CARBONATE RESERVOIR DIAGENESIS ASSOCIATED TO CONNATE WATER / FRESH WATER INTERACTION WITHIN A THERMAL AQUIFER LOCATED IN THE CENTRAL-NORTHERN PART OF THE MOESIAN PLATFORM (ROMANIA)

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Abstract. The Moesian Platform sedimentary basin, which occupies large parts of Romania and of Bulgaria, includes a several hundred meters thick carbonate formation of Late Jurassic – Early Cretaceous age. The regional aquifer hosted by that reservoir formation has been tapped by several deep (up to 3,300 m) wells, drilled in southern Romania during the late 1980s and early 1990s. The main focus of the present study has been to additionally process and interpret previously reported chemistry data concerning groundwater samples which had been collected during the testing of such wells. It accordingly resulted that within the investigated aquifer domain, a significant control on the groundwater chemical properties and on the temperature distribution was exerted by downflowing plumes of cold, meteorically-derived freshwater, which interacted with upflowing plumes of warm, prevalently connate water. In addition, each type of plume was inferred to interact with the host rock in a distinct way, so that two complementary diagenetic processes developed: as downflowing freshwater warmed up – by gradual mixing with connate water – calcite was deposited in the reservoir; and conversely, as upflowing connate water was progressively diluted and cooled by freshwater, the resulting mixture dissolved increasing amounts of calcite. Those processes mirror the specific property of calcite of becoming increasingly soluble, as the aqueous solution progressively cools down (“retrograde solubility”). This overall interpretation is supported by the sampled fluids’ concentrations of Ca^{2+} and HCO_3^-, which for the considered wells display reverse correlations with the corresponding inflow temperatures. On the other hand, the calcite saturation index computed for most water samples proved to be close to zero, accordingly indicating that the inferred groundwater flows – either updip or downdip the reservoir – had to be slow, so that enough time was available for chemical equilibrium to be achieved in correspondence to each new thermal status reached by groundwater.

Key words: sedimentary basin, connate water, freshwater, diagenesis, calcite retrograde solubility, Moesian Platform.

1. INTRODUCTION

The Moesian Platform is a tectonic unit where marine sedimentation has occurred, with occasional interruptions, since Early Palaezoic until Late Pliocene; afterwards, the domain became subject to the continental regime which still exists

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today (PARASCHIV, 1979). While the surrounding orogens (Carpathian and Balkan mountain ranges – Fig. 1 inset) underwent, during the Alpine evolution stages, strong deformations, the coeval behavior of the platform has been far more stable. Consequently, relatively un-deformed sedimentary complexes extend laterally, across the platform, for tens, or even hundreds of kilometers. There are accordingly provided favorable conditions for underground accumulation of natural fluids (oil, gas, drinking water, thermal water). In particular, drilling originally conducted for hydrocarbon exploration has outlined a major reservoir that consisted of carbonate rocks which had been deposited during the Late Jurassic – Early Cretaceous (J_3-K_1) time-interval. That reservoir is continuous over a large area, having been investigated (Fig. 1) both north of the river Danube, in southern Romania (PARASCHIV, 1979; TANASA, 2014), and south of that river, in northern Bulgaria; (SHTEREV *et al.*, 2002 a, b, c).

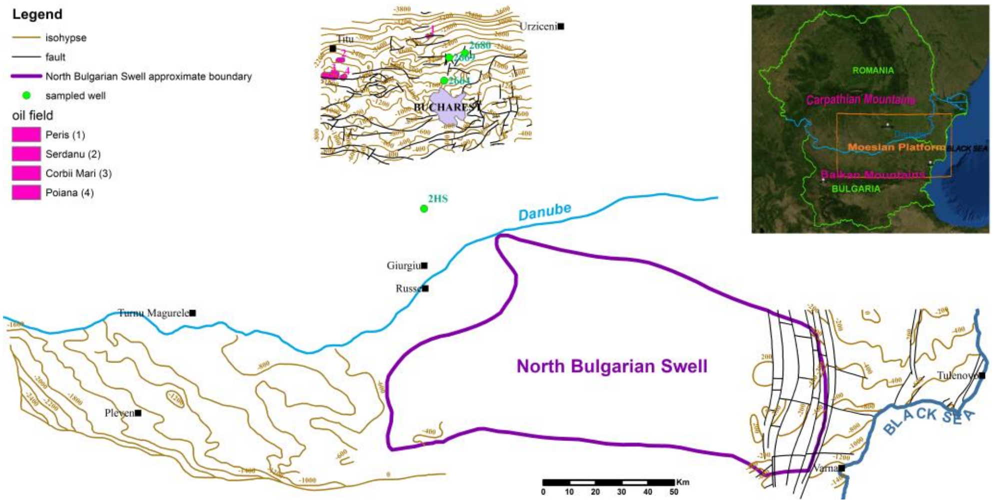

Figure 1. Fragments of a contour map at the top of the J_3-K1 carbonate reservoir (isohypses with respect to sea level; modified from CRĂCIUN *et al.*, 2000, and from SHTEREV *et al.*, 2002 b, c). The locations of the sampled wells addressed by the present study are also shown, as well as the locations of oil accumulations stored (PARASCHIV, 1979; ANASTASIU *et al.*, 2002) in the concerned reservoir. The domain represented on the map is indicated by yellow rectangle within the inset.

Within its thickness, which may be as large as 800-1300 m, the J_3-K_1 carbonate formation includes limestones and dolomites, both of which are, occasionally, cavernous and strongly fractured, consequently displaying a high permeability (a value of 120 mD, derived from a local well test, is indicated in PANU *et al.*, 2002). Siliciclastic, virtually impervious formations of Middle Jurassic (or, occasionally, Late Triassic) age underlie the concerned reservoir.

South of the Danube, the Early Cretaceous carbonate formation crops out in an uplifted structure – the “North Bulgarian Swell” (Fig. 1). Westward, northward and eastward of this doming feature, the carbonate reservoir progressively deepens beneath more recent (Late Cretaceous to Cenozoic), mainly clayey and sandstone formations, that are far less permeable (PARASCHIV, 1979; SHTEREV *et al.*, 2002 b, c).

In terms of water chemistry, bicarbonate-type freshwater saturates the carbonate formation in the regions located E and NE of the North Bulgarian Swell (BANDRABUR *et al.*, 1978; SHTEREV *et al.*, 2002 a, c). Alternatively, within the reservoir section that sinks W and NW of that outcrop area, the dominant dissolved anion is chloride, yet total salinities do not usually exceed 20 g/L (BANDRABUR *et al.*, 1978; CRĂCIUN *et al.*, 2000; SHTEREV *et al.*, 2002 b). It is thus suggested that in those western and northwestern sections of the reservoir, connate water may be interacting with freshwater recharged from the carbonate formation outcrop region. The general presence of connate water is in accordance with hydrocarbon accumulations known to be trapped (PARASCHIV, 1979; ANASTASIU *et al.*, 2002) in particular locations (e.g., Periş, Serdanu, Corbii Mari, Poiana – Fig. 1) within the concerned Early Cretaceous carbonate reservoir.

The present study aims to document specific signatures which might result from the inferred freshwater / connate water interaction. To this purpose, we additionally processed and interpreted previously published groundwater chemistry data which were available (BANDRABUR *et al.*, 1978; PANU *et al.*, 1994; ŢENU *et al.*, 1994; CRĂCIUN *et al.*, 2000) for a domain of the J_3-K_1 reservoir situated on the territory of Romania. Besides chemical analyses, we have compiled, processed and interpreted published data (NEGOIŢĂ, 1970; PARASCHIV, 1979; DANCHIV *et al.*, 1991; MITROFAN & TUDOR, 1992; SHTEREV *et al.*, 2002 b; CRĂCIUN *et al.*, 2000) about the groundwater temperature distribution within the aquifer hosted by the carbonate reservoir.

Groundwater samples that we considered for processing had been collected during pumping tests conducted in several wells that ranged in depth between 660 and 3,300 m, and which had been drilled during the late 1980s and early 1990s for geothermal resources exploration. Unfortunately, the geothermal research program was subsequently abandoned and it has not been possible, to the present day, to collect and analyze any additional water samples from the concerned aquifer.

2. GROUNDWATER CHEMISTRY GENERAL INFORMATION

According to available chemical data (retrieved from ŢENU *et al.*, 1994), groundwater sampled from wells tapping the J_3-K_1 carbonate reservoir seems to be largely derived from connate fluids that had been initially trapped in basin sediments. A preliminary evidence in this respect is provided by the fact that the most saline fluid (which was extracted from the well 2669 Baloteşti – see location in Fig. 1) is remarkably similar, in terms of its relative contents of Cl^-, Na^+, Ca^{2+}, K^+ and Mg^{2+}, with modern seawater (Fig. 2).

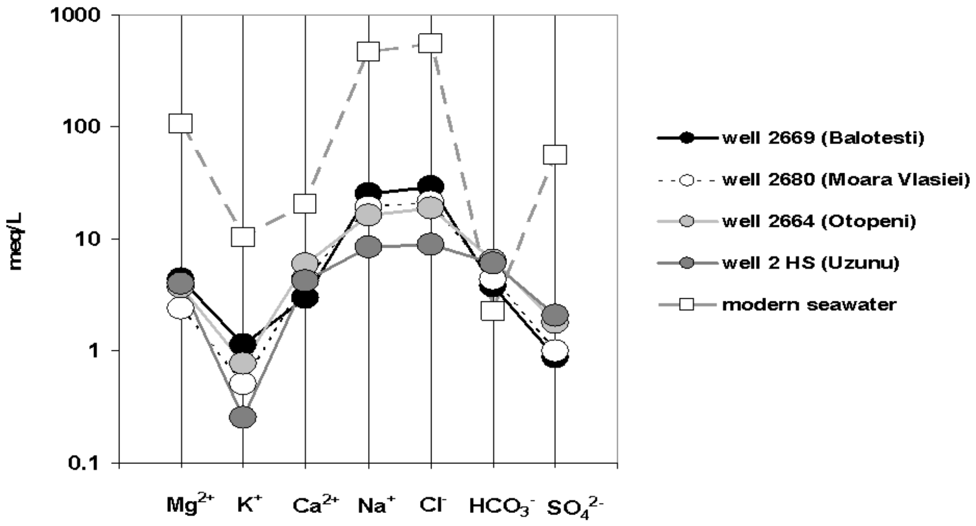

Fig. 2. Schoeller diagram constructed for groundwater samples collected from wells tapping the aquifer hosted by the J_3-K_1 carbonate reservoir.

Additional evidence for a marine provenance of the thermal water stored in the J_3-K_1 carbonate reservoir is provided by the Na^+ vs. Cl^- reciprocal concentration plot, in which groundwater samples from all considered wells are noticed to fall close to the seawater dilution line (Fig. 3): it is thus also indicated a progressive mixing with freshwater, whose contribution gradually increases toward the wells 2680 (Moara Vlăsiei) – 2664 (Otopeni) – 2 HS (Uzunu) (see locations in Fig. 1). Connate, seawater-type fluids are actually known to occur at Periş, Serdanu, Corbii Mari and Poiana (see locations in Fig. 1), in association with oil accumulations stored (PARASCHIV, 1979; ANASTASIU *et al.*, 2002) in the same Early Cretaceous carbonate reservoir.

More specific indications concerning the connate water / freshwater interaction are provided by the SO_4^{2-} ion behavior, which appears to be controlled by the following processes:

- In an initial stage, sulfate-reducing anaerobic bacteria are likely responsible for strongly depleting the original seawater content of SO_4^{2-}: it accordingly results groundwater that is H_2S-rich (concentrations in the 10-30 g/L range are reported in PANU *et al.*, 1994), but sulfate-poor (e.g., the sample collected from the well 2669 Baloteşti - Fig. 2).
- While the contribution of the oxygen-rich freshwater becomes more significant – as indicated by Cl^- concentrations progressively decreasing (Fig. 4) toward the wells 2680 (Moara Vlăsiei), 2664 (Otopeni) and 2 HS (Uzunu) – a gradual SO_4^{2-} enrichment occurs, ensuing to oxidation of larger amounts of the previously generated H_2S.

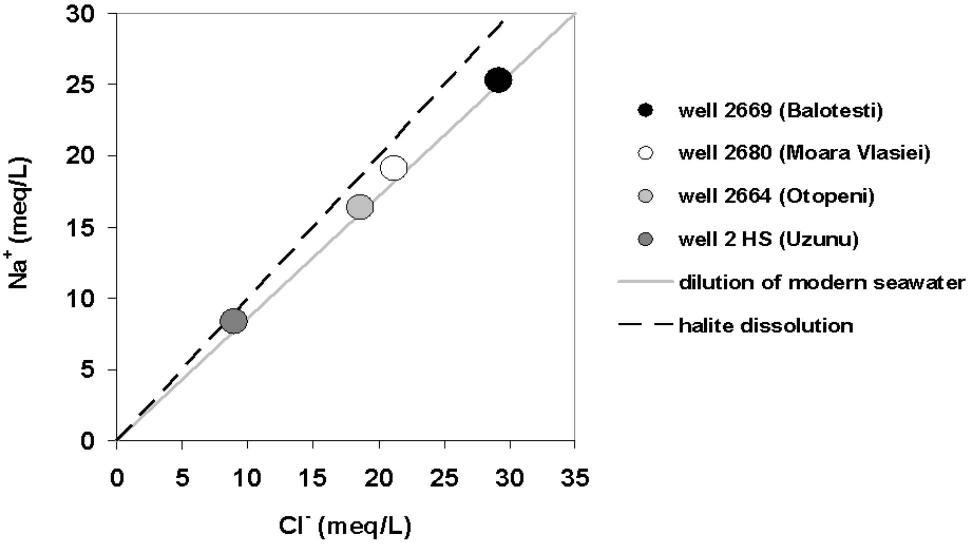

Fig. 3. Na^+ vs. Cl^- reciprocal concentration plot constructed for groundwater samples collected from wells tapping the aquifer hosted by the J_3-K_1 carbonate reservoir.

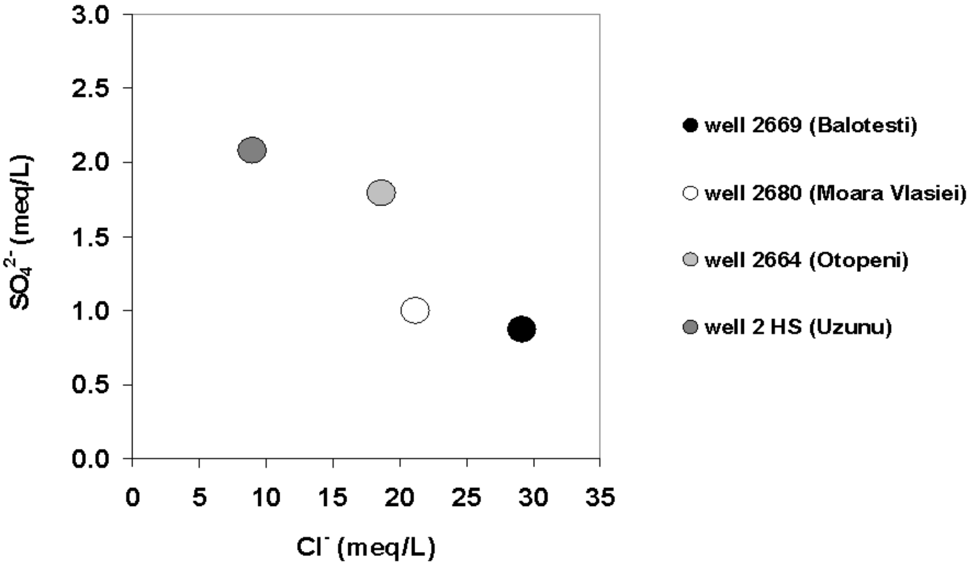

Fig. 4. SO_4^{2-} vs. Cl^- reciprocal concentration plot constructed for groundwater samples collected from wells tapping the aquifer hosted by the J_3-K_1 carbonate reservoir.

3. INFORMATION DERIVED FROM THE UNDERGROUND TEMPERATURE DISTRIBUTION

There are available (e.g., DANCHIV *et al.*, 1991; MITROFAN & TUDOR, 1992) temperature profiles recorded under thermal equilibrium conditions in shut-in wells that had been drilled for investigating the geothermal prospects of the J_3-K_1 carbonate reservoir. It was accordingly indicated that systematically, down the several hundred meters thick carbonate formation, a virtually isothermal regime occurred (Fig. 5); and occasionally, even a decreasing temperature trend was recorded with increasing depth. Those behaviors were in sharp contrast with the essentially linear thermal profiles recorded within the overlying (mostly siliciclastic, and virtually impervious) formations.

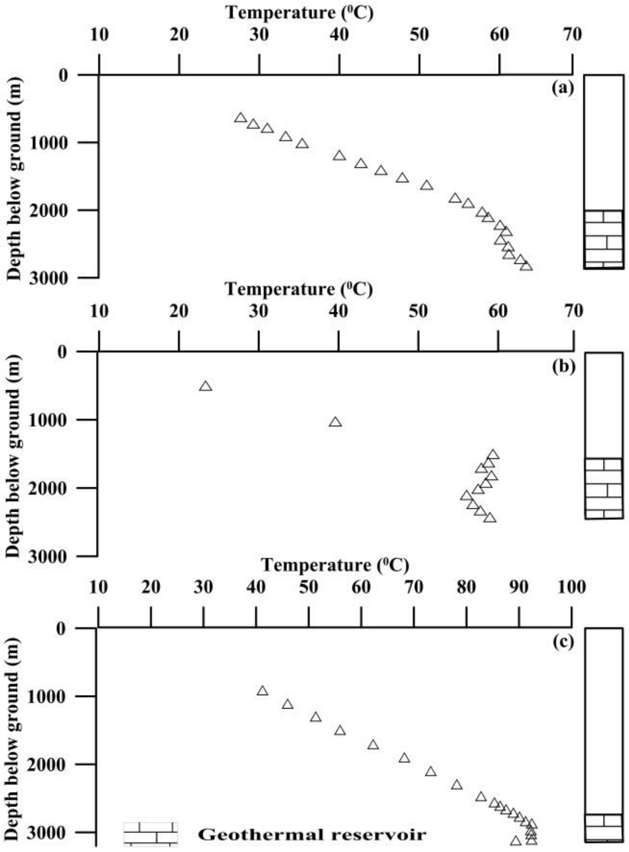

Fig. 5. Examples of temperature profiles (modified from DANCHIV *et al.*, 1991, and MITROFAN & TUDOR, 1992) recorded in shut-in wells which tapped the J_3-K_1 carbonate reservoir: (a) well 2663 (Otopeni); (b) well 2674 (Afumaţi); (c) well 2682 (Snagov). A schematic representation of the lithology intercepted by each well is indicated by the right-side columns, distinction being made only between the geothermal reservoir carbonate formation and the overlying, essentially impervious deposits.

It was consequently inferred (DANCHIV *et al.*, 1991; MITROFAN & TUDOR, 1992; ŢENU *et al.*, 1994) that convective heat transfer within the carbonate reservoir was controlling, to a large extent, the overall thermal regime. This obviously implies that thermal convection patterns should be mirrored also by the temperature lateral distribution. Yet the investigated wellbores are usually located no closer than 2-3 km from one another, hence they can hardly provide the data density necessary for an accurate characterization of an areal, convectively-induced thermal pattern. Therefore, the map which we constructed in order to outline the temperature distribution at the top of the J_3-K_1 carbonate reservoir (Fig. 6) must be viewed as tentative. In devising that image, we have started from an analogous map (DANCHIV *et al.*, 1991), which we additionally adjusted by using supplementary temperature data retrieved from NEGOIŢĂ (1970), PARASCHIV (1979), and CRĂCIUN *et al.* (2000). In our compilation we have included moreover (Fig. 6) analogous maps constructed (SHTEREV *et al.*, 2002 b) for the J_3-K_1 carbonate reservoir section that sinks westward of the North Bulgarian Swell (Fig. 1).

In the absence of a significant convective heat transfer, and admitting a lateral uniformity of the basal heat flow and of the thermal conductivity values, a steady increase of the temperature recorded at the top of the J_3-K_1 reservoir should be noticeable along with the progressive deepening of that carbonate unit under the overlying impervious formations: specifically, isotherms traced at the reservoir top are expected to mimick, fairly rigorously, the isohypses of that geological boundary. (In fact, isotherms should actually emulate the reservoir top isobaths; but since the ground topography is quite flat in the concerned areas, a virtually constant offset is recorded between isobaths and isohypses).

A general trend of temperature increase along with the reservoir deepening is indeed visible both north of the Danube, in Romania, and south of that river, in Bulgaria (Fig. 6). In each of those two settings however, there are also regions that extend roughly perpendicular to the isohypses of the reservoir top, and which display temperatures that are either significantly elevated, or significantly lowered relative to those corresponding to a strictly conductive regime. This specific pattern is likely a result of forced convective heat transfer induced (WOODBURY & SMITH, 1985) by a particular geometry of the concerned aquifer piezometric surface: the latter is supposed to have a general slope in agreement with the reservoir sinking direction, but there are also domains where the local piezometric gradient is transverse to the regional one.

The aquifer hosted by the J_3-K_1 reservoir must indeed have a general gradient of the piezometric surface in agreement with the carbonate formation slope: otherwise, the freshwater recharge from the outcrop areas (a process which had been frequently conjectured, e.g., BANDRABUR *et al.*, 1978; DANCHIV *et al.*, 1991; ŢENU *et al.*, 1994; SHTEREV *et al.*, 2002 b) would not be possible. Moreover, for the aquifer section situated north of the Danube, a tentative map of the piezometric surface had been actually constructed (CRĂCIUN *et al.*, 2000) by converting hydraulic heads recorded in wellbores, into "equivalent freshwater heads" (LUSCZYNSKI, 1961).

It was thus confirmed an overall agreement between the dip (from SSE to the NNW) of the aquifer host formation, and the general slope of the corresponding piezometric surface. Still the map of CRĂCIUN *et al.* (2000) also shows regions where hydraulic head gradients are transverse to the carbonate reservoir dip, thus confirming the possibility that the specific model of forced convective heat transfer proposed by WOODBURY & SMITH (1985) could be applicable to the concerned setting.

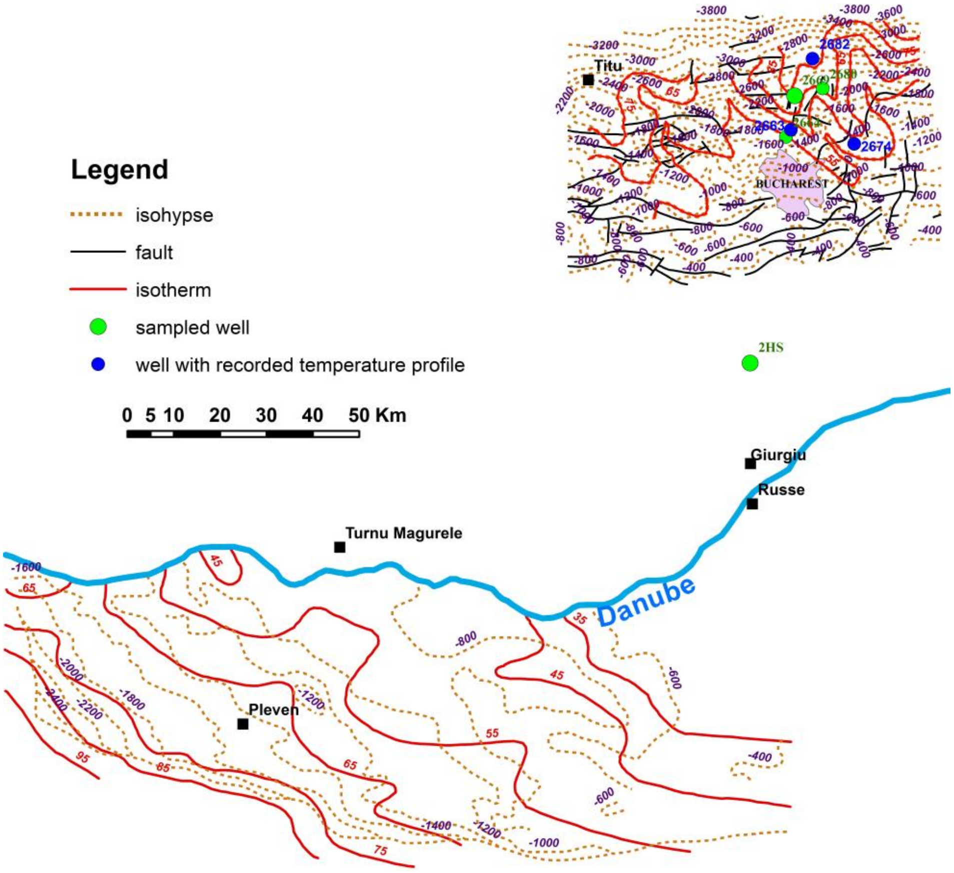

Fig. 6. Maps of temperature distribution (modified from DANCHIV *et al.*, 1991, and from SHTEREV *et al.*, 2002 b) at the top of the J_3-K1 carbonate reservoir, superimposed on contour maps of the same geological boundary (isohypses with respect to sea level – modified from CRĂCIUN *et al.*, 2000, and from SHTEREV *et al.*, 2002 b).

According to that model, subsurface temperatures lower than those expected for the case of a strictly conductive regime correspond to domains of groundwater downflow – specifically, for the considered setting, to domains of prevalently freshwater inflows from the meteoric recharge region associated to the North Bulgarian Swell. Such “colder” domains of the aquifer hosted by the J_3-K_1 carbonate reservoir have been identified beneath the NW and W parts of the city of Bucharest (Fig. 7): by corroborating data provided in DANCHIV *et al.* (1991), and CRĂCIUN *et al.* (2000), it resulted that NW of Bucharest (in a region that at ground surface roughly corresponds to Colentina valley), average thermal gradients in the virtually impervious formations that overlie the carbonate reservoir are as low as 17-18°C/km.

In contrast, similarly computed thermal gradients are almost double (30-33°C/km) north of Bucharest, at Baloteşti: it is thus suggested – according to the WOODBURY & SMITH (1985) model – that in this latter region, groundwater upflow occurs within the aquifer hosted by the J_3-K_1 carbonate formation. Such an inference is in agreement with the previously discussed observation concerning the well 2669 (Baloteşti) water sample: the latter displays the strongest chemical similarities with modern seawater and hence, likely, prevalently includes deeply originating connate water. Corresponding elevated temperatures in the carbonate reservoir seem to extend also SE of Baloteşti, toward Voluntari and Cernica (Fig. 7).

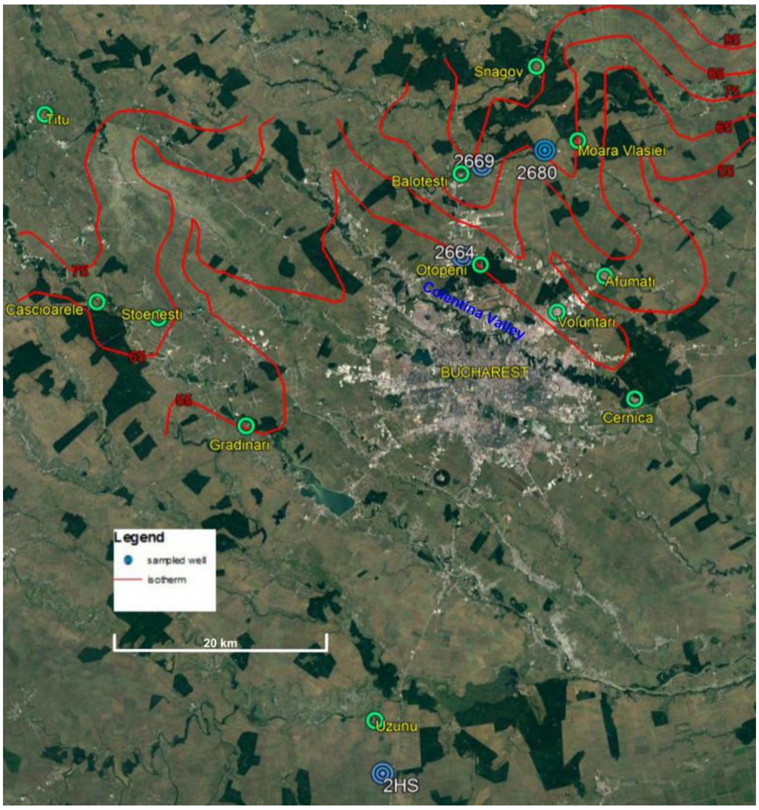

Fig. 7. Temperature distribution map (modified from Danchiv et al., 1991) constructed at the top the J_3-K1 carbonate reservoir for a region underlying the city of Bucharest and its surroundings (isotherms in °C). The locations of sampled wells addressed by the present study are also shown. Ground surface features are illustrated by a Google-Earth image.

Similarly, on a NW-SE striking lineament defined roughly by the villages Căscioarele, Stoeneşti and Grădinari (about 25 km W of Bucharest – Fig. 7), in the virtually impervious formations that overlie the J_3-K_1 formation, average thermal gradients of 40-43°C/km have been determined (PARASCHIV, 1979). Accordingly, it seems that also in the subsurface underneath this lineament, the aquifer hosted by the carbonate reservoir is concerned by a hot upflow of dominantly connate water. Unfortunately however, no water samples are available from wells having tapped the concerned aquifer in this particular region.

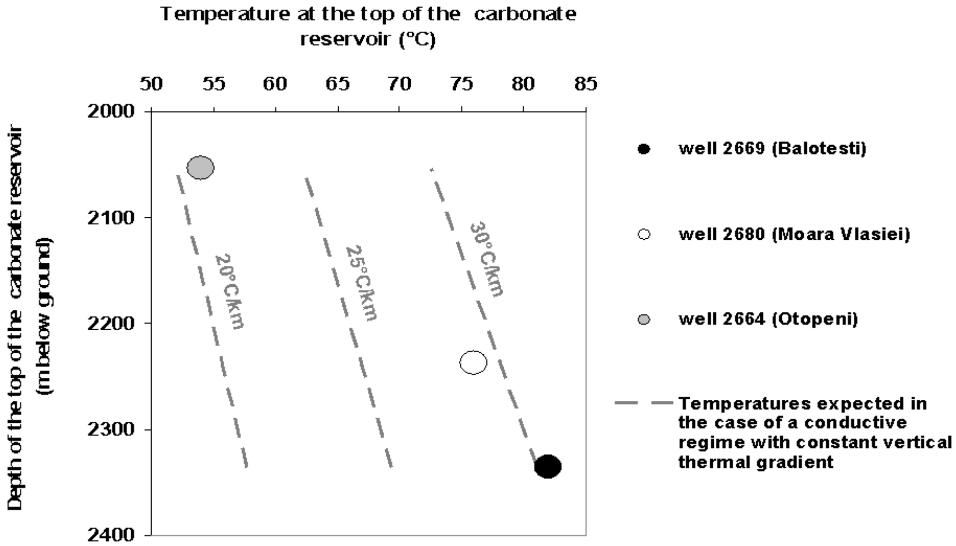

Fig. 8. Temperatures recorded at the top of the J_3-K_1 carbonate reservoir in the three indicated wells. Under a strictly conductive thermal regime and subject to a lateral uniformity of the heat flow and of the thermal conductivities, the concerned temperature values should have plotted approximately on a common linear profile - similar to those illustrated by each of the dashed lines (where the labels indicate the geothermal gradient which was used for constructing each corresponding hypothetical profile). The large discrepancies existing between the actually observed temperature values on one hand, and the temperature distributions hypothesized under a strictly conductive regime on the other, are a clear signature of convection strongly controlling the thermo-chemical characteristics of the aquifer.

4. POSSIBLE IMPLICATIONS CONCERNING RESERVOIR DIAGENESIS

Between the three sampled wells which are positioned relatively close to each other (2669 Baloteşti, 2680 Moara Vlăsiei, and 2664 Otopeni – Fig. 7) there is visible a progressive, and at the same time quite severe lowering of the corresponding temperatures measured at the top of the carbonate reservoir (Fig. 8): from Baloteşti, toward Moara Vlăsiei and Otopeni. The temperature contrasts recorded between the indicated wells are far larger than those which one would expect under the assumption (Fig. 8) of a strictly conductive heat transfer, subject to reasonable values of the geothermal gradient (20-30°C/km); consequently, the observed temperature pattern likely reflects a gradual increase – especially toward Otopeni – of the freshwater-induced cooling and dilution (the dilution process being mirrored – Fig. 9 – by the connate water characteristic constituents, Cl^- and Na^+, becoming, progressively, less concentrated, along with the temperature reduction).

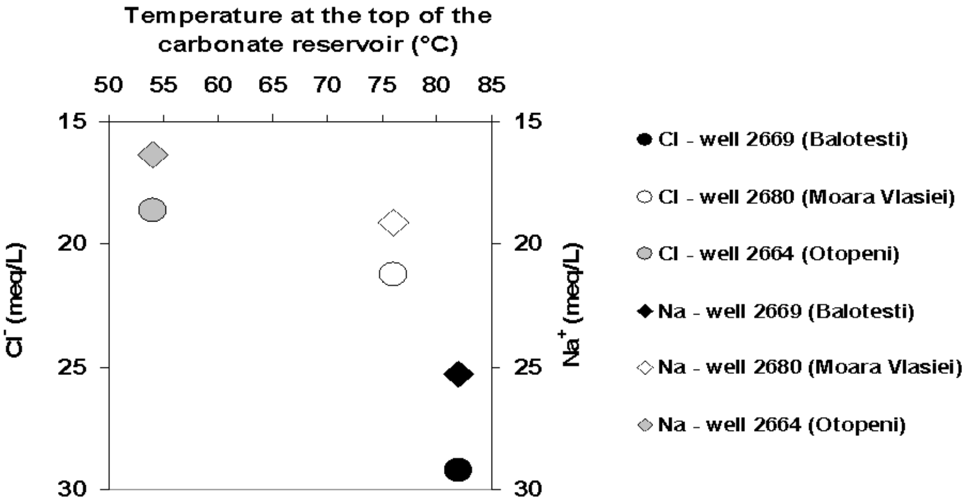

Fig. 9. Cl^- and Na^+ concentrations in thermal water sampled from the indicated wells, plotted against temperatures recorded in the same wells at the top of the J_3-K_1 carbonate reservoir (notice that vertical scales have a downward-increasing values-order). The outlined correlations illustrate that the deeply-originating warm, connate water undergoes simultaneous dilution and cooling, ensuing to progressive mixing with freshwater.

On the other hand, it is noticeable that as the freshwater-induced dilution intensifies, the HCO_3^- and Ca^{2+} concentrations gradually increase, a reverse correlation being outlined (Fig. 10) with the contents of Cl^- – the conservative constituent which can best be used for diagnosing the dilution intensity.

It hence appears that as connate water is progressively diluted by freshwater, the resulting mixture includes increasing amounts of dissolved calcite. Evidence is thus provided about diagenesis currently taking place within the J_3-K_1 carbonate reservoir: calcite is dissolved by upflowing plumes of dominantly connate water; while, conversely, along downflowing freshwater plumes, calcite precipitation is expected to occur. This overall behavior is most likely a consequence of the specific property of calcite of becoming increasingly soluble, as the aqueous solution progressively cools down ("retrograde solubility" – e.g., ANDRE & RAJARAM, 2005). Such an interpretation is also supported by the fact that Ca^{2+} and HCO_3^- concentrations in the sampled wells are reversely correlated with the corresponding temperatures recorded at the reservoir top (Fig. 11).

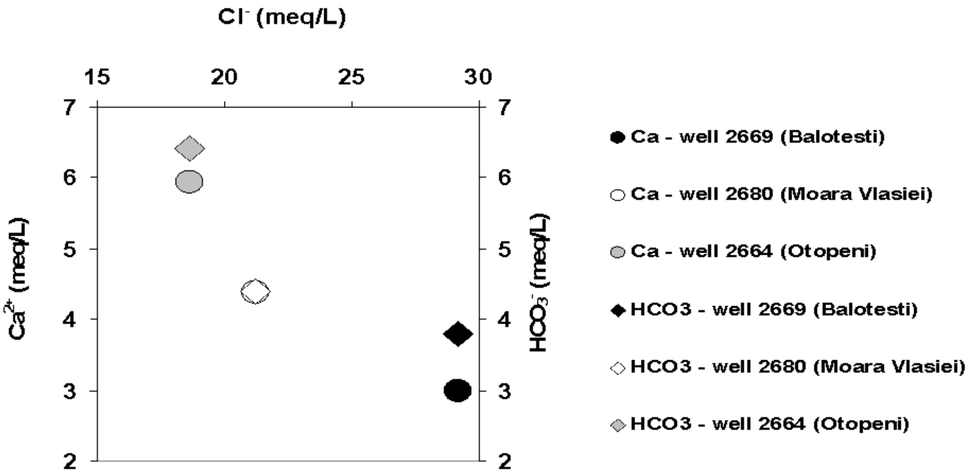

Fig. 10. Ca^{2+} vs. Cl^- and HCO_3^- vs. Cl^- reciprocal concentration plots constructed for thermal water samples collected from the indicated wells. The outlined reverse correlations illustrate a progressive uptake of calcite in solution, along with the increase in freshwater-induced dilution.

Table 1

Calcite saturation indexes

well	Sampling date	Temperature at the top of the carbonate reservoir (°C)	pH	Calcite saturation index
2669 (Baloteşti)	8-Jul-1991	82	6.7	0.01
2680 (Moara Vlăsiei)	15-Sep-1991	76	6.6	0.09
2664 (Otopeni)	25-Jun-1988	54	6.5	-0.02
2 HS (Uzunu)	10-Nov-1991	30	7.5	0.51

Further insights into the conjectured processes could be provided by diagnosing the sampled groundwater condition of being aggressive with respect to calcite, or, conversely, of being prone to calcite precipitation. Such a diagnosis is provided by the calcite saturation index.

For any mineral species, the saturation index *SI* is calculated as the product of the activities a_i of the *i* ions of the solid phase that are present in the solution, divided by the concerned mineral species solubility product *K*, for a given temperature *T*. Specifically, the corresponding equation for calcite is:

$$SI_{calcite} = log \frac{a_{Ca^{2+}} \times a_{CO_3^{2-}}}{K_{T(calcite)}}$$

If the saturation index value is zero, this indicates a chemical equilibrium status, meaning that the concerned solution is saturated with respect to the mineral species for which the index was calculated. Negative *SI* values indicate that the solution is undersaturated with respect to the considered mineral phase – hence the latter may undergo further dissolution. Positive *SI* values are indicative of a supersaturated solution, so that the concerned mineral species has the tendency to get out of the system – usually by precipitation. For the present study, the solute ion activities and the water saturation index values with respect to calcite have been computed by means of the software package PHREEQC 3.4 (PARKHURST & APPELO, 1999).

For each of the three considered samples, calcite saturation indexes computed (Tab. 1) by taking into account the temperatures measured at the top of the J_3-K_1 reservoir are always close to zero. Considering, in addition, the virtually isothermal regime which exists down the several hundred meters thick carbonate formation (Fig. 5), one can actually conjecture that also at the inflow depth (i.e., where each water sample originates) the aqueous solution is close to chemical equilibrium with the calcite in the host rock. Accordingly, the inferred groundwater flows – either updip or downdip the reservoir – must be slow, so that enough time is available for chemical equilibrium to be achieved, in correspondence to each new thermal status reached by groundwater.

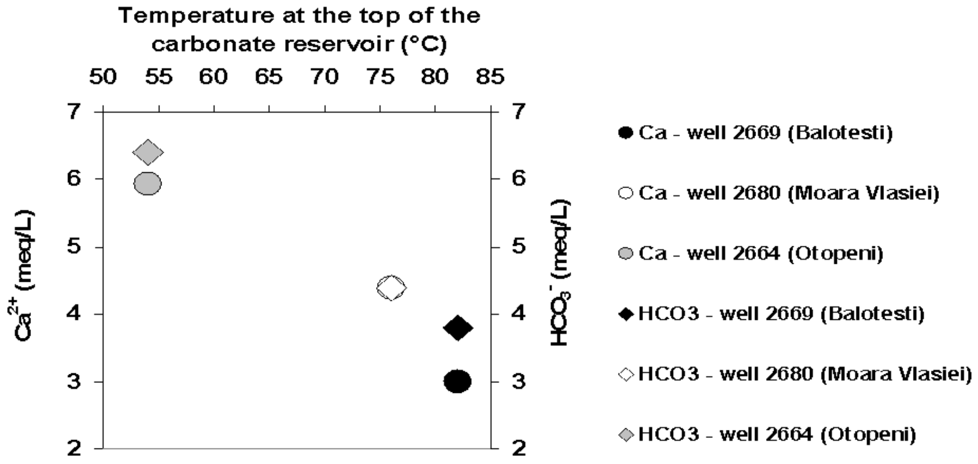

Fig. 11. Ca^{2+} and HCO_3^- concentrations in thermal water sampled from the indicated wells, plotted against temperatures recorded in the same wells at the top of the J_3-K_1 carbonate reservoir. The outlined reverse correlations most likely mirror the "retrograde solubility", which is a characteristic of calcite.

Alternatively, the calcite saturation index computed for the well 2 HS Uzunu indicates (Tab. 1) a non-negligible supersaturation. It consequently seems that the aquifer section located in the proximity of this borehole includes a freshwater downflow, which rapidly reaches an anomalously hot domain. Indeed, if one takes into account that the tapped aquifer occurs here at a quite small depth (in the 234-651 m range – ŢENU *et al.*, 1994), the concerned well discharge proves to be abnormally warm: 30°C – i.e., 19°C above the average ground surface temperature. Hence one may presume that under the inferred circumstances, the originally cool downflow of freshwater is heated up, and it becomes – due to the calcite retrograde solubility – significantly supersaturated: the process occurs faster than it would be necessary for the aqueous solution to chemically re-equilibrate at reservoir temperature – therefore not the entire calcite excess is deposited in the reservoir.

5. CONCLUSIONS

Within the Moesian Platform, an 800-1300 m thick carbonate reservoir of J_3-K_1 age extends laterally over tens, or hundreds of kilometers. From its outcrop area (the “North Bulgarian Swell”, located south of the Danube), the reservoir deepens, in a roughly radial pattern (Fig. 1), beneath more recent siliciclastic – and essentially impervious – formations.

A chemical facies quite similar to that of modern seawater has been outlined for groundwater saturating the reservoir section situated NW of the North Bulgarian Swell: it was thus indicated an origin derived from connate fluids having been initially trapped in basin sediments. Total salinity values are however lower than 20 g/L, which suggests also a significant freshwater-induced dilution.

The freshwater-induced dilution is likely a consequence of groundwater downflow, which is driven by a piezometric gradient that is, mostly, concordant with the J_3-K_1 reservoir dip from SSE to the NNW.

Yet locally, hydraulic head gradients transverse to the reservoir slope also occur. Such gradients are the probable cause of the aquifer being concerned by vigorous convection processes, mirrored by:

(i) vertical temperature profiles that display, across the aquifer large thickness, a virtually isothermal trend, or even a trend of decreasing temperature with increasing depth (Fig. 5);

(ii) significant horizontal temperature gradients recorded (Fig. 6) over aquifer domains which have their impervious top boundary situated at a similar depth;

(iii) concordance (Fig. 9) between such horizontal cooling gradients on one hand, and horizontal gradients of chemical dilution, on the other.

One can consequently infer that within the concerned aquifer, downflowing plumes of cool, prevalently freshwater, coexist with adjacent, upflowing plumes of warmer and dominantly connate water; such adjoining plumes most likely interact with each other, as well as with the host rock.

A probable signature of the connate water / freshwater plumes interaction is the dilution-related SO_4^{2-} enrichment (Fig. 4): the latter occurs when ensuing to an increasing contribution of oxygen-rich freshwater, larger amounts of H_2S associated to the connate water become oxidized.

Interaction with the host rock presumably involves two complementary diagenetic processes: as downflowing freshwater warms up – by gradual mixing with connate water – calcite is deposited in the reservoir; and conversely, as upflowing connate water is progressively diluted and cooled by freshwater, the resulting mixture dissolves increasing amounts of calcite. Such inferences rely on the specific property of calcite of becoming increasingly soluble, as the aqueous solution progressively cools down ("retrograde solubility"). This overall interpretation is supported by the sampled fluids' concentrations of Ca^{2+} and HCO_3^- displaying (Fig. 11) a reverse correlation with the temperatures estimated for the corresponding inflow depths. On the other hand, the calcite saturation index computed for most water samples is close to zero, indicating that the inferred groundwater flows – either updip or downdip the reservoir – must be slow, so that enough time is available for chemical equilibrium to be achieved in correspondence to each new thermal status reached by groundwater.

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