Romanian Reports in Physics, Vol. 62, No. 4, P. 854–864, 2010

SUBSURFACE TEMPERATURE SIGNATURES RELATED TO PARTICULAR FOCAL MECHANISMS, IN ROMANIA (VRANCEA) AND NORTHERN ITALY SEISMIC REGIONS*

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(Received June 30, 2009)

Abstract. Instances of *one* anomalous episode detected in the Na-K-Mg geothermometry records of a spring have been associated by earlier investigations to *one* important seismic event. Alternatively, we address Na-K-Mg geothermometry records that included *two* anomalous episodes, which were, moreover, subject to dissimilar signatures, while different focal mechanisms were also displayed by the *two* associated major earthquakes.

Key words: earthquake, groundwater, hydrochemical monitoring, Na-K-Mg geothermometer, focal mechanism, Vrancea, Northern Italy.

1. INTRODUCTION

Subsurface temperatures of a deep-seated aquifer can be estimated (Fournier and Truesdell, 1970, Fournier, 1979, Giggenbach, 1988) by using Na/K concentration ratios of a groundwater discharge supplied by the concerned fluid-reservoir. Such "ionic geothermometers" provide values of a so-called "Na-K temperature" (henceforth $T_{\text{Na-K}}$). The corresponding temperature estimates are normally subject (Giggenbach, 1988) to certain spurious influences, induced by variable degrees of chemical re-equilibration at shallower depths (lower temperatures), or to the admixture of various amounts of shallow, meteorically-derived waters. There has been, on the other hand, pointed out by a few earlier investigations (Valette-Silver *et al.*, 1985; Idris, 2000) that $T_{\text{Na-K}}$ values could also be subject to some less usual evolutions, related to the occurrence of important ($M > 5$) earthquakes.

* Paper presented at the Annual Scientific Session of Faculty of Physics, University of Bucharest, June 5, 2009, Bucharest-Măgurele, Romania.

A method aimed at discriminating between genuine seismically-related signatures, and inherent "spurious" fluctuations undergone by $T_{Na\text{-}K}$ has been recently described by Mitrofan *et al.* (2009), in association with the processing of observation data pertaining to an important earthquake (M_w=6.0) occurred in Vrancea area (Romania) on 27 October 2004. The indicated method makes use of the "scatterplot" analysis (Cioni *et al.*, 2007), an approach that facilitates the investigation of correlations possibly existing between $T_{Na\text{-}K}$ values, and values of a so-called "maturity index" (henceforth MI), defined by Giggenbach (1988): the latter non-dimensional parameter evaluates – in a certain sense – the "quality" of the $T_{Na\text{-}K}$ assessment (in fact it estimates, by additionally considering the fast-readjusting K/Mg solute ratio, the up-flowing solution departure from the chemical equilibrium mirrored by $T_{Na\text{-}K}$).

By analyzing the considered spring of Vrancea area (specifically located within the Slanic Moldova spa) in terms of the indicated "scatterplot" approach, Mitrofan *et al.* (2009) have distinctively identified:

– a data points "cluster", which assumedly reflected a "routine" behavior;

– another more specific, 18 months-long regime of data-points distribution;

the latter ended just before the M_w = 6.0 earthquake, being consequently, most probably, connected to the preparation stage of that seismic shock.

The present study aims to further extend the investigation of various earthquake-related signatures recorded by means of Na-K-Mg geothermometry / scatterplot analysis. In this respect, the above-mentioned procedure has been employed in the processing of a chemical-analytical data-set already published by Hartmann *et al*. (2005), who addressed a monitoring operation conducted in Vrancea area during 1997–1999, and of another data-set presented by Federico *et al.* (2008), concerning a monitoring operation carried out during 2004-2005 in Northern Italy. There has yet to be mentioned that none of the two above-indicated teams of investigators had specifically considered the Na-K-Mg geothermometry method in their chemical-analytical data processing approach.

In addition, the present study addresses also a more specific issue, namely correlations possibly existing between particular Na-K-Mg geothermometry signatures, and distinct focal mechanisms of the associated earthquakes.

2. OBSERVATION DATA COLLECTION AND CORRESPONDING PROCESSING APPROACH

Between August 1997 and August 1999, there has been monitored (Hartmann *et al*., 2005) a flowing well located at *Turia* (Fig. 1a). That site lies about 70 km outside the epicentral domain of the intermediate-depth seismicity "nest" (Radulian *et al.*, 2000) of Vrancea area (Romania). Sodium-chloride water intermittently discharges from a reservoir consisting of alternating marls and sandstones of Late Aptian – Early Albian age, intercepted by the well in the 175-240 m depth range. Water samples for analyses were generally collected on a regular, two-weekly basis. The corresponding chemical compositions have been published by Hartmann *et al*. (2005).

In northwest Italy, at *Agliano Terme* (Fig. 2a), there has been monitored (Federico *et al.*, 2008) a cold H_2S-rich spring, which discharged sodium-chloride water from Messinian age deposits of prevalently marly character. That spring is located in the Po River plain, in a moderate-seismicity region where most investigators (see, for example, Calais *et al.*, 2002 and references therein) locate the pole around which, assumedly, the counterclockwise rotation of Adria microplate occurs. The analytical results obtained by monthly sampling campaigns conducted at the Agliano Terme spring between January 2004 and December 2005 are provided in the indicated paper of Federico *et al.* (2008).

In the present study, chemical data collected during the two above mentioned monitoring operations have been used to compute, by means of procedures defined by Giggenbach (1988), the values of the $T_{\text{Na-K}}$ and MI parameters. There has been also performed initially, by taking into account the overall chemical-analytical data that were available, a conversion of the Na, K and Mg contents of each of the Agliano Terme spring samples, which in the original paper of Federico *et al.* (2008) were provided as mg/L: that conversion was necessary for obtaining concentrations expressed as ppm, in compliance with the diagnosis procedure stipulated by Giggenbach (1988).

Further specific details concerning the monitoring sites characteristics are provided in Table 1.

Table 1

Groundwater sampling sites characteristics

Sampling site	Turia	Agliano Terme
Latitude N	46.03	44.8
Longitude E	25.92	8.25
Monitoring time-interval	6 September 1997 – 21 August 1999	22 January 2004 – 13 December 2005
Outlet temperature range (°C)	12.5 - 17.0	11.7 - 17.0
pH range	6.01 - 6.84	7.2 - 7.8
Na-K temperature range (°C)	201 - 237	72 - 122
Maturity index range	1.80 - 1.98	2.05 - 2.26

All the considered samples complied with the basic suitability criteria for the Na-K-Mg geothermometry diagnosis (Giggenbach, 1988), i.e. they had NaCl chemical character and close-to-neutral pH values. Different from the spring-water at Agliano Terme, for which MI values always fell within the 2.00-2.66 range, and thus made that fluid fully compliant with the suitability criteria stipulated by Giggenbach (1988), MI values at Turia were always smaller than 2.00, but not lower than 1.80 (Table 1). This minor violation of samples suitability criteria appears to be nevertheless acceptable, considering the internal consistency of the Na-K-Mg geothermometry behavior pattern (as illustrated by the subsequent paragraphs 3.1 and 3.2).

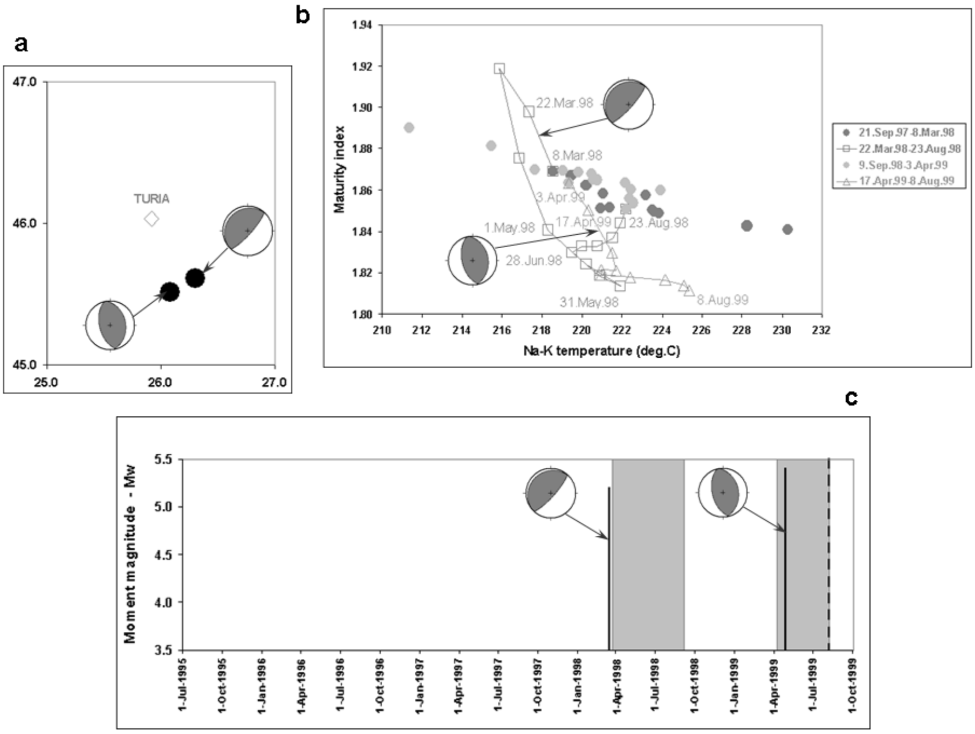

Fig. 1 – a) Location (diamond) of the sampling site at Turia, next to Vrancea seismic zone. On occurrence of the two intermediate depth (~150 km), moderate magnitude (M_w= 5.2-5.4) earthquakes shown on the map as black dots with corresponding beach-balls, specific signatures have been identified in the Na-K-Mg geothermometry records (those seismic events were the strongest that the Harvard CMT catalog listed during that hydrochemical monitoring operation and during the 2 years that preceded it, within a 5 × 5° rectangle centered on the monitoring site at Turia). b) Maturity index (MI) *vs*. Na-K temperature ($T_{Na\text{-}K}$) scatterplot diagram constructed for the groundwater discharge at Turia. Dots indicate "cluster" regimes (see text). Empty squares indicate the first "drift" event (March-September 1998), possibly associated to the 13 March 1998 Vrancea earthquake (M_w = 5.2). Empty triangles indicate the second "drift" event (April-August 1999), possibly associated to the 28 April 1999 Vrancea earthquake (M_w = 5.4). Selected sampling dates during the "drift" events are indicated by labels. c) Time distribution of the significant seismic events ($M_w \geq 4.0$, as listed by the Harvard CMT catalog) which occurred in Vrancea area during the considered hydrochemical monitoring operation and during the previous 2 years. The shaded regions mark the "drift" regime occurrences, with the dashed vertical line indicating that the "drift" regime extended for an additional, unspecified period after the end of the monitoring operation. Beach-balls illustrate, in each of the three panels, the focal mechanisms of the two strongest recorded earthquakes – those which were assumedly associated with specific Na-K-Mg geothermometry signatures.

In order to clearly distinguish key evolution trends, the time-series of the actually computed T_{Na-K} and MI values have been filtered by means of a running average algorithm (Mitrofan *et al.*, 2008). Next, the MI and T_{Na-K} values thus averaged have been used to construct scatterplot diagrams (Fig. 1b, 2b). This latter procedure – analogous to one previously used by Cioni *et al.* (2007) for identifying earthquake-related signals in the time-series of temperature, electrical conductivity and CO_2 concentration values of a specific outlet – made readily apparent certain distinct correlation-regimes which shall be given detailed discussion below (paragraph 3.1).

In order to identify, in the neighborhood of the monitored discharges, significant earthquakes to which specific Na-K-Mg geothermometry signatures could be associated, we have basically taken into account the main seismic events ($M_w \geq 4.0$) listed by the ISC catalog (available at http://www.isc.ac.uk/search/ bulletin/).

There were considered, for each of the two investigated areas, earthquakes having occurred at any depth, within a 5 × 5° rectangle centered on the hydrochemical monitoring site. Yet since the present study showed a particular interest to the focal mechanisms particularities, there were retrieved from the ISC catalog, for each specific area, the entries supplied by that particular contributor who had provided focal mechanisms for all the events we considered in that area: specifically, the Harvard CMT catalog (available at http://www.globalcmt.org/), for Vrancea area, and the Regional Moment Tensor Catalog of the Swiss Seismological Service in Zurich (available at http://www.seismo.ethz.ch/mt/), for Northern Italy.

Table 2

Main seismic events ($M_w \geq 4.0$), that the ISC catalog listed within a 5 × 5° rectangle centered on each of the two considered sampling sites, over periods extending from 2 years before the start of each monitoring operation, until shortly after that operation was completed

Sampling site	**Date of the earthquake**	**Latitude N**	**Longitude E**	**Depth [km]**	**Magnitude [Mw]**
Turia	13 March 1998	45.61	26.30	151.2	5.2
	28 April 1999	45.51	26.08	143.7	5.4
Agliano Terme	8 June 2002	44.360	10.696	33	4.3
	13 November 2002	45.606	10.169	12	4.3
	11 April 2003	44.792	8.892	12	4.9
	23 February 2004	47.272	6.271	12	4.5
	24 November 2004	45.626	10.559	9	5.0
	19 April 2005	44.818	9.786	24	4.0
	8 September 2005	46.032	6.897	8	4.5

Different from the previously discussed case of the Slanic Moldova spring (Mitrofan *et al.*, 2009), where the earthquake-related signature of the Na-K-Mg geothermometer seems to have reached the sampling point at the ground surface virtually "instantaneously", significant delays in the "arrival time" of the seismically-related signals may occur in the case of slower up-flows: for a reasonable range of groundwater flow parameters, computations indicate that an earthquake-related alteration induced at the depth of origin of a fluid up-flow may reach the ground surface within time-intervals ranging from less than one day, to more than one year. That is why a wide enough time interval has been considered, so as to account also for the possibility that significant earthquakes, having occurred many months before the beginning of the monitoring operation, could still exhibit noticeable signatures in the recorded $T_{Na\text{-}K}$ and MI time-series. Specifically, the time-span taken into account for indentifying significant earthquakes has covered a period extending from 2 years before the start of each monitoring operation, until shortly after the concerned operation was completed.

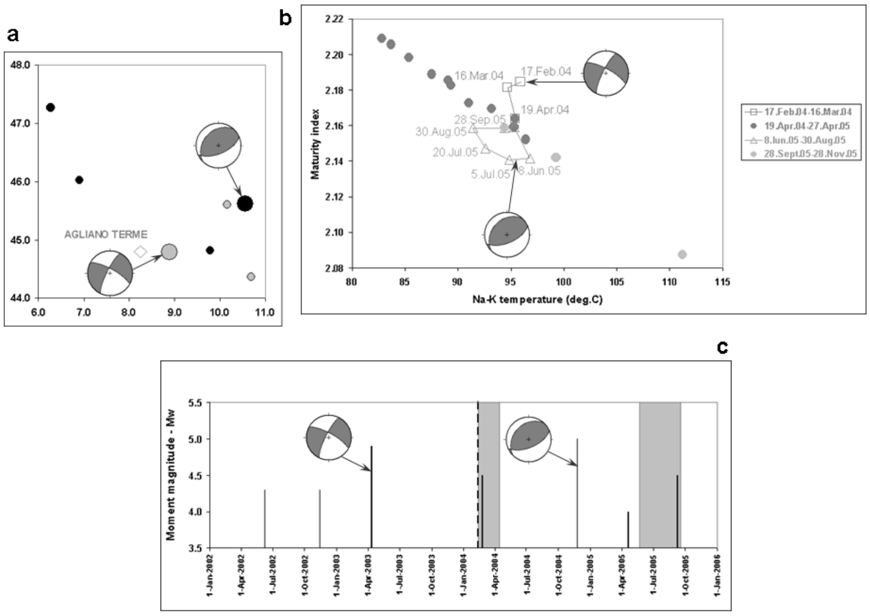

Fig. 2 – a) Location of the sampling site at Agliano Terme (diamond). Dots within the map indicate the significant seismic events ($M_w \geq 4.0$) that the Regional Moment Tensor Catalog of the Swiss Seismological Service in Zurich listed during that hydrochemical monitoring operation (in black), and during the 2 years that preceded it (in grey), within a 5 × 5° rectangle centered on Agliano Terme. Specific signatures noticed in the Na-K-Mg geothermometry records have been ascribed to the strongest ($M_w = 4.9$-5.0) earthquakes occurred during that period (displayed as larger dots, with associated beach-balls). b) Maturity index (MI) *vs*. Na-K temperature ($T_{Na\text{-}K}$) scatterplot diagram constructed for the groundwater discharge at Agliano Terme. Dots indicate "cluster" regimes (see text). Empty squares indicate the first "drift" event (February-April 2004), possibly associated to the 11 April 2003 earthquake ($M_w = 4.9$). Empty triangles indicate the second "drift" event (May-September 2005), possibly associated to the 24 November 2004 earthquake ($M_w = 5.0$). The sampling dates during the "drift" events are indicated by labels. c) Time distribution of the significant seismic events ($M_w \geq 4.0$, as listed by the Regional Moment Tensor Catalog of the Swiss Seismological Service in Zurich) which occurred in the considered area during the Agliano Terme hydrochemical monitoring operation and during the previous 2 years. The shaded regions mark the "drift" regime occurrences, with the dashed vertical line indicating that the "drift" regime extended for an additional, unspecified period before the start of the actual monitoring operation. Beach-balls illustrate, in each of the three panels, the focal mechanisms of the two strongest recorded earthquakes – those which were assumedly associated to specific Na-K-Mg geothermometry signatures.

The seismic event lists prepared in accordance with the above-indicated procedure are provided in Table 2.

3. RESULTS AND DISCUSSION

3.1. DATA-POINTS CORRELATION REGIMES

Results of both monitoring operations, conducted at Turia and at Agliano Terme, exhibit rather similar patterns (Figs. 1b, 2b). Specifically, for each of the two operations, the MI *versus* $T_{\text{Na-K}}$ scatterplot diagram includes:

– a rather narrow domain – which corresponds to what Mitrofan *et al.* (2009) had designated as a “cluster”: the “cluster” consists – in both particular considered cases, of Turia and of Agliano Terme – of two series of rather regularly distributed data-points, which are actually intermingled, being at the same time tightly correlated (corresponding overall correlation values, computed for the intermingled data-point series, score $r^2 = -0.911$ for Turia, and $r^2 = -0.996$ for Agliano Terme);

– two data-points series which appear to “drift away” (Mitrofan *et al.*, 2009) from the main “cluster”. Data points belonging to each “drift away” group appear to be more poorly correlated as compared to those of the main “cluster” (for instance, $r^2 = -0.791$ for the “drift” event recorded at Turia between March-September 1998, and $r^2 = -0.426$ for the “drift” event recorded at Agliano Terme between May-September 2005).

By assuming that, likewise the previously mentioned Na-K-Mg geothermometry signature recorded at the Slanic Moldova spring (Mitrofan *et al.*, 2009), the “drift” regime occurred in response to some anomalous, disturbing processes (which could be, in particular, a significant earthquake), the obvious next step for further investigation was to search for such possible causes.

3.2. POSSIBLE CORRESPONDENCES TO SIGNIFICANT EARTHQUAKES

In Figs. 1c and 2c there are indicated the suites of main earthquakes which, assumedly, could have been associated to the “drift” signatures outlined in the Na-K-Mg geothermometry records of Figs. 1b and 2b. Yet none of the largest earthquakes of the concerned time-periods occurred at the end of a “drift” event – a setting highly contrasting with the behavior that the Slanic Moldova spring had exhibited (Mitrofan *et al.*, 2009) on occurrence of the $M_w = 6.0$ Vrancea earthquake of 27 October 2004. In fact, a reasonable analogy to that latter particular instance requires that 6-12 month-long time-lags actually elapsed between the occurrence of an important earthquake, and the end of the corresponding “drift” period exhibited by the groundwater discharges of Turia or of Agliano-Terme (Figs. 1c and 2c, Table 3).

Significantly longer up-flow durations could be the cause for such delays. Direct comparison between the scatterplots of all three concerned monitoring operations – Slanic Moldova, Turia and Agliano Terme – seems to provide further support for that inference (Fig. 3): outlets subject to *larger time-lags* between the occurrence of an important earthquake and the end of the corresponding “drift” period (~6 months at Turia, 10-12 months at Agliano Terme – Figs. 1c and 2c, Table 3), have their “cluster” regime “envelopes” positioned increasingly near with respect to the axes origin. Such “envelopes” may be viewed as characteristic for *smaller value-ranges of the “maturity index”* (MI), the latter being at its turn – to a certain extent – a proxy of the fluid up-flow duration (the smaller the MI value, the longer the time required by the hydrothermal up-flow to reach the sampling point at the surface).

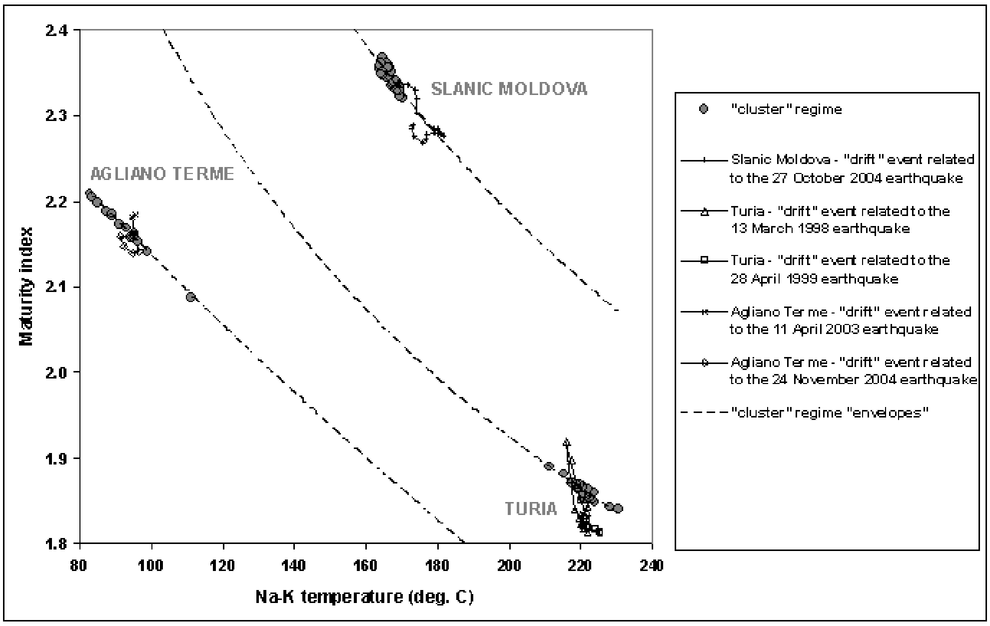

Fig. 3 – Maturity index (MI) *vs*. Na-K temperature ($T_{\text{Na-K}}$) scatterplot diagram, combining the results of monitoring operations conducted at Turia, at Agliano Terme, and at Slanic Moldova (the raw chemical-analytical data for that latter case were retrieved from Mitrofan *et al.*, 2008). The “cluster” regime “envelopes” are arbitrarily traced: they are only meant to illustrate that each outlet could range, in terms of its groundwater up-flow duration, in a significantly different domain (see text).

All things considered, there seems that for “sluggish” up-flows (diagnosed as such by means of their “cluster” regime “envelopes” – ex. the outlets of Turia and of Agliano Terme), the “drift” behavior became manifest in the fluid sampled at the earth surface only long time after the assumedly-related earthquake had actually occurred.

3.3. CORRESPONDENCE TO FOCAL MECHANISMS PARTICULARITIES

There appears that all the previously discussed deep-origin groundwater discharges display rather similar settings of their “cluster” regime data-points (Fig. 3). Conversely, the “drift-away” pathways are quite different, even in the case of the same groundwater outlet. One possibility which we investigated was that such differences in the “drift-away” pathways could be related to particularities in the focal mechanisms of each considered earthquake.

Both major Vrancea earthquakes inferred to be related to the particular, “drift-away” signatures detected in the Na-K-Mg geothermometry records of Turia outlet (Fig. 1, Tables 2, 3) have occurred at intermediate depths (~150 km) and displayed a reverse-faulting mechanism (as indicated by the Harvard CMT catalog, available at http://www.globalcmt.org/); yet while the P-axis of the first event (13 March 1998) displayed a NW-SE strike (which is habitual for most intermediate-depth Vrancea earthquakes – Radulian *et al.*, 2000), the P-axis of the second event (28 April 1999) exhibited a less usual, SW-NE strike. Correspondingly, the Na-K-Mg geothermometry analysis has indicated dissimilar patterns for the subsurface temperature evolutions associated to each of the two seismic events (Fig. 1b).

Table 3

Inferred correspondences between the recorded “drift” events and the significant earthquakes having occurred within an adjoining time-period

"Drift" event			**Earthquake to which the “drift” event was assumedly associated**		
Monitoring site	**"Drift" event record**	**Duration (months)**	**Date of occurrence**	**M_w**	**Time-lag between the earthquake and the end of the “drift” event (months)**
Turia	March – September 1998	5 - 6	13 March 1998	5.2	6
	April – August 1999	> 4	28 April 1999	5.4	> 4
Agliano Terme	February – April 2004	> 2	11 April 2003	4.9	12
	May – September 2005	4 - 5	24 November 2004	5.0	10

The two significant events of Northern Italy which were assumed to be associated with the specific (“drift-away”) Na-K-Mg geothermometry signatures recorded at the monitored spring at Agliano Terme (Fig. 2, Tables 2, 3), occurred at shallow (~10 km) depth. For both events, focal mechanisms (as provided by the Regional Moment Tensor Catalog of the Swiss Seismological Service in Zurich, available at http://www.seismo.ethz.ch/mt/) indicated NW-SE compression. Yet the T-axis changed from near-horizontal, for the first event (11 April 2003), to near-vertical, for the second one (24 November 2004). Accordingly, a pattern of increased subsurface temperatures was recorded at the Agliano Terme spring in the first case, while the opposite pattern (decreased subsurface temperatures) was noticed on occurrence of the second event (Fig. 2b). One possible explanation was that horizontal tension favored deeper cracks opening, and associated intrusions of hotter water from larger depths (a more detailed discussion pertaining to that topic is provided in Mitrofan *et al.*, 2008).

4. CONCLUSIONS

Observation data provided by a couple of hydrochemical monitoring operations conducted over periods of about 2 years in Romania (Vrancea seismic area) and in Northern Italy, have been processed by means of an approach that combined Na-K-Mg geothermometry (Giggenbach, 1988) with scatterplot analysis (Cioni *et al.*, 2007). The indicated procedure has outlined quite distinct anomalous signals, which displayed highly coherent patterns and lasted for several months (between at least 2, and a maximum of about 6 months).

The anomalous signatures were manifest within the several-months time-intervals that followed the occurrence of the most important earthquakes ($4.9 \leq M_w \leq 5.4$) recorded in each of the two study areas. Consequently, there was inferred that seismogenetically-related signals were induced at the depths-of-origin of the concerned groundwater discharge, becoming yet manifest in the fluid sampled at ground surface only after time-lags which ranged between about 6 and 12 months. When compared to the corresponding value-ranges of Giggenbach's (1988) "maturity index" (a proxy of the fluid up-flow duration), the indicated delays appear to be controlled by the "sluggishness" of fluid up-flows which develop between the groundwater depth-of-origin and the earth surface.

At the same outlet, on occurrence of important earthquakes subject to dissimilar focal mechanisms, different patterns of anomalous Na-K-Mg geothermometry signatures have been recorded.

When overall considered, the above-indicated relationships between specific Na-K-Mg geothermometry signatures and the particularities of the corresponding important earthquakes suggest that interactions related to the seismogenesis processes could involve long-range lithospheric domains (that extend – on the horizontal, as well as on the vertical – for more than 150 km). At the same time, the Na-K-Mg signature associated to a particular earthquake could be used – besides amplitude and frequency spectra, focal mechanism, stress drop, magnitude, etc. – as an additional characteristic in the description and the study of that specific event.

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