

## The Origin, Transport, Crustal Storage and Expulsion of CO<sub>2</sub> Associated with Italian Thermal Springs and Travertines

Angelo Minissale (minissa@csmga.fi.cnr.it)<sup>1</sup>, Derrill M. Kerrick (kerrick@pop3server.geosc.psu.edu)<sup>2</sup>,  
Gabriella Magro (g.magro@iggi.pi.cnr.it)<sup>3</sup>, Sophie Rihs (srihs@exchange.anl.gov)<sup>4</sup> &  
Neil C. Sturchio (sturchio@anl.gov)<sup>4</sup>

<sup>1</sup> CNR-Centro di Studio per la Minerogenesi e la Geochimica Applicata, Via La Pira 4, 50121 Firenze, Italy

<sup>2</sup> Dept. of Geosciences, Penn State University, 243 Deike Bldg., University Park, PA 16802, USA

<sup>3</sup> CNR-Istituto di Geocronologia e Geochimica Isotopica, via Alfieri 1, Località San Cataldo, 57017 Ghezzano (PI), Italy

<sup>4</sup> Argonne National Laboratory, Build.203, 9700 South Cass Avenue, Argonne, IL, 60439, USA

In the Tyrrhenian coastal region of central Italy travertine is currently forming at numerous hot springs, and there are extensive fossil travertine deposits (a major world-wide source of travertine for building stone). The thermogenic origin of Italian travertines is compatible with the anomalously high heat flow and late Cenozoic and Recent volcanism in this region. Contemporary travertine precipitation from thermal springs is related to regional circulation of meteorically-derived water through a thick (1-3 km) Mesozoic limestone unit. Geological evidence suggest that CO<sub>2</sub> discharged from thermal springs and the abundant nearby dry CO<sub>2</sub> gas vents have a common secondary deep source inside the buried carbonate sequence. On the other hand, the <sup>3</sup>He/<sup>4</sup>He ratios in the CO<sub>2</sub>-rich gases suggest two distinct CO<sub>2</sub> sources. In the western sector of the Tyrrhenian belt, CO<sub>2</sub> emissions have high <sup>3</sup>He/<sup>4</sup>He ratios (R/Ra ranging 0.5-4.0), thereby implying that CO<sub>2</sub> is partly derived from degassing of primary mantle-derived magmas. In addition to recent volcanism, the presence of subsurface magmas is compatible with the relatively thin crust (20-25 km) and high heat flow in

this sector. In the eastern sector of the Tyrrhenian belt, heat flow is low, the crust is 5-10 km thicker than the western portion, and CO<sub>2</sub> gas vents, although reduced in numbers but not in size, have low crustal <sup>3</sup>He/<sup>4</sup>He ratios (R/Ra ranging 0.02-0.2) suggesting a crustal origin. Accordingly, for the eastern portion of the Tyrrhenian belt we hypothesize the presence of a locked slab of carbonates probably belonging to the Adriatic plate. CO<sub>2</sub> in the eastern sector may be derived by metamorphic de-carbonation of these slab carbonates at 20-35 km. Influx of this CO<sub>2</sub> into the shallower aquifers within the Appennine carbonate sequence would yield dissolution of the carbonate rock and thus formation of gas reservoirs. In the western Tyrrhenian belt, where thermal waters re-emerge after long westward circulation underground, travertines precipitation results in discharge of a huge quantity of CO<sub>2</sub> to the atmosphere. Travertine deposition is clearly modulated by climate; travertines formed mostly during Quaternary pluvial periods, as determined by U-series age determinations of representative deposits in Tuscany and Latium (including those at Tivoli, Canino, Rapolano, and Saturnia).