

ABIOTIC O₂ PRODUCTION FROM CI-LIKE IMPACTORS DURING THE LATE HEAVY BOMBARDMENT PERIOD. K. Kurosawa¹ & H. Kuwahara², ¹Planetary Exploration Research Center, Chiba Institute of Technology (2-17-1, Tsudanuma, Narashino, Chiba 275-0016, Japan, kosuke.kurosawa@perc.it-chiba.ac.jp), ²Dept. of Complexity Sci. & Eng., Univ. of Tokyo.

Introduction: The observation of lunar craters [1] and a theoretical model [2] suggest that dynamically-excited impactors, which are referred to as “E-belt”, collide with inner planets at extremely high velocities around 3.5-4.1 Gyr ago. In the model, the impact velocity of rocky impactors to the Moon reaches 30 km/s [1, 2], which is ~2 times than previously thought [e.g., 3]. Environmental effects after such hypervelocity impacts have not been explored because of the lack of reliable thermodynamic data for silicates under the extreme conditions. In this study, we investigated the chemical composition of the final gas-phase products from shock-heated CI-like impactors after >30 km/s impacts based on recent laser shock data for silicate minerals [4, 5]. According to the new data, hypervelocity impacts at 30 km/s impacts lead to nearly complete vaporization of silicate minerals [5], suggesting that an extremely oxidized vapor plume may be generated during the late heavy bombardment (LHB) period.

Post-impact chemistry: When a hypervelocity impact occurs on a planet, both the impactor and the planetary surface suffer intense irreversible heating, resulting in the entropy gain in the shocked materials. Then, the shock-heated materials expand into an ambient space adiabatically, i.e., $dS = 0$ [7]. The peak shock temperature of silicate minerals due to >15 km/s impacts is higher than 10000 K [5]. Thus, intense gas-phase chemical reactions are driven in the expanding plume and chemical reactions are fast enough to reach a chemical equilibrium at such high temperature [e.g., 8]. As the gas cools due to adiabatic expansion, chemical reactions slow down because the rates of chemical reactions strongly depend on temperature and cease at a quenching temperature [e.g., 8]. Then, the final product gas with a quenched chemical composition is released into the atmosphere. If the expanding plume maintains thermal and chemical equilibrium through an isentropic release and all chemical reactions cease simultaneously at a quenching temperature, the final products of shock-heated materials would be controlled by two factors: the shock-induced entropy gain and the elemental abundance of the plume. Then, we are able to calculate the quenched chemical composition of the expanded plume after an isentropic release using the Gibbs free energy minimization method [6, 9-11].

Calculation procedure: We thermodynamically connected between the shocked

state and the expanded state of impact-generated plumes using the entropy matching technique [10, 11]. In general, the expanded plume is approximated well by an ideal gas/liquid/solid. We calculated the chemical equilibrium composition and entropy for the expanding plume of CI chondrites [12] with a wide range of pressure and temperature (P - T) using the Lewis code [13]. The isentropes in the P - T space as a function of impact velocity were obtained based on the Hugoniot curve on an entropy-pressure plane for forsterite [5]. For simplicity, we included major 8 elements, such as C, H, O, N, S, Mg, Si, and Fe, in the calculation. The quenching temperature T_{quench} depends on the impactor size because the cooling rate decreases as the impactor size increases. We estimated T_{quench} as a function of impactor size based on a scaling relation by [8]. Specifically, T_{quench} are ranged from 1500K to 2000 K for 0.1-1000 km impactors.

Results: Figure 1 shows the isoentropes for shock-heated CI-like impactors as a function of impact velocity on a pressure-temperature plane. The Hugoniot curve [5] and the liquid vapor phase boundary for forsterite [7] are also shown. The isoentropes gradually approaches the liquid-vapor phase boundary for forsterite as the impact velocity increases, but the isoentropes are in “the liquid side” at <40 km/s. This implies that Mg-bearing silicates condense during isentropic release even when the impact velocities of LHB impactors are higher than 30 km/s.

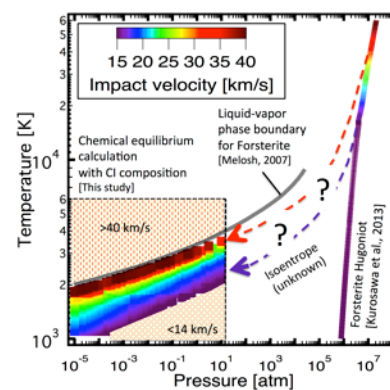


Fig. 1. The isoentropes for the expanding plume as a function of impact velocity on a P - T plane.

Figure 2 shows the quenched chemical composition after isentropic release at 1600 K as a function of impact velocity. This temperature corresponds to T_{quench} for 100 km size impactors. Note that only selected

species are shown here. The vapor fraction increases as impact velocity increases. In contrast, the molar fraction of Fe-bearing condensates, such as FeO (solid), steeply decreases with increasing velocity, whereas that of Mg-bearing condensates is nearly constant. Especially, the entire oxygen in the Fe-bearing condensates releases into the gas phase due to >35 km/s impacts. The molecular oxygen and OH radical were produced from the released oxygen even when impactors are CI-like C-rich materials. A significant amount of Fe atomic gas is also produced as the counterpart of the released oxygen. Thus, the quenched chemical composition generated by >30 km/s impacts differ significantly from the predictions by previous studies [14, 15]. Figure 3 shows the O₂ production, the mass ratio of the produced O₂ mass to the projectile mass as a function of impact velocity, T_{quench} , and P_{quench} . The O₂ production reaches 0.01 – 1 wt% of the projectile mass due to an impact of LHB impactors. Thus, the mass of abiotic O₂ production reaches 10¹³-10¹⁵ kg for LHB impactors with 10-100 km size.

Post-impact consequence: If the impactor size is larger than the atmospheric scale height of a host planet, the impact-generated plume adiabatically expands into the space [e.g., 16]. Then, the part of plume at the velocity higher than the escape velocity of the host planet escapes from the planet [e.g., 17]. The residual of the plume is ballistically re-entered into the planetary atmosphere. Thus, impact-generated Fe gas may initially react with the dense atmosphere. The amount of Fe vapor is estimated to be 10¹⁵ - 10¹⁷ kg for 10-100 km size impactor, corresponding to 200 ppm to 2 wt% of the mass of current Earth's atmosphere. A part of molecular oxygen may be released into the atmosphere for impactors of 10-100 km in diameter although the recombination fraction between released Fe and O₂ should be investigated in the future study. In addition, atmospheric heating due to re-entered solid ejecta [18] may support the delivery of produced molecular oxygen into the atmosphere because O₂ is more stable at higher temperature.

Geologic implications for Earth and Mars:

Here, we discuss the geochemical consequence in the light of the abiotic O₂ production due to >30 km/s impacts. The O₂ concentration may reach 10⁻⁵ - 10⁻³ the present atmospheric level in the Earth's atmosphere after impacts with 10-100 km size. If the released O₂ stay within the Earth's atmosphere, it may erase the signature of the mass-independent fluctuation of sulfur isotopes (MIF-S) in the geologic record [e.g., 19] for a short period of time. Thus, our scenario can be tested using the MIF-S in the impact-related Archean stratifications, such as the spherule beds [e.g., 20]. In the case for Mars, the oxygen isotope measurements of

carbonate from a Martian meteorite ALH84001 suggests that ancient Mars has an ozone layer, produced from molecular oxygen via photochemical reactions [21]. The age for ALH84001, 4.091 Gyr [22], is close to the initiation of the late heavy bombardment around 4.1 Gyr ago [2]. The dynamically-excited impactors at >30 km/s at the LHB period may contribute to the atmospheric photochemistry on the early Mars.

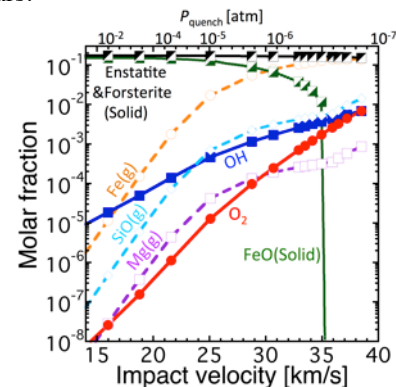


Fig. 2. The quenched molar composition at 1600 K as a function of impact velocity. The quenching pressure P_{quench} is also shown as the top X axis.

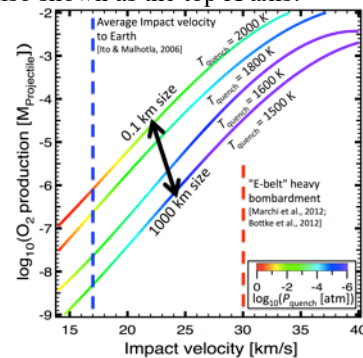


Fig. 3. The O₂ production from CI-like impactors as functions of impact velocity and size.

References: [1] Marchi et al., *EPSL*, **326**, 27, 2012. [2] Bottke et al., *Nature*, **485**, 78, (2012). [3] Ito & Malhotra, *AdSR*, 2006. [4] Kurosawa et al., *44th LPSC*, **1719**, (2013) [5] Kurosawa et al., submitted. [6] Ishibashi et al. *EPS*, **65**, 811, 2013. [7] Melosh, *MAPS*, **42**, 2079, 2007. [8] Gerasimov et al., *Earth, Moon and Planets*, **80**, 209, (1998). [9] Ohno et al., *EPSL*, **218**, 347, 2004. [10] Kuwahara & Sugita, *44th LPSC*, **1982**, 2013 [11] Kuwahara & Sugita, to be submitted [12] Gordon and McBride, *NASA Reference Publication*, **1311**, (1994). [13] Wasson & Kallemeyn, *Philos. Trans. R. Soc. London Ser. A*, **325**, 535, (1988). [14] Hashimoto et al., *JGR*, **112**, E05010, (2007) [15] Schaefer and Fegley, *Icarus*, **208**, 438, (2010). [16] Johnson & Melosh, *Icarus*, **217**, 416, (2012). [17] Vickery & Melosh, *GSA special paper*, **247**, 289, (1990). [18] Goldin and Melosh, *MAPS*, **37**, 1135, (2009). [19] Farquhar and Wing, *EPSL*, **213**, 1, (2003). [20] Lowe et al., *Astrobiology*, **3**, 7, (2003). [21] Farquhar et al., *Science*, **280**, 1580, (1998). [22] Lapen et al., *Science*, **328**, 347, (2010).