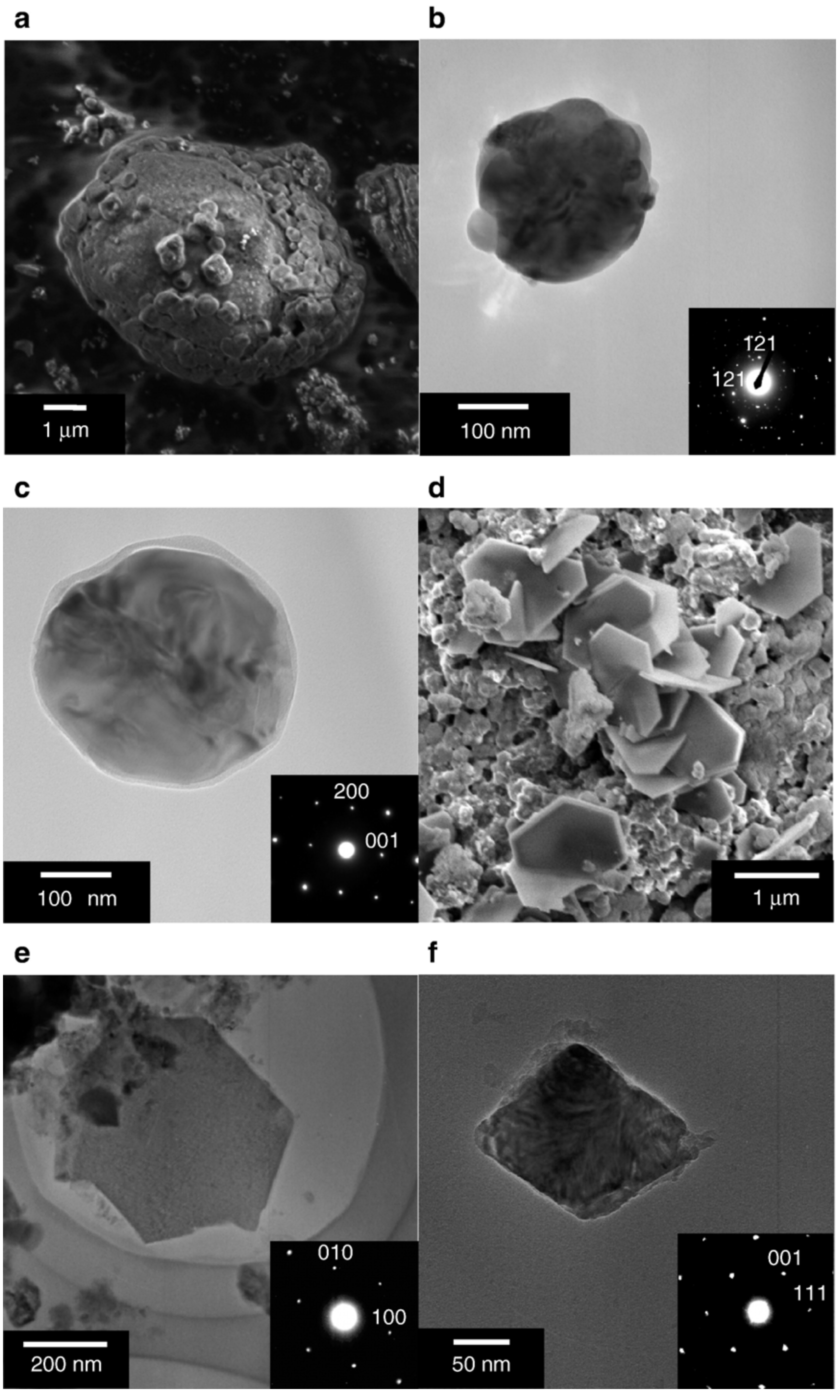

Fig. 2. Typical ultrafine particles observed in the present study. a) SEM image of polycrystalline olivine found in run #1005. Primary UPs of some tens of nanometers in diameter cohered to form a secondary particle of several micrometers in diameter. The secondary particle is spherical with somewhat faceted planes, and a smooth surface with adherent particles of ca. 300-nm diameter. b) TEM image of single-crystalline olivine from run #1005. c) TEM image of coalescent olivine from run #1005. d) SEM image of euhedral hematite from #1005. e) TEM image of euhedral hematite. f) TEM image of magnesiochromite $(Mg0.8, Fe_{0.2})(Cr_{1.2}, Fe_{0.8})O_4$ from run #1010.

of water in the container are shown schematically in Fig. 3. The estimated pressure and temperature of water are about 6 GPa and 580 K, respectively, when a flyer velocity was at about 1 km/s and a shock wave arrived at the interface between the steel container wall and water (point A in Fig. 3) [11].

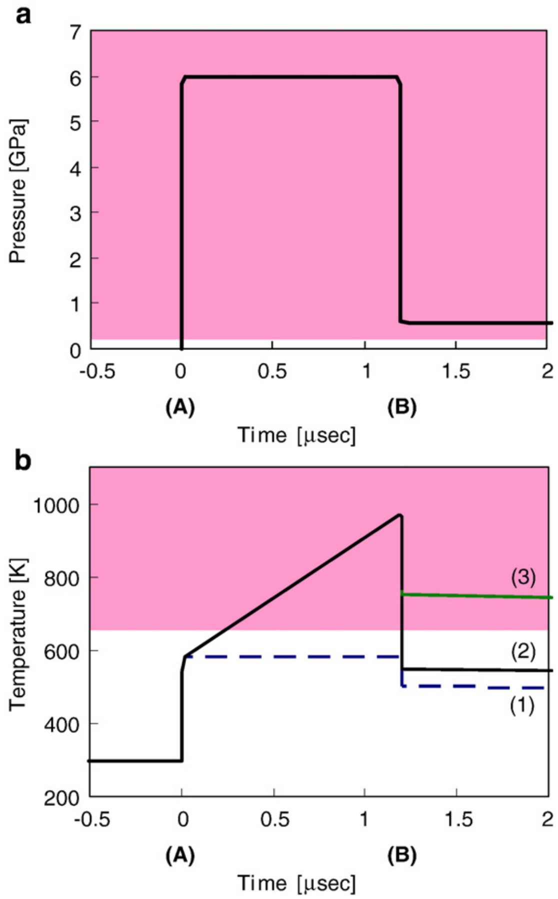

Fig. 3. Schematic diagrams of (a) pressure and (b) temperature changes in the sample cavity during the present shock-compression process. Presence of supercritical water is assumed in this calculation. Point A is the time that the shock wave arrived and B is that of the rarefaction wave. The shaded areas in both figures are the stability field of supercritical water. a) The pressure is estimated by impedance-match calculations with Hugoniots of olivine and water. The time interval between A and B was calculated as 1.2 μs from the present shock wave velocity in the water-olivine mixture (3 km/s) and the sample cavity thickness. After point B, adiabatic decay of pressure is inferred. b) The dashed line (1) shows the temperature change after impact without additional heat, as calculated thermodynamically based on Hugoniots of olivine and water. The solid line (2) shows the case in which oxidation heat is added. The solid line (3) shows the case in which the air turbulence generated additional heat and thereby changed the state of water from liquid to that of a supercritical fluid. Solid and dashed lines after point B trace cooling temperatures, which decrease far more slowly than adiabatic expansion.

The temperature of water at point A is 580 K if no heat is added to the system. We found evidence of exothermic reactions during experiments indicated by the formation of hematite (Fig. 2d and f). This evidence suggests that the temperature of point A is greater than 580 K.

As listed in Table 1, the experimental run with the gold shield (#1012 and #1013) produced fewer ultrafine particles than others. The gold shield reduced the availability of iron from the sample container wall, thereby restricting the oxidation reaction of iron with water and its exothermic heat. The oxidation reaction is expressed as

$$2\mathrm{Fe} + 3\mathrm{H_2O} = \mathrm{Fe_2O_3} + 3\mathrm{H_2},$$

with an exothermic energy of −84 kJ/mol at 600 K [12]. Considering such additional energy, the water temperature will increase by 390 K if half of the initial water reacts with iron. The actual temperature during shock compression is therefore estimated as high as 970 K. The estimated temperature and pressure suggest that the state of water under the present shock condition was that of a supercritical fluid.

After the arrival of the rarefaction wave, the pressure drops adiabatically (point B in Fig. 3), but the container itself must hold the inner pressure. The stainless steel (SUS304) container will explode if the inner pressure increases beyond its tensile strength (0.6 GPa), as observed in some shots. Assuming the tensile strength as the upper limitation of pressure and the water fluid as an ideal gas, we can estimate the temperature when the pressure was released adiabatically down to 0.6 GPa. The temperature is calculated as 550 K if no heat is added to the system. Afterward, it will take a long time to cool down to room temperature by thermal diffusion. The actual peak temperature would be much higher at points A and B because air in the sample cavity might produce turbulence and much higher temperature, as the numerical simulation suggests [13]. Therefore, the state of water immediately after the transition of rarefaction wave is also considered to be that of a supercritical fluid.

4.2. The UP formation process suggested by chemical compositions and morphologies

In general, crystals grown in a free space are surrounded entirely by euhedral facets. Those crystals have been crystallized under flotation from ions, atoms or molecules dissolved in gas or a fluid matrix. The crystals produced in the present experiments showed such characteristic morphologies. Metal particles prepared by evaporation in argon gas at low pressure are typical examples of such euhedral UPs known as *smoke particles* [14–17]. Such a vapor-condensed process is the most common process for UP formation. A high-velocity impact, which corresponds to more than 150 GPa, is necessary to vaporize projectiles when impact events occur. On the other hand, the estimated pressure and temperature conditions of the present experiments indicate that the olivine and metals did not vaporize, postulating an alternative mechanism to produce UPs. For our experiments, we inferred the interaction between solids and the supercritical water as a genetic model of the UPs.

Supercritical water is known for its high capability for dissolving components with low solubility under normal conditions [18–20]. The chemical compositions of the present UPs indicate that starting olivine and metals had once partly dissolved: it is noteworthy that the chemical composition of olivine UPs, $(Mg_{0.7}, Fe_{0.3})_2SiO_4$, is enriched in iron compared with that of the starting olivine of $(Mg_{0.9}, Fe_{0.1})_2SiO_4$. Iron enrichment is the result of the simultaneous dissolution of the starting olivine and also of the surface of the container wall into supercritical water. The chemical composition of magnesiochromite UPs, $(Mg_{0.8},Fe_{0.2})(Cr_{1.2},Fe_{0.8})O_4$, also indicates crystallization from mixed metal sources, i.e. Fe and Cr, from the stainless steel of the container and Mg from olivine (Fig. 2f).

In the present experiments, ions and atoms dissolved into supercritical water from the starting olivine and iron would soon over-saturate when the temperature and pressure decrease after impact. The drastic change of solubility by the rapid decrease of temperature necessitates their rapid crystallization as UPs. In this process, UPs can be formed without vaporization.

The present results show that water and iron-rich samples (#1005, #1010, #1011, #1012 and #1013) produced far more numerous UPs than the sample without water (#1011, Table 1), suggesting an essential role of supercritical water to form UPs. Such interpretation is also supported by recent reports of metal-oxide UPs, which were produced using the great solubility difference between supercritical fluid and liquid water [21,22]. The report indicated that the rapid decrease of pressure and temperature of supercritical fluids, which contained dissolved metal salts, resulted in UP formation of metal oxides (e.g., Fe_2O_3, NiO, and TiO_2). The products also show euhedral morphologies resembling those of the crystals produced in these experiments.

4.3. Possible formation of UPs at ocean impact

The impact magnitude scale is the major difference between laboratory experiments and natural impact events. The shock compression continues for a longer time when the projectile is large. The maximum pressure of the present experiments (ca. 20 GPa) is much lower than the theoretically expected incipient vaporization pressure (150–200 GPa). Even with such low incipient pressure, the present experiment indicates that the projectiles were dissolved easily into supercritical water and UPs were formed, which also suggests that impacts of extraterrestrial objects might have produced far larger masses of UPs if extraterrestrial objects had impacted to an ocean.

The meteorite–ocean impact event is also reported to create a post-impact plume developing in the atmosphere [23]. That post impact plume is composed of supercritical water and/or vaporized water. Our experiments suggest the possibility that UPs are ubiquitous in such a post-impact plume, which further implies that UPs spreading in the atmosphere through the post-impact plume also influenced ultraviolet (UV) shielding and climate, although quantitative estimation of such a UV shield effect and climate impact is beyond the scope of the present study.

Many previous studies suggest that intense impact events, such as Late Heavy Bombardment (LHB) of extraterrestrial objects, seem to have occurred after formation of the early oceans [24–29] and probably before the development of continents. That supposition implies that ocean impact events by extraterrestrial objects occurred more often on the early Earth compared to later geological periods. Large masses of UPs might therefore have been formed and subsequently spread into the atmosphere through the post-impact plume and finally deposited on the early ocean floor. For discussing early Archean and late Hadean surface environments, it might be necessary to consider the presence of such a large volume of UPs.

5. Conclusions

We performed shock-recovery experiments targeting the mixture of olivine, iron, and water. The experimental system simulated low-velocity impact of a meteorite to the ocean. Formation of UPs was confirmed experimentally, even for impact velocities as low as about 1 km/s. The impedance-match method and thermodynamic calculations indicated the formation of supercritical water during shock experiments. Dissolution of projectiles into such supercritical water followed by rapid crystallization is the proposed mechanism to convert projectiles into UPs without vaporization. Results of this study suggest that extraterrestrial objects that impacted oceans might have formed large amounts of UPs, especially during the late Hadean and early Archean ages.

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