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ABSTRACT: The present work concerns the geochemical characterization of the water circulating in the Bossea karst system. In the cavity were sampled, in different hydrodynamic conditions, the waters of the main collector (Mora torrent) and numerous water supplies from drainage network of the unsaturated zone above the cavity and that flow into the main collector. Some seepages are located at the tectonic contact between the rocks of the metamorphic basement (metavolcanic) and carbonate coverage, others come directly from the network of cracks in the limestone and dolomite. The flow of these seepages generally is very low, less than 1 $L \cdot s^{-1}$. The characterization of the individual contributions and the main collector was performed through comparison of the major elements concentration using the Schöeller diagram and have also considered other parameters such as the lanthanides content, the calcite and dolomite saturation index. The data related to the lanthanides (REE - Rare Earth Elements) content normalized using the PAAS (Post-Archean Australian Shale) contribute to diversify the individual contributions that have different anomalies (especially cerium and europium) and/or trends in relation to the sampling period. Finally particularly interesting data have emerged from the correlation between the saturation indices of calcite and dolomite. For all the individual seepages is observed good correlation between the two indices, correlation is less marked when you consider all the values of the karst system under consideration. The data obtained shows, therefore, further differentiation between the individual seepages. From the overall analysis of the geochemical data obtained emerging a substantial complexity of the Bossea Karst system already highlighted by the monitoring data of flow rate, temperature and specific electrical conductivity of the water coming from the individual seepages and from the main collector.

KEYWORDS: *hydrogeochemistry, saturation index, Bossea cave, rare earth elements.*

1 STUDY AREA

The Bossea Karst system is located in the southern Piedmont, in the Ligurian Alps, at an altitude between 800 and 1700 m above sea level. The main absorption area is located between the Corsaglia Valley and the Maudagna Valley.

1.1 *Geological and hydrogeological layout*

The area is characterized by a complex tectonic history that brought the carbonate sediments, originally have built up over an ancient substrate of permo-carboniferous age (represented by metavulcanics and quartzites characterized by a very low permeability), to instead be interspesed in large outcrops separated from each other by important surfaces of dislocation which border compartments hydrogeologically independent, sometimes interconnected with each other in a particularly complex (figure 1).

The Bossea system is characterized by limestone and dolomitic limestone, laterally confined by the rocks of the metamorphic basement, metavulcanics and quartzites, through a series of sub-vertical tectonic contacts.

The carbonate aquifer is characterized by a relatively high permeability, with an underground circulationset to a main collector that receives the contributions coming from limestone-dolomitic storage and from rocks of the metamorphic basement. These rocks form a secondary aquifer, set along the discontinuity that border the carbonate structure and which, through a series of underground transfers, feeds the main aquifer (Peano et al. 2011; Banzato et al. 2011; Vigna & Doleatto 2008).

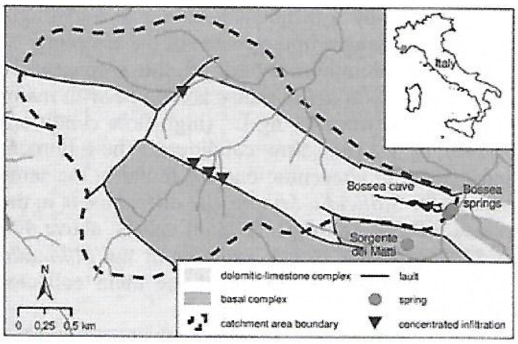

Figure 1. Study area.

1.2 *Groundwater flow description*

The Bossea cave is a cavity crossed by a mainkarst collector, Mora Torrent, that feeds a series of localized springs in proximity of the riverbed of the Corsaglia Torrent. The collector receives the waters by numerous secondary contributions and is fed in part by the circulation in the carbonate rocks and in part also by the surface water contributions flowing in the rocks of the metamorphic basement. The surface water contributions are absorbed by a series of concentrated infiltration in riverbed in proximity of the contact (figure 1).

The seepages more important, called "*polle*", are composed of contributions from fractures relatively open and karstified, usually present at the contact between the carbonate aquifer and the underlying basement (*Polla delle Anatre, Polla dell'Orso and Polletta*). The secondary seepages, denominated "*stillicidi*" and distributed in different sections of the cavity, are located on the cave vault and are usually derived from fractures masked by abundant calcite deposits (*Stillicidio Milano, Stillicidio Torre, Stillicidio Sacrestia*). They have a very low flow, lower than 0.008 $L \cdot s^{-1}$, with variations closely related to external weather conditions and become inactive only in particular situations of drought.

Near the catchment area are present a number of springs with moderate flow, around 0.5-2 $L \cdot s^{-1}$, but rather constant in time, recharged by the rocks of the metamorphic basement. One of these sources, called *Sorgente dei Matti*, was taken as "*sample spring*" representative of the underground circulation set in metavolcanic rocks (figures 2, 3).

2 HYDROCHEMISTRY CHARACTERIZATION OF INDIVIDUAL CONTRIBUTIONS

The water of Bossea Karst system presents an average mineralization between 162.23 and 409.51 $mg \cdot L^{-1}$ in terms of *TDS*. The lowest values are found in the waters of the main collector (*Torrente Mora*) and those circulating in metavulcaniti (*Sorgente dei Matti*) while the higher ones belong to the individual seepages.

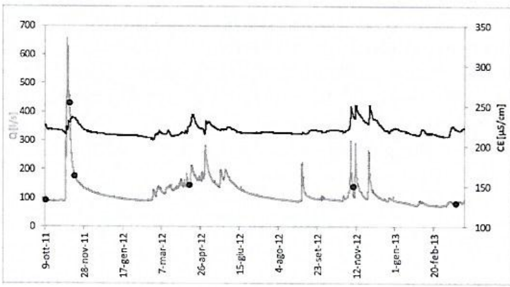

Figure 2. Collector flow and electrical conductivity.

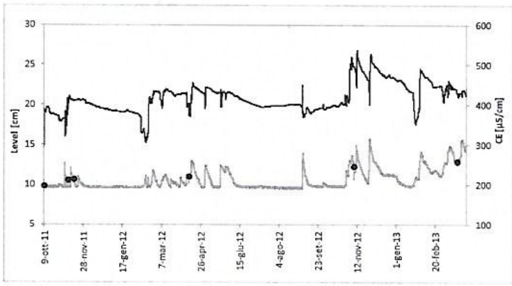

Figure 3. *Stillicidio Milano* level and electrical conductivity.

The hydrochemical facies found in several samples remain essentially constant over time but are substantial differences between the different sampling points (figure 4). *Bicarbonate-calcium-magnesium facies* are observed in the seepages called *Milano* and *Polletta* and *bicarbonate-calcium facies* in other seepages, in the main collector and in water circulating in the metavulcanic rocks. In the *bicarbonate-calcium facies* can be seen, however, differences in the Ca^{2+} / Mg^{2+} ratio ranging from 4.11 (*Polla Anatre* – mean value) to 41.49 (*Sacrestia* – mean value). This ratio report presents average values of 6.99 in main collector and 21.96 in the waters circulating in metavulcanic rocks. The wide variability of the Ca^{2+} / Mg^{2+} ratio is due to the different contents of the ion Mg^{2+} which is the only parameter, including the main ones, to differentiate the different seepages. The parameters with concentrations lower than 0.1 $meq \cdot L^{-1}$ (alkali, chlorides and sulfates) are subject to greater variations in time.

Sorgente dei Matti and *Polla delle Anatre* are characterized by alkali concentrations greater than those of the chlorides. This fact shows the presence of water coming mainly from metavulcanic rocks.

3 LANTHANIDES FOOTPRINT

The lanthanides are a family of 15 chemical elements with chemical properties very similar to each other that in the hydrogeological field can be used for the characterization of the aquifers. The concentrations and distributions depend specifically by the different rocks with which the water came in contact, and despite the low concentrations present specific trends for different waters (Biddau et al. 2009; Banks et al. 1999; Fiorucci & Moitre 2012). Moreover, at present, do not have a full-blown human footprint, and for this reason can be used for the study of the natural geochemical fund.

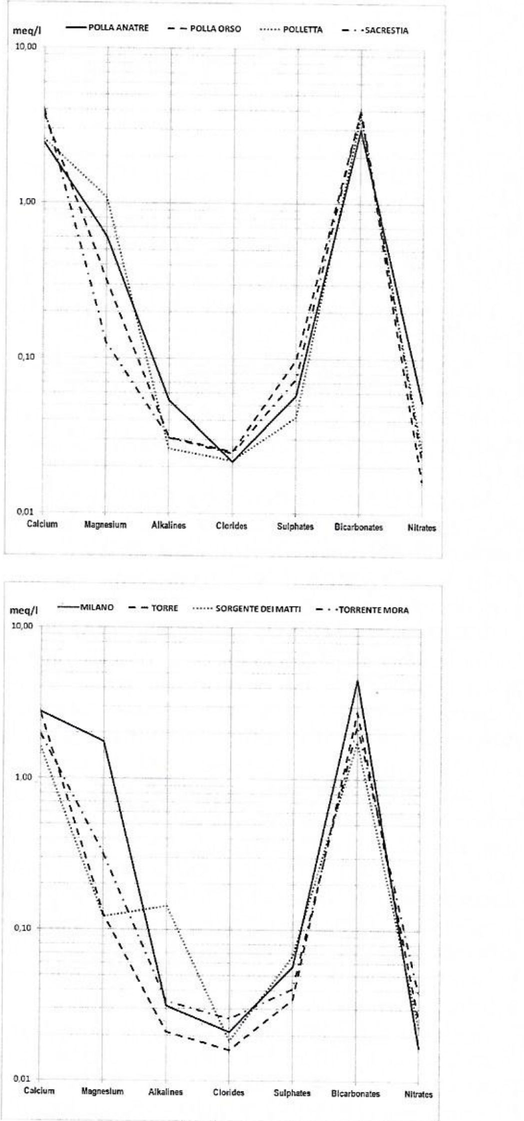

Figure 4. Schöeller diagrams.

The rare earth elements concentration in the basal complex spring remains almost constant in the different sampling and seems quite high (average value equal to 765 ng·L^{-1}). The seepages, instead, are characterized by a different behavior and highlight remarkable changes in the course of the sampling.

The concentrations ranges of the seepages are quite large. *Polla delle Anatre* is the one with major variations, between 21 ng·L^{-1} (high flow condition) to 1481 ng·L^{-1} (low flow condition). The minimum and maximum concentrations are found in the same periods for *Stillicidio Milano*, the difference is in the values (40 and 180 ng·L^{-1}). High values, above 400 ng·L^{-1}, are found in two samples in the *Stillicidio Sacristia* and in a sampling of the main collector (570 ng·L^{-1}).

The concentrations of the *REE* were normalized with the *Post-Archean Australian Shale – PAAS* (McLennan 1989), to highlight the changes in time and the differences between the main collector, secondary seepages and the basal complex springs (figures 5-12).

Unlike Schöeller diagrams, the diagrams which characterize the relationship between the *REE* and *PAAS* not remain constant in time but show differences between the different sampling periods. The only exception is*Sorgente dei Matti*, whose trend remains unchanged in time. These differences may indicate that the Bossea Karst system is a complex system, in which is possible to highlight different catchment circuits between the various seepages and the main collector. Furthermore, important quantitativeand trend changes are observed in the same seepages, in different hydrodynamic conditions.

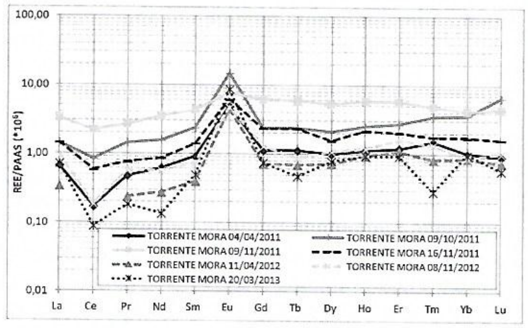

Figure 5. *Torrente Mora* REE/PAAS concentration.

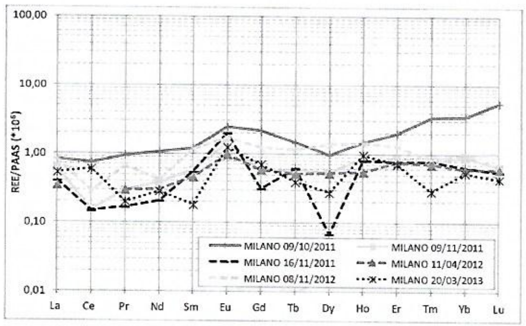

Figure 6. *Stillicidio Milano* REE/PAAS concentration.

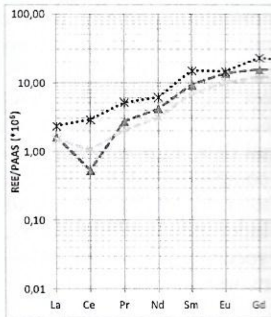

Figure 7. *Sorgente dei Matti* REE

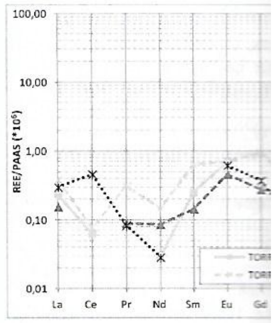

Figure 8. *Torre* REE/PAAS conc

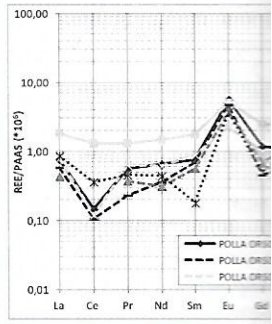

Figure 9. *Polla Orso* REE/PAAS

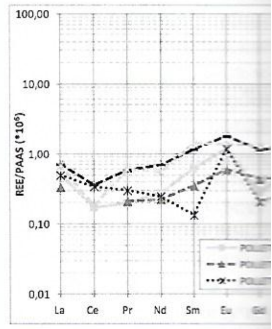

Figure 10. *Polletta* REE/PAAS

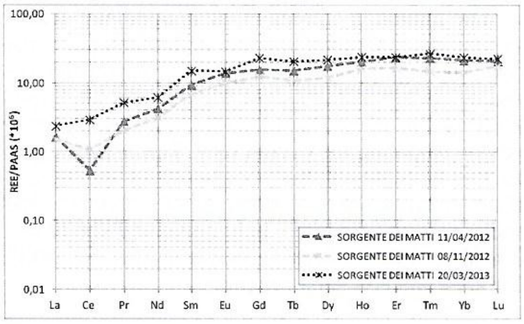

Figure 7. *Sorgente dei Matti* REE/PAAS concentration.

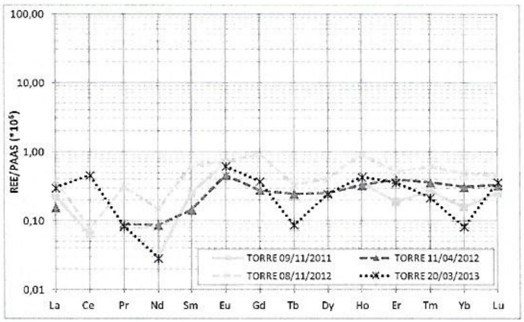

Figure 8. *Torre* REE/PAAS concentration.

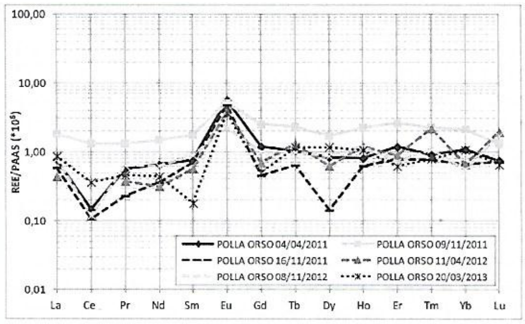

Figure 9. *Polla Orso* REE/PAAS concentration.

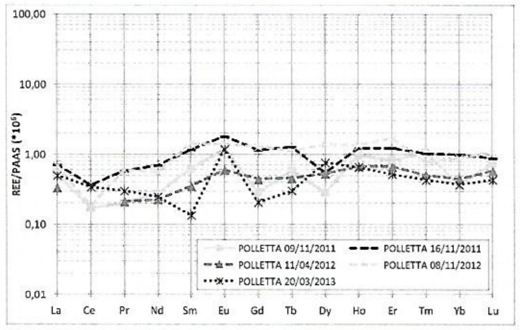

Figure 10. *Polletta* REE/PAAS concentration.

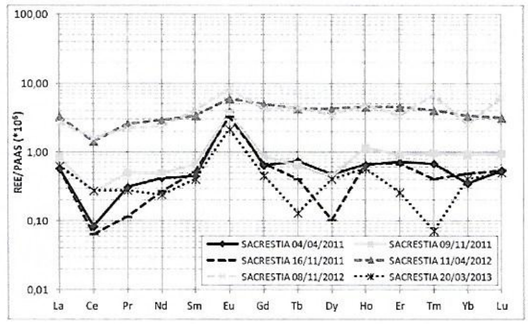

Figure 11. *Sacrestia* REE/PAAS concentration.

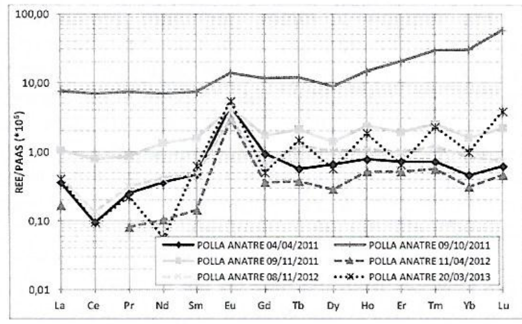

Figure 12. *Polla Anatre* REE/PAAS concentration.

4 SATURATION INDICES

The calcite and dolomite saturation index were calculated using the ratio between the product of ionic activity (with the single ion activity determined with the equation of Debye-Hückel) and the solubility product.

The waters in almost all samples are to be supersaturated in respect of calcite, while recording a considerable number of cases in which they are undersaturated in respect of dolomite.

Considering all the samples there is a fairly good correlation (figure 13) between the two indices (r^2 equal to 0.7738), evaluating the correlation for each contribution is noted that these have values of correlation coefficient always greater than 96 % and angular coefficients of the correlation lines are very similar, varying from a minimum of 0.4330 (*Sorgente dei Matti*) to a maximum of 0.5036 (*Polla delle Anatre*).

5 CONCLUSIONS

The geochemical data show a substantial complexity of the Bossea Karst system already highlighted by the monitoring data of flow rate, temperature and specific electrical conductivity of the water of seepages and main collector.

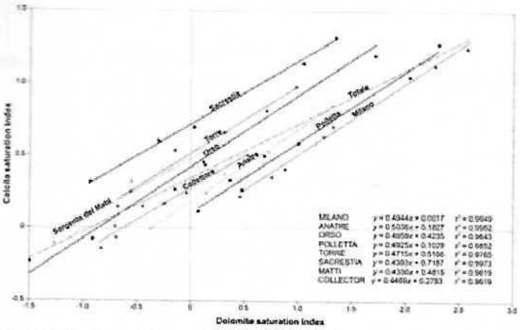

Figure 13. Correlation calcite and dolomite saturation index.

The analysis of facies, performed considering only the major elements, highlights the differences between the individual contributions due substantially to the Ca^{2+} / Mg^{2+} ratio and, in some cases, $(Na^{+} + K^{+}) / Cl^{-}$ ratio. This last, when it assumes values much greater than 1 indicates a water circulation that involves the parts not carbonate of the system (*Polla delle Anatre*, *Sorgente dei Matti* and occasionally also the other seepages).

A clearer distinction between the individual seepages emerges from the data on the lanthanides content, which also seems to show the differences, relative to each seepages, linked to the different sampling periods.

The saturation indices calculated indicate waters almost always supersaturated in respect of calcite and also largely for the dolomite. The correlation between the two indices show high values when considering the individual seepages, while it is lower when comparing the overall data. This aspect seems to further highlight the complexity of the Bossea Karst system as already shown by other geochemical indices. Every circuit is independent of the others, but instead the collector receives the waters of all the karst and non-karst networks.

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О зоне силикатного ти
уралья

А.Я. Гаев
Оренбургский научный центр

АННОТАЦИЯ: Модель карсто
сферно-мантийной средой.
нильной воды в астеносфере
скими породами земной коры
растворимости кристаллически
ликатного карста и разработку

КЛЮЧЕВЫЕ СЛОВА: *карсто*

Г.А. Максимович выделил в
ского фундамента платформ
за, опираясь на терминологию
(Максимович, 1964). Способность
ных недр растворять даже вто
этой зоне он отметил, анализи
мы в разрезах самых глубоких
го золота Южной Африки.
указал на наличие там силикат
(Максимович, 1969). Кристалли
ные породы занимают в разрезе
ности сотни километров в земной
мантии. Это несоизмеримо, как
и по объему с осадочной оболочкой
соизмерима по масштабам области
катного карста.

Однако, традиционно карсту
ми считаются только известняки,
гели, терригенно-карбонатные
гидриты и соли, которые зани
ских разрезах континентов не
ема осадочного чехла и только
ма земной коры. Среди карсту
обладают карбонаты, состав
1.7 % от веса земной коры.
глубин порядка 5 км. Процессы
глубже, почти не изучены.

Эксперименты со «сверхвод
Максом Вильке с коллегами,
ления о породах, подверженных
комбинационного рентгеновского
исследователи подвергли малень