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Free and dissolved gases in Castrocaro spa waters (Italy)

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Abstract

Free and dissolved gases in cold water samples from the Castrocaro spa, Northern Italy, were analyzed for their chemical composition. These gases were interpreted as the result of the binary mixing between a N_2- and a CH_4-rich component. CO_2 is generally a minor constituent. N_2/Ar ratios below the air typical value suggest that air saturated water (ASW) is the most likely source of atmospheric-derived components. This atmospheric end-member is predominant in low-salinity waters. Conversely, CH_4-enriched gases are mainly associated with brackish to saline waters. The occurrence of minor amounts of light hydrocarbons (C_2-C_3) indicates a predominant biogenic origin of CH_4. The He isotopic composition of the CH_4-richest sample ($^3He/^4He$ = 0.22 Ra) is in the range of values measured for cold seeps and mud volcanoes along the Northern Apennines foothills, and indicates a predominant crustal origin of this gas.

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Keywords: dissolved gases; noble gases; Northern Apennines; Castrocaro

1. Introduction

Gas spontaneous seepages widely occur all over the Northern Apennine belt, Northern Italy. Based on their geochemical and geological features, these seepages have been distinguished in: i) seepages associated with water and mud extrusion (mud volcanism); ii) free gaseous emissions, dominated by CH_4. The first group prevalently occurs in the Parma-Reggio sector (Fig.1) and is closely associated with the presence of a hydraulic seal (impermeable Ligurian units) at the top the reservoir (Marnoso Arenacea flysch)[1]. The second group mainly occurs in those areas where the lack of a sealing layer at the top of the reservoir allows for the fluids to migrate from source rocks and/or deep storage layers, and possibly reach the surface.

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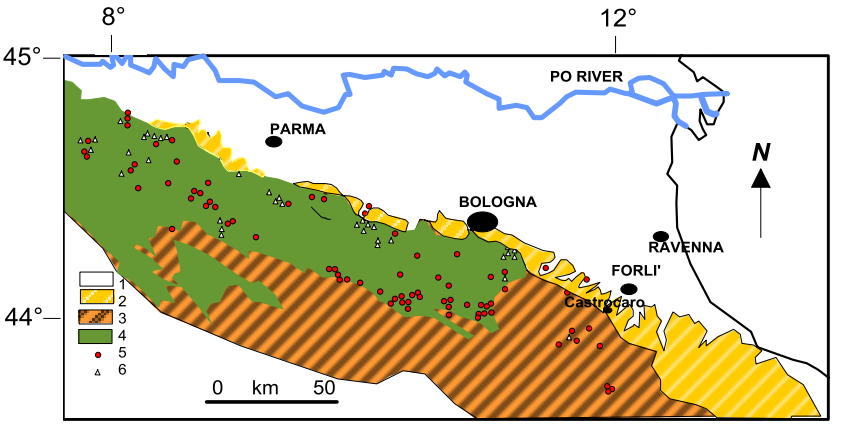

Fig. 1. Geological sketch map and locations of the fluid emissions of the Northern Apennines alongside the Po valley (modified after Borgia et al. 1986). Legend: 1, Continental Quaternary; 2, marine to continental Plio-Pleistocene foredeep units at the foothills; 3, Miocene foredeep units; 4, Ligurian–Epiligurian units; 5, spontaneous fluid emissions and 6, oil and gas from surficial drilled wells.

All these features are strictly connected with the widespread occurrence of hydrocarbon reservoirs all over the region comprised between the Apennine thrust belt, the adjacent foredeep basins, and the Adriatic foreland (Fig.1). Gas fields contain hydrocarbons of predominant biogenic origin, and are concentrated in the Po Plain and in the northern and central parts of the Adriatic Basin. Oilfields have been identified in the western sector of the Po Plain. Based on the chemical and isotopic signature of hydrocarbons, the Marnoso Arenacea Fm., in the Miocene Apennine foredeep succession, has been identified regionally as the source rock and the main reservoir of hydrocarbons[2]. Biogenic methane emissions are associated with the deformed foredeep units of Upper Neogene age, which represent an uplifted portion of the main hydrocarbon system exploited in the eastern sector of the Po Plain[3].

Located in the Northern Apennine belt, the Castrocaro groundwater system (CGS) is part of a wider regional hydrogeological system characterized by the occurrence of saline water, gaseous hydrocarbon spontaneous seepages, and mud volcanoes. Nowadays extending over about 24 km^2, the mineral concession of the Castrocaro spa is a quite narrow area where exploitation wells produce highly variable salinity groundwater. In this paper, the composition of free and dissolved gases has been investigated to gain insights on the origin of chemical compounds of CGS waters, and on the processes controlling their evolution in during the rise towards the surface.

2. Geological setting

The GCS (Fig.1) is located in an area interested by a thrust system deforming the Miocene foredeep succession and allowing the Pliocene to onlap the thrust top with shallow water calcarenites. The most important geological unit is represented by the Marnoso-Arenacea Fm. (Langhian-Tortonian; 16-10 Ma), consisting of an arenaceous-pelitic turbidite sequence of up to 3000 m. In some places, this formation is overlaid by the evaporitic rocks of the Gessoso-Solfifera Fm. (Upper Messinian), and above, by pelitic deposits of Lower Pliocene to Lower Pleistocene age called "Argille Azzurre". Organic-rich laminites (sapropels) are widespread in the Pliocene foredeep succession. Calcarenites of Pliocene age (Spungone Fm.; Lower-Middle Pleistocene) hosts natural fluid seepages, and are locally exploited in the Castrocaro spa with wells drilled down to about 100 m reservoir b.g.l.[3].

Water samples from nine wells were collected and analyzed for their chemical and isotopic composition. These waters are of Na-Cl type, span in composition from fresh, to brackish and saline, have an emergence temperature of 13.2 to 17.7 °C, nearly neutral pH (6.8 to 7.4) and reducing Eh values (between -130 and +30 mV). Cl, Br, Na concentrations and $\delta^{18}O$ values strongly correlate, testifying for the mixing between two components: i) dilute, meteoric waters; (ii) deep, saline waters. Based on the (δ^2H - $\delta^{18}O$) H_2O signature, and on Na/Cl, SO_4/Cl, and Cl/Br ratios, the saline end-member was identified as fossil modified seawater[4].

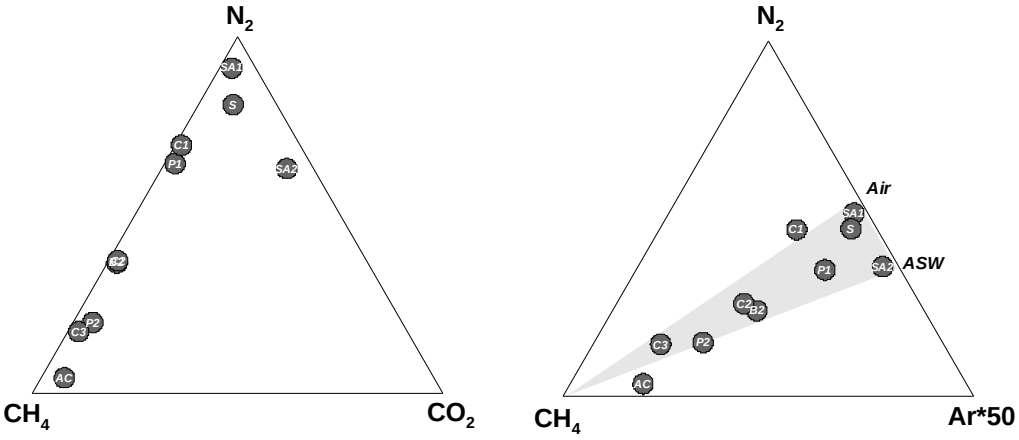

Fig. 2. N_2-CH_4-CO_2 and N_2-CH_4-Ar relative concentrations for Castrocaro samples.

3. Results and discussion

Dissolved gases were extracted from water samples by means of the head space method, and the measured gases concentrations were recalculated to spring water conditions using Henry's law. The bulk chemical composition was measured by gas-chromatography. Abundances of He and Ne were measured using a quadrupole mass spectrometer after separation in a suitable all metal high vacuum line. The He isotopic composition expressed as R/Ra [$(^3He/^4He)_{sample}/(^3He/^4He)_{air}$] was obtained by means of a magnetic mass spectrometer for noble gases (MAP 215–50)[5]. Castrocaro gases are the result of the binary mixing between two N_2– and CH_4–enriched components (Fig.2).

Minor amounts of CO_2 (less 5.44 vol.% in the head space) were also measured, exception made for one sample (SA2) with a concentration of 28 vol.%.

The N_2 and Ar concentrations (Fig.2) are mainly in the range of air and of air saturated water component (ASW), confirming the predominantly atmospheric origin of these compounds. A helium isotopic ratio of 0.22 Ra was measured in the CH_4–richest sample (S2). This value is in the range of $^3He/^4He$ values ($0.03<R/Ra<0.45$) measured in CH_4-dominated gases from mud volcanoes of the Emilia-Romagna region[6], and from natural gas fields of the Po Basins[7]. This signature is clearly indicative of a crustal origin of He.

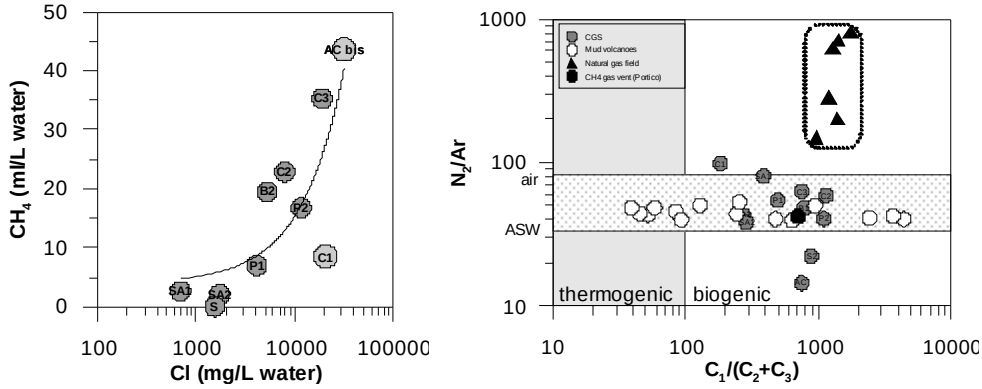

Fig. 3. CH_4 vs. Cl and N_2/Ar vs. $CH_4/(CH_4+C_2H_6)$ diagrams for Castrocaro samples.

Methane (CH_4) contents range from 43.6 to 2.06 ml/L H_2O, and correlate with water salinity (Fig.3). Together with the isotopic composition of methane ($\delta^{13}C$-CH_4), the relative proportions of methane, ethane (C_2H_6) and propane (C_3H_8) allow to decipher the origin of natural gases. Thermogenic and biogenic gases are generally characterized by $CH_4/(C_2H_6 + C_3H_8) < 100$ and $CH_4/(C_2H_6 + C_3H_8) > 100$, respectively[8].

At Castrocaro, $\delta^{13}C$-CH_4 (-75‰ V-PDB;[3] and $CH_4/(C_2H_6 + C_3H_8)$ values (> 100; this work) point to a predominant biogenic origin of hydrocarbons. Further to this, the relatively low concentrations of C_{4+} hydrocarbons in the nearby gas seepage of Portico di Romagna[9], characterized by a similar chemical fingerprinting and geological setting to Castrocaro, suggest a negligible contribution of the thermogenic component.

The occurrence of dissolved to free CH_4-rich gases at Castrocaro is then likely related to anaerobic methanogenesis in local sediments/geological formations, whereas the efficiency of the exsolution process is likely controlled by the interplay between CH_4 production/accumulation rates and groundwater confinement pressure. Methane exsolution is also expected to control the stripping of minor species out of the aqueous solution, and the occurrence of large amounts of gases associated with local aqueous solutions is suspected to enhance the rise of relatively denser saline waters from the deepest levels of the system up to the shallow geological formations currently exploited by the Castrocaro spa.

4. Conclusions

Dissolved and free gases seeping in the Castrocaro area show strong similarities with gases emitted from mud volcanoes and diffuse seeping related to hydrocarbon reservoirs in the Po plain, Northern Italy. These gases are dominated by CH_4 of predominant biogenic origin. The relatively high concentrations of N_2 and the N_2/Ar ratios in the range of air saturated water and air indicates an important contribution of atmospheric-derived gases, likely associated to local meteoric recharge. The $^3He/^4He$ ratio points to a predominant crustal origin of helium.

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