The "Antica Fonte" of Boario (Italy): an hydrochemical and isotopic investigation in support of mineral water development

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Abstract. The "Antica Fonte" mineral water is a valuable resource with well-known therapeutic effects due to its high magnesium and sulphate contents. Hydrochemical and isotopic data indicate that the water is recharged at an elevation exceeding 1000 m asl, derives its mineral content by dissolution of Triassic gypsum and dolomite, and partially mixes with present day recharge from the alluvial aquifer. The results of this investigation provide valuable information for a sustainable development of the resource.

1 Introduction

The Terme di Boario spa are located in the Brescia province, Lombardy, northern Italy. The spa was established in the early 1700, and soon became a well know therapeutic centre. The development of the thermal complex took place in the 20th century with the construction of the main buildings in Art Nouveau style.

This contribution focuses on the "Antica Fonte" mineral water, one of the four springs which naturally outflow in the thermal park of the Terme di Boario. We report results of a hydrochemical and isotopic investigation conducted in recent years, in order to identify the water-rock interaction processes governing its mineral content and elucidate the water circuits.

2 Study area

The Terme di Boario spa are located in the Camonica Valley, in the Southern Alps, at an elevation of 220 m asl. The area is at the foothills of the Monte Altissimo, a thick Triasic sedimentary sequence reaching the elevation of 1707 m asl. The sequence starts with Servino limestone unit (Lower Triasic) that unconformily overlies the crystalline Permian basement (Verrucano Formation). This is followed by the Carniola di Bovegno Formation,

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constituted by dolomitic limestone and dolomites including gypsum and anhydrite lenses with a variable thickness. A series of limestone deposits subdivided in different units and reaching a total thickness of more than 1000 m are attributed to Middle to Upper Triasic. The sequence is topped by the Dolomia Principale Formation, mainly constituted by dolomite [1]. The general slope of the sedimentary sequence is to the N.

The Monte Altissimo therefore represents an important aquifer of highly permeable limestones separated by less permeable aquitards. The general groundwater flow follows the formation slope to the N, but flow through the aquitards is possible due fractures and discontinuities [2]. At the contact with the impermeable pre-Triassic basement, groundwater emerges giving rise to different mineral water types [2, 3].

3 Hydrochemistry

The hydrochemical composition of the "Antica Fonte" mineral water is reported in Table 1.

Table 1. Hydrochemical composition of the "Antica Fonte" mineral water.

Parameter	**Unit**	**08/03/2016**
Temperature	°C	15.2
Conductivity	µS/cm	2400
pH		6.88
Ca^{2+}	mg/L	581
Mg^{2+}	mg/L	95
Na^{+}	mg/L	8.3
K^{+}	mg/L	2.0
Li^{+}	mg/L	0.006
Sr^{2+}	mg/L	10.5
HCO_3^{-}	mg/L	278
SO_4^{2-}	mg/L	1517
Cl^{-}	mg/L	11.8
F^{-}	mg/L	0.78
NO_3^{-}	mg/L	<0.5
Fe	mg/L	0.113
Mn	mg/L	0.022
B	mg/L	0.018
SiO_2	mg/L	12.0

Most groundwaters outflowing at the foothills of the Monte Altissimo range are Ca-HCO_3-SO_4 type, and their mineral content originated from the dissolution of the carbonate host rock, as evidenced by the 1:1 ratio (in meq/L) of Ca to bicarbonate (Fig.1). With increasing mineralization, groundwater samples show an excess of Ca with respect to bicarbonate, that is balanced by an increased sulphate content. The "Antica Fonte" is of Ca-SO_4 type, with a Ca/SO_4 molar ratio of 0.92, close to 1 (Fig.1), suggesting that the mineral content could derive from the dissolution of Gypsum, which is abundant in the Carniola di Bovegno Formation [1]. This evidence is further supported by a Saturation Index close to 0.0 for Gypsum. The slight deficiency in Ca^{2+} is likely due to Calcite precipitation triggered by the Gypsum dissolution. Indeed, the Calcite Saturation Index is 0.19, indicating supersaturation. The water is also rich in Mg, reaching 8 meq/L, whereas most of the Ca-HCO_3 waters display contents of 2 to 4 meq/L. Magnesium is likely derived by the dissolution of Dolomite, as indicated by the Dolomite Saturation Index of -0.3.

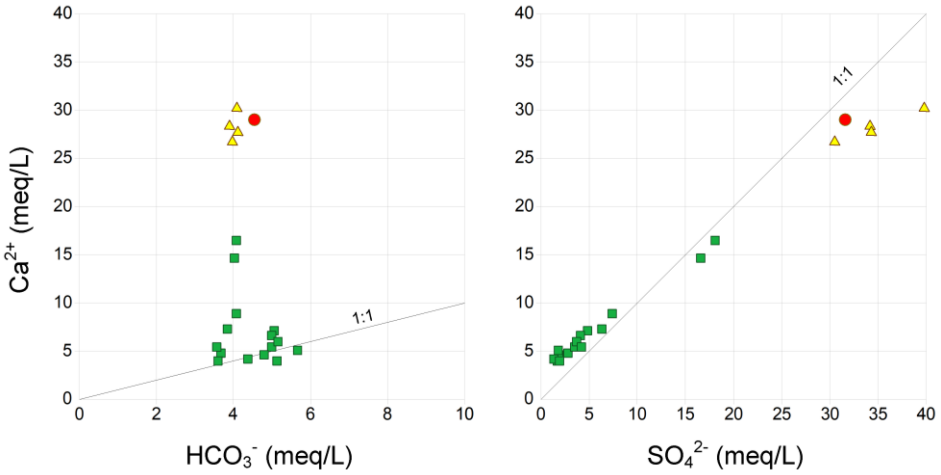

Fig. 1. Ca vs bicarbonate and sulphate contents in groundwaters from the Boario area. The circle represents the composition of the "Antica Fonte" water.

4 Groundwater circulation

Isotope geochemistry was applied to identify the mean recharge altitude, constrain water-rock interaction processes, and define the water "age". The main results are reported in Table 2.

The isotopic gradient with elevation was established using monitoring data of small perennial springs collected in the Monte Altissimo area. This corresponds to the following equations:

$$El.\ (m) = -363.5\ \delta^{18}O - 2153.5\ (R^2 = 0.90;\ n = 19) \quad (1)$$

$$El.\ (m) = -55.6\ \delta^{2}H - 2185.7\ (R^2 = 0.88;\ n = 19) \quad (2)$$

Accordingly, the "Antica Fonte" water is recharged at a mean elevation exceeding 1000 m asl, with a slight discrepancy between the estimates based on the two isotopes.

Sulfate isotopes confirm the origin of this compound by dissolution of Gypsum from the Carniola di Bovegno ($\delta^{34}S_{SO4}$=24.5‰; $\delta^{18}O_{SO4}$=16.2‰) of Lower Triasic age [2]. On the other hand, the Strontium isotope ratio is higher than that expected for waters circulating in Triassic limestones, evidencing a possible contribution from the leaching of the Verrucano

Formation of Permian age ($^{87}Sr/^{86}Sr$=0.7136-0.7211) [4]. Indeed, this formation outcrops close to the Antica Fonte original spring. The boron isotopic composition is compatible with the leaching of marine biogenic carbonates [5].

Table 2. Isotopic and dissolved gas composition of the "Antica Fonte" mineral water.

Parameter	Unit	Value
$\delta^{18}O$	‰ SMOW	-8.58± 0.2
$\delta^{2}H$	‰ SMOW	-56.7 ± 1
$\delta^{34}S_{SO4}$	‰ CD	25.1 ± 0.5
$\delta^{18}O_{SO4}$	‰ SMOW	14.3 ± 0.5
CFC-12	pmol/l	0.51 ± 0.05
CFC-11	pmol/l	0.02 ± 0.05
CFC-113	pmol/l	<0.01
SF_6	fmol/l	1.2 ± 0.2
Tritium	TU	5.3 ± 0.3
$\delta^{11}B$	‰ NBS951	11.4 ± 0.7
$^{87}Sr/^{86}Sr$		0.70846 ± 0.000026

Dissolved gases are dominated by N_2, followed by CO_2, O_2 and Ar, with ratios indicating a crustal rather than an atmospheric origin and suggesting a deep groundwater circulation [3]. Accordingly, the R/Ra ratio shows a clear crustal origin with an end-member of 0.0684, with no (mantle) juvenile addition. Finally, detectable Tritium, CFCs and SF_6 contents in groundwater indicate a contribution (of about 20%) of present day recharge which could derive from the alluvial aquifer.

5 Development of the resource and conclusion

The enhanced sulfate and magnesium contents are responsible for the well-known therapeutic effects of the "Antica Fonte" mineral water. The water has been used for centuries for liver detoxification and for its purgative effect. In 2014, the Ferrarelle group started to bottle the water under the brand name "Fonte Essenziale". Following its launch on the national market, a well-designed advertising strategy, especially targeting women customers with short commercial TV spots scheduled in the morning, allowed to increase the production from an initially estimated of 5 Mliters to 35 Mliters in only 9 months. This

commercial success requested the development of two new wells to satisfy the market demand, which were put in production in early-2017. Hydrochemical and isotopic monitoring of the new wells, in comparison with the "Antica Fonte" composition, helped for a better management and commercial development of the resource,

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