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GEOCHEMISTRY

The Behavior of Gold during Listvenitization: Experimental and Theoretical Simulation

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The metasomatic formation of listvenite is widespread in the ophiolite complexes of different ages and interesting for geologists owing to its high gold potential. The listvenites were first described as the product of hydrothermal alteration of dunites and peridotites in the Urals [1]. Later, the gold-bearing listvenites formed during hydrothermal alteration of serpentinites were studied in the ophiolite complexes of the Appalachian region of Quebec [2], Turkey [3], and the Ust'-Dep block of the middle Amur region [4]. Listvenites are quartz–carbonate rocks with an admixture of chlorite, fuchsite, talc, chromite, sulfides, and magnetite. The carbonates are mainly ankerite, magnesite, and breinerite. The listvenitization of ultramafic rocks is commonly attributed to the late emplacement of orogenic granitoids that produced chloride–carbon dioxide fluids [5]. The elevated contents of As, Sb, and Hg in listvenites confirm the contribution of granite-related hydrothermal fluids [2], whereas the presence of Cr, Ni, Co, and Pt attests to the ultramafic protolith [4, 6].

This work is aimed at experimental and thermodynamic simulation of serpentinite listvenitization in light of the mass transfer of gold with sulfide–carbonic–chloride solutions. The interaction of chloride–carbonic solutions with serpentinite and listvenite was studied at isotherms of 300 and 400°C and P_{tot} = 1 kbar, since the range of listvenite formation is typically within 290–340°C [7].

Experiments were carried out by the ampoule method in Ti-alloy autoclaves. The source of gold during dissolution was the walls of gold ampoules (8 × 0.2 × 80 and 10 × 0.2 × 90 mm). The measurement accuracy was ±5°C and ±30 bar. Aqueous solution 1*m*KCl + 0.1*m*HCl was used as the starting solution. A ground buffer sample together with solution was loaded in the same ampoule to enforce their interaction. The sample consisted of natural serpentinite (150 mg) mixed with a pyrite–hematite–magnetite (PHM) buffer (150 mg) and thus represented a mixed ore–silicate buffer assemblage. This mixture was successfully used previously for studying the solubility of gold in chloride solutions interacting with epidote propylites [8]. To assess the effect of listvenite composition on the behavior of gold in similar sulfide–carbonic–chloride solutions, we performed experiments with natural listvenites in a mixture with PHM in the same proportions. Table 1 shows the composition of starting rocks taken in the Ust'-Dep ophiolite complex. The mole fraction of CO_2 in experiments with serpentinites was defined by the addition of oxalic acid, which decomposed with liberation of carbon dioxide during the experimental regime. In the experiments with starting listvenite, the mole fraction of CO_2 produced by carbonates amounted to ~0.007. Preparation of quenched solutions for the analysis was completed with the extraction of gold in dioctyl sulfide. The Au content was determined by electrothermal atomization and recorded on a Solar atomic absorption spectrometer. The total error was ±10 rel %. Solid run products were analyzed by the XRD method using a DRON-3 apparatus. Run periods were 750 and 480 h at 300 and 400°C, respectively.

To estimate the effect of CO_2 on gold solubility, we studied the interaction of serpentinites with 1*m*KCl + 0.1*m*HCl at variable contents of CO_2 (X_{CO_2} = 0, 0.005, and 0.05) in the presence of the PHM buffer. It was found that serpentinite in the absence of CO_2 is unstable in chloride solution and is replaced by chloritolite. Chlorite corresponds to pennine and is identified on the basis of reflections (*d*/*n*) = 14.03, 7.08, 4.72, and 3.55 Å. The addition of CO_2 leads to the replacement of serpentinite by listvenite with formation of carbonate (Fe, Mg)CO_3, quartz, and pennine. With increasing X_{CO_2} in fluid (0.005 → 0.05), hematite in the run products is replaced by pyrrhotite (*d*/*n* = 2.96, 2.64, 2.08, 1.72 Å). This fact is related to the release of free hydrogen during decomposition of oxalic acid. At a low frac-

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Table 1. Composition of (1) listvenite and (2) serpentinite, wt %

Component	1	2
SiO_2	30.88	38.66
TiO_2	0.02	0.01
Al_2O_3	0.99	0.87
Fe_2O_3	0.18	6.28
FeO	6.90	2.20
MnO	0.11	0.06
MgO	26.23	37.83
CaO	1.17	0.08
Na_2O	0.09	0.02
K_2O	0.25	0.02
P_2O_5	0.003	0.01
H_2O^+	0.65	12.28
CO_2	32.30	0.20
S	0.11	–
Total	99.88	98.52

Table 2. Bulk concentrations of gold in quenched solutions after their interaction with serpentinites and listvenites

Series	Starting assemblage	log*m* Au	
		300°C	400°C
1	Serpentinite + PHM	–7.73 ± 0.30	–7.42 ± 0.40
2	Listvenite + PHM	–7.68 ± 0.35	–7.30 ± 0.30
3	Serpentinite + PHM	–8.13 ± 0.30	–7.55 ± 0.20
4	Serpentinite + PHM	–7.59 ± 0.35	–7.10 ± 0.20

Note: Series: (1) $X_{CO_2} = 0$, products are chloritolite + HPM; (2) X_{CO_2} is defined by rock carbonates; (3) $X_{CO_2} = 0.005$, products are listvenite + PHM; (4) $X_{CO_2} = 0.05$, run products are listvenite mixed with pyrrhotite and magnetite.

tion of CO_2, the oxygen deficiency is buffered by PHM. However, already at $X_{CO_2} = 0.05$, the system is shifted to the more reduced area of magnetite–pyrrhotite stability, which is accompanied by some increase in gold solubility (Table 2).

The experimentally determined behavior of gold can be explained only by thermodynamic calculations. Therefore, we determined the physicochemical parameters of solutions equilibrated with solid products (f_{O_2}, f_{CO_2}, f_{H_2S}, and others) and calculated the contribution of individual soluble Au species in the bulk gold solubility based on the Gibbs minimization method of heterogeneous systems using a Selector-C software package [9] fitted with the SUPCRT98 database (version 2005). The first series of calculations simulated serpentinite listvenitization depending on fluid composition. Starting solutions were H_2O, 1*m*KCl, 1*m*KCl + 0.1*m*HCl, and 1*m*KCl + 0.1*m*KOH with variable amounts of CO_2 ($X_{CO_2} = 0$, 0.005, and 0.05). The mineral composition of the system was maximally close to the composition used in experiments (i.e., model serpentinite + PHM mixture).

The experimental and calculated values of bulk solubility of Au were fairly close (Tables 2, 3), which allowed us to specify theoretically the gold behavior in the framework of the studied model. According to calculations, the interaction of serpentinite with "pure" water produces a weakly alkaline environment and low gold solubility ($\log m$ Au = –7.65 and –6.67 at 300 and 400°C, respectively). The addition of CO_2 to the aqueous solution leads to further decrease of the bulk solubility of Au (Table 3). The bulk solubility of Au in a 1*m*KCl solution environment increases even in the presence of CO_2 owing to the appearance of its chloride species.

The database available in the software package allowed incorporation of $Au(HS)_2^-$, $AuCl_3^{2-}$, $AuCl_2^-$, $AuCl^0$, Au^+, $AuCl_4^{2-}$, and Au^{3+} in calculations. The two latter gold species seemed to be below the detection limit ($1 \cdot 10^{-7}$ mol), while other species are reported in order of their contribution in bulk solubility. This order remained unchanged over the entire range of calculations. The chloride component is always present in the complex fluid, but its fraction in the bulk solubility of Au is usually two to three orders of magnitude lower than that of hydrosulfide species and is determined by $AuCl_3^{2-}$. In the most acid environment (1*m*KCl + 0.1*m*HCl, 300°C, $X_{CO_2} = 0.05$), the maximum significant sum of chloride species is only ~0.5 order of magnitude lower than the hydrosulfide species in terms of $\log m$ Au. Hematite is unstable in the alkaline solution (1*m*KCl + 0.1*m*KOH) due to the growth of the redox potential and pH of the medium. This is accompanied by an increase in the bulk Au content in the fluid, mainly owing to the growth of hydrosulfide activity (Table 3). Thus, although the mechanisms of the formation of models in the KOH-free medium are identical, the capacity of the solid phase buffer (PHM) becomes insufficient with the appearance of this component. In this case, the role of the buffer is probably taken by complexing species. Their proportions diminish the f_{O_2} of the system and provoke the oxygen deficiency. In calculations, this deficiency was eliminated by input of O_2 into the system, which allowed us to specify the effect of f_{O_2} under specific conditions.

The next series of thermodynamic calculations modeled fluid–listvenite interaction at the same P–T–μ_i parameters. The theoretical listvenite was compositionally close to the experimental one and consisted of

Table 3. Parameters of sulfide–carbon dioxide–chloride solutions and bulk gold content after interaction with serpentinite (P_{tot} = = 1 kbar, buffer PHM)

Starting solution	pH	log*m*Au	$\log f_{CO_2}$	$\log f_{H_2S}$	$\log f_{O_2}$	$\log f_{SO_2}$
		300°C	X_{CO_2} = 0.005			
H_2O	5.04	−8.33	1.56	−1.19	−30.98	−6.51
1*m*KCl	5.30	−7.70	1.75	−1.21		
1*m*KCl + 0.1*m*HCl	4.77	−8.20	1.75	−1.21		
1*m*KCl + 0.1*m*KOH	5.96	−7.05	1.75	−1.21		
1*m*KCl + 0.1*m*KOH*	6.16	−6.80	1.75	−1.16	−31.29	−6.92
			X_{CO_2} = 0.05			
H_2O	4.53	−8.88	2.42	−1.21	−30.98	−6.51
1*m*KCl	4.76	−8.27	2.73	−1.22		
1*m*KCl + 0.1*m*HCl	4.27	−8.57	2.76	−1.22		
1*m*KCl + 0.1*m*KOH	5.96	−7.05	1.75	−1.21		
		400°C	X_{CO_2} = 0.005			
H_2O	5.01	−6.61	1.18	−0.27	−24.29	−2.97
1*m*KCl	4.87	−6.03	1.57	−0.29		
1*m*KCl + 0.1*m*HCl	4.70	−6.15	1.59	−0.29		
1*m*KCl + 0.1*m*KOH	5.01	−5.87	1.62	−0.29		
1*m*KCl + 0.1*m*KOH*	6.38	−4.37	1.59	−0.02	−25.91	−5.13
			X_{CO_2} = 0.05			
H_2O	4.81	−6.85	2.04	−0.29	−24.29	−2.97
1*m*KCl	4.89	−6.08	2.42	−0.30		
1*m*KCl + 0.1*m*HCl	4.67	−6.23	2.44	−0.30		
1*m*KCl + 0.1*m*KOH	5.29	−5.70	2.39	−0.27	−24.48	−3.23
1*m*KCl + 0.1*m*KOH*	5.93	−4.95	2.42	−0.13	−25.33	−4.36

Note: (*) Stability field of Mgt + Py, Hem is dissolved (decrease of f_{O_2}, see text for explanation).

quartz, ankerite–magnesite carbonates, chlorite, sericite, pyrite, hematite, and magnetite. The differences in model compositions of serpentinite and listvenite demonstrate the input of Ca and Al in addition to CO_2 and K (Table 1). The calculation results are shown in Table 4. Despite the noted difference between the calculated composition of serpentinite and listvenite, the bulk solubility of gold in both models behaves similarly, satisfactorily explains variations of this parameter in the physical experiment, and suggests the following conclusions.

The bulk solubility of gold in sulfide–carbonic–chloride environments determines the stability of the predominant hydrosulfide species. However, calculations show the universal presence of subordinate amounts of the chloride component. Its role rises with increasing f_{O_2} and reaches a maximum in an acid environment. As was mentioned in [10], the appearance of carbon dioxide in the system decreases the bulk solubility of Au. This effect is enhanced in the KCl environment owing to salting out. The bulk solubility of Au is primarily governed by the redox potential, change of which into the reductive region always fosters the growth of Au concentration in the fluid.

Natural gold-bearing listvenites can form in the upper crust by two mechanisms. Localization of ore during influx of deep-seated reduced fluid with juvenile carbon dioxide is mainly determined by the temperature decrease and geochemical barriers with high redox potential and low pH values. In the zone of mixing of CO_2-free endogenous solutions with CO_2-rich surface waters, precipitation of gold is caused primarily by the presence of carbon dioxide in the system and the growth of the oxidizing potential. This is consistent with data on decrease of the transporting ability of similar complex fluids with respect to gold and other metals [11]. By contrast, the appearance of solutions of elevated alkalinity increases the mobility of Au at the expense of hydrosulfides, resulting in its partial removal from listvenites at the corresponding stages of ore formation. These observations make it possible to define the mechanism of the influence of pH of postmagmatic fluids on the gold potential of listvenites and

Table 4. Physicochemical parameters of chloride solutions and bulk contents of gold after interaction with listvenite (P_{tot} = 1 kbar, buffer PHM)

Solution	pH	log*m*Au	$\log f_{CO_2}$	$\log f_{H_2S}$	$\log f_{O_2}$	$\log f_{SO_2}$
			300°C			
H_2O	5.81	−7.54	1.63	−1.19	−30.98	−6.51
1*m*KCl	5.11	−7.89	1.99	−1.21		
1*m*KCl + 0.1*m*HCl	4.29	−8.54	2.02	−1.21		
1*m*KCl + 0.1*m*KOH	5.61	−7.40	1.95	−1.21		
			400°C			
H_2O*	5.98	−5.58	1.32	−0.21	−24.69	−3.50
1*m*KCl*	5.52	−5.34	1.70	−0.13	−25.25	−4.25
1*m*KCl + 0.1*m*HCl	4.20	−6.33	1.68	−0.29	−24.29	−2.97
1*m*KCl + 0.1*m*KOH*	5.99	−4.83	1.64	−0.06	−25.68	−4.83

Note: (*) Stability field of Mgt + Py, Hem is dissolved.

processes of their mineralization. Thus, the presence of carbonates makes listvenites favorable for the precipitation of Au in systems with repeated influx of ore-bearing fluids.

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