# SPECIFIC BEHAVIOR OF THE "Na-K-Mg MATURITY INDEX" (GIGGENBACH) IN SALINE SPRINGS AT SLĂNIC-MOLDOVA BEFORE AND AFTER THE MAJOR VRANCEA EARTHQUAKE (Mw = 6.0) OF 27.10.2004

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*Particularités de comportement de "l'index de maturité Na-K-Mg" (Giggenbach) des certaines sources naturelles salines de Slănic-Moldova, avant et après le séisme majeur (Mw = 6,0) produit dans la région de Vrancea le 27 octobre 2004.* En fonction des concentrations en Na, K et Mg d'une solution hydrothermale, Giggenbach (1988) a défini "l'index de maturité" (MI) - un estimateur qualitatif de la vitesse d'ascension d'une eau souterraine d'origine profonde. Les valeurs de MI de plusieurs sources naturelles à grande salinité monitorisées à Slănic-Moldova ont subi une fluctuation significative, lors d'un fort séisme (Mw = 6,0) qui s'est produit le 27 octobre 2004 dans la proche région de Vrancea. Cette dernière aire est bien connue pour ses fréquentes séismes intermédiaires (60–200 km de profondeur), dont plusieurs catastrophiques (magnitudes dépassant 7,0). "L'anomalie" géochimique a débuté environ deux mois avant le séisme, son maximum a été atteint encore deux mois après l'événement, puis le déclin s'est étalé sur environ six mois de plus. Ce comportement suggère que pendant la phase préparatoire du séisme, des processus favorisant une ascension accélérée des fluides d'origine profonde étaient déjà actifs, et que cet état "anomal" s'est prolongé, après le séisme, sur près d'une année. L'évolution du MI pourrait donc être prise en considération comme un possible précurseur à moyen terme de forts séismes de Vrancea.

*Key words:* earthquake, geochemical anomaly, Na-K-Mg geoindicator, maturity index, Vrancea.

## 1. INTRODUCTION

In the ionic composition of certain mineral water outlets, earthquake-related anomalies have been identified (Tsunogai, Wakita, 1995; Toutain *et al*., 1997; Favara *et al*., 2001). Such anomalies have been usually inferred to mirror seismically-induced changes in the mixing ratio between a saline up flow of deep origin and shallow inflows of freshwater. No explanation has yet considered changes that might possibly occur just in the deep up flow ionic composition.

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However, as Giggenbach (1988) has indicated, there is a direct connection between the time required by a hydrothermal up flow to reach a sampling point at the surface, and the extent to which the concerned aqueous solution re-equilibrates – in chemical terms – with the surrounding rock matrix. Transients of a so-called "maturity index" (henceforth MI) – defined by Giggenbach (1988) as a function of the Na, K and Mg ions contents of a hydrothermal solution – may be indicative of changes in fluid up flow duration, and implicitly in its up flow velocity.

A model of seismically-induced variations in water up flow velocities has been proposed by Muir-Wood, King (1993), by taking into account transients of the aperture of a vertical, liquid-filled fracture. Woith *et al.* (2003), on the other hand, have invoked a different cause for seismically-induced changes in groundwater up flow rates, namely the "advective overpressure" (Steinberg *et al.*, 1989a, 1989b, 1989c; Sahagian, Proussevitch, 1992; Sahagian, 1993) – a mechanism related to gas bubbles rising through a liquid.

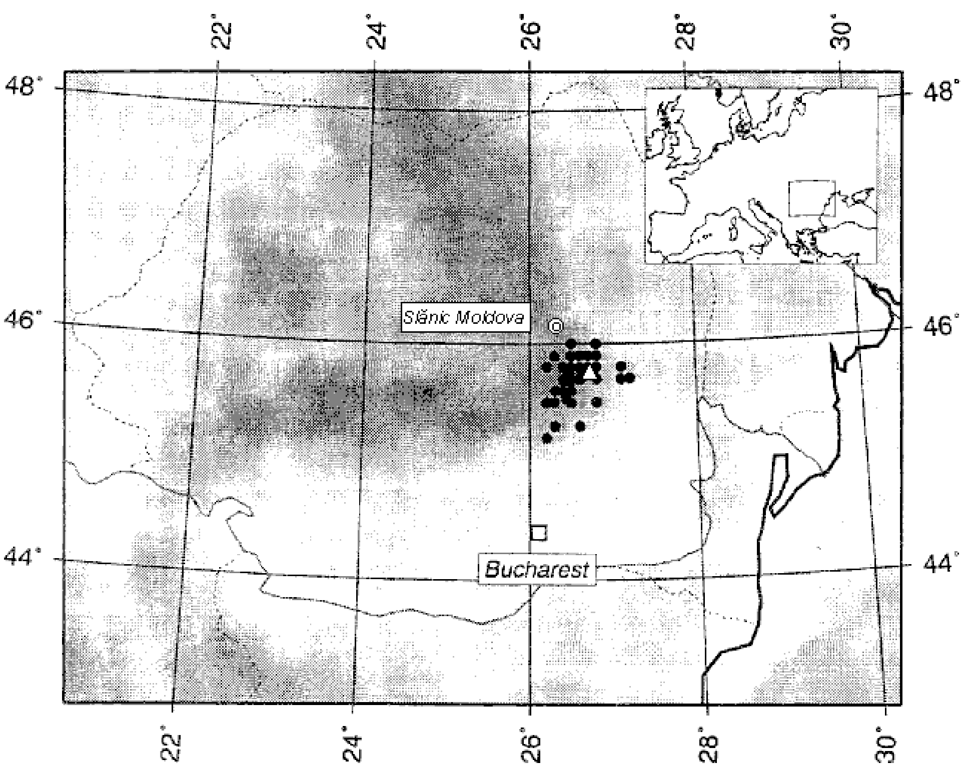


Fig.1 – Location of Slănic-Moldova sampling site with respect to the intermediate depth (>60 km) Vrancea earthquakes. Dots indicate the epicenters of such events having occurred during the XX-th century. The triangle indicates the epicenter of the 27 Oct. 2004, Mw=6.0 earthquake. (Adapted from Wenzel et al., 1999).

In Vrancea region, within a narrow surface area (30 × 70 km), intermediate depth (60–200 km), strong earthquakes occur rather frequently (179 events with $5.0 \leq Mw \leq 7.7$ recorded during the XX-th century – Radulian *et al.*, 2000). Yet no conclusive reports of seismically-related geochemical anomalies have been provided so far for this area. In order to identify whether that specific geodynamic activity might result in characteristic behaviors of the Giggenbach MI parameter - thus possibly hinting to episodic fluctuations in groundwater up flow rates - we have conducted a MI evolution monitoring, by recording ionic compositions in three natural outlets (springs) at Slănic-Moldova. This sampling site is located just 30 km away from Vrancea epicentral area (Fig. 1). Vaselli *et al.* (1997) had already suggested that fluid outlets here could be the most appropriate in terms of earthquakes geochemical monitoring - among the many tens of other discharges they had sampled within a broader territory, assumedly concerned by the Vrancea geodynamic activity effects. Vaselli *et al*. (2002) have additionally provided several pieces of evidence (based on the D and $O^{18}$ isotopes concentrations, and on the $He^3/He^4$ isotopic ratio), which pointed to the existence of a significant constituent of non-meteoric origin in the mineral water discharges at Slănic-Moldova.

## 2. EXPERIMENTAL APPROACH

The geochemical monitoring of the three considered springs at Slănic-Moldova (locally designated as no. 1bis, no. 6 and no. 10) began in April 2003. Water samples have been collected approximately once a month. Sampling frequency has been increased (up to one series of samples per day) subsequently to the significant Vrancea earthquake (Mw = 6.0) of 27 October 2004. A total of 35 series of samples have been collected until May 2005. The chemical analyses (pH, conductivity, TDS, major cations and anions) have been performed within the laboratory of the “Emil Racovitza” Institute of Speleology of the Romanian Academy.

The water of the considered springs is close to neutral (pH values average 6.2 ± 0.2), and it has a NaCl general chemical character, with TDS values ranging between 10,000–17,000 mg/kg. Similarly to other outlets previously investigated at Slănic-Moldova (Vaselli *et al.*, 2002), significant amounts of $CO_2$ and $H_2S$ gases are released from the spring water.

MI values (Table 1) always fall within the “critical” 2.00÷2.66 range, outside which the MI significance becomes less precise (Giggenbach, 1988). This favorable feature, together with the NaCl chemical character and the close-to-neutral pH values, make these spring waters suitable for the MI assessment and interpretation technique described by Giggenbach (1988).

*Table1*

Maturity index (MI) values computed for the three considered springs at Slănic-Moldova

| **Date** | **Spring no. 1bis** | **Spring no. 6** | **Spring no. 10** |
|---|---|---|---|
| 16-Apr-03 | 2.294 | 2.281 | 2.266 |
| 10-May-03 | 2.280 | 2.279 | 2.254 |
| 11-Jun-03 | 2.298 | 2.328 | 2.236 |
| 14-Jul-03 | 2.284 | 2.331 | 2.274 |
| 7-Aug-03 | 2.271 | 2.306 | 2.224 |
| 22-Sep-03 | 2.270 | 2.305 | 2.242 |
| 21-Oct-03 | 2.265 | 2.294 | 2.244 |
| 11-Nov-03 | 2.287 | 2.308 | 2.257 |
| 10-Dec-03 | 2.277 | 2.302 | 2.254 |
| 3-Feb-04 | 2.275 | 2.296 | 2.242 |
| 16-Mar-04 | 2.292 | 2.290 | 2.257 |
| 6-Apr-04 | 2.278 | 2.294 | 2.275 |
| 27-Apr-04 | 2.292 | 2.325 | 2.264 |
| 1-Jun-04 | 2.282 | 2.309 | 2.268 |
| 25-Jun-04 | 2.258 | 2.290 | 2.236 |
| 20-Jul-04 | 2.321 | 2.336 | 2.276 |
| 19-Aug-04 | 2.319 | 2.330 | 2.300 |
| 21-Sep-04 | 2.319 | 2.362 | 2.301 |
| 30-Sep-04 | 2.348 | 2.369 | 2.327 |
| 26-Oct-04 | 2.342 | 2.359 | 2.303 |
| 29-Oct-04 | 2.334 | 2.358 | 2.323 |
| 30-Oct-04 | 2.339 | 2.361 | 2.304 |
| 31-Oct-04 | 2.339 | 2.371 | 2.329 |
| 1-Nov-04 | 2.350 | 2.366 | 2.313 |
| 2-Nov-04 | 2.340 | 2.368 | 2.323 |
| 3-Nov-04 | 2.337 | 2.338 | 2.314 |
| 10-Nov-04 | 2.325 | 2.361 | 2.321 |
| 18-Nov-04 | 2.340 | 2.354 | 2.298 |
| 8-Dec-04 | 2.374 | 2.386 | 2.319 |
| 20-Dec-04 | 2.353 | 2.365 | 2.345 |
| 12-Jan-05 | 2.351 | 2.368 | 2.316 |
| 17-Feb-05 | 2.347 | 2.352 | 2.325 |
| 29-Mar-05 | 2.335 | 2.350 | 2.322 |
| 9-May-05 | 2.343 | 2.347 | 2.300 |

## 3. RESULTS

The strongest four earthquakes recorded in Vrancea area during the geochemical monitoring time interval (April 2003 – May 2005) ranged from Mw = 4.6 to Mw = 6.0 (The Romanian National Institute for Earth Physics, site *www.infp.ro*). They all occurred at intermediate (sub-crustal) depths (100–166 km).

There seems reasonable to assume a correspondence between geodynamic processes operating at large depths and their contemporary MI fluctuations, only if the latter have been manifest at least on the occasion of the strongest event which had occurred within the monitoring period - the Mw = 6.0 earthquake on 27 October 2004.

Such a behavior has been indeed noticed starting approximately from August 2004. All three springs displayed an increasing trend of their MI values (Fig. 2), significantly exceeding the range of the entire previous monitoring period - which was inferred to represent the "normal background". Absolute MI maxima have been recorded in December 2004, when values decayed back toward the "normal background" level.

A more definite outline of the above-mentioned trend has been obtained (Fig. 3) by means of a mobile average filter (average of 3 adjacent values, weighted with the reverse of the time interval between two consecutive samplings).

By analyzing for each spring separately the periods before and after the occurrence of the anomaly (Table 2), one can notice that the pre-anomaly MI averages are by 0.055–0.061 lower than those calculated for the anomalous period. This difference exceeds three standard deviations, irrespective if the latter are computed for the pre-anomaly period (0.016–0.018), or for the anomalous one (0.011–0.013). Additionally, that increment from the pre-anomaly period to the anomalous one amounts to almost 10% of the entire range (2.00÷2.66) for which MI values are accepted (Giggenbach, 1988) to be significant.

It is also important to mention that in relationship with less strong Vrancea earthquakes (for instance those on 5 Oct. 2003, Mw = 4.6, and on 14 May 2005, Mw = 5.2) no analogous anomalies of the MI parameter occurred.

## 4. DISCUSSION

The "anomalous" fluctuation detected in the MI series cannot be ascribed either to hydro-meteorological causes (it is not a cyclic, seasonal occurrence), or to anthropic ones (during that period, the aquifer has not been subject to any anthropic stresses). It is hence reasonable to assume that at its origin there has been a water up flow acceleration, induced for a limited period of time by processes associated with the occurrence of the Mw = 6.0, intermediate depth (100 km) earthquake of 27 Oct. 2004.

*Table 2*

MI average values and standard deviations computed separately for the periods before and after the occurrence of the anomaly, for each of the three considered springs at Slănic-Moldova

| | **Spring no. 1bis** | | **Spring no. 6** | | **Spring no. 10** | |
|---|---|---|---|---|---|---|
| | average | standard deviation | average | standard deviation | average | standard deviation |
| before the anomaly | 2.287 | 0.018 | 2.306 | 0.018 | 2.254 | 0.016 |
| during the anomaly | 2.343 | 0.011 | 2.361 | 0.011 | 2.316 | 0.013 |
| difference between those two time intervals | 0.057 | | 0.055 | | 0.061 | |

About 1-2 months before that major earthquake, an initial, fast increase in the MI values occurred, exceeding by many folds the standard deviations of the pre-anomaly period. This increase may be ascribed to initial changes in the state of stress within the seismogenic zone. We estimate that the indicated stress increase resulted in a more abundant expulsion of the pore water, due to the reduction of the aperture between the walls of the fracture that separates two distinct tectonic blocks of Vrancea geodynamically active zone. Subsequently, when the earthquake was triggered, the phenomenon became more intense, on one hand because of the sudden change in the relative position of the tectonic compartments between which the liquid flows, and on the other hand due to the sudden change of the ascending liquid pressure, as a consequence of the magma degassing that occurred during the release of the elastic energy (micro-fracturing of the concerned material resulted in a sudden expansion of the gas trapped within the magma).

We emphasize the remarkable evolution of the MI values subsequently to the completion of this phenomenon: the absolute maximum recorded virtually simultaneously at all three springs within the 50 days period that followed the earthquake could be ascribed to the expulsion of the liquid from the fault, on one hand because of the additional pressure generated by the magma degassing, and on the other hand because of the enlargement of the voids through which the liquid flowed up toward the surface.

Further on a MI reduction trend occurred, which suggested a progressive return to the previous, undisturbed state (decline of the ascending fluid pressure, restriction of the space available for its up flow).

We estimate that a further check of our hypotheses might be achieved by means of pressure sensors installed in a space next to the spring up flow region. Normally, such sensors should be able to detect the shock triggered by the pressure drop generated by the magma degassing that occurs during the release of the seismic energy. Correlated with the precise time of the earthquake occurrence, such observations will be able to provide an estimate of the shock propagation velocity across the system through which the liquid flows from the deep zone toward the surface. Moreover, apparently the most interesting result of our observations is the possibility to consider that the shift in the MI values, that occurs virtually simultaneously at all three springs, may be an earthquake precursor related to the modification of the fluid conduits size, a phenomenon which occurs when the earthquake generating stress exceeds a certain threshold level.

## 5. CONCLUSIONS

So far published reports on earthquake-related fluctuations in the concentration of certain water dissolved components suggested that such "anomalies" were always a result of changes in the mixing ratio between a saline inflow of deep origin and meteoric fresh water.

Alternatively, the present investigation has outlined that in the composition of the very inflow of deep origin significant changes might occur as well, possibly in relationship with a major (Mw = 6.0) Vrancea earthquake. The detection of this phenomenon has been possible by recording in three saline springs at Slănic-Moldova the fluctuations of the "maturity index" (MI) – a "geoindicator" previously defined by Giggenbach (1988) as a function of the Na, K and Mg ions concentrations of a hydrothermal solution.

A significant MI increase has occurred for about two months before the earthquake and it has continued for another two months, then a decrease followed – for at least six months – toward the "background" state. Since the MI is a "proxy" of the up flow velocity of a hydrothermal solution, the observed behavior seems to indicate that during the earthquake preparation stage there occur processes (rocks mechanical deformations, release of gas) able to induce a noticeable acceleration of the fluid up flow from depth. Subsequently to the earthquake occurrence, the inferred processes progressively diminish, to finally vanish completely, so that liquid up flow velocity returns to normal, smaller values.

The indicated results appear to be promising in terms of devising medium-term forecasts concerning the occurrence of major (Mw ≥ 6.0) Vrancea earthquakes.

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## REFERENCES

FAVARA, R., GRASSA, F., INGUAGGIATO, S., VALENZA, M. (2001), *Hydrogeochemistry and stable isotopes of thermal springs: earthquake-related chemical changes along Belice Fault (Western Sicily)*. Appl. Geochem., **16**, 1–17.

GIGGENBACH, W.F. (1988), *Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators*. Geochim. Cosmochim. Acta, **52**, 2749–2765.
MUIR-WOOD, R., KING, G.C.P. (1993), *Hydrological signatures of earthquake strain*. J. Geophys. Res., **98**, 22.035–22.068.
RADULIAN, M., MÂNDRESCU, N., PANZA, G.F., POPESCU E., UTALE, A. (2000), *Characterization of seismogenic zones of Romania*. Pure Appl. Geophys., **157**, 55–77.
SAHAGIAN, D.L. (1993), *More bubbles in volcanic systems*. Nature, **361**, 308.
SAHAGIAN, D.L., PROUSSEVITCH, A.A. (1992), *Bubbles in volcanic systems*. Nature, **359**, 485.
STEINBERG, G.S., STEINBERG, A.S., MERZHANOV, A.G. (1989a), *Fluid mechanism of pressure growth and the seismic regime of volcanoes prior to eruption*. Mod. Geol., **13**, 3–4, 267–274.
STEINBERG, G.S., STEINBERG, A.S., MERZHANOV, A.G. (1989b), *Fluid mechanism of pressure growth in volcanic (magmatic) systems*. Mod. Geol., **13**, 3–4, 257–265.
STEINBERG, G.S., STEINBERG, A.S., MERZHANOV, A.G. (1989c), *Fluid mechanism of pressure rise in volcanic (magmatic) systems with mass exchange*. Mod. Geol., **13**, 3–4, 275–281.
TOUTAIN, J.P., MUNOY, M., POITRASSON, F., LIENARD, A.C. (1997), *Springwater chloride ion anomaly prior to a* $M_L = 5.2$ *Pyrenean earthquake.* Earth and Planetary Science Letters, **149**, 113–119.
TSUNOGAI, U., WAKITA, H. (1995), *Precursory chemical changes in ground water: Kobe earthquake, Japan*. Science, **269,** 61–63.
VASELLI, O., TASSI, F., MAGRO, G., SEGHEDI, I., SZAKACS, A., MINISSALE, A., ABBADO, D.A., IOANE, D., GRIGORESCU ŞT., BĂDESCU, D. (1997), *Gas geochemistry in the Vrancea Region and surrounding areas (Romania): a preliminary report*. Rare Gases Geochemistry IV International Conference, 8–10 October 1997, Rome, Italy, Book of Abstracts, 1.
VASELLI, O., MINISSALE, A., TASSI, F., MAGRO, G., SEGHEDI, I., IOANE, D., SZAKACS, A. (2002), *A geochemical traverse across the Eastern Carpathians (Romania): constraints on the origin and evolution of the mineral water and gas discharges*. Chemical Geology, **182**, 637–654.
WENZEL, F., LORENZ, P.F., SPERNER, B., ONCESCU, C. M. (1999), *Seismotectonics of the Romanian Vrancea area*, in Vrancea Earthquakes: Tectonics, Hazard and Risk Mitigation, F. Wenzel, D. Lungu (eds.) and O. Novak (co-ed.), Kluwer Academic Publishers, Dordrecht, Netherlands, 15–25.
WOITH, H., WANG, R., MILKEREIT, C., ZSCHAU, J., MAIWALD, U., PEKDEGER, A. (2003), *Heterogeneous response of hydrogeological systems to the Izmit and Duzce (Turkey) earthquakes of 1999*. Hydrogeology Journal, **11**, 113–121.

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