Effect of mineral structure and composition on carbonate clumped isotope measurements

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Carbonate clumped isotope thermometry relies on the temperature-dependent extent of bounding of ^{13}C-^{18}O within CO_3^{2-} ion groups in solid carbonate minerals. The measure of the abundance of $^{13}C^{18}O^{16}O_2^{2-}$ ion groups cannot be performed on the carbonate mineral itself and requires Δ_{47} measurement of CO_2 extracted by phosphoric acid digestion (i.e., the excess of ^{13}C-^{18}O bonds in extracted CO_2 relative to a random distribution). Theoretical studies predict variations in the degree of ^{13}C-^{18}O clumping from one carbonate to another [1] and small but analytically resolvable differences in Δ_{47} of CO_2 extracted from various types of carbonates equilibrated at a given temperature [2]. In contrast, published calibrations of carbonate clumped isotope thermometer do not show distinguishable difference among the different types of carbonate investigated (mostly biogenic and inorganic calcite, aragonite and carbonate-apatite [3]). However, some coexisting carbonate phases supposed to have grown or been re-equilibrated at the same temperature show different Δ_{47} values (e.g., Bonifacie *et al.*, same meeting).

We will present results from a series of experiments on a variety of natural and synthetic carbonate minerals. These experiments have been designed to investigate the possible effects of mineral structure and chemical composition on Δ_{47} values.

This study is relevant for key issues related to the use of Δ_{47}, and in particular in refining application of the Δ_{47} thermometry to the variety of carbonate minerals found in the geological record.

[1] Schauble *et al.* (2006), *GCA* **70**, 2510-2529. [2] Guo *et al.* (2009), *GCA* **73**, 7203-7225. [3] Eiler (2011), *QSR* **30**, 3575-3588

Carbon isotopic composition and flux variations of CO_2 emitted from the soil of Mt Etna

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Since 1987, periodic soil CO_2 flux measurements on the south-western sector and on the eastern flank of Mt Etna have been performed to monitor volcanic activity. Many studies have demonstrated that soil CO_2 flux is closely related to the magma dynamics of Mt Etna. To further confirm this relationship and better understand the influence of rising magma on soil CO_2 emission, we periodically measured the δ^{13}C values as well as the soil CO_2 flux at several points in both areas of Mt Etna. The comparison between δ^{13}C values and soil CO_2 flux revealed two groups of data with different behaviours: (i) data arranged along mixing lines between organic and depth origins of CO_2; (ii) data with high soil CO_2 fluxes and δ^{13}C values with organic marker. The variations in δ^{13}C in (i) are temporally well correlated with the total amount of the soil CO_2 emitted in the areas. This result strongly corroborates the primary role played by magma dynamics in the control of soil CO_2 flux in the analysed areas. In addition, the values of flux of (ii), notwithstanding the organic marker, displayed synchronised variations with the total amount of the soil CO_2 emitted in the area and hence with the δ^{13}C values of group (i). The recorded synchronism suggests that the measurements in group (ii) are also to some extent influenced by magma dynamics. It can be supposed that: increase in flux in (i) is directly derived from the release of CO_2 from ascending magma, whereas the increase in soil CO_2 flux in (ii) is mainly due to the enhancement of stress linked to magmatic intrusion.

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DOI: 10.1180/minmag.2013.077.5.3