

Chloride groundwater discharges out of Ciomadul volcano (Romania): Possible evidence for several distinct deep-reservoirs saturated with high-temperature fluids

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Summary

Solute versus Cl mixing lines constructed for chloride groundwaters discharging from Ciomadul volcano (Romania) outlined the existence of two distinct, deep-origin saline parent-fluids. Chemical geothermometry additionally indicated that both saline end-members derived from hot, yet distinct reservoirs: one of about 310°C, and the other in the 270-290°C temperature range.

Introduction

The most recently extinct volcano of the East Carpathians igneous range is Ciomadul, for which combined U–Th and (U–Th)/He zircon, as well as radiocarbon dating has indicated that it had last erupted about 32 kyrs ago (Harangi et al., 2015). The volcano external slopes host a multitude of mineral groundwater discharges, which might provide significant information on the current status of the still active inflows of magma-derived fluids. Most of the possibly relevant hydrogeological and hydrochemical information published about those groundwater outlets is, however, several decades old (Institutul de Balneologie și Fizioterapie, 1961; 1965; 1970; 1973; Bandrabur et al., 1984), requiring therefore to be - for at least two reasons - updated: (i) many of the previously described groundwater outflows have disappeared, while new wells and artificially dug pools have been commissioned meanwhile; (ii) the chemical-analytical techniques, as well as the data processing and interpretation approaches have undergone, over the elapsed time-period, significant developments.

In this respect, a set of *chloride* groundwater discharges, sampled in the framework of the Electrical Signatures of Groundwater (ESG) project, is considered in the present note in correlation with older hydrochemical data published (Institutul de Balneologie și Fizioterapie, 1961; 1970; 1973) for outflows of the same chemical type. There are specifically addressed a series of tepid (15-23°C) springs (Mikes, Apor, Ana 1 and Ana 2, Ileana, Baia Săracilor), together with the Tisaș artesian well (21.7°C) – all of which are located at Tușnad-Băi, on the Ciomadul volcano NW flank - as well as a previously unreported gas pool (“mofette”), Vallato (13.9°C water temperature), which is situated on the SE slopes of the volcano.

Information provided by linear correlations between various solutes

It is customary to assume that sodium-chloride groundwater discharges derive either from fossil marine fluids (possibly associated also with hydrocarbon accumulations), or ensuing to the leaching of NaCl (halite) deposits. Waters complying with one of those two distinct situations can be readily identified, by plotting the corresponding Na concentration values versus the values of the Cl concentration. Such a diagram (Fig. 1a) includes a line corresponding to the dilution/evaporation of modern-seawater, and another one that corresponds to halite dissolution: experimental points which fall on one of those lines indicate that the concerned waters originate in one of the two indicated processes.

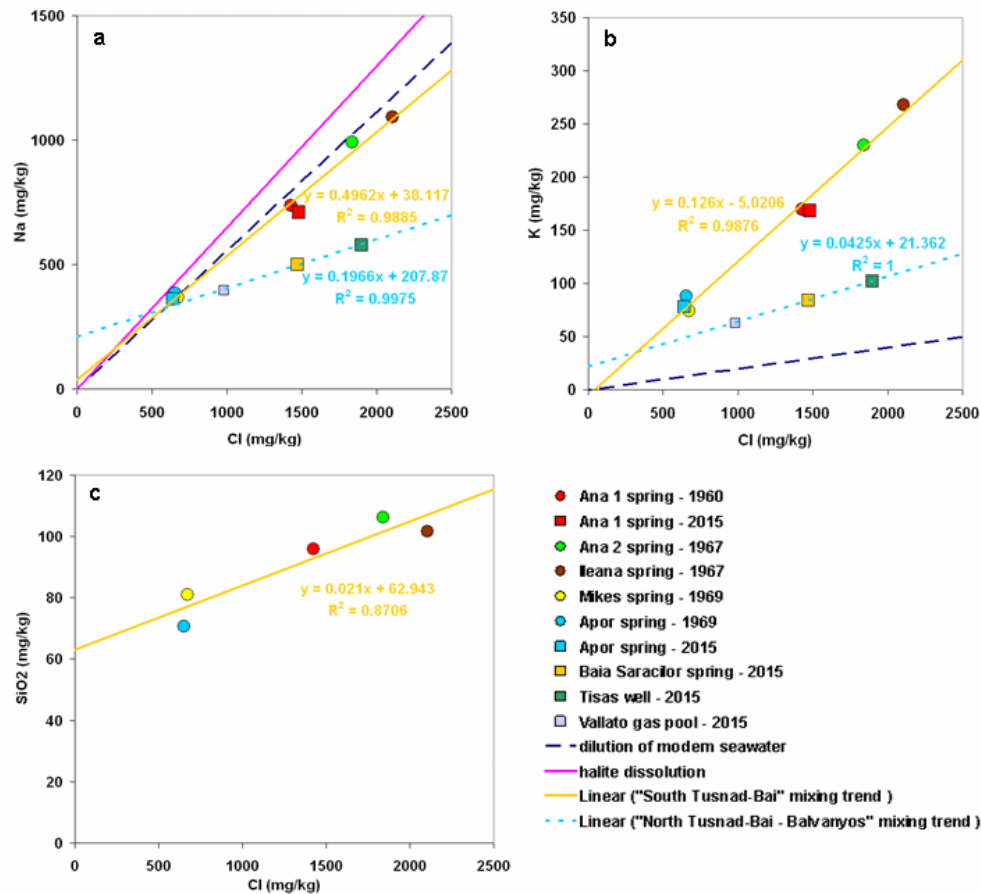


Figure 1 Plot of Na vs. Cl (a), K vs. Cl (b), and SiO₂ vs. Cl (c) concentrations for the considered groundwater discharges.

It is yet clearly visible that chloride water samples of the Ciomadul volcano do not match either the halite dissolution line, or the line corresponding to the modern-seawater dilution: the experimental data-points in Fig. 1a (and those of Fig. 1b as well) are, instead, rather tightly aligned along two separate lineaments: one that corresponds to the springs Ana 1, Ana 2, Ileana, Mikes and Apor (and which we designated as the “South Tușnad-Băi” group), and another one that includes the outflows Baia Săracilor, Tisaș and Vallato (and which we designated as the “North Tușnad-Băi - Balványos” group). It is largely admitted (e.g., Aguilera et al., 2005; Shibata et al., 2008; Taran et al, 2008) that such groundwaters, whose experimental data-points plot along a well-defined line, derive from a common *saline*, deep-origin parent-water, which during its up-flow to the surface underwent mixing, in variable proportions, with a *freshwater* end-member (the latter being, most probably, of local meteoric origin).

And when – like in the case of the Ciomadul volcano outflows - the concerned solutes’ concentrations do not plot either on the halite dissolution, or on the modern-seawater dilution lines, one must admit that the *saline* parent water composition essentially resulted from water-rock interaction having occurred at depth. In this respect, one can invoke a magma-related process, like the one stipulated, for instance, by Giggenbach (1988): HCl released (together with other gases – CO₂, SO₂, H₂S, HF, H₂O vapors) by a cooling magma body, can react with the host rock, finally resulting a near-neutral pH, chloride groundwater, a type which is characteristic to high-temperature, magma-related geothermal systems worldwide.

In the particular case of the chloride groundwater discharges of the Ciomadul volcano, the two linear regressions traced in Fig. 1a (as well as in Fig. 1b) suggest that two distinct saline end-members

contribute to the shaping of the chemical compositions of the sampled outlets. Moreover, the good linear regressions obtained for certain samples collected over a large time-interval (spanning between the years 1960 and 2015) indicate that the contents of the involved chemical species (in this case Cl, Na, and K) remained fairly constant, both in the saline, and in the fresh end-members associated to the “South Tuşnad-Băi” group.

Chemical geothermometry estimates

Chiodini et al. (1996) have suggested that similar linear correlations - between specific solutes and a conservative constituent (usually the Cl⁻ anion) - could also be used as tools for evaluating the apparent response which *chemical geothermometers* exhibited along with variations in the dilution of the concerned groundwater.

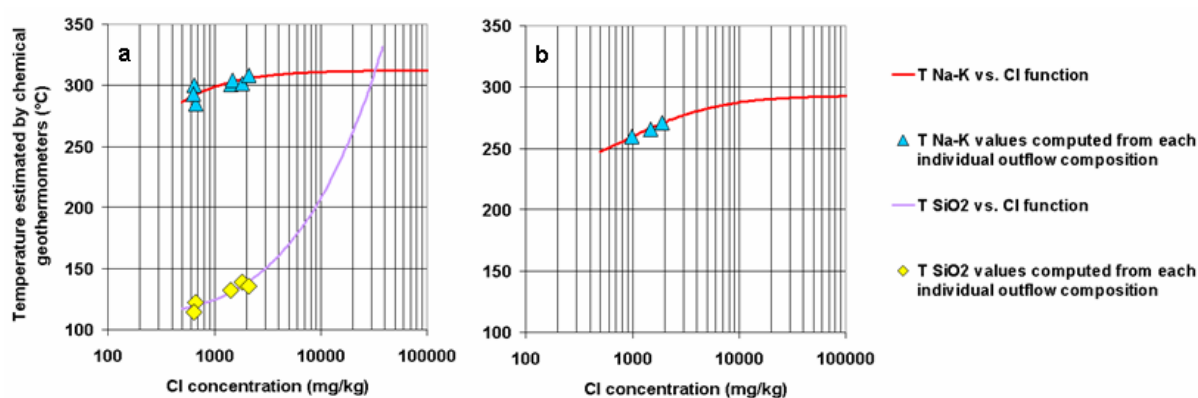


Figure 2 Plot of the temperature estimates based on SiO₂ and Na-K geothermometers (Verma, 2000, and Fournier, 1979, respectively), for (a) - the “South Tuşnad-Băi” group, and (b) - the “North Tuşnad-Băi - Balványos” group.

Chemical geothermometry is an interpretation method which takes advantage of the fact that an aqueous solution is expected to reach, at the temperature of a deep reservoir, chemical equilibrium with its host rock. The fluid will subsequently ascend toward ground surface outlets - becoming thus cooler; yet in spite of that, the concentration of certain dissolved species (or the ratio between the concentrations of two solutes), will undergo - during this upflow - virtually no changes (actually, only a slow chemical re-equilibration will occur).

In many circumstances however, “parasitic” dilution with meteoric freshwater may significantly alter the concentration of the chemical species considered for chemical geothermometry assessments: in this case, the Chiodini et al. (1996) approach becomes applicable. That approach consists in inserting, into the geothermometric formulas based either on the SiO₂ concentration (e.g., Verma, 2000), or on the Na/K concentration ratio (e.g., Fournier, 1979), linear-regression equations corresponding to the solute vs. Cl relationships – in our particular case, those which are illustrated in Figs. 1a, 1b and 1c. As a result there are obtained, for the Na–K and SiO₂ temperatures, variation functions (Fig. 2) that depend on the Cl concentration only: those curves can be used in order to “trace back” the undiluted status (i.e., that which corresponds to the pristine saline parent-water Cl content on the one hand, and to the deep-reservoir “true” temperature on the other); such an estimate was provided for the “South Tuşnad-Băi” group (Fig. 2a), by the intersection of the T_{SiO_2} vs. Cl curve, with the T_{Na-K} vs. Cl one - indicating a deep reservoir temperature of ~310°C, and an associated chloride content of ~30,000 mg/kg. Unfortunately, for the “North Tuşnad-Băi - Balványos” group (Fig. 2b), an analogous T_{SiO_2} vs. Cl curve could not be traced; nevertheless, the corresponding T_{Na-K} vs. Cl line still suggests that this distinct deep reservoir has, as well, an elevated temperature (in the 270-290°C range).

Conclusions

Groundwater reservoirs with temperatures in excess of 270°C, and possibly reaching up to ~310°C - as suggested by the chemical geothermometry assessments performed for chloride fluids discharged from Ciomadul volcano – require that a strong heat-source was located at depth. It hence appears that molten domains could still be present (as hypothesized, for instance, by Harangi et al., 2015) within the magma body existing beneath Ciomadul.

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