## Theoretical calibration on the <sup>13</sup>C-<sup>18</sup>O clumped isotope thermometer

MAO TANG, SI-TING ZHANG, QI LIU AND YUN LIU\*

State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, China. liuyun@vip.gyig.ac.cn (\* Corresponding author)

Equilibrium <sup>13</sup>C-<sup>18</sup>O clumped isotope distribution in carbonates has been applied as a new thermometer for surface temperature systems. However, existing  $\Delta_{47}$ -T relationships calibrated by several different groups are incompatible, which generates substantial confusions in the community. Here we propose a new molecular-level mechanism with three parallel pathways for the kinetic isotope effects during phosphoric acid digestion of carbonates. The new mechanism abandons completely a previously proposed molecular mechanism (i.e., Guo et al., 2009) and explains extremely well the discrepancies of  $\Delta_{47}$ -T relationships provided by different groups. Together with a re-calculated equilibrium clumped isotope fractionation factors using a new volume-variablecluster-model method with higher theoretical-level treatments and higher-order anharmonic corrections, we present an equilibrium  $\Delta_{47}$ -T relationship that varies slightly with different contributions of the three parallel reaction pathways.

Under the absolute reference frame, our new calibration line is only slightly different from the line of Dennis *et al.* (2011), but with large difference from that of Ghosh *et al.* (2006). The slope of our calibration line is almost the same as that of Guo *et al.* (2009).