FORMATIONS OF CALCIUM-CARBONATES BY NATURAL AND ARTIFICIAL SHOCK WAVE IMPACTS: NEW TYPE FORMATION OF CARBONATES. Y. Miura, Inst. Earth Planet. Material Sciences, Graduate School of Science & Engineering, Yamaguchi University, Yoshida 1677-1, Yamaguchi, 753-8512, Japan, yasmiura@yamaguchi-u.ac.jp

Introduction: Calcium carbonates of calcite–group minerals are formed chemically and life process through liquid state on water-planet of Earth. Recently author finds new type of calcium carbonates in natural impact-related limestone and artificial shock wave in air as huge explosions [1-5]. The purpose of this paper is to elucidate new type of calcium carbonates and apply to study on shocked limestone on Earth and formation of carbonates minerals on planetary bodies without large sea-water (esp. on Mars).

Calcium carbonate formation: There are three formation processes of calcium carbonates on Earth:

1) *Life process:* calcium (from life) combines with carbonates (in sea-water or from atmosphere), which can be found in older and known limestone with fossil.

2) *Chemical precipitation under low temperature:* older calcium carbonates dissolved to water, carbon dioxides and younger calcium carbonates found in younger cave used by normal ESR dating method [6].

3) *Shock wave reaction:* Three types of shocked calcium carbonates (calcite group minerals) are found in a) natural impact crater on target rocks of limestone [1-7], b) natural impact on Ca-rich target rock (originally from meteoroids or life production) by carbon-rich projectiles of comets and meteorites [3, 4], and c) artificial shocked wave of huge explosions in air (e.g., Hiroshima atomic bomb) [1, 3-5]. Calcium (from meteoroids or life) combines with carbon and oxygen (from life or atmosphere) to form calcium carbonates (without fossil). This new impact reaction produces easily irregular and intermediate (i.e. non-stoichiometric) compositions between calcium and carbonate ions due to fast reaction [1-5].

Shocked calcites in impact craters: Shocked calcites are found in Barringer (Meteor) meteorite crater in USA (1.2km in diameter), Ries crater in Germany (24km), and Sierra Madera crater in USA (12km). Main characteristics of shocked carbonates of impact craters are high contents of Fe, C, Ni, Co and Ir (Fig. 1).

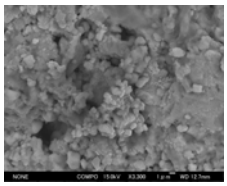


Fig.1 Electron-micrograph of shocked calcite grains (with carbon-rich particles) from Sierra Madera crater in Texas, USA. Sample collected by author in 2006.

Shocked calcite formed by artificial impact experiment: Carbon-rich calcite grains are synthesized by re-crystallization from pure marble limestone at laboratory of Yamaguchi University. Electron micrographs show carbon-rich calcium carbonate with micro-grains [3-5] (Fig.2).

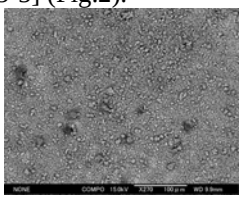


Fig.2. Electron micrograph of shocked carbon-rich calcite grains by impact experiment from pure limestone at laboratory of Yamaguchi University, Japan.

Shocked calcite formed by Hiroshima A-bomb explosion in air with materials on surface: Melted fragments formed by Hiroshima Atomic-bombs explosion at 600 m above surface of Hiroshima City, together with long existence of high temperature show carbon-rich or poor calcium carbonates analyzed by using analytical electron microscopy (JEOL7000F; Fig.3). Melt fragments collected at 150m from explosion center site on surface show calcite grains with crystal shape and composition, whereas those at 1100m are surrounded by FeSi-rich grains. Irregular fragments at 850m from explosion site on surface show calcium-rich and carbon-poor compositions as shown in Fig.3 [1, 3-5]

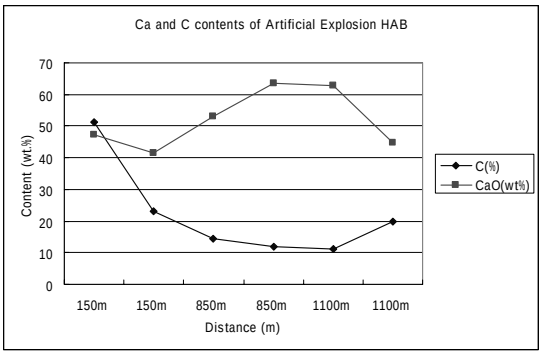
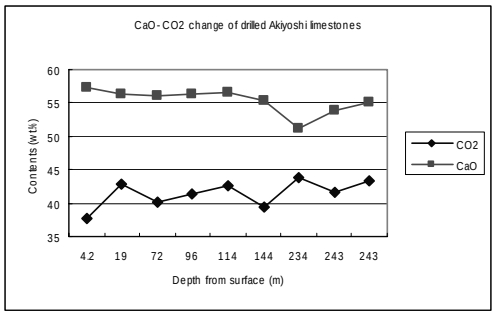


Fig.3. Compositions of calcium carbonates formed by Hiroshima Atomic-bomb explosion. Data are obtained by analytical scanning electron microscopy. Samples are used from the Hiroshima Peace Memorial Museum by permission of the director.

Carbon-rich grains of the drilled Akiyoshi Permian limestone breccias: Drilled Akiyoshi breccias of Permian limestone from Yamaguchi, Japan are used as related samples originally from Equator region transported by continental-drift after impact event [1, 2, 5-7]. Main characteristics of drilled samples of Akiyoshi limestone are higher amounts of carbon, carbon-rich calcite, Fe, Ni Co and Ir elements (esp. in 243m in depth) which are considered to be mixed from impact materials [4, 5] (Fig.4).



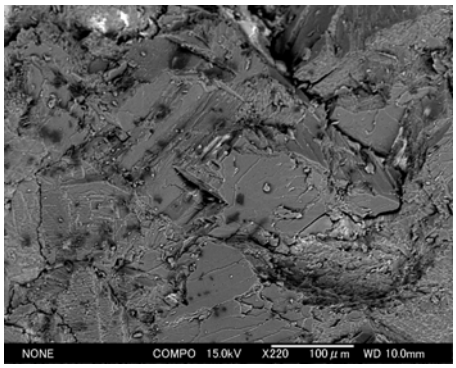


Fig.4. Compositions of calcium carbonates formed by Permian Akiyoshi limestone. Data are obtained by XRF analyses with depth from surface (above). Electron-micrograph of shocked calcite with carbon-rich grains which are obtained by analytical scanning electron microscopy (below). Drilled samples are used from the Akiyoshi Science Museum by permission of the director.

Applications to formation of new types of shocked carbonates: In order to make carbonates, the elements of carbon and oxygen are required on Earth and Mars as carbon compounds (carbon dioxide etc.) on atmosphere, sea water and/or rocks of limestone. On airless Moon, carbon compounds are only from extra-lunar materials of comets and carbonaceous chondrites. In order to supply calcium, main sources are crustal rock of earth, carbonaceous chondrites and human body. Crustal rock and human body are main source of calcium on Earth. In fact, shocked calcite from terrestrial impact craters is supplied from crustal rock of limestone originally from life process in water. Calcium carbonates from melt blocks of Hiroshima Atomic Bomb explosion are human body, because compositions of the matrix are carbon and nitrogen [4].

Shocked carbonates on the Moon: Calcium elements from anorthite on lunar highland should be mixed with elements from carbonaceous chondrites or comets (esp. crater bottom of South Pole). This is other target to next lunar project to find carbonate materials.

Shocked carbonates on Mars: Older Martian meteorite (ALH84001) [8] indicates that there are formation of carbonate minerals and magnetite bacteria with Fe- or Mg-rich elements under local carbon cycle system at an older age (ca.4.5Ga), because carbon-bearing carbonate rocks of limestone formed in wide sea-water cannot be found so far on Martian surface. If there are no wide calcium carbonates on Mars, main source of calcium on Mars should be supplies from carbonaceous chondrites or comets by impact process. In this sense, shocked calcium carbonates on Mars are considered to be formed from impact explosion on Martian atmosphere, or Martian Polar regions with calcium-bearing projectiles to Mars. Magnesium or iron carbonates on Mars should be mixed with elements of Martian atmosphere by local impact process. Spherule shape of Martian meteorite (ALH84001) indicates that formation of the spherules can be explained by impact process to the meteorite body [9, 10].

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