

**HABILITATION THESIS**

**Geochemical signature of natural and anthropogenic environmental changes**

**ABSTRACT**

Human civilization along the history placed an increasing pressure on natural environment. This pressure increased during the industrial revolution. Among industrial branches, mining industry has always been a strong source of environment pollution. “*De re Metallica*”, the first book on “modern” mining written by Georgius Agricola (1556), contains the clear description of the negative effect of the mining industry upon the environment. Discovery of the steam engines at the beginning of 18<sup>th</sup> century revolutionized the mining industry by allowing the exploitation of the deeper part of the mines. The mining of Au, Ag, Pb, Zn, Cu, and coal increased dramatically. After 1859, the petroleum industry started. These changes not only increased the pollution of the environment with potential toxic elements but also with CO<sub>2</sub> from fossil fuel burning (coal and petroleum). Tracking environmental changes caused by mining and fossil fuel burning represents the author main research topic.

The habilitation thesis titled “Geochemical signature of natural and anthropogenic environmental changes” summarizes candidate’s activity in the field of geochemistry, after defending his PhD thesis titled “Geochemistry of the environment in the areas of mining works from Aries Valley (Apuseni Mountains, Romania)”. There are three major research directions in the fields of geochemistry that he follows.

The first research area is related to mine industry pollution, a continuation of the research begun while working on the PhD thesis. Here, the candidate focused on obtaining new thermodynamic data for minerals (*e.g.* jarosites, yavapaiite, alunites, beaverite, beudantite) produced by the weathering in mining fields (related especially to acid mine drainages). Jarosite mineral family, with the chemical formula  $A^+\text{Fe}^{3+}(\text{SO}_4)_2(\text{OH})_6$ , belongs to the alunite supergroup of minerals, is a common mineral in mining sites. The ‘A’ sites in jarosite minerals are commonly occupied by alkali ions such as K<sup>+</sup> or Na<sup>+</sup>, but numerous substitutions have been reported, partly due to the flexibility of the jarosite structure toward ion size accommodation. This feature makes jarosite-like minerals especially suitable for trapping unwanted, potentially toxic elements in the environment. Using the newly obtained thermodynamic data, it is possible to predict the fate of different toxic elements in the environment.

The enthalpy of formation from the elements of a well-characterized synthetic Pb-jarosite sample was measured by high temperature oxide melt solution calorimetry using a custom-built Tian-Calvet twin calorimeter. Comparison with the thermochemical properties of hydronium jarosite and plumbojarosite end-members strongly suggested the existence of a negative enthalpy of mixing probably related to the non-random organization of Pb<sup>2+</sup> ions

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within the jarosite structure. Based on these considerations, the following thermodynamic data are proposed as the recommended values for the formation from the elements of the ideal stoichiometric plumbojarosite  $\text{Pb}_{0.5}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ :  $\Delta G^\circ_f = -3118.1 \pm 4.6$  kJ/mol,  $\Delta H^\circ_f = -3603.6 \pm 4.6$  kJ/mol and  $S^\circ = 376.6 \pm 4.5$  J/(mol·K). These data should prove helpful for the adjustment of phase diagrams of the Pb–Fe– $\text{SO}_4$ – $\text{H}_2\text{O}$  system, or for estimating the solubility product of pure plumbojarosite. For illustration, the evolution of the estimated solubility product of ideal plumbojarosite as a function of temperature in the range 5 – 45 °C was evaluated ( $\log K_{\text{sp}}$  ranging from –24.3 to –26.2).

The enthalpy of formation from the elements of well characterized Pb–As, Pb–Cu, and Pb–Zn synthetic jarosites, was measured by high temperature oxide melt solution calorimetry and gave  $\Delta H^\circ_f = -3691.2 \pm 8.6$  kJ/mol,  $\Delta H^\circ_f = -3653.6 \pm 8.2$  kJ/mol, and  $\Delta H^\circ_f = -3669.4 \pm 8.4$  kJ/mol, respectively. Using estimated entropies, the standard Gibbs free energy of formation from elements at 298 K  $\Delta G^\circ_f$  of the three compounds were calculated to be  $-3164.8 \pm 9.1$  kJ/mol,  $-3131.4 \pm 8.7$  kJ/mol, and  $-3153.6 \pm 8.9$  kJ/mol, respectively. Based on these free energies, their  $\log K_{\text{sp}}$  values are  $-13.94 \pm 1.89$ ,  $-4.38 \pm 1.81$  and  $-3.75 \pm 1.80$ , respectively. For this compounds, a  $\log_{10}\{\text{Pb}^{2+}\} - \text{pH}$  diagram is presented. The diagram shows that the formation of Pb–As jarosite may decrease aqueous arsenic and lead concentrations to meet drinking water standards. The new thermodynamic data confirm that transformation of Pb–As jarosite to plumbojarosite is thermodynamically possible.

Heating jarosite species above ca. 400 °C, yavapaiite mineral can form. Thermal decomposition indicates that the final breakdown of the yavapaiite structure takes place at 700 °C (first major endothermic peak), but the decomposition starts earlier, around 500 °C. The enthalpy of formation from the elements of yavapaiite,  $\text{KFe}(\text{SO}_4)_2$ ,  $\Delta H^\circ_f = -2042.8 \pm 6.2$  kJ/mol, was determined by high-temperature oxide melt solution calorimetry. Using literature data for hematite, corundum, and Fe/Al sulphates, the standard entropy and Gibbs free energy of formation of yavapaiite at 25 °C (298 K) were calculated as  $S^\circ$  (yavapaiite) =  $224.7 \pm 2.0$  J·mol<sup>-1</sup>·K<sup>-1</sup> and  $\Delta G^\circ_f = -1818.8 \pm 6.4$  kJ/mol. The equilibrium decomposition curve for the reaction jarosite = yavapaiite +  $\text{Fe}_2\text{O}_3$  +  $\text{H}_2\text{O}$  has been calculated, at  $\text{pH}_2\text{O} = 1$  atm, the phase boundary lies at  $219 \pm 2$  °C.

Jarosite, a potassium iron sulphate hydrated mineral, has recently been found on the Martian surface by the Opportunity rover. Based on recent thermochemical data (Drouet and Navrotsky, 2003; Forray et al., 2005), we calculated the equilibrium decomposition curve of jarosite and show that it is thermodynamically stable under most estimates of present Martian pressures and temperatures. If jarosite has been within its thermodynamic stability field since its formation, this curve gives the relation between maximum temperature and minimum water fugacity through a large part of Martian history. Its stability makes jarosite potentially useful to retain textural, chemical, and isotopic evidence of past history, including possible biological activity on Mars.

Beside the thermochemical studies, a classical but detailed research was carried out in Roşia Montană mine site (Apuseni Mountains, Romania). Hop mine waste-rock dump was sampled and analysed for bulk chemistry, for selected potential toxic elements (Ag, As, Cu, Ni, Pb and Zn), mineralogy, colour, grain size and acid mine drainage producing potential. Two main waste rock groups were identified, one with bulk composition dominated by

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dacite, the other one by andesite. The concentrations of potential toxic elements are below the regulatory limits for soils, with the exception of As, for both waste rock types. In terms of acid mine drainage producing potential, dacite-dominated rocks has a net acid producing potential, while the andesite-dominated type has a net neutralizing potential.

The second research area is the study of the past environmental changes using the  $\delta^{13}\text{C}$  values measured in bat guano deposits. These environmental changes can be of natural origin and/or related to human activity (*e.g.* fossil fuel burning). Understanding the complex drivers behind Earth's past climate changes may help predict the likelihood, extent, and patterns of future changes.

The  $\delta^{13}\text{C}$  values of guano samples from a 17-cm long sediment profile from Gaura cu Muscă Cave (SW Romania), made it possible to reconstruct the paleoprecipitation (MAP-mean annual precipitation) through the Medieval Warm Period (MWP).

A 1.5-m-long core from a bat guano deposit in Zidită Cave (Hunedoara County, Romania) has provided a 900 yr record of environmental changes. Shifts in  $\delta^{13}\text{C}$  values of bulk guano (between  $-24.1$  and  $-27.6\%$ ) show significant changes in the structure of vegetal assemblage. The vegetation dynamics is linked with changes in the hydrologic regime. The  $\delta^{13}\text{C}$  values of guano did not changed markedly over the Medieval Warm Period (MWP) and Little Ice Age (LIA) transition. Instead, an overall decreasing trend of  $\delta^{13}\text{C}$  values between *ca.* AD 1200 and 1870–1900 defines the duration of LIA.

The aforementioned investigations on an exciting topic are new research direction not only for Romania but for the word scientific community interested in paleoclimatic reconstructions. If the financial support for this type of research will be granted in the future, our current worldwide leading position in this research can be maintained. Is worth to mention, in 2015, Romania caves had the most research using the bat guano  $\delta^{13}\text{C}$  as proxy for paleoclimate.

The third research area focuses on the geochemical signature (major, minor, and trace elements,  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ , and  $\delta^{34}\text{S}$ ) of surface and ground water in order to understand how climate change affects the water resources and possible health effect of minor and trace toxic elements in various non-monitored drinking water resources (*e.g.* hundred of sparkling and still mineral water springs are used for domestic consumption).

While the present research mainly focuses on the first two areas, the third one will be the future direction, for which we already measured samples and results are ready to be published in 2016.

The habilitation thesis is covered by the following ISI publications:

- Forray F.L.**, Onac B.P., Tanțău I., Wynn J.G., Tămaș T., Coroiu I., Giurgiu A. (2015) A Late Holocene environmental history of a bat guano deposit from Romania: an isotopic, pollen and microcharcoal study. *Quaternary Science Reviews*. doi:10.1016/j.quascirev.2015.05.022 (**Current IF: 4.572**).
- Onac B.P., Hutchinson S.M., Geantă A., **Forray F.L.**, Wynn J.G., Giurgiu A.M., Coroiu I. (2015) A 2500-year Late Holocene multi-proxy record of vegetation and hydrologic

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- changes from a cave guano-clay sequence in SW Romania. *Quaternary Research* 83:437-448. doi:10.1016/j.yqres.2015.01.007 (**Current IF: 2.544**).
- Forray F.L.**, Smith A.M.L., Navrotsky A., Wright K., Hudson-Edwards K.A., Dubbin W.E. (2014) Synthesis, characterization and thermochemistry of synthetic Pb-As, Pb-Cu and Pb-Zn jarosites. *Geochimica Cosmochimica Acta* 127:107-119. doi:10.1016/j.gca.2013.10.043 (**Current IF: 4.331**).
- Onac B.P., **Forray F.L.**, Wynn J.G., Giurgiu A.M. (2014) Guano-derived  $\delta^{13}\text{C}$ -based paleo-hydroclimate record from Gaura cu Musca Cave, SW Romania. *Environmental Earth Sciences* 71:4061-4069. doi:10.1007/s12665-013-2789-x (**Current IF: 1.765**).
- Servida D., Comero S., Dal Santo M., Capitani L., Grieco G., Marescotti P., Porro S., **Forray F.L.**, Gál Á., Szakács A. (2013) Waste rock dump investigation at Roşia Montană gold mine (Romania): a geostatistical approach. *Environmental Earth Sciences* 70:13-31. doi:http://dx.doi.org/10.1007/s12665-012-2100-6 (**Current IF: 1.765**).
- Pop D., Ionescu C., **Forray F.**, Tămaş C.G., Benea M. (2011) "Transylvanian gold" of hydrothermal origin: an EMPA study in an archaeological provenancing perspective. *European Journal of Mineralogy* 23:911-923. doi:10.1127/0935-1221/2011/0023-2156 (**Current IF: 1.483**).
- Forray F.L.**, Smith A.M.L., Drouet C., Navrotsky A., Wright K., Hudson-Edwards K.A., Dubbin W.E. (2010) Synthesis, characterization and thermochemistry of a Pb-jarosite. *Geochimica Cosmochimica Acta* 74:215-224. doi:http://dx.doi.org/10.1016/j.gca.2009.09.033 (**Current IF: 4.331**).
- Forray F.L.**, Drouet C., Navrotsky A. (2005) Thermochemistry of yavapaiite  $\text{KFe}(\text{SO}_4)_2$ : Formation and decomposition. *Geochimica Cosmochimica Acta* 69:2133-2140. doi:http://dx.doi.org/10.1016/j.gca.2004.10.018 (**Current IF: 4.331**).
- Navrotsky A., **Forray F.L.**, Drouet C. (2005) Jarosite stability on Mars. *Icarus* 176:250-253. doi:http://dx.doi.org/10.1016/j.icarus.2005.02.003 (**Current IF: 3.038**).