Sr isotopes and U series radionuclides in the Sangemini area (Central Italy): Hydrogeology implications

Maurizio Barbieri[1], Angela Nigro[1], Mario Voltaggio[2]

[1] Department of Earth Science, Sapienza University of Rome, P.le A. Moro, 5 - 00185 Rome, Italy
[2] NationalRresearch Council, Institute of Environmental Geology and Geoengineering, Montelibretti, Via Salaria Km 29 – Rome, Italy

Corresponding author: Prof. Maurizio Barbieri, Department of Earth Science, Sapienza University of Rome, P.le A. Moro, 5 - 00185 Rome, Italy. Tel. +39-06 4991 4593; e-mail: maurizio.barbieri@uniroma1.it

Abstract

The strontium isotopic ratio (expressed as $^{87}Sr/^{86}Sr$) of groundwater represents a useful method for studying and understanding the groundwater circulations, also, the U and Ra isotopic compositions can vary as function of the groundwater residence time.

This paper reports an evaluation of the probable recharge area of the Sangemini mineral water springs (Terni-Umbria Central Italy) and an estimate of the residence time of the aquifer by coupling Sr and U series isotopic systematics. For this study have been analyzed four water sample for the isotope ratio of $^{87}Sr/^{86}Sr$, and eleven samples, shallow waters and groundwaters, for U and Ra, furthermore were determined the values of isotopic ratio for sample of typical rocks of the area. The results of this study allow to identify: a recharge area in a restricted sector of the Meso-Cenozoic carbonates a longer and more effective water/rock interaction in the Quaternary series. U and Ra recoil models allow to estimate a groundwater residence time of about 350 years and a total water volume whose value ($64*10^6$ m^3) agrees with the limited extension of the aquifer.

The extension of the aquifer was constrained by comparing Sr isotopic composition of waters and local geological formations. Groundwaters seem mainly to circulate in clayey sandy Quaternary series characterized by low redox conditions.

1.Introduction

The strontium isotopic ratio (expressed as $^{87}Sr/^{86}Sr$) of groundwater represents a useful method for studying and understanding the lithological characteristics of a sedimentary basin. In effect $^{87}Sr/^{86}Sr$ isotopic ratio can be used as a tracer for understanding the lithological composition in which the groundwaters circulated and for the reconstruction of the potential areas of recharge for the aquifer levels [1]. This is possible by the comparison between the value of the strontium isotopic ratio measured in the waters and in the rocks from the local lithological series. It is well known [2] that the Sr isotopic ratio measured in the marine limestones is the same of the $^{87}Sr/^{86}Sr$ isotopic ratio characteristic of the marine water during the $CaCO_3$ deposition. The

scientific literature records the Sr isotopic curve as a function of time for the Phanerozoic and for well-defined chronological intervals [3]. This curve show high and low values which are in relationship with the orogenetic events occurred in the Earth during its geological past.

Moreover groundwaters can be characterized by their Uranium content and their $^{234}U/^{238}U$ ratios as well as by their radium content and their $^{228}Ra/^{226}Ra$ ratios.

In particular the U and Ra isotopic compositions can vary as function of the groundwater residence time, with rates which largely depend on the kind of aquifer model has been assumed [4, 5].

The Sangemini hydrogeological Basin is located in the Western part of the Monti Martani, between Spoleto and Terni towns (Central Italy). The Monti Martani

complex during Plio-Pleistocene divided the old Tiberin lake in two branches, Western and Eastern respectively.

The spring waters analyzed in the present paper are all included between Monti Martani and the sandy and gravelly deposits from the old Tiberin lake. The bedrocks of the Torrente Naia, to which the Sangemini and Fabia waters belong, show a composite lithology. The western area is constituted by Plio-Pleistocenic sedimentary terranes filling of the old Tiberin lake. The eastern area is delimited by the Monti Martani crest formed from the top to the bottom by a large plate of travertine, by Jurassic-Cretaceous calcareous terranes and by calcareous marls of Cretaceous age, typically of the "Umbria sedimentary series".

The "calcare massiccio", "maiolica" and "scaglia rossa" constitute the "permeable" terranes useful for the underground circulation [6]. The Quaternary continental terranes are mainly constituted by lacustrine deposits formed by sandy series which in the lower part of the outcrop show an high content of clay minerals and organic matter resampling the characteristics of a peat. The higher levels are clearly arenaceous terranes.

From the hydrogeological point of view, the continental terranes are formed by impermeable and permeable levels: the sandy levels are permeable for porosity, whereas the clayey levels are not permeable and finally the peaty levels are quite impermeable.

2. Material and Methods

For $^{87}Sr/^{86}Sr$ isotopic ratio measurements were analyzed two of the water samples analysed arise from springs near Sangemini basin. Other two samples come from waters taken from bottles labeled as "Sangemini" and "Fabia".

The analytical methods are the following: 50 ml of water are mixed with 50 mg of Na_2CO_3 (Sr free) and the solution is heated to 70°C. Then the residue is dissolved with 2.5N HCl acid and soluble Sr (Sr related to $CaCO_3$ content of the samples) is separated from the bulk of other elements by means of ion exchange columns.
Isotopic ratios are measured and compared with standard $SrCO_3$ (SRM NBS 987) for which a ratio of 0.71024 has been assumed. Measurements are made using a VG 54E mass spectrometer. $^{87}Sr/^{86}Sr$ values have been normalized to $^{87}Sr/^{86}Sr$ = 0.1194.

For lithology, 100 mg of ground sample and 1 g of Na_2CO_3 were treated with 40 ml H_2O for 6 h at 70°C the sample obtained was subsequently dissolved with 2.7 N HCl. After evaporation to dryness, the resulting $CaCl_2$

was dissolved in HCl and the solution passed through a cation exchange resin to separate strontium.
Eleven samples of mineral water (eight bottled as "Sangemini" and two bottled as "Fabia") from the study area have been analysed for Uranium content and $^{234}U/^{238}U$ activity ratios. These samples were extracted both from deep levels (T6, T9, S10 at about - 80 m) and from the shallow ones (S3, S15, S13, S9, SG7, Piagge, F2, F4 at about -30 m).

Uranium content and activity ratios were determined by isotope dilution with 232U, using anionic exchange resins and liquid/liquid extractions with TTA to separate and purify the uranium isotopic complex. Final solutions were evaporated onto stainless steel discs and analysed by alpha mass spectrometry. Four samples (S3, S15, T9, F2) were analysed for Radium content and $^{228}Ra/^{226}Ra$ activity ratios, by precipitating quantitatively radium with barium sulfate and analysing the precipitate by high resolution gamma spectrometry.

Table 1. $^{87}Sr/^{86}Sr$ isotopic ratios, Sr content and total residue in water samples.

Sample	$^{87}Sr/^{86}Sr$	Sr mg/l	Total Residue mg/l
Sg7	0.708159	n.d	n.d
Piagge	0.708380	n.d	n.d
Fabia	0.708318	1	437
Sangemini	0.708490	3	955

3. Results

Analytical results for $^{87}Sr/^{86}Sr$ isotopic ratio of groundwaters are presented in table 1, while in table 2 are presented the values of isotopic ratio of some deposits outcropping in Sangemini area.

The groundwaters shows a numerical ratio included between 0.708159, for SG7 sample, and 0.708490 for Sangemini sample. The deposits show a concentration of Sr included between 250 ppm for the Scaglia and 1200 ppm for the Travertine, while the isotopic ratio for the carbonate fraction change between 0.706803 for the Calcare Massiccio and 0.708980 for Clayey material. The $^{87}Sr/^{86}Sr$ isotopic ratios of the groundwaters are different from that of each permeable lithology U content of the aquifer rocks, (Ur), ranges between a maximum of 480 ppb (mixed sample of local marine carbonatic rocks) and 50 ppb, (the average of ten continental carbonate samples from the travertine plate outcropping in the study area).

Table 2. ^{87}Sr/^{86}Sr isotopic ratios, Sr content of some deposits outcropping in Sangemini area.

Sample	^{87}Sr/^{86}Sr Carbonate Fraction	^{87}Sr/^{86}Sr Silicate Fraction	Sr ppm
Clayey material	0.708980	0.716890	600
Travertine	0.707874	n.d	1200
Scaglia	0.707893	n.d	250
Calcare Massiccio	0.706803	n.d	280
Maiolica	0.707236	n.d	320

The ^{228}Ra/^{226}Ra isotopic ratio were analyzed for four samples (Table 3), the results show a values about 0.52. U contents of studied waters (U_w) are notably variable (<0.001-4.4 ppb) whereas 234U/238U activity ratios range between 1.09 and 2.07 (tab. 3). If one compares the U content with other elements sensitive to variable redox conditions, as Fe or Mn, it may be noted how U (whose mobility is linked to the presence of uranyl ion, unstable in poor oxigenized waters) decreases in waters characterized by reduced conditions (that conversely allow high Fe and Mn concentrations). Here reduced conditions are matched in waters extracted by deeper levels (T6, T9, S10), conversely S13, S15 and S3, from the shallow horizons, show the opposite trend.

4.Discussion

The strontium isotopic ratio (expressed as ^{87}Sr/^{86}Sr) of groundwater represents a useful method for studying and understanding the groundwaters circulations [7, 8, 9, 10]. The analysis of the values of this isotopic ratio both of some waters and of some lithologies considered as a possible place for a groundwater circulation, suggest that these waters are unlikely fed only by local absorption.

In fact the sedimentary covering is formed by water-proof clayey levels, intercalated with the continental Quaternary series.

If these waters had been in some kind of relation with the clayey covering, their isotopic ratio should have been really close, if not equal, to that measured in the clayey sediments of the lake series. It is important to point out that the ^{87}Sr/^{86}Sr waters isotopic ratio is not even correlated to the travertines (tab. 2) placed on the top of the lake series. It has been possible, comparing the waters ^{87}Sr/^{86}Sr isotopic ratio with the rocks (Fig. 1), to indicate a probable pathway of the groundwaters. This pathway has been suggested by some previous hydrogeological studies [6] which mention a recharging

area at an average height of about 700 m (a.s.l.) for waters labeled Sangemini and for the Piagge sample [11]. This means that on the carbonatic area of Martani Monti, standing between 400 and 1000 m (o.s.l.), an absorption area reflects the regional hydrological network.

The ^{87}Sr/^{86}Sr isotopic tracer feels the effects of the geochemical characteristics of the different permeable lithologies outcropping in the area.

The ^{87}Sr/^{86}Sr isotopic ratios of the waters are different from that of each permeable lithology (fig. 1 and tab. 1-2). Consequently, the final value of the ^{87}Sr/^{86}Sr isotopic ratio should represent a mixing value between the different lithologies regarded as possible places for infiltration and underground water circulation. Probably this is due to the fact that the water, after the infiltration in the carbonatic series, takes up its course through the lacustrine series.

Concerning the springs placed on the edge of Sangemini basin, such as Fabia and the SG7 sample (tab.1), the values of the ^{87}Sr/^{86}Sr isotopic ratio, close to those of the travertines and the clayey sediments, should demonstrate a long timing of the rock-water interaction at shallow depth.

However the Sangemini total residue (tab.1) is higher than that of Fabia water; whose lower value could depend on a diluition of the most superficial aquifer (Fabia water) due to the meteoric waters.

In fact, according to Giglia et al. (1977), the recharge of these waters should occur through the precipitations which fall at a lower height than those which are recharging the Sangemini basin, placed between the valley bottom and the nail of Monti Martani.

In addition it is interesting to observe that, thanks to the isotopic studies (^{87}Sr/^{86}Sr), has been possible to reconstruct the probable recharge area of the paleo-waters which caused the formation of the travertines.

In fact the values of the isotopic ratio for the travertines is very close to that of the "scaglia" (range: 0.707800 - 0.708000): so this formation is likely responsible for the Ca (and consequently for the Sr) contained in the travertines.

The analysis of U and Ra allowed to determine the residence time of groundwaters. These radionuclides are ubiquitous in all groundwaters and are each represented by several isotopes with widely different half-lives and chemistries.

In the following discussion we assume a mean value of 265 ppb for Ur, deriving from a 1:1 weighted ratio of local marine carbonatic rocks and continental carbonate

Table 3. U series radionuclide data and some chemical features of Sangemini waters.
All errors are at 1-σ·levels eU = equivalent Uranium n.d. = not determinate

Sample	Ca (mg/l)	CO² (mg/l)	Mn (mg/l)	Fe (mg/l)	U (ppb)	Ra Eu (ppb)	U-234/U-238	Ra-228/Ra-226
S-3	344	511	0.2	0.055	4.4±0.3	6.59±1.20	1.39±0.02	0.52±0.12
S-9	272	296	0.4	0.06	0.25±0.01	n.d	1.25±0.08	n.d
S-10	424	682	1.2	0.64	<0.001	n.d	n.d	n.d
S-13	256	233	0.06	0.072	2.11±0.06	n.d	1.12±0.02	n.d
S-15	240	215	0.07	0.014	2.56±0.10	3.90±0.50	1.34±0.02	0.51±0.10
T-6	392	584	1	0.7	0.005±0.0005	n.d	2.07±0.24	n.d
T-9	384	540	1	1.6	0.015±0.001	4.42±0.50	1.45±0.11	0.54±0.11
F-2	130	64	0.001	0.01	0.43±0.01	7.52±1.40	1.26±0.03	0.54±0.12
F-4	116	38	0.001	0.035	0.82±0.02	n.d	1.09±0.03	n.d

samples from the travertine plate outcropping in the study area.

This equation describes the temporal evolution of the $^{234}U/^{238}U$ activity ratio in an aquifer which undergoes reduced conditions. Indeed under reduced conditions, the recoil effects causing enrichment of ^{234}U prevail over dissolution processes, causing ^{234}U enriched.

The equation, proposed by Andrews and Kay [12] is:

U activity ratio=1+(initial U activity ratio-1)*
exp($-\lambda_{234}$*t)+(Ur*A/Uw)*(1-exp($-\lambda_{234}$*t))

(1)

Where initial U activity ratio is referred to the water before entering the reduced zone and A is a constant. Normally it is difficult to work with this equation as A, that represents the ratio of the rock volume interested by effective recoil into water and the ground water volume, depends on four factors such as rock density, recoil efficiency, recoil range and fracture surface area. However we use this equation only by a modelling point of view, just to support the model of a recoil dominated aquifer.

In fact, in such an aquifer the residence time can be easily calculated by knowing the $^{228}Ra/^{226}Ra$ activity ratios in the water and in the aquifer rock [13]:

$(^{228}Ra/^{226}Ra)$w=$(^{228}Ra/^{226}Ra)$r*(1-exp($-\lambda_{228}$*t))/
(1-exp($-\lambda_{226}$*t))

(2)

The ^{228}Ra specific activity in the travertines (0.011 dpm/g) and marine carbonates (0.016 dpm /g)

outcropping in the area is comparable, whereas ^{226}Ra specific activity, due to secular equilibrium with variable U content, is notably different (0.037 in travertines, 0.355 in marine carbonates); as before, we assume a mean ^{226}Ra and ^{228}Ra specific activities resulting from a weighted ratio 1:1 of the two lithotypes. Therefore we estimate a radium isotopic ratio of the rock equals to 0.069. The same ratio in the analyzed waters is quite constant (0.500) (tab. 2). By using the equation (2) we calculate that the residence time of the water is close to 350 years. Since the product of residence time and mass rate equals the total volume of the aquifer, we deduce that under condition of maximum mass rate (350 liters/minute) the maximum water volume of the Sangemini aquifer is about 64*10^6 m^3. Such a water volume represents about 1/7 of the total volume that yearly infiltrates, 15 m^3/sec, [14] in the carbonatic complex comprising the Monti Martani.
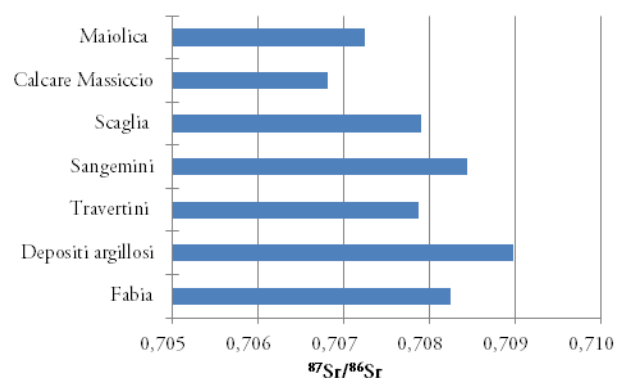

Figure 1. $^{87}Sr/^{86}Sr$ isotopic ratios of the groundwaters and lithology

Sr isotopes and U series radionuclides in the Sangemini area

4.Conclusion

This paper present the results of geochemical investigations of Sangemini waters (Terni-Umbria, Central Italy). Were evaluated the $^{87}Sr/^{86}Sr$ isotopic ratio for identify the recharge area of the aquifer, and U-Ra radionuclides for calculate the residence time of waters.

The study of isotopic strontium composition of the mineral waters of the Sangemini basin show that waters are unlikely fed only by local absorption, since these present a different values o isotopic ratio in respect to the lithology. The results of this study allow to identify:
1) a recharge area in a restricted sector of the Meso-Cenozoic carbonates;
2) a longer and more effective water/rock interaction in the Quaternary series.

On the basis of these preliminary findings, a temporal evolution model of the U-series radionuclides has been applied, giving an estimate of the aquifer potentiality in terms of groundwater residence time and total water volume.

The results show that the residence time of the water is close to 350 years, furthermore were calculated that the maximum water volume of the Sangemini aquifer is about $64*10^6$ m^3.

References

1. Barbieri M, Battistel M, Garone A. The geochemical evolution and management of a coastal wetland system: a case study of Palo Laziale protected area. J Geochem Explor, 2013; 126-127: 67-77.

2. Burke WH, Denison RE, Hetherington EA, Koepnick RB, Nelson HF, Otto JB. Variation of $^{87}Sr/^{86}Sr$ throughout phanerozoic time. Geol, 1982; 10: 516-19.

3. Bunner JL. Radiogenic isotopes: systematics and applications to earth surface processes and chemical stratigraphy. Earth-Sci Rev, 2003; 65: 141-94.

4. Porcelli D, Swarzenski PW. The behaviour of U and Th series nuclides in groundwater and the tracing of groundwater. Rev Mineral Geochem, 2003; 52: 317–61.

5. Rapaglia J, Ferrarin C, Zaggia L, Moore WS, Umgiesser G, Garcia-Solsona E, Garcia-Orellana J, Masque P. Investigation of residence time and groundwater flux in Venice Lagoon: comparing radium isotope and hydrodynamical models. J Environ Radioact, 2010; 101: 571–81

6. Giglia G, Ronga G, Trevisan L, Longinelli A. Ricerche di geologia e di geochimica isotopica sul bacino idrominerale di Sangemini. Centro di Studi Sangemini Roma. Tipografia Arti Grafiche Panetto & Petrelli Spoleto, 1977.

7. Barbieri M, Sappa G. Application of geochemical and isotopic analysis methods (87Sr/86Sr) in hydrogeological characterization of some springs in Simbruini Mountains. In: Beddow, J.K. (Ed.) Proceedings of Geoenv '97 International Symposium on Geology and Environmental,1997; pp. 77-81.

8. Barbieri M, Boschetti T, Petitta M, Tallini M, 2005. Stable isotope (2H, 18O, and 87Sr/86Sr) and hydrochemistry monitoring for groundwater Hydrodynamics analysis in a karst aquifer (Gran Sasso, central Italy). Appl Geochem, 2005; 20: 2063-81

9. Dogramaci SS, Herczeg AL. Strontium and carbon isotope contraints on carbonate-solution interactions and inter-aquifer mixing in groundwaters of semi-arid Murray Basin, Australia. J Hydrol, 2002; 262: 50-67.

10. Katz BG, Bullen TD. The combined use 87Sr/86Sr and carbon and water isotopes for evaluation of groundwater and lakewater in mantled karst. Geochim Cosmochim Acta, 1996; 60: 5075-87.

11. Longinelli A. Relazione sulle ricerche di Geochimica Isotopica condotte sul bacino dell'acqua minerale Sangemini (1972-1976). Centro di Studi Sangemini Roma. Tipografia Arti Grafiche Panetto & Petrelli Spoleto, 1976.

12. Andrews JN, Kay RLF. 234U/238U activity ratio of dissolved uranium in groundwaters from a Jurassic limestone aquifer in England. Earth Planet Sci Lett, 1982; 57:139-51.

13. Voltaggio M, Andretta D, Taddeucci A. Dating of newly formed minerals in geothermal fields trough 232Th series short lived isotopes: check on mineral of known age and implications to fluid-rock interactions. Geothermics, 1987; 16: 255-61.

14. Boni C, Bono P, Capelli G. Schema idrogeologico dell'Italia Centrale. C.N.R. e Università di Roma "La Sapienza", 1987.