



Natural CO₂ degassing in Tuscany (Central Italy)

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Tuscany, as most of the central-southern peri-Tyrrhenian side of Italy, is characterised by a large non-volcanic CO₂-degassing, generally associated to the NW-SE trending fault systems at the boundary of basins formed during the Plio-Pleistocene extensional event that followed the Apenninic belt-originating compressive phase.

Naturally discharged gases in this region, mainly constituted by CO₂, are well known to be lethal for animal and human beings, due to both indirectly depletion of O₂ in the atmosphere and increased CO₂ solubilization in the blood, the latter causing hypercapnia and acidosis. Fatalities associated to the CO₂-rich sites, especially where gases are discharged in morphologically depressed areas where CO₂ tends to be accumulated, are not uncommon, the last death occurring in November 2003 in the Mt. Amiata area.

The main aim of this study was to provide a census of the main thermal/mineral and gas discharges in Tuscany, together with new geochemical analyses, in order to identify the most hazardous sites and to promote recommendations to the Italian Civil

Protection for the risk mitigation. Accordingly, in this work, carried out in the framework of a project funded by the Italian National Institute of Geophysics and Volcanology (V5-Diffuse Degassing in Italy), we present the geochemical and isotopic characterization of 81 and 103 free- and dissolved-gases, respectively, and 150 thermal and mineral waters from emission sites located in Tuscany with the exception of the Larderello and Travale geothermal fields, along with the measurement of CO₂ flux from the highest CO₂-discharging rate manifestations.

Typologies of the sampled gas discharges are highly variable since they include hot and cold bubbling and mud pools, dry vents, thermal and cold wells in either spas or CO₂-producer industries. The chemistry of the samples evidences as like most of the discharges are characterised by CO₂ whose concentration reaches at places 990,000 μmol/mol. In terms of carbon and helium isotopes, the CO₂-rich manifestations are generally referred to a thermometamorphism process with a mantle imprinting occurring at variable extent.

The degassing phenomenon often involves impressive amount of CO₂ release with values up to 50-100 ton/day. On the other hand, N₂- and CH₄-rich gases are also found, mainly in correspondence of the edges of Mesozoic limestone and related to brines discharging from Miocene evaporite outcrops, respectively.

The thermal waters discharges cover a large compositional variability, i.e. Na-HCO₃, Ca-SO₄, Na-Cl and Ca(Mg)-HCO₃ with subordinate Mg-HCO₃ and Ca-Cl geochemical facies. Oxygen and hydrogen isotopes suggest a meteoric-related origin for both thermal and mineral waters, whereas the large variability of δ¹³C-DIC (Dissolved Inorganic Carbon) values indicates the presence of multiple sources of HCO₃, dissolution of carbonate formations, solubilization of thermometamorphic and meteoric CO₂, decomposition of organic matter.

The main result of the present study is to have recognised sensitive areas where CO₂ emissions are potentially dangerous to human beings. To mitigate the risks associated to these areas we suggest to modify the common way of seeing these potentially dangerous sites, which are indeed considered as unsafe and unapproachable. Instead, local communities and authorities should exploit them as attraction and geo-tourism localities, where guided tours should be led by instructed and prepared personnel to let population and tourists understand the importance of these geological events and perceive the effects of CO₂.