



Water-gas-rock interactions in carbonate-evaporite aquifers sited in CO₂ degassing areas

C. Cardellini (1), S. Caliro (2), G. Chiodini (2), **F. Frondini** (1), N. Morgantini (1)

(1) Dipartimento di Scienze della Terra, Università di Perugia, Italy, (2) INGV-Napoli, Osservatorio Vesuviano, Napoli, Italy (frondini@unipg.it / Fax: +39 0755852603)

Central and southern Italy are interested by a strong process of CO₂ degassing partly related to a deep mantle source (Chiodini et al., 1999; Chiodini et al., 2000; Rogie et al., 2000; Chiodini and Frondini, 2001; Gambardella et al., 2004). For these areas Chiodini et al. (2004) presented the first regional map of CO₂ Earth degassing, showing that a globally significant amount of deeply derived CO₂ (2.1×10^{11} mol/y) is released by the region. The presence of large carbonate-evaporite aquifers in the Apennine sector of central Italy strongly influences the regional degassing process. In fact groundwater can dissolve and transport important quantity of CO₂. Field evidences and aqueous speciation calculations show that a large part of the dissolved gas is degassed towards the atmosphere during circulation of groundwater or after their emergence from springs. In order to investigate both the role of the regional aquifers in the degassing process and how the influx of a deep gas phase influences the chemical evolution of groundwater, several springs from some of the main regional carbonate-evaporite aquifers of central Italy (Narnese-Amerina, Monti Martani structures) were sampled and analysed. For each sample the chemical composition and carbon isotopic composition of the total dissolved inorganic carbon were determined, furthermore in some selected samples we analysed the dissolved gas content. The comparison of the data with a theoretical water-gas-rock interaction model show how the continuous addition of a CO₂ rich gas phase to groundwater cause the progressive increase in the total pressure of dissolved gases. When total pressure of the reservoir fluid exceeds the hydrostatic pressure, a degassing process take place. At the beginning, this process causes the progressive loss of N₂, Ar (atmospheric components) and He (partly deriving from the atmosphere and partly from the deep gas) and a relative enrichment of the solution in dissolved CO₂. The CO₂ buffering effect related to the dissolution

of calcite and dolomite, further increase the amount of CO₂ that can be dissolved by the solution. When TDIC reach a threshold value (variable depending on total pressure) the degassing process interests mainly the CO₂ and TDIC increase at a lower rate. Depending on the CO₂ influx rate and on the hydrostatic pressure of the aquifer, the gas-water separation process may take place after the emergence of groundwater from springs or at aquifer conditions. In the second case, a free gas phase forms gas reservoirs from which gases may escape generating gas emissions at the surface. This model explains both the formation of CO₂ rich spring-waters and the gas emissions of the region (Montecchie, Monte Castello, Fersinone, San Faustino). The contrasting behaviour of N₂, noble gases and CO₂, allow to discriminate the waters degassed prior the emergence from springs from the non-degassed water. The CO₂ flux computed for these structures considering both the CO₂ released from gas emissions and the CO₂ dissolved by groundwater is about 9×10^6 mol/ y km².

References: Chiodini et al., 1999. Chem. Geol., 15, 205-222; Chiodini et al., 2000. J. G. R., 105, 8423-8434; Rogie et al., 2000. J. G. R., 105(B4), 8435-8445; Chiodini and Frondini 2001. Chem. Geol., 177, 67-83; Gambardella et al., 2004 J. V. G. R., 136, 31-52.