

Mineralogical and geochemical characteristics of drinking water salt deposits

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Abstract. The article presents the research results on the features of element and mineral composition of salt deposits (limescale) formed in household conditions in heat exchanging equipment. The major part of limescale is represented by two species of calcium carbonate - calcite and aragonite. We have shown that high concentrations of chemical elements in the limescale promote the formation of their own mineral forms (sulphates, silicates, native forms) in salt deposits. Detecting such mineral formations suggests the salt deposits of drinking water to be a long-term storage media which can be used in the course of eco-geochemical and metallogenic studies.

1. Introduction

According to several encyclopedias and reference books, salt deposits, or limescale, are "... solid deposits that form on the inner walls of steam boilers, water economizers, super-heaters, evaporators and other heat exchangers in which the evaporation or heat of water containing certain salts takes place" [1]. The study of the salt deposits formed in drinking water systems at various stages of water treatment and transportation is the relevant issue all over the world. Usually most of the studies deal with methods of treatment and removal of salt deposits. The issues discussed there are: 1) development and influence of various factors on these processes [2-4]; 2) their mineral composition [5-9]; 3) disposal processes and methods. However, all these studies characterize the processes taking place in industrial production systems: water treatment, water heating in boilers of thermal power plants, etc.

Our research is based on the data of the studies of drinking water salt deposits which are formed directly in household conditions (enamelled and electric kettles, pots, pans) in the process of multiple boiling and cooling of water. In our opinion, such data could be a source of information on chronic, "long-term" input of chemical elements in a human body. Investigations of the Department of Geoecology and Geochemistry (GEGC) (Tomsk Polytechnic University (TPU)) carried out for over 20 years have shown that the study of limescale element composition is an informative way to assess the quality of drinking water as well as environmental and geochemical conditions of the sites. Furthermore, element composition of these formations can be used in metallogenic forecasting [10-16].



According to our data, the information on the mineral composition of limescale formed directly in the household conditions appears to be absent. Therefore, the aim of this work is to study the characteristics of the mineral composition of drinking water salts.

2. Materials and methods

So far, the research covers the territory of southern part of Urals and Siberia: Irkutsk, Tomsk, Chelyabinsk Oblasts, the Republic of Altai and Buryatia (Russia), as well as Pavlodar Oblast (Kazakhstan).

We collected samples of limescale from different utensils, which were repeatedly used to boil drinking water (enamelled and electric kettles, pans, pots, samovars). In most cases, the selected materials presented powdered mass or separate plate aggregates on the walls of utensils. If limescale was firmly fixed on the walls, the samples were taken with a knife made of stainless steel: salt deposits were carefully removed from the walls of the heat exchanging household utensils. Selected samples were packed in plastic bags. Each sample was labeled with the following information: kind of vessel where water was boiled and the depth of the aquifer. If we had the opportunity to take samples from different type of dishes (plastic pots, metal teapots and samovars) in the same yard, we necessarily did it. In the laboratory, samples were dried at room temperature and prepared for analyzes according to the relevant standards.

At the first stage, all samples were sent to an instrumental neutron activation analysis (INAA) to determine the concentrations of 28 chemical elements (Na, Ca, Sc, Cr, Fe, Co, Zn, As, Br, Rb, Sr, Ag, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Au, Th, U). The analysis was performed in the nuclear geochemical laboratory of the International Innovation Research and Educational Center (IIREC) "Uranium Geology" (TPU) (accreditation number ROSS RU.0001.518623, October 10, 2011, analysts are senior researcher A.F. Sudyko, and L.V. Bogutskaya).

The samples with elevated concentrations of chemical elements were studied in detail by other methods for the mineral composition analysis: 1) X-ray diffraction (DRON-3M, GEGC, TPU, head of the laboratory is G.A. Babchenko; D2 Phaser, Bruker AXS GmbH, Moscow, analyst is Dr. S.N. Putilin); 2) scanning electron microscopy (Hitachi S-3400N, IIREC "Uranium Geology", analyst is S.S. Il'enok). U occurrence modes were determined using the method of fission radiography (f-radiography).

3. Results and discussion

Analysis of more than 600 samples showed that the element composition of limescale is changed within the wide ranges. The leading group includes such elements as Ca, Na, Fe, contents of which in all samples exceed $n \cdot 100$ ppm. In our opinion, these elements are structure-forming for the minerals of drinking water salts. This is also reflected in the composition of the limescale matrix. Our studies show that most of them have a composition identical to travertine – natural carbonate rocks formed by the deposition of Ca, Mg, Fe, Na carbonates out of carbonated springs water [17]. Both travertine and limescale consist of two modifications of calcium carbonate (90-95 %) – calcite and aragonite – with impurities of magnesium and iron species (figure 1). It should be noted that whereas calcium carbonate in travertines is almost always crystallized in the form of calcite, this trend is not observed in limescale. For instance, in some cases it crystallizes in the form of pure calcite, sometimes aragonite and calcite are formed together in various proportions.

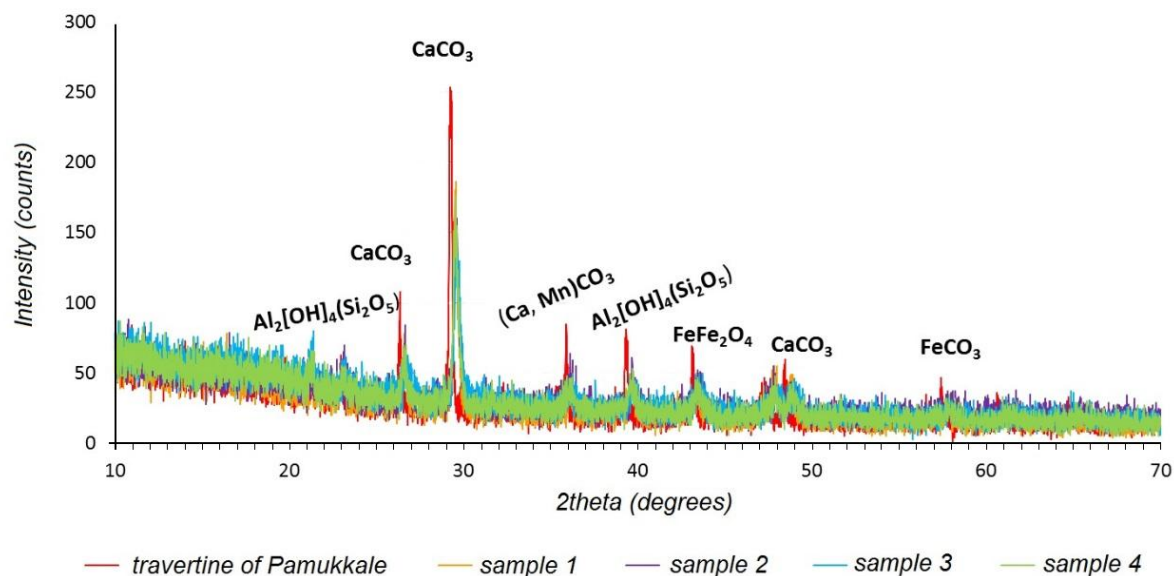


Figure 1. Comparison of mineral composition of Pamukkale travertine and drinking water salt deposits.

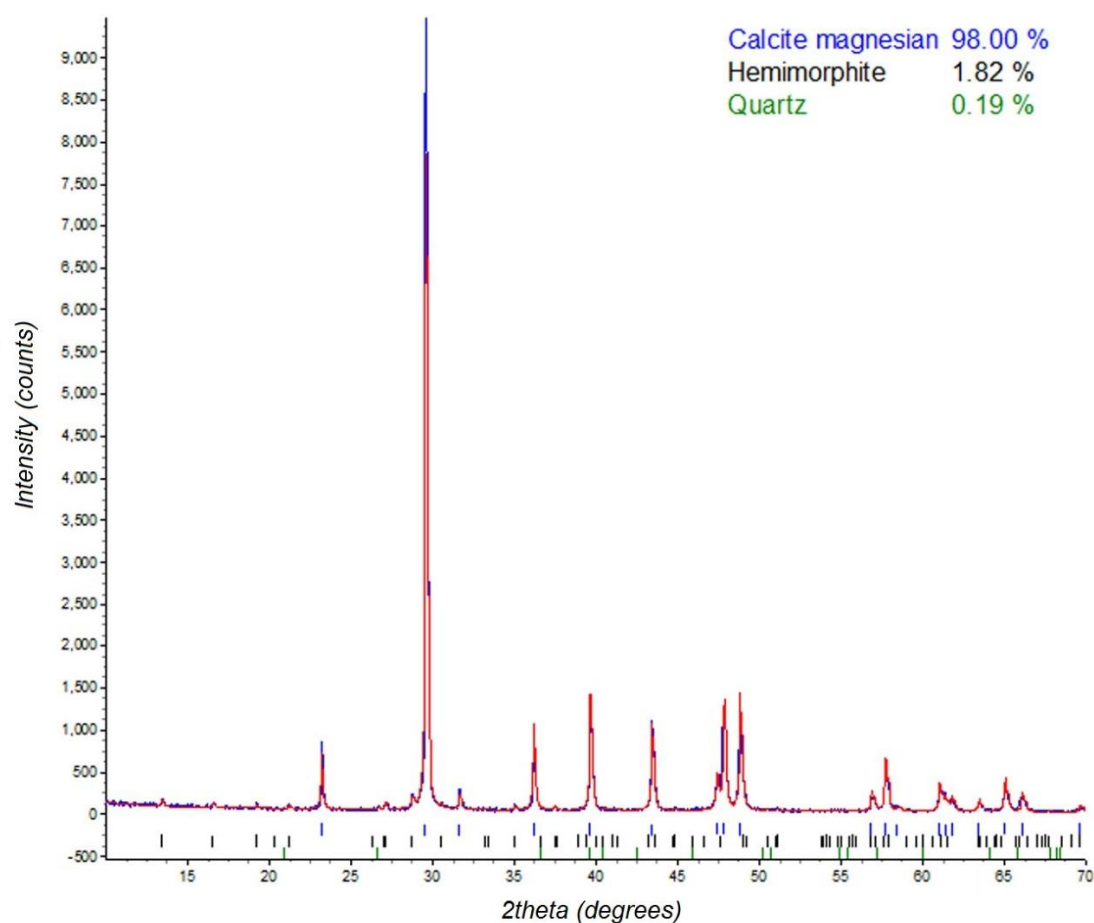


Figure 2. Diffractogram of drinking water salt deposits sample (content of Zn – 3%, Ba – 0.8%).

Issues of formatting aragonite and calcite in travertines are widely discussed in literature. According to various researchers, among the possible factors influencing the formation of aragonite in travertine, there are water temperature [18, 19], the ratio Mg/Ca [18, 20], saturation coefficient [21], Sr^{2+} and SO_4^{2-} [22], pCO_2 and CO_2 rate [23], Fe^{2+} , Ba [21]. On drinking water limescale we found only one research [6], where the high content of Fe ions in water is stated as the factor preventing formation of aragonite.

The elements with high concentrations ($> \text{n} \cdot 10$ ppm) in salt deposits are also Zn, Sr, Ba. They seem to isomorphically substitute Na, Ca, Fe ions in the structure of aragonite-calcite, and form their native mineral phases due to their similar geochemical properties. We observed mineral native forms of Zn (hemimorphite) (figure 2), Ba (barite), etc.

Elevated concentrations of some trace elements are also reflected in the mineral composition of limescale. For instance, native minerals of Ag, Au, Ba, Co, Cu, Ni, Ta, Th, Ti, REE (particle sizes range from $\text{n} \cdot 10$ to $\text{n} \cdot 100$ μm) (figure 3) were revealed by scanning electron microscopy (SEM).

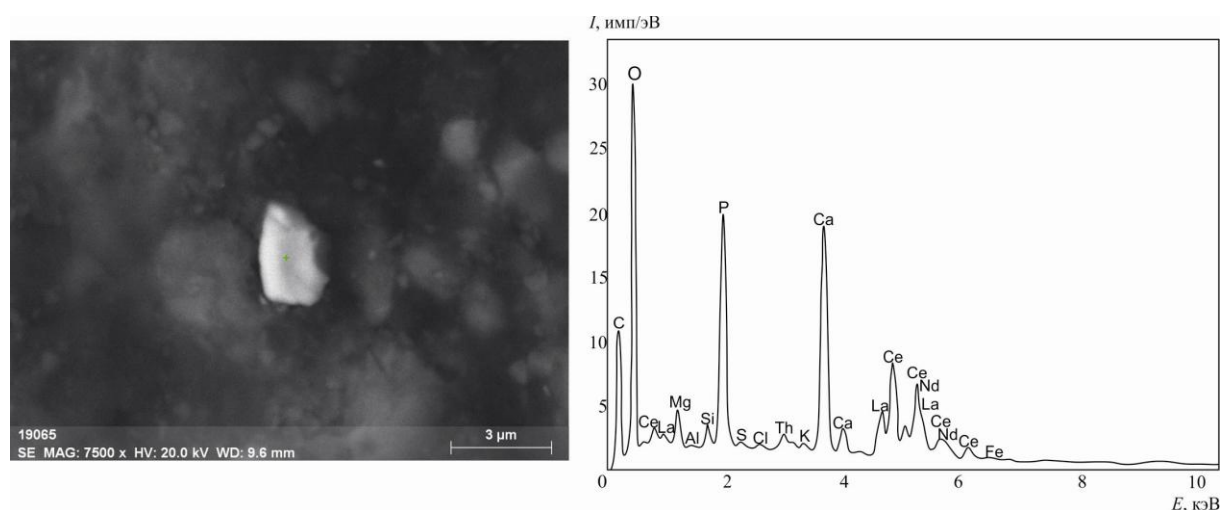


Figure 3. Rare-earth elements phosphate in drinking water salt deposits according to SEM.

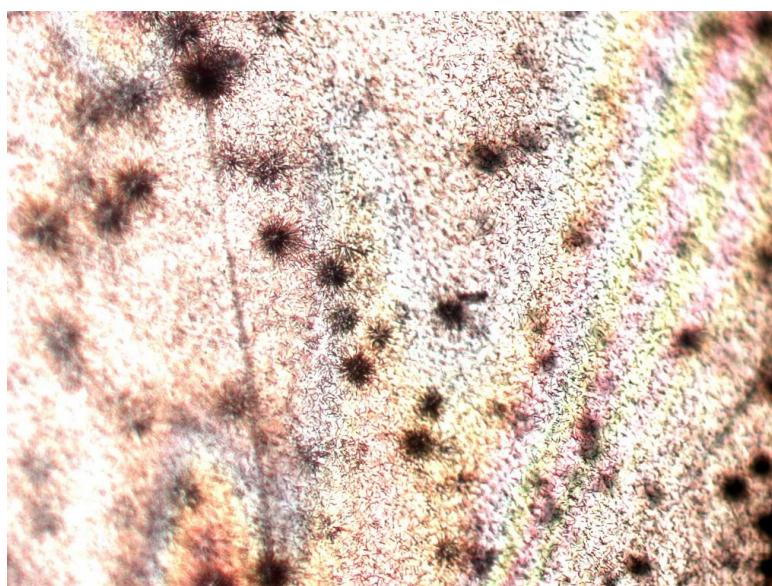


Figure 4. Uranium modes of occurrence in drinking water salt sediments according to fission radiography.

The study in U modes of occurrence in limescale performed by the f-radiography indicates that even at the U concentrations of 1.8 ppm it can be found both in the form of native uranium microminerals (observed as "stars") and molecular form of nonstructural scattering, uniformly distributed in the matrix of salt deposits (Fig. 4).

4. Conclusion

The study in mineral composition of the drinking water salts shows that main matrix minerals are calcite and aragonite in various ratios. Elevated concentrations of several chemical elements allow revealing their own mineral forms using methods of X-ray diffraction and scanning electron microscopy. It is also of importance that the elevated contents of elements and minerals in limescale are not always confirmed by the analysis of water chemical composition. This suggests that the drinking water salt formations are depositing media that can provide information on the long-term accumulation of chemical elements.

References

- [1] Amjad Z (ed.) 2014 *Mineral scales in biological and industrial systems* (Boca Raton, FL: Taylor & Francis Group)
- [2] *Encyclopedia of Desalination and Water Resources*, 2012. URL: <http://www.desware.net> (date of access 12.12.2013).
- [3] Gal J-Y, Fovet J and Gache N 2002 Mechanisms of scale formation and carbon dioxide partial pressure influence. Part I. Elaboration of an experimental method and a scaling model *Water Research* **36** 755–63.
- [4] Gal J-Y, Fovet J and Gache N 2002 Mechanisms of scale formation and carbon dioxide partial pressure influence. Part II. Application in the study of mineral waters of reference *Water Research* **36** 764–73
- [5] Pokrovskiy D S (ed.) 2002 *Mineral growths on the water intakes in Tomsk region* (Tomsk: Publishing House of Scientific and Technical Literature) (in Russian)
- [6] Potapov S S, Votyakov S L and Borisov D R 1998 Mineralogy and spectroscopy of technogenic and anthropogenic (domestic) limescale *Ural'skiy mineralogicheskiy sbornik* **8** 151–70 (in Russian)
- [7] Cowan J C and Weintritt D J 1976 *Water-formed scale deposits* (Houston: Gulf Publishing Co)
- [8] Clark L M 1948 The identification of minerals in boiler deposits. Examples of hydrothermal synthesis in boilers *Mineralogical Magazine* **28** 359–66
- [9] Candeais J P, de Oliveira D F, ods Anjos M J and Lopes R T 2014 Scale analysis using X-ray microfluorescence and computed radiography *Radiation Physics and Chemistry* **95** 408–11
- [10] Mongolina T A, Baranovskaya N V and Soktoev B R 2011 Element composition of drinking water salt sediments in Tomsk Oblast *Bulletin of Tomsk Polytechnic University* **319(1)** 201–11 (in Russian)
- [11] Soktoev B R, Rikhvanov L P, Taisaev T T and Baranovskaya N V 2014 Geochemical characteristics of drinking water salt deposits of Baikal region *Bulletin of Tomsk Polytechnic University* **324(1)** 209–23 (in Russian)
- [12] Soktoev B R, Rikhvanov L P, Usenova S Z, Mongolina T A and Baranovskaya N V 2014 Drinking water salt sediments as an indicative media in ecogeochemical and metallogenic investigations *Herald of Irkutsk State Technical University* **1(84)** 40–45 (in Russian)
- [13] Yazikov E G, Rikhvanov L P and Baranovskaya N V 2004 Indicative role of salt sediments from water in geochemical monitoring *Izvestiya vuzov. Geologiya i razvedka* **1** 67–69 (in Russian)
- [14] Yazikov E G, Rikhvanov L P, Baranovskaya N V and Yankovich E P 2009 Features of element composition of drinking water salt sediments in the south of Tomsk Oblast *Environmental Geoscience* **4** 375–81 (in Russian)
- [15] Rikhvanov L, Baranovskaya N, Soktoev B and Mongolina T 2011 Evaluation of drinking water

- according to geochemical composition of its salt deposition *Proc. of 8th Int. Conference Environmental Engineering (19-20 May 2011) (Vilnius: Vilnius Gediminas Technical University Press)* pp 337–42
- [16] Tapkhaeva A E, Taisaev T T, Rikhvanov L P, Yazikov E G and Baranovskaya N V 2010 Geochemical specialization of limescale of water sources illustrated by two regions in Siberia *Contemporary Problems of Ecology* **3** 498–507
- [17] Pentecost A 2005 *Travertine* (Berlin Heidelberg: Springer-Verlag)
- [18] Folk R L 1994 Interaction between bacteria, nannobacteria, and mineral precipitation in hot springs of Central Italy *Geographie physique et Quaternarie* **48** 233–46
- [19] Fouke B W, Farmer J D, Des Marais D J, Pratt L, Sturchio N C, Burns P C and Discipulo M K 2000 Depositional facies and aqueous-solid geochemistry of travertine depositing hot springs (Angel Terrace, Mammoth Hot Springs, Yellowstone National Park, U.S.A) *Journal of Sedimentary Research* **70** 565–85
- [20] Leitmeier H 1915 Zur kenntnis der carbonate. II. Teil *Neues Jahrbuch fur Mineralogie Beilageband* **40** 655–700
- [21] Buczynski C and Chafetz H S 1991 Habit of bacterially induced precipitates of calcium carbonate and the influence of medium viscosity on mineralogy *Journal of Sedimentary Petrology* **61** 226–31
- [22] Malesani P and Vanucci S 1975 Precipitazione di calcite o di aragonite dalle acque termominerali in relazione alla genesi e all'evoluzione dei travertini *Accademia Lincei, Rendiconti Scienze fisica, matematica e naturale* **58** 761–76
- [23] Kele S, Demeny A, Siklosy Z, Nemeth T, Maria T and Kovacs M B 2008 Chemical and stable isotope compositions of recent hot-water travertines and associated thermal waters, from Egerszalok, Hungary: depositional facies and non-equilibrium fractionations *Sedimentary Geology* **211** 53–72
- [24] Meyer H J 1984 Influence of impurity on the growth rate of calcite *J. Cryst. Growth* **66** 639–46