HOW TO MAKE OTHERWORLDLY OXYGEN ISOTOPE SIGNATURES ON EARTH AND TO PRESERVE THEM IN ROCKS. Huiming Bao[1], [1]Department of Geology & Geophysics, Louisiana State University, E235 Howe-Russell Geoscience Complex, Baton Rouge, LA 70803, USA. bao@lsu.edu

Introduction: Triple oxygen isotope measurement was once an exclusive practice in meteorite research [1]. Since 1980s, many compounds on Earth have been found to possess triple oxygen isotope compositions that deviate from terrestrial fractionation line [2, 3]. Some of them form minerals and rocks, which can be preserved in geological records and serve as a solid archive for past Earth system history.

Sulfate or sulfate-bearing minerals have the best geological usage due to their low solubility and wide geographic and temporal occurrences in Earth history. I identify here two major pathways by which ^{17}O-anomalous sulfate oxygen isotope compositions can be generated with ^{17}O enrichment (positive anomaly) and ^{17}O depletion (negative anomaly), respectively. Both pathways points to the same ultimately source of non-mass-dependent oxygen isotope signature: atmospheric zone.

Pathway I:
Sulfate formed by secondary oxidation of sulfur compounds (e.g. H_2S, SO_2, HSO_3^-, SO_3^{2-}) in the atmosphere by ozone or related oxidants (e.g. H_2O_2, NO_x) in aqueous or gas phase, without an exception, bears a positive ^{17}O anomaly. Due to a much faster reaction rate [4], aqueous oxidation overwhelms the gas phase oxidation in the quantity of sulfate produced in the atmosphere. The aqueous reactions themselves do not generate non-mass-dependent signatures; they merely transfer the anomalous signatures from ozone or its associated oxidants to sulfate [5]. Such formed sulfate is constantly raining down from the atmosphere [6, 7] but only accumulates as minerals (e.g. gypsum or anhydrite) to measurable quantities in arid to hyperarid surface environments. Massive ^{17}O-anomalous sulfate deposits are found in major hyperarid deserts on Earth, e.g., the Central Namib Desert [8, 9], the Atacama Desert, and the Antarctica Dry Valleys [10]. Some of these surfaces are as old as 15 million years. Similar hyperarid deposits should have existed in other parts of the world at certain time periods in the geological past. None of those massive, $\Delta^{17}O$-positive desert sulfate deposits, however, has been discovered in geological records older than the Miocene. Under special circumstances, such as a series of sulfur-rich volcanic eruptions, large quantity of ^{17}O-anomalous sulfate can be accumulated in a short period of time in a semi-arid environment. An Oligocene eruption event (~ 28 million years ago) in northern Colorado laid down gypsum-bearing ash deposits in western Nebraska, from which we have found the most positive sulfate ^{17}O anomaly ($\Delta^{17}O$ = ~+6.0‰) known so far [11] (Fig. 1). It is also the oldest such record on Earth. A depositional environment favorable for an early precipitation of gypsum and a subsequent burial helped the preservation of the anomalous sulfate[12, 13].

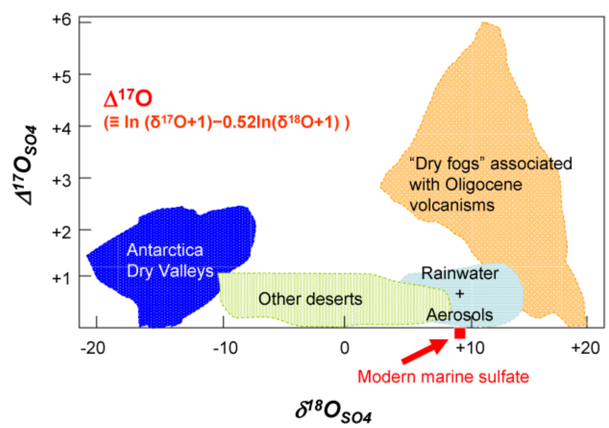

Fig. 1. Sulfate deposits with positive $\Delta^{17}O$ values (in VSMOW) on Earth

Pathway II:
Sulfate formed by oxidative weathering of sulfide minerals (most commonly, FeS_2) by atmospheric O_2 in surface environments can bear a negative ^{17}O anomaly. The negative anomaly comes from the O_2, as the result of stratospheric O_2–CO_2–O_3 chemistry in which the exchange reaction between O_3 and CO_2 results in a negative ^{17}O anomaly in O_2 [14-16]. The magnitude of the ^{17}O anomaly for O_2 is also determined by biosphere O_2 fluxes (photosynthesis and respiration) [17]. Other variables being the same, increasing pCO_2 can increase the magnitude of the negative ^{17}O anomaly for atmospheric O_2 [18]. Since sulfate produced by oxidative weathering of sulfides has part of its oxygen derived from O_2 [19], the negative anomaly of O_2 is therefore recorded by the sulfate. At the present atmosphere the pCO_2/pO_2 ratio and the biosphere flux are such that the ^{17}O anomaly of O_2 is barely above analytical noise, with $\Delta^{17}O \sim -0.20$‰. However, past Earth surface condition, especially the pCO_2/pO_2 ratio can be very different. The ^{17}O anomaly of O_2 can be sufficient large so that it is measurable. At surface, sulfate can form evaporitic minerals (e.g. gypsum),

barite, or be trapped in carbonate mineral structure as a stable, solid sulfate archive. Recent data revealed distinctly negative sulfate $\Delta^{17}O$ values at the end of Marinoan glaciation at ~ 635 million-years ago, reaching as low as −1.64‰ [18, 20] (Fig. 2), suggesting probably an extremely high pCO_2 atmosphere at that time. This is so far the strongest evidence that supports the "snowball Earth" hypothesis for the Marinoan global glaciation.

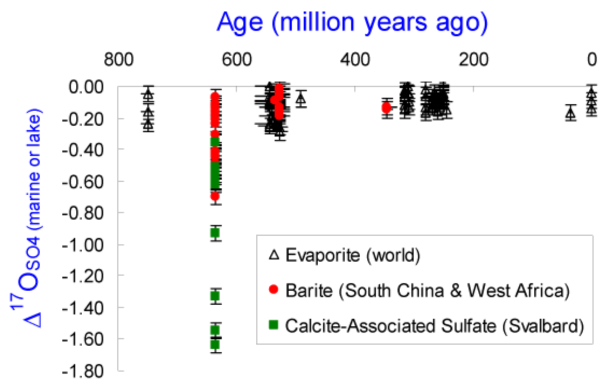

Fig. 2. Sulfate deposits with negative $\Delta^{17}O$ values over the last 750 million years. The negative spike is at ~ 635 million years ago.

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