

ADSORPTION AND COPRECIPITATION OF METALS ON THE SILICEOUS SINTER

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Notwithstanding the source of heat and the nature of high-enthalpy gas-water mixture, siliceous sinter usually deposits from already overheated chloride-sodium therms - the most high-temperature boiling springs rich in silicic acid and frequently oversaturated by it before the unloading. Water, forming siliceous sinter, is polygenetic: partly it is the water of meteorites with the vapor phase connected not only with volcanogenic complex of bearing strata, but with apparently tertiary marine sediments. This specific rock forms around the craters of the geysers. Formation occurs under the condition of fast cooling of springs, whose water temperature reaches the boiling point. High mineralization for hydrothermal solutions of such systems, which periodically build up their enthalpy reserve (resource?), is not typical because of the blending of gas-vapour phase with fresh meteoric water. They are actually colloidal solutions generally saturated during the cooling only by silica.

Micelles of silica are charged negatively in the majority of natural conditions, in which they form, including thermal waters. Just as the self-coagulation of Fe and Al (hydr)oxides is possible on colloidal particles of silica in continental waters because of the negative charge of siliceous micelles in alkaline conditions and down to pH=2-2.5, and due to the positive charge of the surface of Fe and Al (hydr)oxides, self-coagulation may take place in hydrothermal solutions. It seems that only a small part of these particles precipitates at once, while another part remains in the solution with a size not exceeding the maximum possible for stable colloidal particles and can not coagulate for a sufficiently long period of time revealing an important characteristic of hydrothermal solutions of SiO₂ – the capability for hardening.

There exist several well-known versions in the world about the mechanisms of the geyser activity under the conditions of a balance change of heat and mass. Alternative mechanisms are possible too. We are actually interested in them in respect to the sources which form the composition. Gas enters the camera together with the high-enthalpy water vapour and dissolves in the liquid which fills it permanently in the period between eruptions. This gas is an important factor in forming the composition of this thermal water in regard to the easy volatile components and complexes, transferred in the gas-vapour phase. Simultaneously with heating of the wholly kremastic water, for example, saturation of liquid with gases reaches the condition in which gases can not be dissolved wholly without changing its composition. Gas holes extract recurrently a part of the earlier dissolved gases and gases of kremastic water simultaneously with heating. They are partly coalesced and enlarged during the floating-up, becoming quite large on the rise. At the moment when the gas hole becomes larger than the diameter of the camera canal, it forms a gas piston which pushes water out of the camera. It provokes the first moment of dynamic instability of the system when a phase with a less density than others does not have a possibility for a free barbotage. Gas approaches the surface and then dilates, forming a type of a slug regime (gas lift). It separates rapidly from the water phase when the camera gets empty after blowing out of the gas-water mixture. The most interesting point in all these processes is the size of the dense phase share of deep thermal water, raised to the surface together with the gas-vapour phase. There arise other problems consisting in the following. Are the chemism and the microcomponents' composition determined by the dominating part of surface meteoric water with its short and labored processes of the camera walls' solution during the infill and heating? And is it possible to make this problem clear particularly according to the microelements when comparing compositions of the geyserites and the water, forming them?

It is evident that in the rapid outpouring of solution, only a part of colloidal particles remain suspended while another-precipitates quickly. Spontaneous deposition of siliceous sinter and not of tuff, is a result of this precipitation. If the falling-out (and accumulation) of this part of sediment is a fast process, then the composition of siliceous sinter is essentially opalescent (the chalcedony fraction in silica is quite small) with chemical admixtures, adsorptively seized by colloidal particles, and mechanical admixtures, seized by oversaturated gel-silica on the stage of its ageing after it has been raised to the surface.

The specific character of the siliceous sinter formation in the process of rapid cooling of thermal water is accompanied by the capture of all the complexes of soluted components with macro elements forming during the hardening colloids of (hydr)oxides which are hydrolyzates in the matrix. If we

suppose that the opal of geyserites is a typical depositing medium for thermal water and that it preserves its composition, then it means that the role of the specific chemisorption and adsorptive fractionation of components in the solution – gas-vapour phase –opal-silica system should be scarcely revealed. According to this version, the elements, different in characteristics, almost do not have time for the relocation between the water of thermal springs and the water of opals. It presents an easy way for paleo-reconstructions.

It is well known that the low quantity of pH of zero charge point for SiO_2 (2.2 – 2.5 for 20-100°C) not only determines the cation-exchange properties of surface but also the adsorption of protons hinders other cationic forms from chemisorption in acid solutions, up to pH = 4-4.5 and more. Ordinary pH for water of siliceous sinter are 7.5-9. We considered that under such conditions the differentiation of microelements in the process of adsorption and coprecipitation is hardly a process to take place but which in any case demands thorough studying. This version could be confirmed only by the distributing coefficients (K_d) close to one for different elements, which contrast in their chemical properties, natural occurrence and principal ionic forms.

To confirm the given version there were determined contents of 20 microelements by the method RFA SE in 40 samples of siliceous sinter. K_d were found by normalizing the composition of siliceous sinter on the quantity of water in it. The significance of this procedure is evident as the specific surface area available for adsorption could vary in different samples at the moment of their formation. It is a well-known fact that in the structures of water-saturated silica (including water of opals) water represents initially hydroxyl water of silanol and protonated silanol groups and it correlates with the surface, available for adsorption. The content of microelements in the rock was normalized on the quantity of this water because it is its presence that determines the quantity of centers, available for adsorption microelements'. This quantity is a specific surface area of the siliceous sinter in the moment of opals' formation.

Our calculations didn't confirm the version about the inheritance of thermal water composition. K_d as ratio (m_{Me} in opal water) / (m_{Me} in thermal water) have quantities, normal for adsorption ranks. They increase regularly from $n \cdot 10^1$ for some singly charged and alkaline elements and $n \cdot 10^4$ for many of the alkaline-earth elements via $n \cdot 10^5$ for most of d-metals to $n \cdot 10^6$ - $n \cdot 10^7$ for many of microelements-hydrolyzates. Thus, the supposition that siliceous sinter is a typical depositing medium was refuted by realized investigation.

Distribution coefficients for microelements:

Element	Ag	< Cd	< Mn	< Mo	< Sr	< Ni	< Cu	< Zn	< Rb	= Y	<
K_d	$1,15 \cdot 10^1$	$3,9 \cdot 10^3$	$1,1 \cdot 10^4$	$1,2 \cdot 10^4$	$2,1 \cdot 10^4$	$2,8 \cdot 10^4$	$4,3 \cdot 10^4$	$7,0 \cdot 10^4$	$0,85 \cdot 10^5$	$0,85 \cdot 10^5$	

Element	< Sn	< Nb	< Pb	< Ge	< Cr	< V	< Ti	< Fe	< Zr	< Ga
K_d	$0,9 \cdot 10^5$	$4,6 \cdot 10^5$	$5,6 \cdot 10^5$	$0,8 \cdot 10^6$	$0,98 \cdot 10^6$	$1,1 \cdot 10^6$	$1,3 \cdot 10^6$	$3,1 \cdot 10^6$	$1,1 \cdot 10^7$	$5,0 \cdot 10^7$

The main reasons for differences between the microelemental composition of siliceous sinter and the composition of thermal water are selective chemisorption and coprecipitation. Particular qualities of the dynamics of unloading and accretion, shown in morphology, can play a positive role in concentration of some components, including coprecipitated hydrolytically, mechanically and with thermophilic algae. They include rapid cooling during the evaporation, water trickling from the geyserite edifice, slow forming from gel in lower parts of relief with contamination by clayey and ash material.

Differences in microelemental composition of geyserites and palaeogeiserites from composition of thermal water found in some areas of Kamchatka (Paujetskaya and Uzon-Geyzernaya hydrothermal systems, the springs of Academiya Nauk, Karymshinskie and Dachnye springs/thermae) confirm the peculiarity of the formation of these rocks with respect to the source, transport medium and processes of bearing strata changes. The findings of investigation prove the small appropriateness of siliceous sinter for the paleo-reconstruction of thermal water composition and the necessity to take into account the distribution coefficients between water of geyserites and thermal water. Though it complicates the reconstruction of hydrothermal systems' composition, it provides us with the opportunity to reveal in contrast the differences in composition and genesis of thermal water.

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