Solubility of monazite chemical components in humic acid solutions

E. V. Polyakov · I. V. Volkov · V. T. Surikov ·
L. A. Perelyaeva

Abstract Using physicochemical methods we showed that continuous (15 days) exposure of monazite powder in humic acid (HA) solutions with different acidity gives rise to one to two orders of magnitude growth in the concentration of the monazite' p-, d- and f-elements of Periodic Table (Mg, Al, Si, P, Pb, Ti, Bi, Sc, Ti-Zn, REE, Th, U). The growth in the elements concentration in the humic solutions contacting monazite is shown to depend on the initial concentration of HA in the solutions, pH. It is concluded that these factors should be taken into consideration when inorganic phosphates and alike phases are used as a matrix for the radionuclide wastes solidification.

Keywords Monazite · Humic acid · Solubility · Rare earth elements · Phosphates

High chemical stability and small solubility in water and mineral acids make phosphatic ceramics applicable as a biomaterial, tooth ceramics, construction and heat resisting materials [1, 2]. Structural and radiation stability of d- and f-elements phosphates aroused interest in them as potential matrices for immobilization and long-term storage of highly active actinides [1, 3–6]. These compounds are also used as sorbents of trace elements and nuclides from soil, as well as in order to suppress of their assimilability by plants [7, 8]. Storage of phosphatic compounds in the environment assumes their contact with soil, surface and ground waters, in which inorganic complexing agents and dissolved organic matter (first of all humic substances: humic and fulvic acids) are present. Humic acids (HA) are natural complexing agents [9, 10], and the interest in their functional properties grows constantly. According to our analysis of recent publications, the attention to the problem of humic acid interaction with minerals grows significantly. However, we did not find any data which give an insight into physical and chemical consequences of HA interaction with components of inorganic (amorphous and crystalline) mineral. The purpose of the present work was to answer these questions experimentally for a particular system [monazite(Ce,La,Nd,Th)PO_4—HA solution in natural water]. Monazite was chosen for its natural radioactivity due to the presence of Th-232, U-238 radioactive series and also because it is considered as a model of phosphatic immobilization matrices for highly active actinides.

Experimental

A sample of natural mineral monazite (Ce,La,Nd,Th)PO_4 containing (mass%) ThO_2—4.9, U_3O_8—0.2, sum REE_2O_3—51, Ce_2O_3—25.2, P_2O_5—33.3, Fe_2O_3—2.4, TiO_2—5.5, SiO_2—1.6 was chosen for experiments. The estimates phase and chemical composition of the sample are in agreement with literature data for natural monazite [11]. The specific surface area of monazite samples, defined by low-temperature nitrogen adsorption, was 1,28 m^2/g. A powder of monophase lanthanum orthophosphate $LaPO_4$ synthesized by a standard technique was used as a synthetic analogue of monazite. The influence of pH and HA concentration (natural water samples diluted with river water with a known chemical composition and pH 7.2–10.0) on the results of monazite dissolution were

E. V. Polyakov (✉) · I. V. Volkov · V. T. Surikov ·
L. A. Perelyaeva
Institute of Solid State Chemistry, Ural Branch of the Russian
Academy of Sciences, 91 Pervomayskaya Str, 620990
Yekaterinburg, Russia
e-mail: polyakov@ihim.uran.ru

analyzed in experiments. pH and temperature of batch solutions were controlled by pH-meter ANION with glass electrode. Batch dissolution experiments were carried out by 15 days exposure of monazite powder (50.0 mg, fraction size 0.1–0.2 mm) to 10.0 ml water solutions in isothermal conditions while mixing. Natural solutions with a high level of organic carbon (to 1000 mg/L) and 97% humic acids (HA) were chosen for investigation [12]. The dissolution of phosphates in natural HA-containing water in batch conditions was compared to the phosphates behavior in synthetic HA solutions.

The latter were prepared by mixing a commercial grade product—20 mass% solution of sodium humate and river water with addition of NaCl 0.068 mol/L. The influence of pH and HA concentration (natural water samples diluted with river water with a known chemical composition and pH 7.2–10.0) on monazite dissolution was analyzed in the experiments. The pH and temperature of batch solutions were controlled by a pH-meter ANION with a glass electrode. All synthetic chemical reagents used in the experiments were "very pure" or "chemically pure". IR-spectra of HA molecular fragments isolated from natural and synthetic solutions were registered by a FTIR spectrometer Vertex-80 (Bruker) in KBr tablets in the frequency range 4000–400 sm^{-1}. IR-spectra of natural (1,3) and synthetic (2) HA are shown in Fig. 1. Electronic absorption spectra of HA solutions were obtained with a SP46 spectrophotometer.

The HA in the water is well known to accompany by background chemical elements [12]. Some of these chemical elements are presented both as a background in humic solutions and as impurities in the monazite (Fig. 2). To take the background elements interference in the
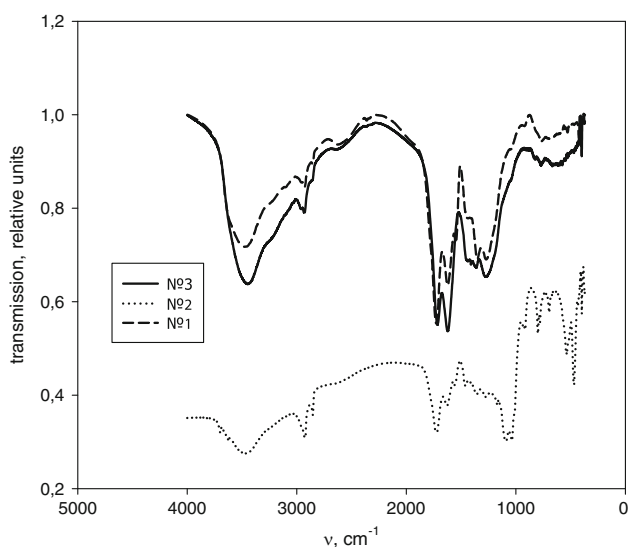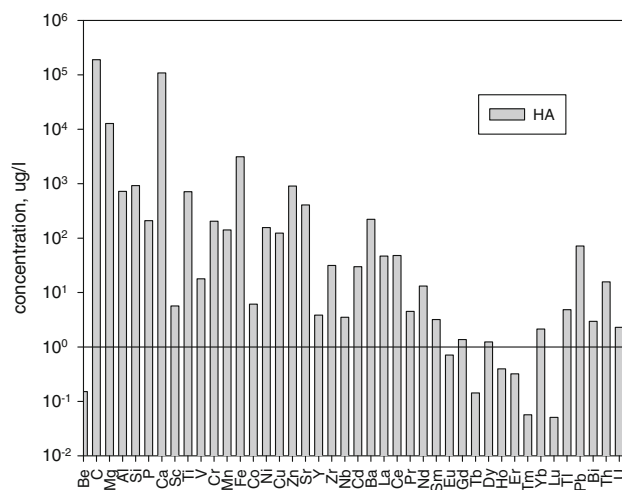
Fig. 2 Background level of chemical elements in natural water sample (µg/L) with humic acids (HA) concentration 900 mg HA/L, used in the solubility experiments. pH = 7.8

solubility experiments into consideration, the following chemical procedures were used. Solid HA was isolated from an aliquot of a solution (i) contacted with the monazite by precipitating with nitric acid and then by filtering through the paper filter, dried and ashed on air at 400 °C; ash-laden residual matter was then quantitatively transferred to a glass test tube with 10 ml of nitric acid (ii). Filtrate originated from HA acidic precipitation was also collected in a glass test tube, acidified by nitric acid and diluted up to the volume 10 ml (iii). Concentrations of chemical elements extracted in each solubility experiment from the sample of monazite in the solutions (i–iii) were then determined by the method of inductively coupled plasma mass-spectrometry (ICP-MS, ELAN 9000). By using these data overall concentrations of controllable elements in each of the HA solutions (iv) contacted with the monazite (overall monazite solubility) at given pH or HA concentration were then calculated. To determine solubility of monazite (C) resulted from the interaction between monazite and HA, the background concentrations of the elements in the HA solution were subtracted from the concentrations estimated in the solutions (iv) by using previously determined general concentration of these elements in the natural or model HA solutions (Fig. 2). The total randomized error of concentration (C) measurements in three parallel experiments was smaller than 25% in the concentration range $n10^{-2}$—$n10^{-}$ µg/L.
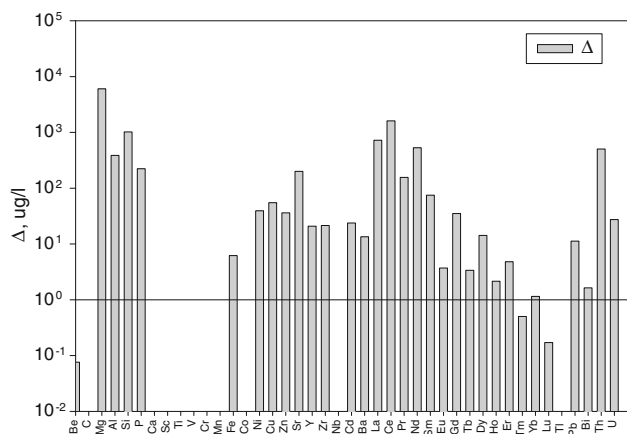
Results and discussion

The experimental data show that in the absence of HA the concentrations of the basic monazite components (REE, U, Th, P) in contacting aqueous solutions are in agreement

Fig. 1 IR-spectra of humic acids samples isolated from natural water (no. 1,3) and synthetic solution (no. 2)

with the literature data on REE orthophosphates and monazite solubility [4] those do not exceed 90 µg/L. Thus, empirically chosen contacting time in these experiments provides equilibrium in the system [monazite—aqueous solution].
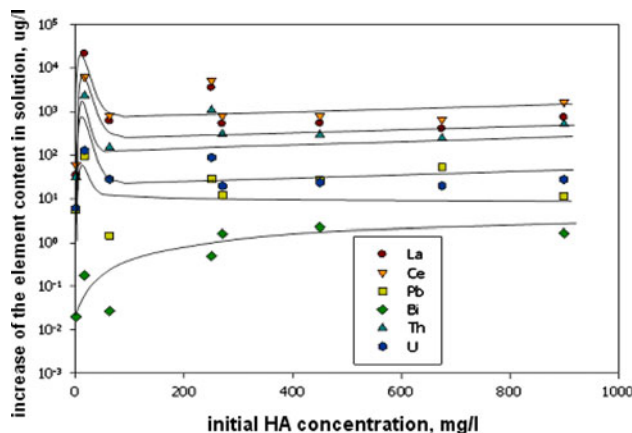
After contacting of HA with monazite the chemical stability of the latter changes drastically. Typical chemical elements concentration change in natural water HA solution with concentration 900 mg/L after its 15 day contact with monazite is depicted on Fig. 3. In this figure are plotted differences (Δ) between monazite elemental concentrations in final HA solution and their background level in the initial HA solution.

It is seen that the concentration of some p- (Mg, Al, Si, P), d- (Fe, Co, Ni, Cu, Zn, Zr, Nb, Cd, La) and f-elements (La, REE, Th, U) in monazite-water solutions increase several orders of magnitude. Omitted data on the Fig. 3 for some of the elements mean that for these elements the difference values Δ are negative. This could be only due to their adsorption by monazite powder surface as a result of the overall solubility products partitioning.

As it is seen from Fig. 4, the increase in the dissolved substance concentration is nonlinear function of HA concentration. A slight increase in the HA concentration in neutral solution in the range 0–20 mg/L results minimum in 10 times growth of La, Ce, Pb, Bi, Th, U and another d- and f-elements concentration. The appearance of maxima on the isotherms (Fig. 4) correlates qualitatively with the known liability of concentrated humic acid solutions to polymerization. The observed non-monotonic optical density versus concentration dependence for HA solutions in the same concentration range (Fig. 5) does not contradicts

Fig. 4 Influence of initial HA concentration on elements content (*C*) growth in a solution over monazite with regard to the background content in HA solution at pH = 7.8, 23 °C
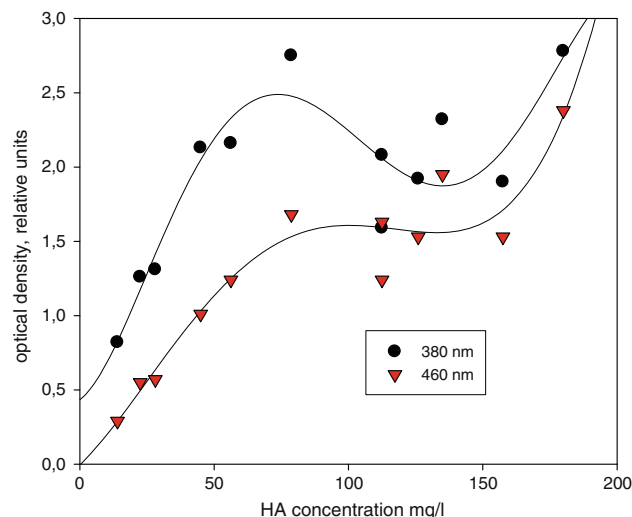
Fig. 5 Optical transmission density variation of solutions with different HA concentration (pH = 10.0), measured at two wavelengths. Solutions are obtained by dilution at 23 °C
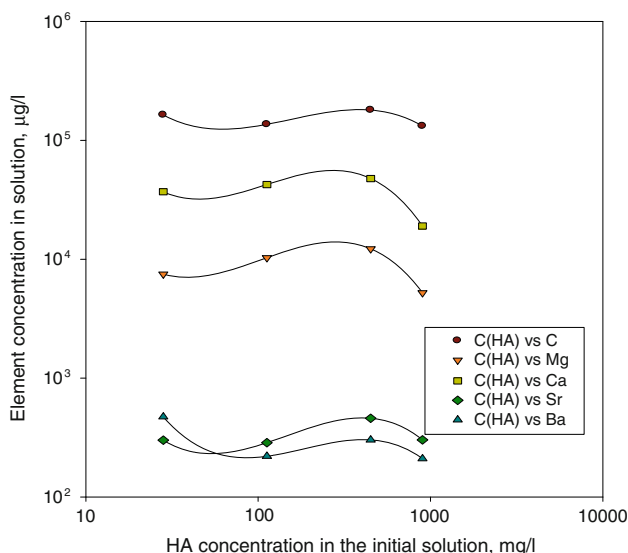
to the polymerization hypothesis. It is known that HA polymerization includes formation of at least two types of polymeric particles in the HA concentration range 20–800 mg/L [13, 14]. In accordance with the assumed interpretation of a HA polymerization role in its complexation activity, monomeric HA in diluted solutions should have the highest stability and thereby liability to monazite components complexes.

Therefore polymer forms of HA in concentrated solutions have less affinity toward metal cations. It is confirmed by FTIR spectroscopy of HA isolated from acidic solutions of natural and synthetic HA (Fig. 2). IR data show that natural and synthetic HA differ by its functional structure (in the synthetic HA free phenolic and alcoholic OH-groups and higher content of aliphatic groups

Fig. 3 Difference (Δ) between monazite elemental solubility in the natural water sample with initial HA concentration 900 mg/L after 15 days of contact with monazite and their background level in HA solution, µg/L. Omitted data on the plot regarding Δ for some of the elements means its adsorption (negative differences Δ) by monazite powder surface. Mass of monazite powder—50.0 mg, solution volume—10.0 ml, pH = 7.8, 23 °C
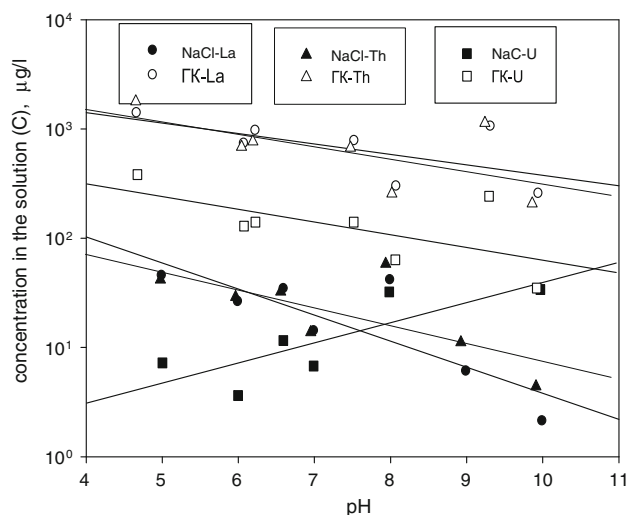
prevailed). In both cases HA IR spectra show wide and difficult absorption in the frequency range of 1725–154 cm^{-1}, confirming the presence of aromatic and aliphatic carboxylates. Noted strong low-frequency absorption shift of valence vibrations νOH in 400–3450 cm^{-1} area testifies intermolecular hydrogen bonds formation in HA macromolecules, that is to be considered as a direct sign of HA polymerization. Carboxylic, hydroxylic and carbonyl groups are considered as a carriers of HA liability to polymerisation. In combination with aromatic structures these groups provides HA ability to participate in ionic and donor–acceptor reactions, to form hydrogen bonds and adducts with various classes of organic compounds [15].

Another important factor which may be responsible for the limitation of monazite dissolution in concentrated HA solutions is a property of HA to form sparingly soluble interface layers which can block transition of monazite components in a solution. For example, in accordance with experimental data (Fig. 6) monazite solubility in HA solution with regard to the alkaline-earth elements passes through a maximum and have a tendency to decrease at high HA concentrations possibly due to formation of sparingly soluble calcium and magnesium humates on monazite surface grains. Such an interpretation is in good agreement with the experimental data [16].

The role of complexation in monazite solubility growth in the presence of HA is visible from comparison of solubility concentration "C-pH" dependences of the systems, in which HA ligands and reference chloride ligands are present (Fig. 7). The presence of HA in solution over monazite not only sharply increases the degree of monazite components dissolution, but also changes the form of
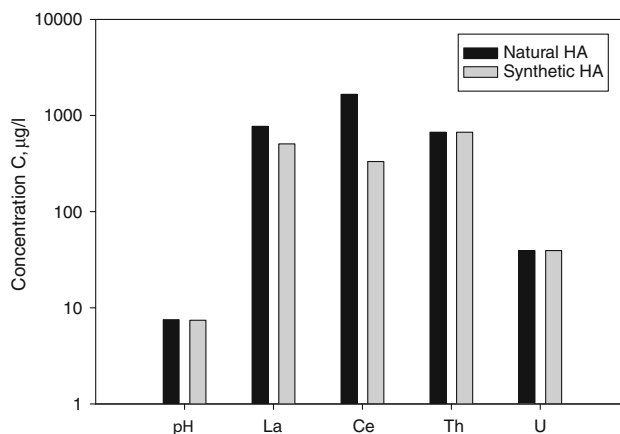

Fig. 7 La (III), Th(IV), U (VI) concentration (C) growth against the background owing to monazite dissolution in 0,098 mol/L NaCl solution (*black symbols*) and natural HA 990 mg/L solution (*light symbols*) at 23 °C as a function of pH

element concentration dependence on pH, possibly suppressing the formation of carbonate uranium complexes. The polyfunctional character of carboxylic groups and their presence in HA are apparently the determining factors of humates ability to complexation, which is very well seen from comparison of monazite solubility in natural HA solutions and in synthetic humate solutions (Fig. 8). Comparison of the dissolution rate values calculated from experimental data for lanthanum and phosphate ions (RL, g/m^{2}day [4]) and the lanthanum orthophosphate phase in natural water with HA concentration $\sim$1 g/L shows that the RL LaPO$_4$ value in comparable conditions is almost two orders of magnitude higher than that of monazite (Fig. 9). Judging from the correlation of lanthanum and phosphorus concentration in a solution, the dissolution of

Fig. 6 Alkaline-earth elements concentration (C) change in HA solution in contact with monazite. Initial pH value 8.8; 23 °C

Fig. 8 Comparison of monazite dissolution (C) in natural HA solution (990 mg/L) and in synthetic HA solution (10000 mg/L) at similar pH at 23 °C
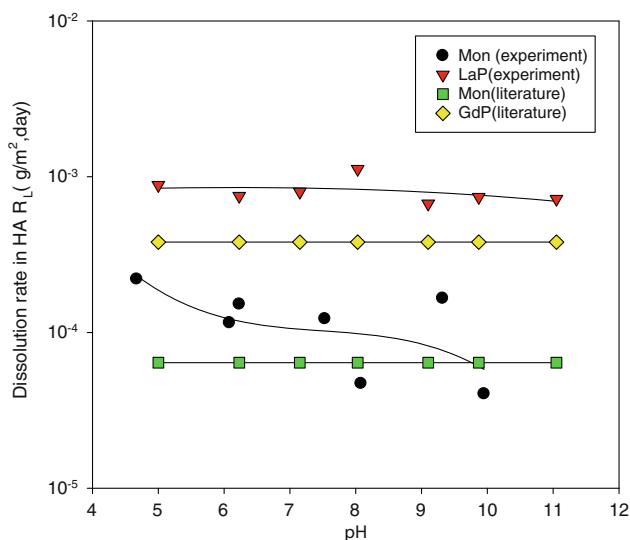
Fig. 9 Experimental dissolution rates of lanthanum orthophosphate (LaP) and natural monazite (Mon) in natural water with 1 g/L HA at 23 °C as a function of water pH. The literature data on monazite ($6.4 \cdot 10^{-5}$) and GdPO4 orthophosphate (GdP, $3.8 \cdot 10^{-4}$) dissolution rates in HNO_3, RL (g/m^2, day) at pH = 1 in batch conditions [4] are cited for comparison

both types of phosphates have an incongruent character due to complexing side reactions. It is especially visible from comparison of the molar ratio (La/P) in a solution equilibrated with the $LaPO_4$ phase: the average value of this ratio in HA solution is 0.60 ± 0.06.

The observed sharp increase in the concentration and monazite dissolution rate for uranium, thorium, REE, and other elements reached the absolute levels of chemical components content of a strong phosphatic matrix. This shows promise for potential technological application of humic solutions for more effective processing of mineral raw materials and technogenic wastes.

Thus, direct experimental supervision indicates that long-term exposure of monazite to solutions containing natural or synthetic HA essentially increases its dissolution with respect to heavy p-, d-, and f-elements of the Periodic system.

Conclusion

This data requires improvement of the existing notions on chemical resistance of phosphatic compounds, which are based on examination of their solubility in nitric-acid solutions [1, 3, 4, 17]. The increase in monazite dissolution rate and in the general concentration of monazite elements both in natural and synthetic humic solutions shows that the deposition of phosphatic compounds similar to monazite in natural systems containing aqueous HA solutions may lead to harmful ecological and radioecological effect caused by release of natural and technogenic radionuclides from the phosphatic matrix. However, the problem of monazite dissolution product behavior in humic solutions calls for further research since humic complexes of uranium, thorium, REE, strontium, cesium and other chemical elements and radionuclides are not only rather stable at natural pH. Those also can be actively sorbed by both inorganic and bioorganic ecosystem components.

References

1. Wagh AS (2004) Chemically bonded phosphate ceramics, twenty-first century materials with diverse applications. Argonne National Laboratory, USA
2. Wilson AD, Nicholson JW (1993) Acid–base cements. Cambridge University Press, Cambridge
3. Wagh AS, Singh D, Jeong SY (2001) Handbook of mixed waste management technology. CRC Press, Boca Raton
4. Terraa O, Dacheuxa N, Audubertb F, Podorc R (2006) J Nucl Mater 352:224–232
5. Clavier N, Dacheux N (2006) Inorg Chem 45:220–229
6. Veilly E, de Kerdaniel E, Roques J, Dacheux N, Clavier N (2008) France Inorg Chem 47:10971–10979
7. Tyler G (2004) Plant Soil 267:191–206
8. Barroso CB, Nahas E (2005) Appl Soil Ecol 29:73–83
9. Ure AM, Davidson CM (2002) Chemical speciation in the environment, 2nd edn. Blackwell Science Ltd, Glasgow
10. Polyakov EV, Egorov YV (2003) Russ Chem Rev 72:985–994
11. Libman EP (1947) Rare earth elements. In: Handbook of geologist (in Russ.). Gosgeolisdat, Moscow
12. Polyakov EV (2007) Radiochemistry (in Russ) 49:378–383
13. Bergelin A (2003) In: Dissertation abstracts international. Proquest. Royal institute of technology, Stockholm
14. Christensen JB, Jensen DL, Gron C, Filip Z, Christensen TH (1998) Wat Res 32:125–135
15. Perminiva IP (2000) Analisys, classification and prognosis of humic acid propertied (in Russ.). Moscow State University, Moscow
16. Yoon SH, Lee CH, Kim KJ, Fane AG (1998) Wat Res 32:2180–2186
17. Poitrasson F, Oelkers E, Schotta J, Montela JM (2004) Geochim Cosmochim Acta 68:207–222