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Title: Sorption of the Rare Earth Elements and Yttrium (REE-Y) in calcite: the mechanism of a new effective tool in identifying paleoearthquakes on carbonate faults

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A new tool for identifying paleoearthquakes on carbonate faults has been successfully tested on two carbonate faults in southern Europe (the Magnola Fault in Italy and the Spili Fault in Greece): the Rare Earth Element and Yttrium (REE-Y) method (Manighetti et al., 2010; Mouslopoulou et al., 2011). The method is based on the property of the calcite in limestone scarps to absorb the REE and Y from the soil during its residence beneath the ground surface (e.g. before its exhumation due to earthquakes). Although the method is established, the details of the enrichment mechanism are poorly investigated. Here we use published data together with new information from pot-experiments to shed light on the sorption mechanism and the time effectiveness of the REE-Y method. Data from the Magnola and Spili faults show that the average chemical enrichment is $\sim$45%, in REE-Y while the denudation rate of the enriched zones is $\sim$1% higher every 400 years due to exposure of the fault scarp in weathering. They also show that the chemical enrichment is significant even for short periods of residence time (e.g., $\sim$100 years). To better understand the enrichment mechanism, we performed a series of pot experiments, where carbonate tiles extracted from the Spili Fault were buried into soil collected from the hanging-wall of the same fault. We irrigated the pots with artificial rain that equals 5 years of rainfall in Crete and at temperatures of 15^{o}C and 25^{o}C. Following, we performed sorption isotherm, kinetic and pH-edge tests for the europium (Eu), the cerium (Ce) and the ytterbium (Yt) that occur in the calcite minerals. The processes of adsorption and precipitation in the batch experiments are simulated by the Mineql software. The pot experiments indicate incorporation of the REE and Y into the surface of the carbonate tile which is in contact with the soil. The pH of the leached solution during the rain application range from 7.6 to 8.3. Nutrient release like Ca is higher in the leached solution at lower temperature (15^{o}C) probably due to higher calcite solubility (higher dissolved $CO_{2(g)}$ content) and to less adsorption capability of the soil in elevated temperatures. The isotherm sorption modeling showed that REE-$(CO_3)_2$ precipitation is the dominant mechanism in the incorporation of REE into calcite, while the kinetic tests showed instant REE sorption (within few hours). Our experiments show that pH>7.5 and temperatures $\sim$25˚C favor REE-Y sorption on calcite surface. Hence, due to the REE-Y fast interaction with carbonate scarp face and the low denudation rate due to later weathering, the REE-Y method is considered a reliable method for tracing paleoearthquakes along carbonate fault scarps when the scarp is in contact with soil at temperate climates. The resolution of identifying frequent paleoearthquakes with low residence time in contact with soil is also considered high.

References

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