Introduction: Central to the question of life on Mars is whether liquid water ever existed on the surface of Mars, and if so, under what climatic conditions. Secondary minerals such as carbonates, sulfates can provide important clues in understanding the aqueous history of Mars [1]. Carbonate minerals are precipitated in a saturated solution, thus potentially preserving a record of atmosphere, hydrosphere and geosphere, subject to concentration ratio values. The Martian atmosphere is rich in CO₂ (95% v/v), and by analogy with terrestrial carbonate sediments, CO₃ minerals are regarded as a potential sink of a thicker CO₂ and water rich past Martian atmosphere. However, the enigma of missing carbonates spurred a high level of interest to explore Mars via telescope, space craft and robotic rovers and have indicated only 3-5% carbonate in the regolith. The lack of a significant fraction of carbonates in most Martian meteorites (Shergottite-Nakhalite-Chassignite), except ALH84001 (~1% carbonate) have further accelerated the quest for the missing CO₂ sink. Stable isotopes of oxygen ([18]O) in atmospheric carbonate, relationship between CO₂ and water were used to measure excess [17]O ([17]O/10₃) and anomaly was attributed to photochemical fractionation processes on Mars [3-4], similar to those known to occur in the Earth’s upper atmosphere [5]. An oxygen isotope anomaly in stratospheric CO₂ has been measured and shown to occur via excited oxygen atom produced by the UV dissociation of ozone molecule [6-9].

Materials and Methods: An oxygen isotopic anomaly in terrestrial atmospheric carbonates has been measured for the first time. Size fractionated aerosol samples were collected weekly in La Jolla, CA using a high volume air sampler and cascade impactor. Aerosol samples (coarse > 1µm and fine < 1 µm) were reacted with 100% H₃PO₄ to release CO₂(1). Controlled laboratory experiments indicated that CO₂ produced during this reaction is strictly from inorganic carbonates and not other atmospheric oxygen bearing species. To obtain independent measurements of O-isotopes, purified CO₂ gas was fluorinated to produce oxygen and analyzed using isotope ratio mass spectrometry (Delta-253, Thermo Finnigan, USA). To uniquely resolve the source of the O-isotope anomaly in atmospheric carbonates, two sets of laboratory experiments were performed. In first set ozone was reacted with pre-existing carbonates and in second set of experiments ozone and CO₂ were reacted with basic aerosols (CaO, MgO, Ca(OH)₂, Mg(OH)₂) for in-situ carbonate production. The oxygen isotopic composition of carbonates in soil samples was analyzed in order to determine the source of mass independent anomaly and to distinguish atmospheric carbonate chemistry from other equilibrium and kinetic isotope processes associated with pedogenic and sedimentary carbonate formation.

Results and Discussions: The Atmospheric carbonates showed excess [17]O ranging from 0.4 to 3.9‰ [10] and coarse fraction of aerosols indicated higher oxygen isotope anomaly (Fig. 1).
Fig. 1. Oxygen isotope anomaly ($\Delta^{17}O = \delta^{17}O' - 0.524* \delta^{18}O'$) in the coarse ($\Box$) and fine ($\square$) fraction of atmospheric carbonates collected in La Jolla, California, USA. For comparison isotopically normal carbonate standards ($\Phi$) and soil carbonates ($\times$) are also shown. Here $\delta^{17}O' = 10^3 \ln(1+\delta^{17}O/10^3)$ and $\delta^{18}O' = 10^3 \ln(1+\delta^{18}O/10^3)$.

The soil and commercial cement samples (carbonate content 3%) did not show excess $^{17}O$ and followed a mass dependent relation ($\delta^{17}O \approx 0.524 \delta^{18}O$). The carbonate fractions of soil samples are enriched in both $^{17}O$ and $^{18}O$ ($\delta^{17}O' = 15-21\%$ and $\delta^{18}O' = 27-40\%$) compared to the atmospheric carbonates ($\delta^{17}O' = 7.4 - 18.1\%$ and $\delta^{18}O' = 12.9 - 31.6\%$). Laboratory experiments indicated that the ozone anomaly is transferred to carbonates from intermediary hydrogen peroxide which is produced when $O_3$ reacts with surface adsorbed water. Oxygen produced from hydrogen peroxide was also measured and was found to be anomalously enriched with $\delta^{17}O=0.74\delta^{18}O$ (Fig 2).

Both static and continuous flow laboratory experiments elucidate the incorporation of oxygen isotope anomaly from ozone to the carbonates with hydrogen peroxide as intermediate via two different pathways. One mechanism involves the isotopic exchange reaction on existing carbonates and the second involves in-situ formation of carbonates on mineral particles. These findings further shed light on the origin of isotope anomaly reported in Martian carbonates. Even if the kinetics of the process are different at low Martian temperatures, adsorbed surface water is critical for the solid-gas interaction. We suggest that oxygen isotopic anomaly in carbonates extracted from SNC meteorites ($\Delta^{17}O = 1.1-0.7\%$) arise from ozone, $CO_2$ and water interaction on the particle surfaces in Martian regolith with an intermediary peroxide formation. The proposed mechanism of secondary carbonate formation via hydrolysis of mineral particles and evaporative enrichment of ions in the micro-environment on aerosol surfaces may also account for the presence of 2-5% carbonates in the Martian soils [11].