Diagnosing Non-Meteorically Induced Variations in the Chemistry of Saline Springs of the Vrancea Seismic Area (Romania)

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1. Introduction

Abstract-A monitoring operation conducted over more than seven years has been addressing chemical fluctuations displayed by several cool, low-discharge springs located close to the highly seismic Vrancea area (Romania). Those outflows compositions proved to be strongly controlled by binary, essentially isochemical mixing between a deep-origin brine and meteoric freshwater. By taking advantage of this particular setting, there have been constructed diagrams aimed at investigating how the groundwaterdischarges Na-K-Mg geothermometric parameters fluctuated as a function of the chloride content (taken to be an estimator of the freshwater-induced dilution). We made use of the reciprocal algebraic relationships existing between the equations describing the Na-K-Mg geothermometric parameters "Na-K temperature" and "K-Mg temperature" on the one hand, and the so-called "maturity index" (MI) on the other. In an accordingly derived plot of MI against the logarithm of the chloride concentration, a series of data-points being quite uniformly off-set from the MI dilutioncurve constructed for an apparently "regular" period, suggested that, episodically, all concerned springwaters were simultaneously subject to some similar changes in the controlling geochemical processes. One such modification intervened 3-4 months before the occurrence of the strongest earthquake ($M_w = 5.8$) of the hydrochemical monitoring period. The consequently derived interpretation was that then, the numerical values of certain geothermometric coefficients were likely altered: such a process could be consistent with changes in the alkali feldspars solubility relationships, possibly in response to episodic Al-Si complexing which might develop within a hypothesised, still active, exhumationchannel.

Key words: Geochemistry, Na–K–Mg geothermometry, binary mixing, Al–Si complexing, earthquake, Vrancea.

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A combined Na-K-Mg geothermometric technique has been devised by GIGGENBACH (1988), by taking advantage of the fact that the dissolved cation pair Na-K likely responded most slowly to temperature changes undergone by an up-flowing hydrothermal solution, while, in contrast, the relative contents of K and Mg were much faster to adjust to shallower (and implicitly cooler) thermal conditions. Two different temperature estimates could be accordingly derived, by separately taking into account the constituent-pairs Na-K and K-Mg: a "Na-K temperature" ($T_{\text{Na-K}}$), which was inferred to correspond to the deep-reservoir equilibrium conditions, and a "K-Mg temperature" (T_{K-Mg}), which progressively departed from T_{Na-K} along with the increasing chemical re-equilibration that likely occurred during the solution ascent from the deepreservoir to the ground surface. Also a non-dimensional maturity index (MI) has been defined by GIGGENBACH (1988), as an estimator of the departure intervening between T_{K-Mg} and T_{Na-K} .

It has yet to be emphasized that since $T_{\text{Na-K}}$, $T_{\rm K-Mg}$ and MI are defined as a function of the Na⁺, K⁺ and Mg²⁺ concentrations, their values reflect not only the more or less important amount of water-rock interaction having occurred since the hydrothermal (and usually saline) aqueous solution left the fullequilibrium deep reservoir; they also vary as a function of the intensity of the freshwater dilution undergone by that parent-water. In fact, mixing of two distinct endmembers (specifically, a deep-origin brine and meteorically-derived freshwater) appears to be a quite ubiquitous process involved in shaping the chemical "profile" of thermal and mineral

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groundwater discharges in tectonically active areas (e.g., AHMAD *et al.* 2002; TOUTAIN *et al.* 2006; GRASSA *et al.* 2006; CIONI *et al.* 2007). Linear correlations between pairs of solutes (anions, cations) normally provide, for such a mixing setting, a straightforward diagnosis tool (e.g., MARINI *et al.* 2000; LEVET *et al.* 2002; AGUILERA *et al.* 2005; SHIBATA *et al.* 2008; TARAN *et al.* 2008; TARAN and PEIFFER 2009).

In order to assess the apparent response that the parameters of the combined Na–K–Mg ionic geothermometer exhibited along with variations in the concerned solution dilution, CHIODINI *et al.* (1996) have suggested to directly use the corresponding linear correlations between the involved main cations and a conservative constituent—usually, the Cl⁻ anion: by inserting those cation-versus-Cl⁻ binarymixing linear-regressions into the Na–K and K–Mg geothermometers equations, the Na–K and K–Mg temperatures variations having been obtained as a function of the Cl⁻ concentration only. The same algorithm has been later on utilized also by AHMAD *et al.* (2002) and DOTSIKA *et al.* (2006, 2010).

It seems at the same time that such plots of the Na–K–Mg geothermometric parameters versus the chloride concentration might also be used as reference "baselines", against which possible departures from a mixing-only scenario could be outlined, and, as a result, one could detect and monitor the occurrence of additional, less frequent hydrochemical processes.

Accordingly, the present study aimed to highlight which were the specific variations that the Na–K–Mg geothermometer parameters values—actually recorded at several saline springs in the highly seismic Vrancea area (Romania)—still displayed after the subtraction of the binary-mixing effect estimated by means of the CHIODINI *et al.* (1996) algorithm.

As a result, two highly distinct regimes have been outlined, with the transition between them occurring 3–4 months before an $M_w = 5.8$ earthquake which had been, by far, the strongest occurring in that area since 1990. A certain analogy might exist between such results, and previous reports of distinct cationic geothermometry regimes having been recorded before and after a significant earthquake ($M_w = 5.8$) occurred in Egypt (IDRIS 2000). Yet in contrast with the scenario invoked by that earlier investigation, the well-documented binary mixing setting considered by the present study allowed one to rule out the hypothesis that in response to seismically-related processes, an alteration of the mixing ratio between two chemically contrasting fluids had occurred. Instead, our results suggest that the coefficients of some geothermometric relationships might have been, episodically, modified. The occurrence of such changes could be consistent with a series of earlier results (STEFÁNSSON and ARNÓRSSON 2000; ARNÓRSSON *et al.* 2002; GUDMUNDSSON and ARNÓRSSON (2005) concerning the Al–Si complexing influence on the alkali feldspars water-solubility functions and on the accordingly-derived water-rock chemical equilibrium relationships.

2. General Conceptual Background

2.1. General form Equation Describing the MI Variation as a Function of Dilution

For computing the Na–K and the K–Mg temperatures, the most widely-used expressions [and also the ones originally proposed by GIGGENBACH (1988)] are of the type:

$$T_{\text{Na}-\text{K}} = \frac{\alpha_{\text{Na}-\text{K}}}{\beta_{\text{Na}-\text{K}} - \log\left(\frac{c_{\text{K}}}{c_{\text{Na}}}\right)} - 273.15 \qquad (1)$$

and respectively:

$$T_{\rm K-Mg} = \frac{\alpha_{\rm K-Mg}}{\beta_{\rm K-Mg} - \log\left(\frac{c_{\rm K}^2}{c_{\rm Mg}}\right)} - 273.15, \qquad (2)$$

where c_{Na} , c_{K} and c_{Mg} are the concentrations (expressed as mg kg⁻¹) of the cations indicated by the subscripts. The geothermometer equation coefficients α and β (with their corresponding subscripts specifying the particular geothermometer to which they apply) had been obtained empirically from fielddata, by regressing the concentration-ratios of the concerned constituents, against actually measured temperatures.

For a binary-mixing setting, the actually determined concentrations of the concerned cations Na⁺, K⁺ and Mg²⁺ (c_{Na}^{\star} , c_{K}^{\star} and c_{Mg}^{\star}) can be regressed against the actually determined concentrations of Cl⁻ (c_{Cl}^{\star}). The resulting set of equations is:

$$c'_{\rm Na} = s_{\rm Na}c'_{\rm Cl} + i_{\rm Na},\tag{3}$$

$$c'_{\rm K} = s_{\rm K} c'_{\rm Cl} + i_{\rm K},\tag{4}$$

$$c'_{\rm Mg} = s_{\rm Mg} c'_{\rm Cl} + i_{\rm Mg}, \qquad (5)$$

where c' are the concentrations that exactly fit the above equations, with their subscripts indicating the involved constituent, while *s* and *i* are the regression coefficients (slope and intercept, respectively), with their subscripts specifying the cation involved in the regression.

The original algorithm of CHIODINI *et al.* (1996) stipulates that by substituting the regression Eqs. (3, 4 and 5) into the geothermometer functions (1) and (2), there could be obtained the variation-pattern displayed by $T_{\text{Na-K}}$ and $T_{\text{K-Mg}}$ in response to dilution. The corresponding $T'_{\text{Na-K}}$ vs. c'_{Cl} and $T'_{\text{K-Mg}}$ vs. c'_{Cl} relationships are:

$$T'_{\rm Na-K}(c'_{Cl}) = \frac{\alpha_{\rm Na-K}}{\beta_{\rm Na-K} - \log\left(\frac{s_{\rm K}c'_{\rm Cl} + i_{\rm Na}}{s_{\rm Na}c'_{\rm Cl} + i_{\rm Na}}\right)} - 273.15$$
(6)

and, respectively:

$$T'_{\rm K-Mg}(c'_{\rm Cl}) = \frac{\alpha_{\rm K-Mg}}{\beta_{\rm K-Mg} - \log\left[\frac{(s_{\rm K}c'_{\rm Cl} + i_{\rm K})^2}{s_{\rm Mg}c'_{\rm Cl} + i_{\rm Mg}}\right]} - 273.15$$
(7)

It is important to emphasize that the mixing process implicitly addressed by the algorithm of CHIODINI *et al.* (1996) is an *isochemical* one AHMAD *et al.* (2002): otherwise stated, the concerned cation-concentration variations are inferred to result, practically, only from dilution fluctuations (i.e., no significant water-rock reequilibration occurred—either before, or after the mixing of the two distinct water-types). Accordingly, also a "zero-dilution" status implicitly exists, which is defined by the saline parent-water chloride content (c_{Cl}^{max}) on the one hand, and by the deep-reservoir "true" temperature on the other: those two values are provided by intersection of the T'_{Na-K} vs. c'_{Cl} curve (Eq. 6) with the T'_{K-Mg} vs. c'_{Cl} one (Eq. 7).

Analogous to Eqs. (1) and (2), also the particular definition provided by GIGGENBACH (1988) for MI can be expressed by a general formula:

$$MI = G \log\left(\frac{c_{\rm K}^2}{c_{\rm Mg}}\right) - \log\left(\frac{c_{\rm K}}{c_{\rm Na}}\right) \tag{8}$$

with *G* being a function of the Na–K and K–Mg geothermometers equation coefficients, namely:

$$G = \frac{\alpha_{\rm Na-K}}{\alpha_{\rm K-Mg}}.$$
 (9)

There can be shown, on the other hand, that Eq. (8) can also be rewritten as a function of $T_{\text{Na}-\text{K}}$ and $T_{\text{K}-\text{Mg}}$, specifically:

$$\mathbf{MI} = F - \alpha_{\mathrm{Na}-\mathrm{K}} \left(\frac{1}{T_{\mathrm{K}-\mathrm{Mg}} + 273.15} - \frac{1}{T_{\mathrm{Na}-\mathrm{K}} + 273.15} \right)$$
(10)

with F being another function of the coefficients of the Na–K and K–Mg geothermometers equations, namely:

$$F = \frac{\alpha_{\text{Na}-\text{K}}}{\alpha_{\text{K}-\text{Mg}}} \beta_{\text{K}-\text{Mg}} - \beta_{\text{Na}-\text{K}.}$$
(11)

Equation (10) indicates that *F* is the maximum value which the maturity index can reach (i.e., under full equilibrium conditions, when $T_{K-Mg} = T_{Na-K}$): as T_{K-Mg} and T_{Na-K} progressively depart from each other ($T_{K-Mg} < T_{Na-K}$), MI values gradually decrease below *F*.

Next, into the maturity index definition-formula (8), written as:

$$\mathbf{MI}' = \log\left(c_{\mathrm{Na}}'c_{\mathrm{K}}'^{2G-1}c_{\mathrm{Mg}}'^{-G}\right) \tag{12}$$

there can be substituted the regression Eqs. (3)–(5), to further obtain the following dependence of the maturity index (MI') on the chloride concentration (c'_{CI}) only:

$$MI(c'_{Cl}) = \log\left[\left(s_{Na}c'_{Cl} + i_{Na}\right)\cdot \left(s_{K}c'_{Cl} + i_{K}\right)^{2G-1} \cdot \left(s_{Mg}c'_{Cl} + i_{Mg}\right)^{-G}\right].$$
(13)

Notice that for one and the same chloride concentration value $(c'_{CI} = c^{\star}_{CI})$ there exist two distinct MI values which are, as a general rule, different from one another: MI[´]—which exactly fits Eq. (13), and MI^{*}— which is computed from the actually determined concentrations of Na⁺, K⁺ and Mg²⁺ (c^{\star}_{Na} , c^{\star}_{K} , and c^{\star}_{Mg} , respectively) by means of Eq. (8).

For large concentrations of Cl⁻, if all *s* values are positive, the coefficients i_{Na} , i_K and i_{Mg} in Eq. (13) become increasingly negligible. Under such circumstances, Eq. (13) can be written in the asymptotic approximation:

$$\mathrm{MI}' \approx G \log \left(c_{\mathrm{Cl}}' \right) + \log \left(s_{\mathrm{Na}} s_{\mathrm{K}}^{2G-1} s_{\mathrm{Mg}}^{-G} \right). \tag{14}$$

It is, thus, indicated that the plot of MI as a function of $log(c'_{Cl})$ asymptotically tends to a straight line of slope *G*.

For the considered binary-mixing assumptions, one must expect the maximum possible MI['] value namely *F*, see Eq. (10)—to be obtained simply by imposing zero-dilution conditions: therefore, within an MI['] vs. c'_{Cl} plot, the Cl⁻ concentration corresponding to *F* is the maximum possible one (c'_{Cl}^{max}) assuming, that of the saline parent-water involved in the mixing with shallow meteoric water CHIODINI *et al.* (1996). The coordinates (c'_{Cl}^{max} , *F*) of the corresponding particular point of the MI['] vs. c'_{Cl} curve are provided by the following relationship, obtained by rewriting Eq. (13) as:

$$F = \log \left[\left(s_{\text{Na}} c_{\text{Cl}}^{\prime \text{max}} + i_{\text{Na}} \right) \times \left(s_{\text{K}} c_{\text{Cl}}^{\prime \text{max}} + i_{\text{K}} \right)^{2G-1} \times \left(s_{\text{Mg}} c_{\text{Cl}}^{\prime \text{max}} + i_{\text{Mg}} \right)^{-G} \right].$$
(15)

2.2. Selecting Numerical Values for α_{Na-K} , β_{Na-K} , α_{K-Mg} and β_{K-Mg} .

In different places, fluids may interact with rocks including different mineralogical phases, and/or structural states of the concerned minerals (HELGESON et al. 1978; FOURNIER 1990; MICHARD and BEAUCAIRE 1993; STEFÁNSSON and ARNÓRSSON 2000). Therefore, an appropriate description of the aqueous solutions chemical equilibrium may require the utilization of different sets of numerical values for the coefficients α_{Na-K} , β_{Na-K} , α_{K-Mg} , and β_{K-Mg} (e.g., Verma *et al.* 2008). In particular, it has been frequently debated (e.g., MARINI et al. 2000; AHMAD et al. 2002; TARCAN and GEMICI 2003; SHIBATA et al. 2008; DELALANDE *et al.* 2011) whether the α_{Na-K} and β_{Na-K} coefficients proposed by GIGGENBACH (1988) were (or were not) more suitable than those provided by the FOURNIER (1979) Na-K geothermometer function, for being used—in conjunction with the K-Mg geothermometer

Table 1

The numerical values utilized for the Na–K–Mg geothermometric equations coefficients in the present study

Reference	$\boldsymbol{\alpha}_{K-Mg}$	$\beta_{\rm K-Mg}$	$\boldsymbol{\alpha}_{Na-K}$	$\beta_{\rm Na-K}$	G^{a}	F^{b}
GIGGENBACH (1988)	4,410	14.0				
GIGGENBACH (1988)			1,390	1.75	0.315	2.663
Fournier (1979)			1,217	1.483	0.276	2.380

The values of $\alpha_{\text{Na}-\text{K}}$, $\beta_{\text{Na}-\text{K}}$, $\alpha_{\text{K}-\text{Mg}}$ and $\beta_{\text{K}-\text{Mg}}$ are retrieved from the indicated references. In addition to the already published *G* and *F* values associated with the Na–K and K–Mg geothermometers equations proposed by GIGGENBACH (1988), we have also computed the analogous *G* and *F* coefficients for the Na–K equations proposed by FOURNER (1979)

 a Computed by means of Eq. (9), utilizing for α_{K-Mg} the value proposed by Giggenbach (1988)

 b Computed by means of Eq. (11), utilizing for α_{K-Mg} and β_{K-Mg} the values proposed by GIGGENBACH (1988)

equation provided by GIGGENBACH (1988)—in various specific Na–K–Mg geothermometric diagnoses.

We started by assuming that for the investigated springs of the Vrancea area, any of the two abovespecified Na–K experimental relationships might be applicable, in conjunction with the GIGGENBACH (1988) K–Mg geothermometer equation (we have accordingly indicated in Table 1 the corresponding values-sets that we utilized for the $\alpha_{\text{Na}-\text{K}}$, $\beta_{\text{Na}-\text{K}}$, $\alpha_{\text{K}-\text{Mg}}$, $\beta_{\text{K}-\text{Mg}}$, *G* and *F* parameters). Yet eventually, by corroborating additional geochemical evidence (Appendix 1), we managed to pinpoint the FOURNIER (1979) Na–K geothermometer function as being the one which best suited the hydrogeological setting considered by our study.

3. Geological and Hydrogeological Setting

Vrancea (Fig. 1) represents one of Europe's most active seismic regions: large earthquakes (M_w up to 7.7 according to the so far available instrumental records—ISMAIL-ZADEH *et al.* 2012) occur in a high P-wave velocity lithospheric body (e.g., TONDI *et al.* 2009; POPA *et al.* 2012), which occupies a steeplydipping position at mantle-depths (60–180 km), within a tightly confined area (just 25 km × 70 km lateral extent). The latter develops beneath the Eastern Carpathians fold-and-thrust belt, which consists MATENCO and BERTOTTI (2000) of northward-trending



Figure 1

General setting of the study area (geology after SĂNDULESCU 1984). The approximate boundary of the epicentral domain of the mantle-depth Vancea earthquakes is indicated by the dashed, roughly oval contour: the star inside it marks the epicenter of the strongest seismic event ($M_w = 5.8$) which occurred in Vrancea area during the hydrochemical monitoring operation. The *light-grey triangle* indicates the monitoring site at Slănic Moldova. *Small white dots* labeled DP represent the DACIA PLAN seismic experiment profile track-fragment where increased P wave velocities were assumed to indicate (BOCIN *et al.* 2009) a crystalline rocks occurrence; while the approximate overall extent of that conjectured crystalline body is illustrated (cf., LANDES *et al.* 2004; TONDI *et al.* 2009) by the dotted contour. The site displaying the maximum GPS uplift velocity (according to data provided by HEIDBACH *et al.* 2007) is indicated by the *plus* sign. TSB designates the Tîrgu Secuiesc Basin. The location of the study area within Romania is indicated in the *inset* map

successions of Cretaceous-Neogene flysch deposits. The laterally constricted Vrancea seismicity "nest" has been frequently ascribed to the last remnant of an oceanic slab being subducted toward the NW, beneath the Intra-Alpine plate.

The considered springs are located at Slǎnic Moldova and they discharge from the so-called Marginal Folds (or Vrancea) nappe, built up of tubiditic and other clastic deposits ranging in age from Lower Cretaceous to Lower Miocene (MAT-ENCO and BERTOTTI 2000; AMADORI *et al.* 2012). Beneath the tectonic half-windows where the southernmost outcrops of the Marginal Folds nappe are met (and where also the Slǎnic Moldova discharge area is located), a crustal structure with increased P-wave velocities was detected by means of 3-D tomography studies. That P-wave anomaly, positioned somewhere between 4.5 and 12.5 km depth, was inferred to mirror (LANDES *et al.* 2004; BOCIN *et al.* 2009) crystalline rocks belonging to the flysch nappes basement.

The earliest-mentioned indication concerning a possible deep-origin of the saline springs at Slănic Moldova had been derived (TSCHERMAK 1881) from their average discharge-temperatures. The latter exceeded by a few degrees C (Table 2) the 7 °C multiannual average air temperature of that region (general physiographic data provided, for instance, in CANTUNIARI 1939). In order to explain why closely-spaced outlets at Slănic Moldova discharged waters of quite different salinities, TSCHERMAK (1881) suggested a conceptual model consisting of a network of poorly interconnected groundwater flow-paths, analogous, to a certain extent, to the setting that ROWLAND

General data concerning the 2003–2010 hydrochemical monitoring operation conducted at the considered saline springs of Slănic Moldova

	Spring No. 10	Spring No. 1bis	Spring No. 3
Outlet location Latitude N(°)	46.2035	46.2035	46.2028
Outlet location Longitude E (°)	26.4309	26.4309	26.4302
First sampling date	16-Apr- 2003	16-Apr- 2003	14-Jul-2003
Last sampling date	22-Jun- 2010	22-Jun- 2010	8-May-2010
Total number of samplings	83	84	26
Outlet temperature range (°C)	5.4-12.8	5.1-13.0	n.a. ^a
Flow-rate range (Ls^{-1})	0.009-0.016	0.016-0.022	0.095-0.154
pH range	5.4-6.9	5.6-7.0	5.7-6.9
Range of computed TDS values (g L^{-1})	6.9–10.0	9.1–11.8	14.1–15.2

^a The natural outlet was never accessible during the monitoring operation; therefore, any temperature measurements of the flow discharging from the complex water-intake equipments were inevitably altered by outer environment temperatures

et al. (2008) imagined for certain chloride-rich springs in the California Coast Ranges: while a common, deep-origin saline endmember assumedly supplied all the springs, the concentration of a particular outflow was controlled by the variable degrees of dilution induced by the actual amounts of meteoric freshwater that reached the up-flow path of that specific spring.

Much more recently, by taking into account a noticeable ¹⁸O isotope enrichment relative to local meteoric waters, as well as Na–K–Mg geothermometry diagnoses which indicated deep-equilibration temperatures in excess of 150 °C, VASELLI *et al.* (2002) conjectured that at Slănic Moldova there were discharged deep-seated chloride waters whose origin should be non-meteoric. In "Appendix 2", a more detailed discussion is provided about isotopic evidence on the origin of the Slănic Moldova mixed waters.

4. Data Collection and Analysis

Different from the time-interval 1977–1990 when in the Vrancea mantle-depth seismogenic body there had occurred no less than four strong earthquakes (in a magnitude range $6.3 \le M_w \le 7.5$ according to the Harvard CMT catalog)—the 5.5 magnitude threshold has been subsequently exceeded by only one event: that of 27 Oct. 2004 (depth 93.8 km, $M_w = 5.8$). The present investigation made use of chemical data derived from a large number of samples which had been collected from the considered springs at Slănic Moldova during a hydrochemical monitoring operation conducted over the time-interval 2003–2010, and, which, thus, implicitly encompassed the 27 Oct. 2004 strong earthquake. General information concerning that monitoring operation is provided in Table 2.

Each of the three monitored springs (locally designated as No. 1bis, No. 3 and No. 10) discharge by the present time via more or less intricate watertapping facilities. Therefore, logistic impediments prevented on certain occasions the access to the natural outlets of the springs No. 1bis and No. 10, while the natural outlet of the spring No. 3 has not been accessible at any sampling date; so samples have been collected—as a function of the actually existing conditions—either from the natural outlets, of from the water-intake facilities.

Although just about 2 m separate the spring No. 1bis from the spring No. 10 (and because of that, identical co-ordinates have been ascribed in Table 2 to both discharges), each of these two outflows displayed, on every occasion, dissolved constituents concentrations which were quite distinct from those of its neighbour. In fact, the three considered springs exhibited, on each sampling date, the same "hierarchy" in terms of salinity—with No. 10 always being the most dilute, while No. 3 (located about 100 m away) was always the most concentrated.

For the entire hydrochemical monitoring period, the prescribed water-sampling frequency should have been, on the average, once a month. It has yet been possible to broadly conform to this sampling frequency only in the case of the springs No. 10 and No. 1bis; due to various constraints, sampling with the indicated frequency has started at the spring No. 3 only in October 2007. Fortunately, additional samples had been collected from this latter spring on two previous isolated occasions—in July 2003 and in June 2004. That was within a time-period during which there was manifest a different chemical behaviour (see Sect. 5)—with the transition between the two behaviour regimes being possibly related to the occurrence of the strong (magnitude 5.8) Vrancea earthquake of 27 Oct. 2004.

The water sampling and analysis procedures, together with the accordingly derived solute concentrations are listed as Electronic Supplementary Data.

An estimate of the error associated with the analytical determinations was provided by the relative standard deviation (%RSD). To this purpose, for enough large numbers of samples selected over the entire duration of the monitoring operation, 3–5 aliquot samples have been analyzed in parallel. Computed %RSD values refer to the concentrations expressed as mg kg⁻¹, specifically: for Na, the variation range is 0.040 %RSD to 2.041 %RSD (the arithmetic average is 0.832); for K, the variation range is 0.057 %RSD to 2.903 %RSD (average 1.068) and for Mg, the variation range is 0.046 %RSD to 1.789 %RSD (average 0.644).

5. Distinguishing Between Preseismic and Postseismic Geochemical Regimes

In defining and constraining distinct behaviour regimes possibly displayed by the hydrochemical data-series, two separate stages have been involved.

5.1. Stage One: Diagnosing the Binary-Mixing Behaviour

Within this first stage, in order to outline possible differences between preseismic and postseismic regimes, the concentrations of the main cations Na^+ , K^+ and Mg^{2+} have been plotted against the concentration of the conservative element Cl^- (Fig. 2): there was, thus, an attempt to detect distinctions in terms of binary-mixing behaviour.

A binary-mixing setting has been quite frequently invoked in previous studies (e.g., TOUTAIN *et al.* 1997, 2006; BIAGI *et al.* 2000; RAMIREZ-GUZMAN *et al.* 2005; TARAN *et al.* 2005; SONG *et al.* 2006; SKELTON *et al.* 2008; SÜER *et al.* 2008), in order to explain earthquake-related changes detected in the ionic composition of groundwater. Such changes were inferred to mirror enhancements (or, alternatively, reductions) in the water flow between a pair of adjacent aquifers whose groundwater chemical compositions were highly contrasting. The actual triggering phenomena were assumed to be straininduced changes in the differential pore-pressure, and/or alterations of the overall aquifer-system permeability. Implicitly, in such earthquake-related investigations there was additionally adopted the inference that the "seismically-controlled" datapoints, while still remaining positioned on the same linear mixing-trend as the "routine" data-points assemblage, would, nevertheless, plot significantly far away from the latter (TSUNOGAI and WAKITA 1995; NISHIZAWA et al. 1998; FAVARA et al. 2001; ITALIANO et al. 2005; Pérez et al. 2008; WOITH et al. 2013). Yet environmental factors, like rainfall and infiltration, can also exert a considerable control on the mixing processes intensity. There are as a consequence instances when, due to the comparatively large amplitude of the meteorically-induced fluctuations, only modest (if any!) changes in the mixing regime could be plausibly ascribed to earthquake-related phenomena (CIONI et al. 2007; FAVARA et al. 2007; MANGA and ROWLAND 2009).

In an attempt to diagnose the considered springs at Slănic Moldova in terms of the above discussed possible patterns, it was assumed—as a first-order approach—that a significant time-reference for separating the two regimes from one another could be provided by the important earthquake of 27 Oct. 2004. Consequently, each series of samples of a specific spring has been divided into:

- "preseismic regime" samples, collected during the approximately 18 month long interval elapsed between April 2003 (when the monitoring operation had started), and the occurrence of the 27 Oct. 2004 earthquake;
- "postseismic regime" samples, collected after the 27 Oct. 2004 earthquake, and till the hydrochemical monitoring operation was concluded.

There can be noticed that for all the "postseismic regime" samples, the experimental data-points are rather tightly aligned (Fig. 2; Table 3). This setting





Springs No. 10, No. 1bis and No. 3 at Slănic Moldova: plots of Na⁺ versus Cl⁻ (**a**), K⁺ versus Cl⁻ (**b**), and Mg²⁺ versus Cl⁻ (**c**). "Preseismic regime" and "postseismic regime" refer to the samples being collected (within the 2003–2010 monitoring operation) before and after the 27 Oct. 2004 earthquake, respectively. In addition to the samples collected during the 2003–2010 monitoring operation, there are also plotted several "historical" samples (*symbols* labelled with the corresponding sampling date). In computing the mixing-trend linear regressions (*solid lines*), there were taken into account only the samples collected from all three considered springs during the October 2004–June 2010 "postseismic regime" period. When comparison is made with a fluid derived from seawater dilution (*dotted line*), the computed mixing trends indicate significant Na⁺ and K⁺ enrichments, as well as a strong Mg²⁺ depletion (due to space reasons, the seawater dilution line for Mg²⁺ is not shown). In addition, there is an obvious excess of Na⁺ with respect to the stoichiometric dissolution of halite (*dashed line*)

points to the fact that a common saline endmember, of constant composition, supplied all the Slănic Moldova springwaters. When the computed mixing trend for Na^+ (Fig. 2a) is compared with the halitedissolution line, it becomes obvious that the considered springs do not owe their saline character to salt-leaching. In addition, significant Na^+ and K^+ enrichments are noticed (Fig. 2a, b) with respect to a simple setting involving seawater dilution. As for the Mg^{2+} concentrations, they are much lower than those

Parameters of the linear regressions corresponding to the mixingtrends between the conservative anion Cl⁻, and each of the constituents Na⁺, K⁺, Mg²⁺ and total dissolved SiO₂

Table 3

	Postseismic regime ^a					
	Na ⁺ vs. Cl ⁻	K ⁺ vs. Cl ⁻	Mg ²⁺ vs. Cl ⁻	SiO_2 vs. Cl^-		
Goodness of fit— r^2	0.962	0.904	0.978	0.572		
s $i (mg kg^{-1})$	0.8945 -170.83	0.03341 1.76	0.005349 1.67	-0.001135 22.23		

The *s* and *i* coefficients represent the slope and intercept, respectively

^a It concerns the samples collected from all three springs over the time-interval 29 Oct. 2004–22 Jun. 2010 (Figs. 2, 8)

corresponding to the seawater dilution trend. It consequently appears that the basic factor controlling the cationic composition of the involved saline endmember is water-rock interaction.

The saline parent-water is next subject, during its up-flow to the surface, to variable mixing with freshwater (probably, of local meteoric origin). The corresponding behaviour remained unchanged over the entire time-interval (of almost six years) during which the hydrochemical monitoring operation continued to be performed subsequently to the occurrence of the 27 Oct. 2004 earthquake.

For the springs which we considered in this paper, chemical analyses have been also provided by several previous studies that had addressed-in the late nineteenth and early twentieth centuries-the hydrogeological setting of Slănic Moldova (Konya 1887; SUMULEANU and POPOVICI 1923; GHIMICESCU et al. 1951). There can be noticed (Fig. 2) that such "historical" data-points exhibit just a moderate scatter with respect to the mixing trend regressions that had been computed based only on samples collected during the "postseismic regime" period of the 2003–2010 hydrochemical monitoring operation. Unfortunately, seismic records contemporary to the historical samplings are poor in reliablity, and, therefore, relevant comparisons cannot be made (especially in terms of magnitude estimates-e.g., SHEBALIN et al. 1998) with recently documented Vrancea earthquakes. With this caveat in mind, it, nevertheless, appears that the "historical" chemical data provide a rough indication that within the last 125 years or so, a regime similar to the one, which we designated as "postseismic", has been repeatedly present in that area (for possible correlations with the 1886, 1915 and 1932 Slănic Moldova samplings, one may still consider, tentatively, a list of mantle-depth major events occurred in Vrancea area - for instance in RADULIAN *et al.* 2000).

It can next be seen (Fig. 2) that most samples collected during the "preseismic regime" period plot in the same Cl^- concentration-range as the "postseismic regime" ones. It is, hence, suggested that essentially, the involved mixing ratios underwent no changes. Yet in terms of their concentrations of K⁺ (Fig. 2b), and especially of Mg²⁺ (Fig. 2c), many "preseismic regime" data-points display significant departures with respect to the linear trends which mirrored a simple, essentially isochemical mixing between two fluids of contrasting compositions.

Water composition data-points which—similarly to those illustrated in Fig. 2b, c-exhibited significant excursions with respect to a linear, environmentallycontrolled binary-mixing pattern have been previously reported by LAWLER et al. (1996): concomitantly with enhancements in the local seismic activity, those investigators had monitored the composition of geothermally-influenced meltwater derived from a glacier in Iceland; there have been accordingly noticed obvious departures in the SO_4^{2-} concentrations, with respect to the linear, mixingcontrolled correlation that during aseismic periods existing between the SO_4^{2-} and Cl^- contents. The proposed explanation was that the deviations from the "routine" mixing regime were due to an extra amount of SO_4^{2-} , the latter being derived from the near-surface oxidation of the fresh H₂S inputs which accompanied the seismicity burst.

It is obvious that an analogous mechanism cannot be invoked for explaining the preseismic excess concentrations of K^+ and Mg^{2+} detected in the monitored springs of the Vrancea area (Fig. 2b, c). Therefore, in order to obtain further insights into the processes that were likely responsible for the observed modifications, we have considered, alternatively, how the Na–K–Mg geothermometric parameter MI varied along with dilution.

5.2. Stage Two: Discriminating Between Preseismic and Postseismic Signatures in the MI Fluctuations of the Considered Springs

As already mentioned (Sect. 2.1), the prerequisite for utilizing the "mixing-effect" algorithm of Chio-DINI *et al.* (1996) is that the concerned cationconcentration variations are induced, preponderently, by fluctuations in the saline parent-water amount of dilution: such a circumstance is expected to be outlined by highly-correlated linear trends of cation vs. Cl^- data-points; alternatively, if a notable chemical re-equilibration additionally takes place between the ascending solution and the host-rock, an important scatter in those data-points will be noticed (see, on that topic, discussion in MARINI *et al.* 2000).

The highly correlated cation versus Cl⁻ linear trends illustrated in Fig. 2 suggested in this respect that a binary, essentially isochemical mixing regime indeed controlled, during the "postseismic regime" time-period, the behaviour of the concerned spring discharges. With this prerequisite being, by and large, fulfilled, we have constructed a MI vs. c_{Cl} diagram (Fig. 3) which included:

- experimentally obtained MI* values plotted versus the corresponding c^{*}_{Cl} (they are represented as individual data points, illustrated by various symbols): those MI* values are computed, for each analyzed sample, by substituting the actually determined concentrations c^{*}_{Na}, c^{*}_K and c^{*}_{Mg} into Eq. (8);
- the MI vs. c'_{Cl} dilution function (dashed line), computed by means of Eq. (13) relying only on the "postseismic regime" samples (with the values of the involved regression coefficients *s* and *i* being accordingly retrieved from Table 3);
- the maximum possible MI value (namely *F*, retrieved from Table 1 for the adopted set of $\alpha_{\text{Na}-\text{K}}$ and $\beta_{\text{Na}-\text{K}}$ values—the latter being those proposed by FOURNIER 1979 in accordance with discussion in "Appendix 1").

A logarithmic scale was also used for the chloride concentration, in order to visualize the asymptotic behaviour that Eq. (14) predicted for the MI vs. Cl^- dilution function.

By considering each of the three monitored springs at Slănic Moldova, it can be noticed (Fig.



Figure 3

Plot of MI vs. Cl, constructed for the considered springs at Slănic Moldova. Symbols as specified in Fig. 2. The Na–K geothermometer equation coefficients used in computing the MI values are those proposed by FOURNIER (1979) (in accordance with discussion in "Appendix 1"). Only the "postseismic regime" samples and the "historical" samples plot reasonably close to the MI vs. $c'_{\rm Cl}$ dilution line (*dashed curve*) [the latter was computed by means of Eq. (13), relying only on the "postseismic regime" samples—see Sects. 2.1, 2.2 and 5.2 for details]. Most of the samples collected during the "preseismic regime" time-period plot quite far away from that *curve*

3) that both for the "postseismic regime" samples collected during the 2003–2010 monitoring operation, and for the "historical" samples, all individual data-points fall reasonably close to the constructed MI vs. c'_{Cl} curve. In contrast, for most of the samples collected during the "preseismic regime" time-period, the experimental data-points plot rather far away from that curve.

Further looking for a quantitative assessment that would support the above considerations, there has been computed, for each individual water sample (which had the actually determined concentrations c_{Na}^{\star} , c_{K}^{\star} , c_{Mg}^{\star} and c_{Cl}^{\star}), a "maturity index" residual (designated as Δ MI):

$$\Delta MI = MI^{\star} - MI', \qquad (16)$$

where MI['] was provided by Eq. (13), for $c'_{Cl} = c^{\star}_{Cl}$.



Figure 4

Springs No. 10 (a), No. 1bis (b), and No. 3 (c) at Slănic Moldova: time series of Δ MI —the deviations between the experimentally-derived values of MI (*various symbols* in Fig. 3), and the MI vs. Cl dilution line computed by means of Eq. (13) (*dashed curve* in Fig. 3—see Sect. 2.1, 2.2 and 5.2 for details). *Symbols* as specified in Fig. 2; still notice that the "historical samples" are plotted at an arbitrary position on the time scale. The *dashed horizontal lines* indicate the $\pm 3\sigma$ interval (σ being computed for the entire Δ MI data-set associated with the "postseismic regime" samples collected from all three springs during the 2003–2010 monitoring operation). The *vertical solid bar* marks the strong $(M_w = 5.8)$ Vrancea earthquake of 27 Oct. 2004

In an approach somehow analogous to that of BIAGI *et al.* (2000), the possible occurrence of earthquake-related modifications has been investigated by checking if the Δ MI values were contained within an interval of six standard deviations ($\pm 3\sigma$), or if they exceeded that interval. The adopted standard

deviation values referred to the entire data-set of ΔMI values computed for all "postseismic regime" samples collected from all three Slănic Moldova springs.

When the Δ MI variation in time is considered, it can be noticed (Fig. 4) that for the samples collected during the "preseismic regime" period, most Δ MI

6. Discussion

A feature immediately discernible in Fig. 3 is that most "preseismic regime" data-points are shifted with respect to the MI[′] vs. c'_{C1} dilution line constructed for the "postseismic regime" time-period; and seemingly, for all three considered springs, by rather similar amounts (see in this respect also Fig. 4).

One possible cause for such signatures (Fig. 3) could be a major increase (almost twofold) in the saline parent-water Cl⁻ content. It, however, seems probable that the latter concentration actually was not changed during the "preseismic regime" period—otherwise significant differences should have been noticed also in the Na vs. Cl correlation of Fig. 2a, as compared to the "postseismic regime". In principle, episodically (i.e., during the "preseismic regime"), mixing with a third, more saline endmember could have occurred as well: it is yet difficult to imagine one such "exotic" endmember, that displays exactly the same Na⁺/Cl⁻ ratio as the "routine" parent-water (Fig. 2a), but highly increased K⁺/Cl⁻ and Mg²⁺/Cl⁻ ratios (Fig. 2b, c).

It appears, consequently, that the shifted datapoints outline an alternative MI['] vs. c'_{Cl} dilution curve, to which a different set of α_{Na-K} , β_{Na-K} , α_{K-Mg} and β_{K-Mg} numerical values could be associated. For further exploring the implications of that latter inference, some additional data-processing was performed, by using the significant amount of sampling-data having been collected during the TDPR time-interval (as defined in Sect. 5.2).

6.1. Separately Processing the Data Associated to the "Truly Distinct Preseismic Regime"

We chose to empirically investigate the possibility (suggested by Figs. 3, 4) that the MI values had been diminished, during the TDPR, by a more or less constant amount.

Our approach simply consisted in uniformly shifting, down the MI scale, the MI['] vs. c'_{Cl} curve previously derived for the "postseismic regime" samples (Fig. 3), until there was achieved a best-fit

values are negative, with a large number of them falling even below the -3σ reference-line. Actually, it was until sometime between 25 Jun. and 20 Jul. 2004 that the ΔMI values computed for the Springs No. 10 and No. 1bis (Fig. 4a,b respectively) remained, on the whole, below the -3σ referenceline (just two samples of the Spring No. 10 were positioned slightly above); whereas subsequently, for the next six years or so (i.e., until the end of the hydrochemical monitoring operation), the ΔMI values computed for any of the three monitored springs never again plotted outside the $\pm 3\sigma$ range. (In the case of the Spring No. 3, Fig. 4c-the two samplings performed during the "preseismic regime" period are included in the particular time-interval spanning approximately from 16 Apr. 2003 to 25 Jun. 2004, i.e., within the period predating the 27 Oct. 2004 earthquake by more than four months: hence, by assuming an analogy with the previously discussed behaviour displayed by the springs No. 10 and No. 1bis, one would expect the corresponding "preseismic" ΔMI values computed for the Spring No. 3 to plot below the -3σ reference line; and indeed—as indicated by Fig. 4c-this anticipation is confirmed.)

Overall , such a systematic behaviour suggests that, for a specific preseismic time-interval that extended until 3-4 months prior to the occurrence of the important ($M_w = 5.8$) 27 Oct. 2004 earth-quake, the computed MI values mirrored the influence of certain processes which, subsequently - in particular, during the postseismic regime—were presumably altered.

By considering the period during which most ΔMI values plotted below the -3σ reference-line, one can define a "truly distinct preseismic regime" (TDPR), which covers the monitoring time-interval spanning until about four months prior to the important 27 Oct. 2004 earthquake.

Finally, another significant observation concerns the Δ MI values associated with the "historical" samples: they all plot within the $\pm 3\sigma$ interval (Fig. 4), that circumstance strengthening the suggestion that they had been collected during time-periods similar to the one which we designated as "postseismic".





Empiric derivation of a MI vs. Cl dilution line associated to the Slănic Moldova springs "truly distinct preseismic regime". *Symbols* designate, accordingly, samples collected just during the "truly distinct preseismic regime" (as defined in Sect. 5.2). The *dashed curve* represents the same MI vs. Cl dilution line as in Fig. 3—i.e. the one derived for the "postseismic regime" samples: by uniformly shifting this *curve* along the MI scale till the residuals (ΔMI) were minimized in the least squares sense [as stipulated by Eq. (17)—see Sect. 6.1 for details], a new, hypothetical MI vs. Cl dilution line was empirically traced (the *solid curve*)

to all the TDPR data-points (Fig. 5). The adopted optimization criterion has been:

$$\sum (\Delta MI)^2 = \min \tag{17}$$

and the accordingly derived off-set value resulted to be 0.062.

The empirical procedure we developed has a few straightforward implications:

- for geometric reasons, the asymptotic slope G (see Eq. 14) of the MI['] vs. $\log(c'_{CI})$ curve associated with the TDPR (the solid line in Fig. 5), remains the same as the asymptotic slope of the analogous "postseismic regime" curve (the *dashed line* in Fig. 5);
- by subtracting the obtained off-set value (0.062) from the *F* value associated to the "postseismic regime" curve (i.e., 2.380—as retrieved from Table 1), there is obtained the *F* value corresponding to the empirically traced TDPR curve (the solid line in Fig. 5)—namely 2.318.

When the above-indicated shifting in the F value is considered simultaneously with the F definitionequation (11), one may in the first place assume that no significant changes have intervened in the first term on the right hand of Eq. (11): consequently, the above-calculated 0.062 off-set was in fact experienced just by $\beta_{\text{Na-K}}$, so that the latter coefficient accordingly "shifted" from the "standard" value of 1.483 (proposed by FOURNIER 1979 and indicated as such in Table 1), to an "anomalous" one of 1.545.

Such an inference seems to be supported by a couple of simultaneous plots of $T_{\text{Na-K}}$ vs. c_{Cl} , and $T_{\rm K-Mg}$ vs. $c_{\rm Cl}$ (Fig. 6). One such plot—Fig. 6a—has been constructed by using for β_{Na-K} , in all the computations, the "standard" numerical value (i.e., that provided by FOURNIER 1979 and indicated as such in Table 1). In the other plot-Fig. 6b-the only difference was that in calculating (by means of Eq. 1) the Na-K temperatures for the individual samples collected during the TDPR, there has been used the newly-derived value of β_{Na-K} (1.545), instead of the "standard" one (1.483): as a result, the TDPR datapoints that scatter around the $T'_{\text{Na}-\text{K}}$ vs. c'_{Cl} dilution curve became (Fig. 6b) much more similar to the scatter exhibited by the "postseismic regime" datapoints; in contrast, in Fig. 6a, most of the $T_{\text{Na}-\text{K}}$ experimental data-points associated to the TDPR



Figure 6

Springs No. 10, No. 1bis and No. 3 at Slănic Moldova: plots of T_{Na-K} and T_{K-Mg} vs. Cl. (a). For all the computations, the numerical values used for α_{Na-K} , β_{Na-K} , α_{K-Mg} and β_{K-Mg} have been retrieved from Table 1, as explained in Sect. 2.2 and in "Appendix 1"; (b). In computing the T_{Na-K} data-points associated with the "truly distinct preseismic regime" (as defined in Sect. 5.2), a newly-derived numerical value was used for β_{Na-K} (see Sect. 6.1 for details), all other computations being performed as in (a). *Various symbols* represent: the T_{Na-K} values computed from the actually determined concentrations of Na⁺ and K⁺, plotted versus the actually determined concentrations of Cl⁻; and similarly, the T_{K-Mg} values computed from the actually determined regime" refer to the samples being collected before and after the 27 Oct. 2004 earthquake, respectively. *Solid curve*: the T_{Na-K} vs. Cl dilution line computed by Eq. (6); *dashed curve*: the T_{K-Mg} vs. Cl dilution line computed by Eq. (7)

samples were significantly shifted "upwards" with respect to the cluster of the "postseismic regime" data-points.

Figure 6 indicates on the other hand that for T_{K-Mg} , the TDPR experimental data-points are anyway intermingled with the "postseismic regime" ones (otherwise stated, the scatter of both groups around the T'_{K-Mg} vs. c'_{Cl} curve is comparable). This largely unperturbed behaviour suggests that when the "postseismic regime" time-period is compared to the

period of TDPR, it appears that neither was the ascending solution subject to more advanced chemical re-equilibration, nor did the numerical values of α_{K-Mg} and β_{K-Mg} undergo substantial changes. When additionally considering that our empiric approach (as illustrated in Fig. 5) implied that the *G* coefficient did not change either, it results from Eq. (9) that also the α_{Na-K} numerical value remained, probably, more or less the same. Evidence is, thus, provided for the conjectured stability of the first term on the right hand





Na⁺/K⁺ mass-concentration ratios versus the reciprocal of the absolute temperature (K) at which the aqueous solution reaches chemical equilibrium with alkali feldspars. The *solid line* is the Na–K temperature *curve* proposed by FOURNIER (1979): accordingly, for data-points (*symbols*) plotting exactly on this line, the Na–K temperature had been calculated by using for β_{Na-K} the "standard" value of 1.483 (retrieved from Table 1). Alternatively, the data-points shifted to the left correspond to the "truly distinct preseismic regime" T_{Na-K} values, which were recalculated by using for β_{Na-K} the newly-derived value of 1.545 (see Sect. 6.1 for details). As a result, these recalculated "truly distinct preseismic regime" data-points plot in the same temperature range as the "postseismic regime" ones, while in terms of $\log(c_{Na}/c_K)$, they are off-set toward lower values by 0.062 log units

of Eq. (11): this implicitly supports the inference that only the value of $\beta_{\text{Na-K}}$ was presumably subject to a notable change during the TDPR, as compared to the "postseismic regime" period.

We next assumed that this modification of the $\beta_{\text{Na-K}}$ numerical value mirrored, probably, some kind of alteration undergone by any of the water-rock interaction parameters. However, there was by no means involved also a significant change of the chemical equilibration temperature. Had that temperature been modified, it should have likely induced noticeable effects also in the $T_{\text{K-Mg}}$ values, as well as in the actually measured temperatures of the considered groundwater discharges; yet no such symptoms have been detected.

As a first-order approach, one can imagine a simple formal scheme for intuitively addressing the behaviours illustrated in Fig. 6: when the water-rock interaction environment is altered, this also implies a $\beta_{\text{Na-K}}$ parameter numerical value adjustment that would compensate for the anomalous changes of the $c_{\text{Na}}/c_{\text{K}}$ ratio - so that, on the whole, the value of $T_{\text{Na-K}}$ provided by Eq. (1) remains virtually the same.

In order to shed further light on this issue, we constructed a more familiar diagram (Fig. 7), based on a simplified form of the Van't Hoff equation (e.g., FOURNIER 1981; GIGGENBACH 1988). The straight line in this diagram corresponds to the Na-K temperature curve proposed by FOURNIER (1979), and which has been estimated ("Appendix 1") to be the most appropriate for describing the behaviour of the Slănic Moldova "postseismic regime" samples. It shows that for an aqueous solution subject to simultaneous equilibrium with Na- and K-feldspars, the logarithm of the Na/K ratio varies linearly (Eq. 1) with the reciprocal of the absolute temperature (K). Obviously, the data-points whose T_{Na-K} value had been calculated by using for β_{Na-K} the "standard" value of 1.483 (retrieved from Table 1) plot exactly on this line, both for the "postseismic regime" samples, and for the samples collected during the TDPR. Alternatively, when the T_{Na-K} values for the TDPR samples were recalculated by using for β_{Na-K} the newlyderived value of 1.545 (i.e., the situation illustrated in Fig. 6b), the corresponding data-points in Fig. 7 were off-set toward lower temperatures-actually, in a

temperature-range very similar to that of the "postseismic regime" samples. At the same time, in this new position, the recalculated data-points appear to have been shifted—with respect to the "standard" Na–K geothermometer curve—by 0.062 log-units toward smaller $\log(c_{\text{Na}}/c_{\text{K}})$ values: accordingly, these datapoints lie on an alternative akali-feldspars/aqueoussolution equilibrium curve, positioned below the one that we had adopted as "standard".

6.2. A Surmised Cause for Changes Undergone by the β_{Na-K} value

A likely explanation for the previously conjectured departure of the $\log(c_{\rm Na}/c_{\rm K})$ values from the adopted "standard" Na-K geothermometer function (Fig. 7) may be provided by changes in the stability of groundwater-dissolved dimer the $Al(OH)_{3}H_{3}SiO_{4}^{-}$: on the one hand, it has been established by speciation modelling (STEFÁNSSON and Arnórsson 2000; Arnórsson et al. 2002; GUDM-UNDSSON and ARNÓRSSON 2005) that the presence or absence of that specific Al-Si dimer induced significant changes in the alkali feldspars water-solubility functions-being otherwise well-known that those functions provided the theoretical grounds for the concerned cationic geothermometry approaches (e.g., GIGGENBACH 1988; STEFÁNSSON and ARNÓRSSON 2000); on the other hand, it has been conjectured that the corresponding Al-Si aqueous complexing could be favoured by increased pressures (BUCHOLZ and AGUE 2010), and/or by an enhanced abundance of aqueous silica (TAGIROV and SCHOTT 2001; MANNING 2007; BEITTER et al. 2008) possibly induced by pressure solution (e.g., PILI et al. 2002; ANZALONE et al. 2006). It is interesting to consider in this respect the SiO_2 vs. Cl⁻ plot constructed (Fig. 8) for the Slănic Moldova discharges: as a general rule, the total dissolved silica content of each spring appears to be supplied by the relatively SiO₂-rich freshwater endmember, with the highly SiO₂-depleted parent-brine acting-in this respect—as a diluent; some noticeable departures from this habitual trend are recorded only during the TDPR, when large extra amounts of total dissolved silica are present in the springwaters. In order to elucidate this rather atypical behaviour, additional investigations are required.

It appears, anyway, that large uncertainties are still subsisting in terms of the Al–Si complexing processes that occur in crustal aqueous fluids (STEF-ÁNSSON and ARNÓRSSON 2000; GUDMUNDSSON and ARNÓRSSON 2005; BEITTER *et al.* 2008; NEWTON and MANNING 2010; MANNING *et al.* 2010). Therefore, it would be beyond the scope of the present paper to additionally elaborate on the particular mechanisms which might contribute to the observed Na–K–Mg geothermometry signatures.

6.3. Possibly Involved Long-Range Interactions

In utilizing the Na-K geothermometer, it was implicitly assumed that the aqueous solution chemical equilibrium at depth is controlled by alkali feldspars. Such an inference is in conformity with a previously discussed (Sect. 3) local occurrence of crystalline rocks having been tomographically delineated in that area (LANDES et al. 2004; BOCIN et al. 2009) somewhere between 4 and 12.5 km depth. The latter depth-interval is at the same time consistent with the Slănic Moldova springwater depth of origin, which we estimated to amount to about 6km. In deriving that depth-value, we have used an approach similar to that of DAVISSON et al. (1994) and MELCHIORRE et al. (1999): linear thermal profiles (recorded by DEMETRESCU et al. 2005, in nearby hydrocarbon exploration wells) were extrapolated down to the depth at which there was reached the most plausible equilibrium temperature indicated by our Na-K-Mg geothermometry diagnoses (146 °Ccf. derivation in "Appendix 1"); accordingly, that was the depth where the water-rock chemical equihad assumedly been established-or librium otherwise stated, the "depth of origin" of the concerned springwaters.

It was, thus, suggested in addition (by taking into account the previously inferred relationships between the strong, 93.8 km deep earthquake of 27 Oct. 2004, and the Na–K–Mg geothermometry signatures detected in springwaters) that long-range interactions could operate in this region over lithospheric domains which extended, on the vertical, for about 100 km. A possible explanation for such a setting might be related precisely to the above-mentioned crystallinerocks occurrence delineated by elevated seismic



Figure 8

SiO₂ versus Cl⁻ crossplot constructed for the considered springs. "Preseismic regime" and "postseismic regime" refer to the samples being collected (within the 2003–2010 monitoring operation) before and after the 27 Oct. 2004 earthquake, respectively. In addition to the samples collected during the 2003–2010 monitoring operation, there are also plotted several "historical" samples (*symbols* labeled with the corresponding sampling date). In computing the mixing-trend linear regression (*solid line*), there was taken into account only the samples collected from all three considered springs during the October 2004–June 2010 "postseismic regime" period. With respect to this trend, noticeable departures (consisting of large extra amounts of silica) were recorded during the "truly distinct preseismic regime"

wave velocities: that high velocity body westward extension (as delineated by TONDI et al. 2009) roughly corresponds to the western boundary of the Tîrgu Securesc Basin (TSB-Fig. 1), a depression which unconformably developed during the Quaternary onto the Carpathians fold-and-thrust belt (LEEVER et al. 2006. According to Gîrbacea et al. (1998), that basin was generated by local extension which basically operated along a NW-SE direction. Fracture-sets indicating a radial-extension regime have been observed, however, as well. It is worth mentioning that a radial-diverging deformation pattern is suggested also by the present-day horizontal displacement velocities (with values as large as 5 mm year⁻¹) having been recorded by HEIDBACH *et al.* (2007) at several closely spaced GPS measurementsites located within and around the concerned region. Moreover, at a site located in this basin, there has been recorded (Fig. 1) the largest uplift velocity derived by GPS observations in Vrancea area (about 5 mm year⁻¹, HEIDBACH *et al.* 2007).

Accordingly, we tentatively considered the possibility that beneath the TSB there might be present a sub-vertical channel, filled at its top with highpressure/ultra-high pressure crystalline rocks, generated by an exhumation process that was currently still active. Exhumation of mantle-lithosphere (frequently together with oceanic crust) has been recognized (e.g., AGARD et al. 2009) in several paleosubduction environments: in the early stages of subduction, oceanic crust was acting like a "plunger" (sensu WARREN et al. 2008), inserted into the subduction channel that was filled with hydrated serpentinized—hence buoyant—lithospheric and mantle; as a result, oceanic crust and lithospheric mantle (scraped off from the subducting plate), together with lower crust fragments from the upper plate, built up an exhuming body that was moving upward, through the crust and the accretionary prism. The possibility that in the lithosphere some lighter material could exist, whose positive buoyancy might assist in its exhumation, is consistent with a highly localized gravity minimum outlined beneath the TSB by a 3D "stripped" map constructed (IOANE and ION 2005) at Moho level. Such a sub-vertical structure could also explain asymmetrical seismic wave attenuation patterns which had been ascribed (IVAN 2007; OTH et al. 2008) to a strongly attenuating (scattering ?) volume, assumed to be present down to about 100 km depth, roughly above the Vrancea seismogenic body. In addition, the very location of the extensional-collapse structure of the TSB above the inferred exhumation channel indicates a general compliance with scenarios (JOLIVET *et al.* 2003; BUTLER *et al.* 2011; LI *et al.* 2011; MALUSÀ *et al.* 2011) having addressed possible interactions between an exhumation setting and the orogenic wedge extension. Previously, the existence of an ongoing exhumation process has been advocated (SEARLE *et al.* 2001; WARREN *et al.* 2008) also for the Hindu Kush geodynamic environment, which is well-known (e.g., PRIETO *et al.* 2012), and references therein) to be the closest analog of the Vrancea seismicity nest and its particular features.

Overall, it appears that around the occurrence date of the concerned significant Vrancea mantledepth earthquake, an alteration intervened in the geochemical processes that developed within a still active exhumation channel assumedly extending beneath the TSB (and, implicitly, close to the sampled springs at Slănic Moldova). Anyway, the concerned processes should not develop at depths shallower than 4 km, given that the corresponding geochemical signatures were manifest just in connection to the solubility of feldspars-minerals which were likely present only in the crystalline rock body outlined by the seismic wave anomalies beneath 4 km depth. It is at the same time important to notice that the actual occurrence of an important earthquake did not act, for the concerned modifications, as an "instantaneous switch": it rather appears that only a rough time-coincidence existed between certain earthquake-related phenomena, and possibly accompanying process-changes which took place in the conjectured exhuming body.

7. Summary and Conclusions

The chemistry fluctuations of several cool, lowdischarge springs located close to the highly seismic Vrancea area (Romania) are clearly dominated by binary, essentially isochemical mixing between a saline endmember of deep-origin and meteoric freshwater. By relying on this particular circumstance, specific behaviours were investigated such that each of the Na–K–Mg geothermometric parameters $T_{\text{Na-K}}$, $T_{\text{K-Mg}}$ and MI were displayed in response to dilution. To this purpose, an algorithm initially devised by CHIODINI *et al.* (1996) has been expanded, while being additionally developed also as a general formulation for the particular equations that GIGGENBACH (1988) had originally proposed in the framework of the Na–K–Mg geothermometry approach.

It was consequently possible to outline (by processing chemical data derived from a monitoring operation, which had been conducted for more than seven years), that in addition to an apparently "routine" control (due, at least during a "postseismic regime" period, to the meteoric water inflow fluctuations), episodic alterations of certain geothermometric relationships coefficients might have occurred as well. In particular, a truly significant modification seems to have been specifically undergone by the β_{Na-K} coefficient (defined by Eq. 1). The signature assumedly due to this alteration was especially conspicuous in the MI vs. $log(c_{CI})$ plots (Figs. 3, 5): series of successive data-points were quite uniformly off-set along the MI scale, a setting which suggested that all concerned springwaters had been simultaneously subject to a similar change in the controlling geochemical processes. That specific alteration was noticed to have occurred 3-4 months prior to the strongest earthquake $(M_w = 5.8)$ of the hydrochemical monitoring period.

All things considered it appears that occasionally, significant deviations can be discerned with respect to the general framework that the Na–K–Mg geothermometry approach provides for diagnosing chemical equilibrium between alkali feldspars and subsurface saline solutions: such deviations are assumedly due to Al–Si complexing which may develop in the concerned aqueous fluids episodically (possibly, in association with an ongoing-exhumation process, "modulated"—presumably—by the generation of a mantle-depth strong earthquake).

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Appendix 1: Selecting the Na–K Geothermometric Equation Coefficient-Values that Would be Suitable for the Considered Springwaters

A couple of simultaneous plots of $T_{\text{Na-K}}$ vs. c_{Cl} and $T_{\text{Na-K}}$ vs. c_{Cl} have been constructed, by taking into account only the samples collected from the considered springs during the "postseismic regime" time-period (as defined in the main text, Sect. 5.1). For one such plot (Fig. 9a), in the computations there were utilized the $\alpha_{\text{Na-K}}$ and $\beta_{\text{Na-K}}$ coefficient-values (Table 1) proposed by GIGGENBACH (1988); in the other plot (Fig. 9b), the computations used the corresponding values proposed by FOURNIER (1979). Each of the two diagrams includes:

• experimentally obtained $T_{\text{Na}-\text{K}}^{\star}$, and $T_{\text{K}-\text{Mg}}^{\star}$ values plotted versus the corresponding c_{Cl}^{\star} (they are represented as individual data points, illustrated by various symbols): for each analyzed sample, those $T_{\text{Na}-\text{K}}^{\star}$, and $T_{\text{K}-\text{Mg}}^{\star}$ values have been computed by substituting—into Eqs. (1) and (2), respectively– the actually determined concentrations c_{Na}^{\star} , c_{K}^{\star} and c_{Mg}^{\star} ; • the dilution functions $T'_{\text{Na}-\text{K}}$ vs. c'_{Cl} (solid line), and $T'_{\text{K}-\text{Mg}}$ vs. c'_{Cl} (dashed line): they are computed by means of Eqs. (6) and (7), respectively, with the values of the involved regression coefficients *s* and *i* being retrieved from Table 3.

It is assumed (CHIODINI *et al.* 1996) that the coordinates of the intersection-point between the $T'_{\rm Na-K}$ vs. $c'_{\rm Cl}$ curve and the $T'_{\rm K-Mg}$ vs. $c'_{\rm Cl}$ one, should provide a reasonably accurate estimate both for the actual temperature of the deep-reservoir, and for the corresponding chloride content of the saline parent-water ($c^{\rm max}_{\rm Cl}$). It appears, however, that such a derivation is not quite unequivocal: when the Na-K geothermometer values proposed by GIGGENBACH (1988) are used (Fig. 9a), the estimates strikingly differ from those obtained when using the FOURNIER (1979) $\alpha_{\rm Na-K}$ and $\beta_{\rm Na-K}$ coefficient-values (Fig. 9b).

Fortunately, in the particular case of the Slănic Moldova springs, an independent estimate of the saline endmember chloride concentration (c_{Cl}^{max}) could be derived by means of the SiO₂ vs. Cl⁻ crossplot constructed for the "postseismic regime" samples (Fig. 8). In this respect, advantage has been taken of the fact that silica in the deep-origin brine proved to be significantly less abundant than in the freshwater component (low-mineralized shallow groundwater displaying SiO₂ concentrations larger than those of nearby mineral or thermal springwatersthat have been previously mentioned also by Gökgöz and TARCAN 2006, and by WEAVER *et al.* 2006).

There was consequently possible to extrapolate the reverse linear mixing-trend displayed by the SiO₂ vs. Cl⁻ plot (Fig. 8, with regression parameters indicated in Table 3), down to a zero-silica concentration. It was obtained, as a result, a maximumpossible Cl⁻ content of about 19.6 g kg⁻¹. Accordingly, it was inferred that Na–K geothermometric equations coefficients, which provided larger chloride values for the Slănic Moldova parent-water were not applicable: in particular the GIGGENBACH (1988) Na–K geothermometer function, which led to a maximum Cl⁻ content of 40.7 g kg⁻¹ (Fig. 9a). Alternatively, a much more plausible description of the concerned springwater behaviour appears to be provided by the





Springs No. 10, No. 1bis and No. 3 at Slănic Moldova: plots of T_{Na-K} vs. Cl, and T_{K-Mg} vs. Cl, constructed only for the samples collected during the "postseismic regime" time-period. The α_{Na-K} and β_{Na-K} values utilized in the computations were: in (**a**), those proposed by GIGGENBACH (1988); in (**b**), those proposed by FOURNIER (1979). *Symbols* and *curves* as specified in Fig. 6 of the main text. The intersection of the two *curves* should assumedly provide "true" values for the saline parent-water chloride content, as well as for the deep-reservoir temperature. The maximum possible chloride content derived from the SiO₂ versus Cl linear mixing trend (Fig. 8 in the main text) is marked by the *vertical solid bar*

Na–K geothermometer coefficients proposed by FOURNIER (1979): the indicated parent-water Cl⁻ content is then 14.6 g kg⁻¹ (Fig. 9b), thus, authorizing one to assume that the saline component still possessed a small amount of dissolved SiO₂ when it mixed with the shallow freshwater. Correspondingly, the deep reservoir temperature resulted in being 146°.

We, consequently, concluded that in the case of the considered springs, the α_{Na-K} and β_{Na-K} coefficient-values provided by FOURNIER (1979) were the most appropriate for being further used—in conjunction with the α_{K-Mg} and β_{K-Mg} geothermometric coefficients provided by GIGGENBACH (1988)—in the MI values computations.

Appendix 2: Extending to the Currently Addressed Springwaters Previous Isotopic Evidence About the Involvement of a Non-Meteoric Component

On two distinct occasions (14 July 2003 and 25 June 2004), simultaneously with the springs No. 1bis, No. 3 and No. 10, we had also sampled two saline

water discharges located nearby. They had been previously discussed also by VASELLI *et al.* (2002), who designated them as Slanic 14 and Slanic 15.

It is important to stipulate that for the Slănic 15 water sample, VASELLI *et al.* (2002) have provided both chemical, and isotopic (δD and $\delta^{18}O \%$ SMOW) analytical results. The only other groundwater discharge at Slănic Moldova for which the indicated authors had provided a similar kind of information was that designated by them as Slănic W2 (which we did not sample). Both the sample Slănic 15, and the sample Slănic W2 display in the $\delta^{18}O - \delta D$ diagram discussed in VASELLI *et al.* (2002) significant ¹⁸O enrichments with respect to the meteoric water line, thus, strongly suggesting a non-meteoric fluid contribution to the corresponding discharges.

While for all the samples we collected on 14 July 2003 and 25 June 2004, complete chemical analyses were performed, we did not have the possibility of conducting isotopic determinations as well. Therefore, we attempted to check (by means of a Na^+ vs. Cl^- cross-plot—Fig. 10) if the same deep-origin endmember was involved both in the supply of the





Plot of Na⁺ versus Cl⁻, aimed at comparing Slănic Moldova samples included in the study of VASELLI *et al.* (2002) (*dots*), with samples collected (at 14 Jul. 2003 and 25 Jun. 2004) in the framework of the present study (*triangles*). Most data-points are tightly aligned, which suggests that except for the sample "Slanic W2", all spingwaters originate in a common saline endmember (presumably, of deep-origin), that is subject to various amounts of freshwater dilution. When comparison is made with a fluid derived from dilution of seawater (*dotted line*), the computed mixing trend indicates a significant Na⁺ enrichment; there is also an obvious Na⁺ excess with respect to the stoichiometric dissolution of halite (*dashed line*)

springs chiefly addressed by the present study (No. 1bis, No. 3 and No. 10), and in that of the discharges Slănic 15 and Slănic W2, which had already been proven, by means of isotopic data VASELLI *et al.* (2002), to include a non-meteoric component.

In Fig. 10 there can be noticed a very good alignment of most data-points—the Slănic 15 samples included—on a well-defined Na vs. Cl mixing line. It, hence, seems quite probable that the water discharged by the springs No. 1bis, No. 3 and No. 10 includes the same non-meteoric origin endmember as that involved in the supply of the Slănic 15 outflow. In contrast, the sample Slănic W2 plots rather far away from the indicated mixing line, suggesting that certain additional components—or processes—probably contribute to shaping its composition.

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