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Origin and migration of gases in the Pannonian sedimentary basin

J. Pezdič

Department of geology, Faculty of Natural Sciences and Engineering, University of Ljubljana, 1000 Ljubljana

Abstract. The study took place at the Southwestern part of Pannonian basin called Pomurje area. The highly mireralzed water has a big ammount of pure CO_2. Sources of this gas was the aim of detailed studies during several years. At broader region the possibilities of juvenil endogenic origin, organic mater maturation as well as carbonate decomposition products were indicated. Using structural, sedimentological, geochemical and mostly isotopical methods the inorganic origin due to dolomite decomposition at temperature range between 70 and 170°C was found as mostly probable.

1 Introduction

The Pomurje area lie at the Southwestern part of Pannonian basin called Pomurje nearby the known mineral water resource Radenci. Geologicaly it belong to Tertiary sedimentary clastic basin of the Miocene and Pliocene age. Using the data of previous investigations (Pezdič, 1991; Pezdič et al., 1991, 1995) a basic fluid dynamic model is developed, which consists of three basic water types with particular directions of flow, mixing, and sedimentation processes. The model is based upon previous hydrogeological studies, the possibilities of fluid transport, assumed aquifer compaction, isotope measurements, and species concentrations (such as Cl^- and HCO_3^-). Various equilibrium conditions may be found in the basin, which depend on temperature, rate of mixing, mineral composition of the rocks, and permeability of the aquifer.

The main processes take place near the surface at the Boračevo fault (a fractured zone) in the Radenci area and Ščavnica valley. The faults are active and partially contribute to migration of waters towards the surface. Mobility is also enhanced by porous zones of Miocene to Pliocene layers, which slope upward to the surface in this area and along the border between Palaeozoic metamorphic rock in Tertiary sediments at the Sobota massive.

Correspondence to: J. Pezdič (joze.pezdic@ntfgeo.uni-lj.si)

The capacity of the water flow in the system depends on the hydraulic gradient and the porosity of the stratigraphic layers. The reservoirs large volume and frequently low permeability of sediments limits fluid circulation. The dynamics of mixing can be seen in various isotope, chemical species, and pressure conditions in connected aquifers. The proposed and possible hydraulic pressures and directions of flow, characteristic of the Radenci region, are shown in Fig. 1. The final composition of water and dissolved species are expressed as the mixing ratio between the three basic water types (A – young meteoric, B – stagnant fresh and M – marine formation water). Over ten year long period of testing the stable isotope data of oxygen in water and chemical composition, especially sulphate ions show that old meteoric waters (type B) drained intensively to the pumped area, with velocity of around 6.3×10^{-6} m/s.

2 Modelling CO_2 production by decomposition of dolomite

The controlling factor of mobility and mineralization in the system is carbonate ionisation. The majority of gaseous CO_2 and aqueous HCO_3^- in both Radenci and the wider area was created by the intensive decarbonization of dolomite in the presence of silica and silicates (mainly clay minerals) at temperatures between 80 and 150°C. The reaction is slowly active also at atmospheric conditions (Pezdič et al., 1999). The system has a sufficiently large quantity of ancient dolomite. In contact with clastic sediments, the dolomite rapidly degrades also in the Tertiary sediments, which consist of up to 20% of clastic dolomite content (Pezdič, et al., 1995).

Thermodynamic calculations using the computer simulation, PHREEQE (Parkhurst, 1987–1993) shows a great amount of CO_2 can be produced at relatively low temperatures:

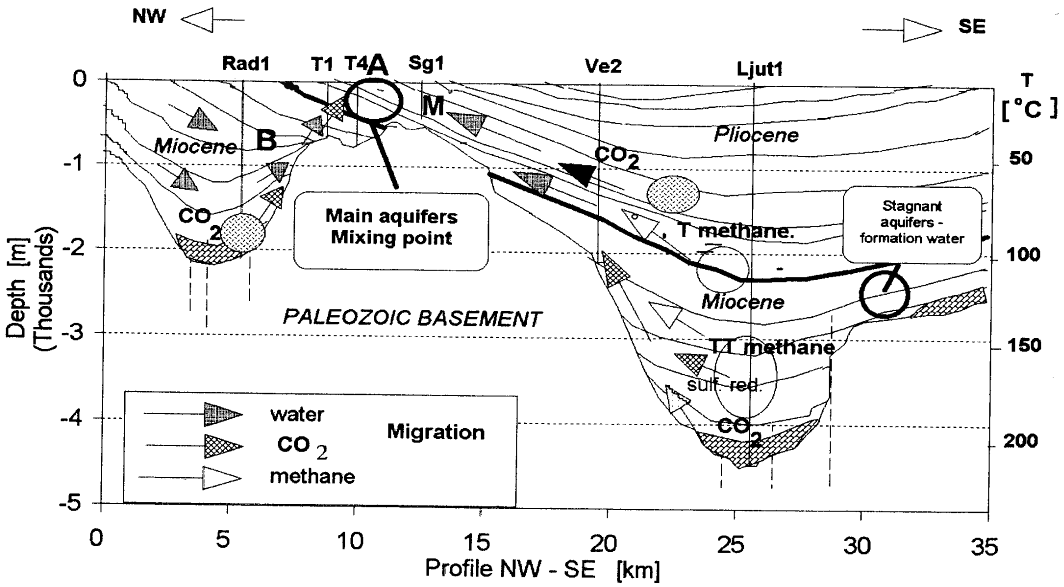

Fig. 1. Fluids transport through tertiary sediments over the Palaeozoic basement.

$$5\text{Dol} + 8\text{SiO}_2 + \text{H}_2\text{O} \Rightarrow \text{tremolite} + 3\text{CaCO}_3 + 7\text{CO}_2$$
$$5\text{Dol} + 4\text{SiO}_2 + \text{H}_2\text{O} + \text{kaolinite} \Rightarrow \text{chlorite} + 5\text{CaCO}_3 + 5\text{CO}_2$$
$$5\text{Dol} + 8\text{SiO}_2 + \text{H}_2\text{O} \Rightarrow \text{talc} + 3\text{CaCO}_3 + 3\text{CO}_2$$

In a closed system, the partial pressure of CO_2 (1 bar) is attained in the temperature range 70 to 120°C. These conditions are particular to the formation of clay minerals such as:

$$\text{tremolite}: \text{Ca}_2\text{Mg}_5(\text{SiO}_{11})_2(\text{OH})_2,$$
$$\text{chlorite}: (\text{Mg, Fe})_5\text{Al}(\text{AlSi}_3)\text{O}_{10},$$
$$\text{talc}: \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$$

In the presence of marine-like water or iron in dolomite (ankerite), the reactions are more rapid and temperature required for dissolution is lower. Minimal production of CO_2 occurs at the base of Tertiary sediments which are composed of metamorphic rocks and contain only marble. Marbles can be thermally decomposed at temperature over 700°C (Fyfe et al., 1978) but they are not found in the Radenci system.

Carbon isotope fractionation in carbonate species shows the origin of CO_2 as from the decomposition of dolomite (with δ^{13}C around +4‰) in the temperature range from 80 to 170°C (Pezdič, 1991). Specifically, this is seen from of δ^{13}C (CO_2) the range −5 to −2‰ measured in most of Radenci mineral waters.

Furthermore, some gaseous CO_2 is created by the processes of sulfate reduction and maturation of organic matter (kerogen). Both processes are related to the presence of organic matter in sediment layers. The isotopic composition of methane (Pezdič, 1991) and vitrinite reflection defined the intensity of production, processes of maturation, and isotopic composition of CO_2 (which has in this case δ^{13}C around −12‰).

Miocene and mainly Pliocene post-volcanic exhalative deposits are possible where $\delta^{13}C_{(CO_2)}$ does not negate this. However, considering other parameters, physical, and chemical characteristics of the system, the quantity of CO_2 from this source is marginal. Additionally, the origin of CO_2 from the mantle is not probable. This assumption may be checked by measuring the isotopic composition of helium, which was found in some waters but only in minimal quantities.

The gas flow through the surveyed system is expected to be very rapid since the areas where CO_2 is produced are several kilometres away, compared to locations of measurement. Nonequilibrium states are observed in the carbonate species and their isotopic composition differs between phases. In addition to the inclination of layers between fractured zones, the flow of CO_2 is facilitated by large grained clastic sediments whose porosities can reach up to 20% and permeability up to 10–3 cm/s.

3 Conclusion

The study draws conclusions of properties of the sedimentation basin, (particularly its fluid parts), possible sources and origin of its components, mixing processes of various types of fluids, and their interactions with the host rocks.

– Based on previous studies, possible thermodynamically favourable reactions, isotopic composition, and sample analysis, the principal source of carbon dioxide is attributed to reactions of dolomite with silica and clay minerals at temperature range between 80 and 150°C. A smaller part of carbon dioxide originates from the maturation of organic matter in the particulate strata and from reduction of the sulphate, and exhalations of carbon dioxide from the mantle plays a subordinate role.

– The established sedimentation and hydraulic model of the basin, supported by known hydrogeochemical characteristics, allowed us to draw conclusions on the likelihood of fluid transport towards Radenci. In addition, proportions of mixing between water and gas of various origins were demonstrated.

– Thermal gradients and heat flows contribute to the origin and transport of large quantities of CO_2 from dolomite decomposition. Temperature over 100°C is achieved at the depth of 2000 m and at the border between Tertiary sedimentary basin and Palaeozoic basement around Sobota massif degraded layers of Triassic dolomite relicts are seen.

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