Uranium groundwater anomalies and L’Aquila earthquake, 6th April 2009 (Italy)

Wolfgang Plastino, Pavol P. Povinec, Gaetano De Luca, Carlo Doglioni, Stefano Nisi, Luca Ioannucci, Marco Balata, Matthias Laubenstein, Francesco Bella, Eugenio Coccia

Abstract

Monitoring of chemical and physical groundwater parameters has been carried out worldwide in seismogenic areas with the aim to test possible correlations between their spatial and temporal variations and strain processes. Uranium (U) groundwater anomalies were observed during the preparation phases of the recent L’Aquila earthquake of 6th April 2009 in the cataclastic rocks near the overthrust fault crossing the deep underground Gran Sasso National Laboratory. The results suggest that U may be used as a potential strain indicator of geodynamic processes occurring before the seismic swarm and the main earthquake shock. Moreover, this justifies the different radon patterns before and after the main shock: the radon releases during and after the earthquake are much more than during the preparatory period because the process does not include only the microfracturing induced by stress–strain activation, but also in radon increases accompanying groundwater U anomalies.

1. Introduction

Earthquake prediction is widely recognized as being among the most challenging scientific problems, both due to its societal relevance and to the intrinsic complexity of the problem, and it has been analyzed with several controversial discussions, debates, and reviews (e.g. Geller et al., 1997; Wyss, 1997; Nature Debates, 1999; Keilis-Borok and Soloviev, 2003; Peresan et al., 2005).

Radon (222Rn) as a possible candidate for earthquake's precursor has been studied for a long period, but there is no clear evidence that it is really a good precursor. It has been suggested as one of several possible early signals, and its groundwater anomalies associated with earthquakes and water-rock interactions were detected in several seismogenic areas worldwide indicating possible transport of radon through microfractures or the crustal gas fluxes along active faults (Ulomov and Mavashev, 1967; Scholz et al., 1973; Wakita et al., 1980, 1989; Hauksson, 1981; Monnin and Seidel, 1992; Virk and Singh, 1994; Igarashi et al., 1995; King et al., 1995; Plastino and Bella, 2001; Richon et al., 2003; Plastino, 2006; Kawada et al., 2007). The physical processes associated with radon groundwater anomalies are based on changes of radon emanation rates occurring due to strain signal near the earthquake's nucleation point. Particularly, it is unclear its behaviour before, during and after the main shock, considering the consolidated scheme for radon release due to stress–strain processes in the rock.

In the geological environment, the radon groundwater concentration depends on the isotopic abundance of its parent radionuclides (238U and 226Ra), and on their geochemical patterns with reference to environmental redox and pH characteristics. The geodynamic processes associated with earthquakes can modify radon migration patterns in groundwater as a potential indicator of strain. However, to predict the activity of radon in fractured lithologies is difficult and the measurement of radon concentration does not uniquely characterize the rock deformation or the chemical inhomogeneity (Torgersen et al., 1990), as well as its relationship with the transient crustal strain signals from 'aseismic' fault slip near the earthquake’s nucleation point (Roeloffs, 1999). Moreover, non-tectonic factors related to variations of chemical and physical groundwater parameters may be of importance (Shapiro et al., 1985; Plastino, 2006), requiring proper geological, hydrological and hydrogeological settings (Trique et al., 1999), so only the variations induced by stress–strain processes should be considered in...
evaluations. Important issues are the stability and reliability of the monitoring system which should be checked continuously during the measurement time (Plastino and Bella, 2001) or the development of new detectors independent of environmental noise parameters such as temperature, acid concentrations, humidity, and air pressure (Plastino et al., 2002).

Therefore, uranium (U) groundwater monitoring was planned and performed at Gran Sasso National Laboratory of the National
Institute of Nuclear Physics (LNGS-INFN), Italy, to study the possible pattern for radon sources in groundwater, because anomalies were detected during the Umbria-Marche (Italy) seismic sequence in 1997, located about 80 km from the laboratory (Plastino, 2006). The aim was to test U as a potential strain indicator of geodynamic processes occurring before an earthquake, rather than the consolidated scheme for radon release due to stress-strain processes in the rock.

Although, in order to assess the utility of U isotopes as fluid phase earthquake precursors, U concentrations and $^{234}$U/$^{238}$U activity ratios have been monitored in thermal waters (Gorbushina et al., 1973; Kuleff et al., 1980; Finkel, 1981), this monitoring at LNGS-INFN was performed in a shallow aquifer with a high dynamic behaviour due to high permeability of the cretaceous limestones that form part of the Gran Sasso massif (Plastino and Bella, 2001). Moreover, these measurements were performed to test a possible contribution to the variation of the neutron flux background (Plastino et al., 2009), because it plays a key-role in several research activities for Neutrino Physics and Dark Matter detection in the underground environment.

The concentration of U in groundwater is usually in the range 0.1–50 mg L$^{-1}$ (Giammar, 2001). In groundwaters, the weathering of U-bearing rocks and minerals is the source of dissolved U, which is most concentrated in sedimentary rocks, particularly organic shales, and is also found in significant amounts in metamorphic and igneous rocks, with higher concentrations in granites than in basalts (Gascoyne, 1992). Uranium solubility in aqueous systems is predominantly controlled by three factors: Oxidation-Reduction Potential (ORP), pH, and dissolved carbonate (Langmuir, 1980; Murphy and Shock, 1999). In aqueous solution U can exist in oxidation states of +III, +IV, +V, and +VI; however, under environmental conditions only the tetravalent and hexavalent states are stable. Clay minerals have high specific surface areas and reactive surface groups for binding metals and radionuclides through two different mechanisms: sorption can occur either in the interlayer space (fixed-charge sites) between sheets by an ion-exchange mechanism, or at the edges of the sheets through specific coordination (Zachara and McKinley, 1993; McKinley et al., 1995; Turner et al., 1996). At low ionic strength, significant sorption occurred at fixed-charge interlayer sites even at low pH, but at higher ionic strength U sorption decreases because sodium and calcium ions occupy the fixed-charge sites (Giammar, 2001).

### 2. Experimental

The mountain chain of Gran Sasso is formed by carbonatic rocks of marine origin settled during the long period of time going from the upper Trias and the upper Miocene. A series of tectonic events going from the end of the upper Miocene until the Pleistocene produced the complex structure of the present chain characterized by an anticline-syncline structure with its outmost side upturned. The main structure evolved during the first tectonic phase in a sort of break thrust and successively in an over-thrust structure. The great overthrust event pushed the northern block, representing the main syncline component (Fig. 1a) (Catalano et al., 1973; Kuleff et al., 1980; Finkel, 1981), this monitoring at LNGS-INFN is performed in a shallow aquifer with a high permeability of the cretaceous limestones that form part of the Gran Sasso massif (Plastino and Bella, 2001). Moreover, these measurements were performed to test a possible contribution to the variation of the neutron flux background (Plastino et al., 2009), because it plays a key-role in several research activities for Neutrino Physics and Dark Matter detection in the underground environment.

Fig. 2. Schematic view of the LNGS-INFN. The overthrust fault (red line) and monitoring sites (E1, E3 and E4) are also shown. At site E3 there are two sampling points: E3 which is parallel to the overthrust fault in the North direction; and E3dx which is orthogonal to the fault in the E4 direction into the cataclastic rocks.

The water samples were collected weekly in three sites located inside the LNGS-INFN underground laboratories (Fig. 2). Each sample was 1 L, and was stored in cleaned and rinsed polyethylene bottles after five minutes of water flushing at maximum flow. The pH measurements were performed by an electrometric method using a traditional glass electrode. The instrument used was the Accumet® pH meter 50 by Fisher Scientific with accuracy of ±0.1 pH units. The potentiometric determination of electron activity was carried out with an inert indicator electrode and a reference electrode. The ORP measurements were performed using the Accumet® pH meter 50 by Fisher Scientific with precision of ±2.2 mV (one standard deviation) in a closed flow cell. The conductivity of the water samples was measured with a conductivity meter MC 226 from Mettler Toledo® with a relative accuracy of 1%.

The flow rate measurements of the Traforo spring, located under the tunnel close to the monitoring area, and which collects percolation water from the LNGS-INFN and the highway tunnel (Fig. 1b and 2), were performed by a Venturi flow meter with precision of ±30 L/s (one standard deviation). This monitoring is managed by Ruzzo Waterwork Society.

### 2.1. Sampling and chemical analysis

The water samples were collected weekly in three sites located inside the LNGS-INFN underground laboratories (Fig. 2). Each sample was 1 L, and was stored in cleaned and rinsed polyethylene bottles after five minutes of water flushing at maximum flow. The pH measurements were performed by an electrometric method using a traditional glass electrode. The instrument used was the Accumet® pH meter 50 by Fisher Scientific with accuracy of ±0.1 pH units. The potentiometric determination of electron activity was carried out with an inert indicator electrode and a reference electrode. The ORP measurements were performed using the Accumet® pH meter 50 by Fisher Scientific with precision of ±2.2 mV (one standard deviation) in a closed flow cell. The conductivity of the water samples was measured with a conductivity meter MC 226 from Mettler Toledo® with a relative accuracy of 1%.

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### 2.2. Sample treatment and multi-element determination by ICP-MS

The water samples were diluted 10 times and acidified with 2.5% of nitric acid to stabilize traces in the sample. Reagents of trace analysis grade (HNO3, super pure by Fisher Scientific with accuracy of ±0.1 pH units. The potentiometric determination of electron activity was carried out with an inert indicator electrode and a reference electrode. The ORP measurements were performed using the Accumet® pH meter 50 by Fisher Scientific with precision of ±2.2 mV (one standard deviation) in a closed flow cell. The conductivity of the water samples was measured with a conductivity meter MC 226 from Mettler Toledo® with a relative accuracy of 1%.

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Fig. 4. U concentration of groundwater sampled at E1, E3, E3dx and E4 sites from June 2008 to May 2009, and the cumulative seismic moment from January 2008 to May 2009 in the region of 42.00–42.75 N and 12.75–13.75 E (see Fig. 3a and b). The cumulative seismic moment has been estimated from Italian Seismicity Catalogue (CS) (Chiarabba et al., 2005; Del Pinto, 2005): \( M_r - 1.85 \times 10^6 \times S + 272 \), where \( M_r \) is the seismic moment and \( S \) is the local magnitude. The jump-like in the cumulative seismic moment indicates the main shock on 6th April, 2009. The seismic data are from the Italian Seismic Bulletin, Istituto Nazionale di Geofisica e Vulcanologia.

Carlo Erba Reagenti, ultra-pure water (produced by Millipore MilliQ-Q-Element), plastic containers and ancillary equipment were used during preparation of water samples because long-lived U radioisotopes at trace levels had to be measured. The ICP-MS measurements were carried out using a quadrupole mass spectrometer from Agilent Technologies, model 7500a. The tuning of the instrument was optimized in order to reach high sensitivity, stable signal, and low background. A Rabbington nebulizer was installed as well. The concentration values were determined in quantitative mode using an external calibration curve, because the matrix effect of the ten times diluted groundwater samples is negligible. During the measurements, a multi-element solution was used as internal standard to correct for possible instability and drift of the ICP-MS device. This solution was added on line using the third line of the peristaltic pump. The calibration curve of U response was corrected using \(^{209}\)Bi. The accuracy reached in this way generally was better than 5%, which is reasonable for the ICP-MS technique.

3. Results and discussion

The area was under investigation from November 2008 to May 2009, a time marked by a seismic swarm with the main shock occurring at 01:33 UT on April 6th, 2009 (moment magnitude, \( M_r = 6.3 \)) located about 18 km far from LNGS-INFN (Fig. 3). In the period 2002–2007, the local seismicity was widespread in the NW sector of the epicentral area of the L’Aquila earthquake with depths ranging from 10 to 20 km and magnitudes from 0.8 to 3.5. The L’Aquila sequence started in November 2008 close to the location of the main event of 6th April, 2009. The depths were between 8 and 12 km and the magnitudes were up to 4.1 (less than 2000 events). After 6th April, 2009, the seismicity continued, migrating to the SE sector of the epicentral area of the L’Aquila earthquake with depths ranging from 10 to 20 km and magnitudes from 0.8 to 3.5. The L’Aquila sequence started in November 2008 close to the location of the main event of 6th April, 2009. The depths were between 8 and 12 km and the magnitudes were up to 4.1 (less than 2000 events).

Within the framework of the INFN scientific program ERMES (Environmental Radioactivity Monitoring for Earth Sciences), radon (Plastino and Bella, 2001; Plastino, 2006), radiocarbon (Plastino et al., 2001) and tritium (Plastino et al., 2007) were monitored in groundwater inside the LNGS-INFN, showing different chemical, physical and fluid-dynamic characteristics of groundwater. The U groundwater monitoring was carried out from June 2008 with the aim to better define the radon groundwater transport processes through the overthrust fault (Plastino and Bella, 2001; Plastino, 2006), as well as to check its contribution to the neutron background at the LNGS-INFN (Plastino et al., 2009). The U groundwater results obtained between June 2008 and May 2009 (Fig. 4) showed two different water groups, which were also supported by stable isotope (\( ^{8}\)H, \( ^{8}\)O), \(^{14}\)C and \(^{3}\)H analyses (Rozanski, private communication). While the second group (sites E3 and E3dx, Fig. 2) showed clear U variations (correlated at both sites) with slightly depleted stable isotopes in water (about 0.25\(^{\text{ppm}}\) in \(^{18}\)O and 2.1\(^{\text{ppm}}\) in \(^{2}\)H), the first group (sites E1 and E4, Fig. 2) showed much lower U levels, with a weaker correlation between the sites (Table 1). This indicates that the U groundwater changes strongly depended on the position of monitoring stations and the overthrust fault (Fig. 2).

The highest \(^{14}\)C concentration was found at site E4 (71.7 pMC (percent modern carbon)) and the lowest at site E3 (57.1 pMC), documenting a longer groundwater–rock interaction time in the latter case. Tritium levels were in the range between 6 and 13 TU (Tritium Unit), higher than the current tritium content in rainfall of the Gran Sasso region, indicating transit times of groundwater of the order of some decades.

The observed U variations (Fig. 4) were indicative of a seasonal trend of the water table in the Gran Sasso aquifer due to its recharge modulated by percolation effect related to snow melting during summer period, and some spike-like anomalies not related to hydrological pattern. These U anomalies in groundwater were detected until beginning of March, 2009 about one month before the L’Aquila earthquake of 6th April, 2009. However, during the main shock and aftershocks the variations in the U content were small. Groundwater pH (Fig. 5), ORP (Fig. 6), and electrical conductivity (Fig. 7) did not support the observed U anomalies (Langmuir, 1980; Murphy and Shock, 1999).

The flow rate observed at the Traforo spring located in the tunnel close to the monitoring area (Fig. 8), which collected percolation water from the LNGS-INFN and the highway tunnel, showed a seasonal trend due to snow melting during summer period. This trend was modified, however, from November 2008 with starting of the seismic swarm located about 20 km far from the spring, and drastically during the main shock on 6th April, 2009 with a jump-like anomaly of about 120 L/s. This behaviour emphasized hydrological links between the Gran Sasso aquifer and seismic activities before, during and after the main shock.

The U anomalies observed at site E4 could be explained with the seismic swarm activities, which trigger diffusion processes through the overthrust fault (Plastino, 2006). A correlation between the shear strain in cataclastic rocks and the U content of groundwater was investigated, suggesting a progressive increase in U enrichment with deformation (McCaig, 1989). This behaviour was detected in thermal waters and environments characterized by U

<table>
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<th>Table 1</th>
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<tr>
<td>Mean values of U, tritium, radiocarbon, ( ^{13})C, ( ^{18})O, ( ^{3})H, pH, ORP, and EC (electrical conductivity) of groundwater sampled at E1, E3, E3dx, and E4 from June 2008 to May 2009.</td>
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<tr>
<th></th>
<th>U 10(^{-9}) g/g</th>
<th>( ^{18})H TU</th>
<th>( ^{14})C pMC</th>
<th>( ^{13})C ( _{\text{%}} )</th>
<th>( ^{18})O ( _{\text{%}} )</th>
<th>( ^{2})H ( _{\text{%}} )</th>
<th>pH</th>
<th>ORP/mV</th>
<th>EC ( \mu S/cm )</th>
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<tbody>
<tr>
<td>E1</td>
<td>0.29 ± 0.01</td>
<td>6.6 ± 0.4</td>
<td>59.5 ± 1.0</td>
<td>−9.64</td>
<td>−72.2</td>
<td>−10.93</td>
<td>8.2 ± 0.1</td>
<td>231 ± 22</td>
<td>159.1 ± 2.0</td>
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<tr>
<td>E3</td>
<td>1.79 ± 0.02</td>
<td>8.8 ± 0.5</td>
<td>57.1 ± 1.0</td>
<td>−6.68</td>
<td>−74.6</td>
<td>−11.28</td>
<td>8.2 ± 0.1</td>
<td>232 ± 22</td>
<td>169.1 ± 2.0</td>
</tr>
<tr>
<td>E3dx</td>
<td>1.47 ± 0.02</td>
<td>11.2 ± 0.6</td>
<td>57.1 ± 1.0</td>
<td>−6.68</td>
<td>−74.6</td>
<td>−11.22</td>
<td>8.2 ± 0.1</td>
<td>228 ± 22</td>
<td>169.1 ± 2.0</td>
</tr>
<tr>
<td>E4</td>
<td>0.54 ± 0.01</td>
<td>10.1 ± 0.6</td>
<td>71.7 ± 1.0</td>
<td>−5.74</td>
<td>−72.6</td>
<td>−11.07</td>
<td>8.2 ± 0.1</td>
<td>240 ± 22</td>
<td>159.1 ± 2.0</td>
</tr>
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concentrations of rocks of several milligram per kilogram. The Gran Sasso karst aquifer, however, does not have similar characteristics, and the U content of the rock is very low, ranging from 0.42 ± 0.10 to 6.80 ± 0.67 × 10⁻⁶ g/g (Esposito and Pelliccioni, 1985; Wulandari et al., 2004).

The fluids are crucial for the mechanics of faults (Sibson, 1992), as they play both passive and active roles during deformations. Variations in the fluid fluxes were observed during seismic sequences, likely associated with variations in the state of stress of the crust. Moreover fluids (CO₂) can increase pore pressure, and thus trigger a fault rupture along asperities (Miller et al., 2004). The crustal rupture may follow the fault-valve behaviour (Sibson, 1992), with cyclic changes in the transit, accumulation and release of fluids. As fluids decrease the friction on the fault plane, their variation in time could control the episodic activity of faults.

The presence of a locked normal fault in the brittle upper crust does not inhibit an active shearing at depth in the viscous regime, as shown by the steady state strain rate measured by Global Positioning System (GPS) (Kreemer et al., 2002). During the interseismic period, the stick-slip behaviour of the upper crust may correspond to an active stationary shear in the lower ductile crust. The deep strain rate implies an area beneath the locked fault plane where the crust is stretched and the consequent fracturing is expected to be filled by fluids. When the shear stress acting on the locked area of the fault reaches the threshold determining the rupture, the hanging wall of the normal fault starts moving downward. This initial movement could be represented by foreshocks and an increase in fluid pressure. The fluids that filled the cracks are then squeezed out by closure of previously generated vacuum. During the coseismic evolution, the hanging wall may move, squeezing out again the remaining fluids, which had filled the dilated volume during the interseismic period. Long-lasting aftershocks are interpreted as primarily related to the gradual settlement of the hanging wall to the new lower position, and distributed all over the volume within and above the previously dilated rocks. The recent L’Aquila earthquake sequence may be explained using this hypothesis as the area is cross-cut by several NW-SE trending active normal faults (Vezzani and Ghisetti, 1998).
4. Conclusions

The underground anomalies observed before the seismic swarm and the main shock, which occurred on 6th April, 2009 in L’Aquila, were probably associated with geodynamic processes occurring before the earthquake, which triggered diffusion processes through the overthrust fault. This would indicate that more attention should be devoted to the pre-earthquake studies of geodynamic processes, especially on characteristics of fluids filling the fractures before the main shock. Uranium in groundwater can be used therefore as a potential indicator of pre-earthquake processes as it may be associated with geodynamics of preparation phases of earthquakes. Moreover, another possible physical process during the pre- and post-phases of the earthquake could be investigated: the first stage seems to be characterized by U variations in groundwater that can modulate the radon concentration, the second one (after the main shock) do not show any U anomalies, justifying the different radon patterns before and after the main shock.

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References


Rozanski, K., Private communication.


