

A CONTRIBUTION TO THE GEOCHEMISTRY OF BERYLLIUM: BERYLLIUM IN SYSTEMS WITH ORGANIC COMPOUNDS

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Abstract: Experimental work was directed towards investigation the influence of selected organic compounds on the formation of soluble and insoluble systems (bonds) of beryllium for further conclusions about the migration or accumulation of beryllium in geochemical and environmental processes. We found that the optimal conditions of solubility of most Be-systems are in the pH interval 3-5, formation of insoluble hydrolytic Be(OH)₂ in the interval 5-7, non-hydrolytic insoluble compounds of Be are formed in the pH interval 1-3. The presence of certain organic compounds causes specific deviations. The obtained data are applied to different natural and medicinal conditions.

Key words: beryllium, organic compounds, analytics, soluble and insoluble systems, geochemistry, medicinal influence.

Introduction

The basic features of the geochemistry of beryllium have been investigated widely. The content of beryllium in different rock types as well as the content of beryllium in soils and waters are known.

Many more questions about Be transport remain still unanswered, as well as transfer of Be from one rock type to another, or from one species to another. Generally, these geochemical processes are elucidated on the basis of fundamental knowledge from inorganic chemistry, applying mostly to the magmatic processes. It is much more difficult to explain the behaviour of Be in supergene conditions, in biological systems, or transport of Be by hydrothermal solutions.

The biogeochemical function of Be in plant and animal organisms is not clear. We do not know the limiting boundary of usefulness of Be for plant and animals. However, much experimental data and observations exist about its harmfulness for both animals and people.

The toxicity of beryllium was not recognized until the beginning of the technical usage of Be metal and its compounds. High doses of beryllium gained during the preparation of these materials attacked people, with consequent serious health damage and deaths. Inhalation of Be and its salts seemed to be most hazardous. Experiments with animals also pointed to the toxic effect of Be materials in direct exposure to injuries (Marhold 1980).

The ways of Be migration in natural conditions, in addition to its transport in living organisms including plants are more or less subject of guesses. Soluble beryllium hydroxo and fluorocomplexes are supposed to exist in water solutions. They are released in the process of weathering of different rock types, becoming a constituent in the water cycle and can be absorbed by clay minerals, or be involved in forming some organic compounds, etc.

Speculations about Be transport do not involve any proofs of the presence of organic compounds in these processes. After experience with other elements (Babčan & Ševc 1989, 1991, 1994) we attempt to investigate the properties of beryllium derivatives with different organic substances. The aim of the study is to determine influence of these compounds upon formation of soluble or insoluble compounds, or different bonds of beryllium in environments with pH values changing from 1 to 13.

Methods and material

a) Used chemicals

Reagents of industrial production with the highest purity, usually the purity p.a. were used in experimental study: amino acids L-alanine and cysteine, D-glucose, tartaric acids (company Lachema, Brno), cellulose (Chemička Ústí nad Labem), starch (Slovenské škrobárne, Boleráz), charcoal (Slovenské lúčobné závody, Hnúšťa). We isolated humic and fulvic acids from peat exploited near the village of Hroboňovo, Dunajská Streda Co., according to the procedure described in Babčan & Ševc (1989).

Beryllium chloride used in experimental practice was prepared from oxide (of company Popelka, Brno).

b) Procedure

The primary goal of the study was to determine how the above mentioned organic compounds (OC) influence the solubility of Be²⁺ (used as BeCl₂) in solutions with chosen pH values. The solution pH was adjusted by adding either HCl or NaOH. We used 80 ml of water and 100 mg of given OC in each run. The solution pH was checked by the pH-meter MS

11 (company Laboratorní přístroje, Praha). Finally, the solution of BeCl_2 (1 millimole in 10 ml of water) was added to the prepared solution, and the pH value was adjusted again. After 24 hours with occasional stirring the final pH value of the solution was determined. The insoluble fraction was separated by filtration or centrifugation. The content of Be was measured by the AAS - ICP.

The difference between the content of Be^{2+} added to the original solution and the content determined after the run is considered to be bound to the OC, for the present without further specification between the formation of an insoluble complex or the result of adsorption.

c) Analytics of beryllium

In order to determine the content of Be in the studied solutions we used a modified method utilized to measure Be content in mineral waters (Kubová et al. 1994). Be was measured directly because no substances with interfering influence were expected in the solutions.

We employed the AAS spectrometer with inductively coupled plasma in sequence arrangement (PLASMAKON S 35, company KONTRON, FRG) with these conditions: wavelength Be I 234.861 nm, wavelength of background 234.912 nm. Argon flows: the external $14.5 \text{ l}\cdot\text{min}^{-1}$, internal $0.7 \text{ l}\cdot\text{min}^{-1}$, carrier $1.2 \text{ l}\cdot\text{min}^{-1}$. Plasma capacity 1.5 kW. Observing height 12 mm, integration time 5 s. The sample flow $1.2 \text{ l}\cdot\text{min}^{-1}$, (through the peristaltic pump). Sprayer: concentric, glassy, type Meinhard B.

Results

Figs. 1 to 10 depict the relationships between the Be^{2+} content in solution and the pH value of the solution. The presence of soluble systems with Be^{2+} , including soluble complexes, is indicated by values of graphic symbols close to the line "basic solution" and vice versa, insoluble systems with low content of Be^{2+} in solution correspond to the values closer to the x axis of the diagrams.

a) System Be^{2+} - water

The behaviour of Be^{2+} in water solutions is shown in the Fig. 1. pH value was adjusted by the addition of HCl or NaOH. These solutions are designated as "purely water" ones.

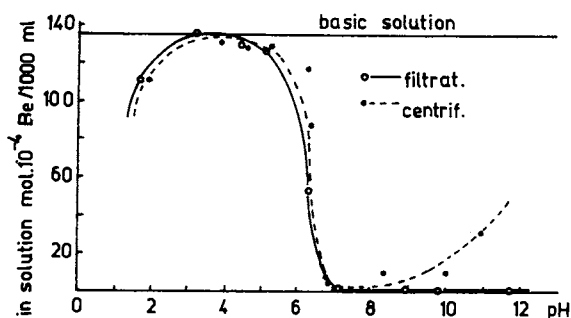


Fig. 1. System Be^{2+} - water. (a) — after filtration, (b) — after centrifugation of the solutions.

Notice the different values of content of soluble Be^{2+} compounds in alkaline region, depending on the method used to separate the soluble and insoluble fraction. Filtration is probably accompanied by sorption of beryllium to the paper filter and is consequently lowering the concentration of Be^{2+} in solution.

Nevertheless, the relationship Be^{2+} vs. pH does not fit with the common understanding of Be^{2+} properties in solution. Even if the symbol Be^{2+} is a working one because only complex aquation $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ exists in the solution, the very low Be solubility in the strongly acid region ($\text{pH} < 3$) is surprising. It is probably caused by formation of complicated complexes, probably on the basis of chlorides. Hydrolysis of the Be^{2+} species or formation of $\text{Be}(\text{OH})_2$ in water environment ($\text{pH} 5.5\text{--}6.5$) is in agreement with the published data (e.g. Jilek & Kofa 1951).

b) System Be^{2+} - humic acids

Humic acids have practically no influence upon Be^{2+} behaviour in water solutions (Fig. 2).

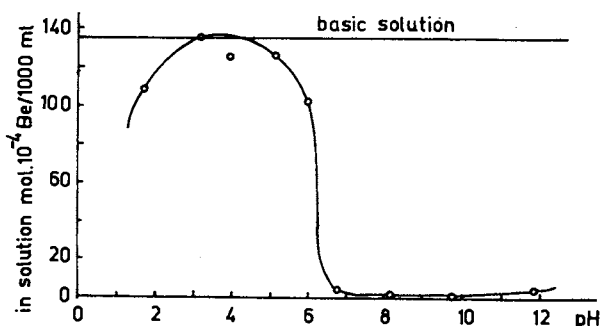


Fig. 2. System Be^{2+} - humic acids.

c) System Be^{2+} - fulvic acids

The behaviour of Be^{2+} in acid solutions with fulvic acids differs markedly from that of systems Be^{2+} with humic acids. Fig. 3 illustrates lower Be^{2+} solubility in the pH range 1-5. Because the fulvic acids themselves are soluble over a wide pH range 1-13 it is clear that the reason for the decrease of Be solubility is the formation of insoluble complexes with the fulvic acids.

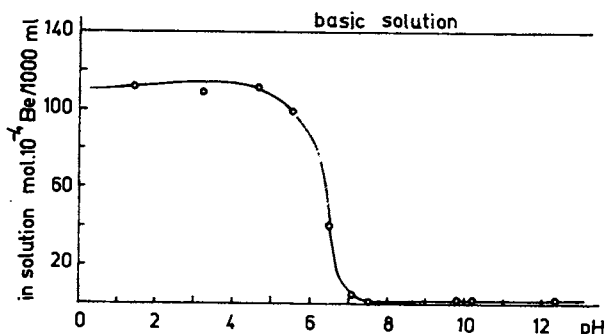


Fig. 3. System Be^{2+} - fulvic acids.

d) System Be^{2+} - amino acids

We investigated the influence of simple amino acids such as alanine $C_3H_7O_2N$ (Fig. 4) and a little more complicated cysteine $C_3H_7O_2NS$ (Fig. 5) with a sulphur atom in the molecule. Their influence on Be^{2+} in solutions is similar to that of the fulvic acids. Both amino acids are soluble and therefore the overall characteristics of these systems must be the same as in the previous case.

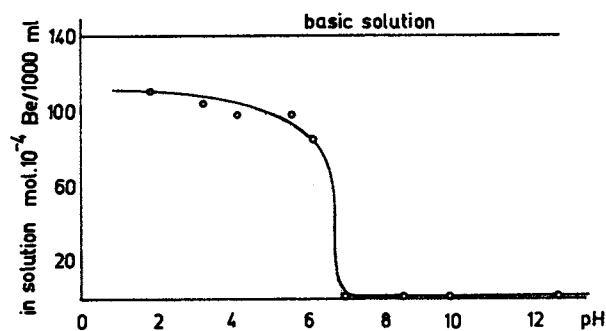


Fig. 4. System Be^{2+} - alanine.

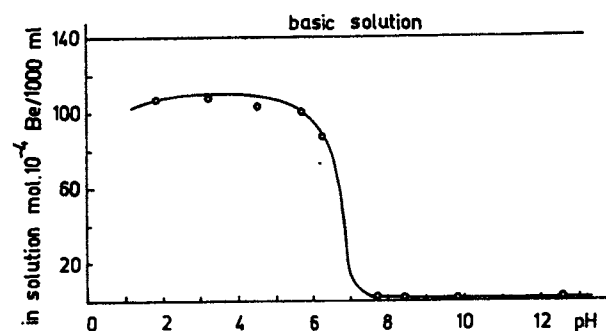


Fig. 5. System Be^{2+} - cysteine.

e) System Be^{2+} - tartaric acid

The tartaric acid or the tartarates are used in analytical practice to inhibit the hydrolysis of beryllium (II) compounds.

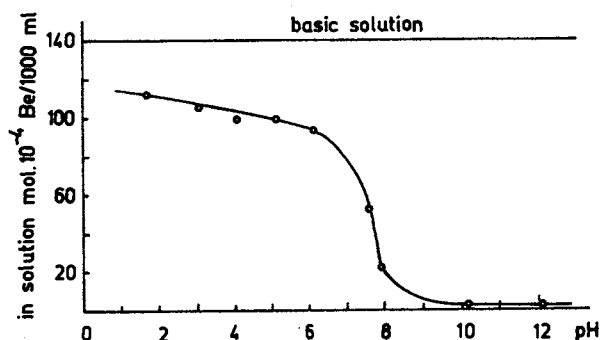


Fig. 6. System Be^{2+} - tartaric acid.

This fact was manifested in our experiments only to a limited extent probably due to a lower concentration of tartaric acid in the solution (100 mg in 100 ml). However, we recorded a clear shift of hydrolysis in a greater extent of the Be^{2+} compounds toward the higher pH values (Fig. 6).

f) System Be^{2+} - saccharides and polysaccharides

Systems with glucose, cellulose and starch (Figs. 7 thru 9) are mutually rather similar, especially in the acid region and they differ in the alkaline region. They are like the "purely water" systems in acid region but the region of maximal Be solubility is considerably narrower and shifted toward higher pH values (5-5.5).

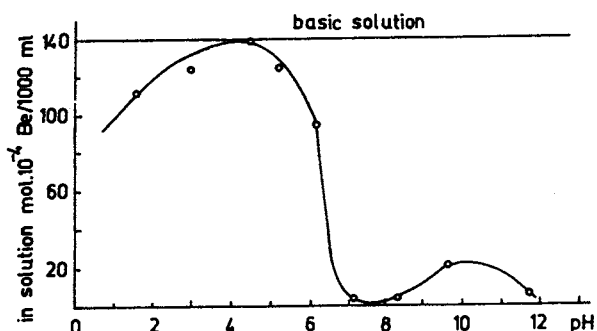


Fig. 7. System Be^{2+} - D-glucose.

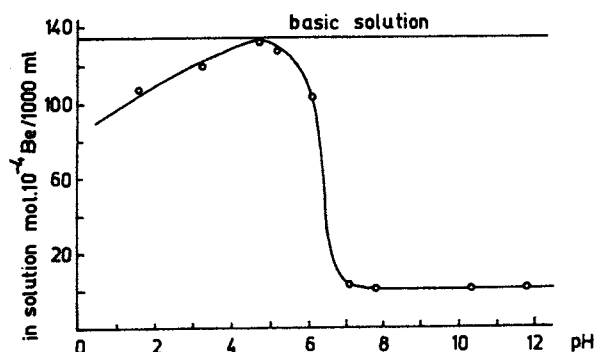


Fig. 8. System Be^{2+} - cellulose.

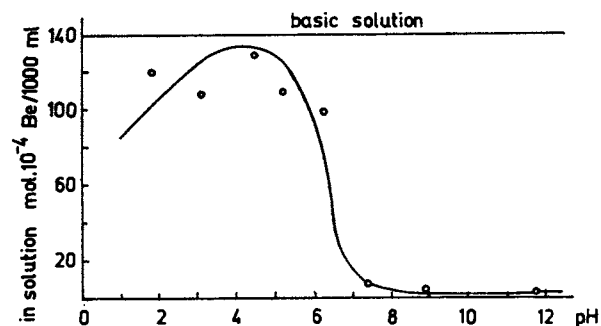


Fig. 9. System Be^{2+} - starch.

g) System Be^{2+} – charcoal

Be^{2+} behaves in the presence of charcoal almost as in the purely water systems (Fig. 10). Many questions arise concerning the relationship between Be^{2+} and charcoal especially with regards to the common natural phenomenon of a higher concentration of Be in some coal types (Sokolovo Basin, etc.). Yet another problem is the presence of sparingly soluble compounds of Be^{2+} in strongly acidic water solutions.

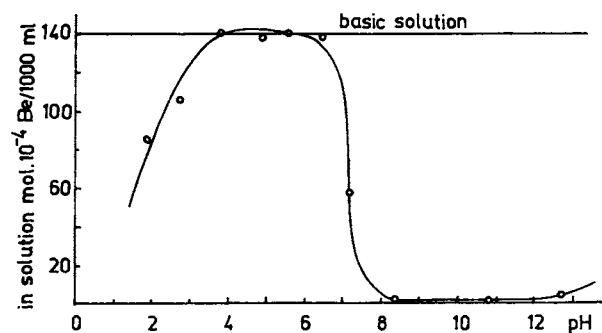


Fig. 10. System Be^{2+} – charcoal.

Discussion

Certain specialities of beryllium systems, especially those with organic compounds were mentioned above in description of the experiments. In the discussion part we attempt to evaluate the geochemical or environmental importance of the obtained data.

Purely water systems of beryllium compounds (according to our definition) do not occur in nature. Our experiments serve only as a comparison. They are used as standards for comparison. As we already mentioned, soluble hydroxo and fluorocomplexes are supposed to be responsible for Be transport in water environment. These may be represented in our experiments by hydroxocomplexes but only in a very narrow pH region (3–5). This may concern only mineral waters or generally underground waters, where, moreover, fluorides could be present.

The common feature of all the studied systems is the marked hydrolysis of the Be^{2+} compounds in the pH range 5–7. It corresponds to the most common natural conditions in many sediments, weathering crusts, waters, soils, etc. Be in these conditions precipitates as sparingly soluble (and therefore immobile) $\text{Be}(\text{OH})_2$. Among the investigated OC, only tartaric acid shifts Be compounds hydrolysis to the more alkaline region (6–8). Its influence may be expected for example in soil systems.

In the alkaline region with pH above 8, the migration ability of Be may be affected to a small extent by saccharides and polysaccharides, namely glucose and cellulose. They may occur especially in soils, underground and surface waters, etc.

Several systems in the acidic and strongly acidic region yielded unexpected results, e.g. considerable drop of Be solubility was also observed in pure water at pH < 3. The systems with humic acids, glucose and starch behaved similarly. Influence of these OC may overlap certain extent with the influence of the pH of the water solutions. Remarkably, the maximal solubility in these systems was reached in the pH range

3–5. It is worth mentioning that a strongly acidic environment should be taken into account in the volcanic processes, in process of sulphidic minerals weathering, etc.

Another group of organic compounds — fulvic acids, amino acids and tartaric acid — exhibit different influence on beryllium. Systems of Be are formed already in very acidic solutions (pH \approx 2). Their solubility is limited but they are not so markedly insoluble as in the case of previous group of OC. Their insolubility is approximately identical from the acid region to the region of Be^{2+} hydrolysis but maximal solubility values are not reached.

The given experimental results are in full agreement with the field observations of e.g. Skřivan et al. (1991), Veselý (1993), Kvidová et al. (1994).

Charcoal, a well-known adsorbent of both organic and inorganic compounds was found to be inactive in the relationship towards beryllium. According to our experimental data, accumulation of Be in coal could not have taken place after the coal formation but it occurred most probably in the stage of humification or peat formation when many organic compounds able to bind Be into insoluble complexes were present in this environment (Hak & Babčan 1967). However, we cannot exclude the assumption that the accumulated Be was gained during the plant lives (Bouška 1981). Different types of OC (humic acids, saccharides, etc.) simplify transport of Be and its access to the plant root system.

The results of our experiments also provide an explanation the contradictions in medicinal observations of beryllium toxicity. Inhalation of some Be compounds as well as intravenous application and the consequent toxic effect share one common transporting medium — blood. In contrast, if used orally, they come into contact with completely different OC. The reduction of insoluble systems is also supported by strongly acidic environment of the stomach (pH \approx 1) and they can be expelled from the body.

The processes in living organisms with an active role of Be need not to be so simple. A great variety of organic compounds may cause in these systems other, so far not investigated effects.

Conclusion

The realized experiments pointed at some specific relationships of beryllium to organic compounds as well as their possible participation in geochemical processes.

1 — We confirmed the marked tendency of Be^{2+} to hydrolyze already in the pH range 5–7. Tartaric acid shifts hydrolysis to more alkaline region (pH 6–8).

2 — Insoluble systems of Be may be formed by non-hydrolytic reaction in:

a) relatively strongly acidic environment (pH 1–3) in so called pure water systems and with humic acids, cellulose and starch;

b) solutions with fulvic acids, amino acids and tartaric acid where slightly more soluble complexes originate in the acidic region (pH \leq 2).

3 — The highest solubility and therefore the maximal migration ability of Be^{2+} compounds was recorded in weakly acidic environment (pH 3–5). Solubility of Be compounds in alkaline solutions depends upon the presence of tartaric acids, OH^- ions (formation of beryllate), glucose and cellulose.

4 — Experiments with charcoal lead to the conclusion that

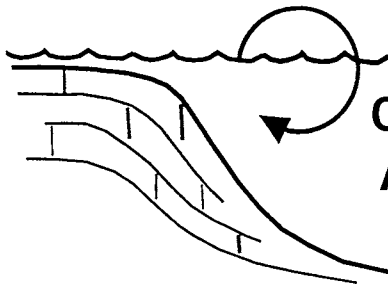
Be is most probably introduced to some coal types during the period lives of plants or during the processes of humification and peat formation of coal substances.

5 — Medicinal-geochemical or toxic-environmental paradoxes of the behaviour of beryllium compounds are caused by the presence of different organic compounds and different pH values (blood ~ 7, digestive system ~ 1).

Translated by J. Majzlan

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SEPM/IAS Research Conference

**CARBONATES AND GLOBAL CHANGE:
AN INTERDISCIPLINARY APPROACH**

Wildhaus, Switzerland, June 22-27, 1996

Convenors: Maria Mutti & Helmut Weissert (ETH Zürich, Switzerland), Toni Simo (Univ. Wisconsin, USA), Paul Baker (Duke University, USA).

Around 100 scientists and 20 earth science students from all over the world attended the SEPM/IAS Research Conference on carbonates and global change, held in Wildhaus, Switzerland. The conference locality was situated in the heart of the Helvetic Alps. Impressive Cretaceous carbonate platform sequences in the nearby Säntis and Churfirten ranges provided a scenic and stimulating framework for the lively discussions on carbonates and past global change.

The conference focussed on three major topics: (1) oceanographic and biotic aspects of carbonate systems, (2) controls over carbonate platform growth

and demise, (3) platform response to changes in the ocean and atmosphere. We reserved one day for each session. Key note talks introduced the audience into questions of current interest and case studies were given as oral and poster presentations.

(1) The first session provided the actual framework for the discussions on the link between carbonate sedimentation and paleoenvironmental change. John Milliman reminded us on the many open questions concerning the present-day global carbon budget. He provided an important link to the IGBP (International Geosphere — Biosphere Programme) research groups studying

the present-day marine carbon budget. Other topics addressed by the key note speakers of the first session included the use of geochemical tracers in carbonates as proxies for paleoceanography. The Sr/Cr-ratio may serve as a tracer of past sea level position (P. Baker), phosphorus accumulation rates seem to reflect low frequency and high amplitude fluctuations in paleoproductivity (K. Föllmi). H. Spero confronted us with unsolved problems in oxygen and carbon isotope geochemistry. He specifically discussed questions on oceanic carbonate chemistry and its impact on isotope signatures in foraminiferal calcite. E. Erba provided a micropaleon-