minerals

Supplementary Materials

Physicochemical Model of Formation of Gold-Bearing Magnetite-Chlorite-Carbonate Rocks at the Karabash Ultramafic Massif (Southern Urals, Russia)

Valery Murzin, Konstantin Chudnenko, Galina Palyanova, Aleksandr Kissin and Dmitry Varlamov

[1] A.N. Zavaritsky Institute of Geology and Geochemistry, Ural Branch of Russian Academy of Sciences, Vonsovskogo str., 15, Ekaterinburg 620016, Russia; murzin@igg.uran.ru (V.M.); kissin@igg.uran.ru (A.K.)
[2] A.P. Vinogradov Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences, Favorskogo str., 1a, Irkutsk 664033, Russia; chud@igc.irk.ru
[3] V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of Russian Academy of Sciences, Akademika Koptyuga pr., 3, Novosibirsk 630090, Russia
[4] Department of Geology and Geophysics, Novosibirsk State University, Pirogova str., 2, Novosibirsk 630090, Russia
[5] Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia; dima@iem.ac.ru
* Correspondence: palyan@igm.nsc.ru

Table S1. Trace-element composition of rocks (ppm).

No. Sample	1512	1422	1410	1421
Li	4.622	7.275	96.061	2.483
Be	0.217	0.014	0.000	0.152
B	27.074	3.533	0.300	9.794
Sc	7.89	21.99	63.46	62.36
Ti	89.6	24.5	2762.4	4095.2
V	25.19	66.37	138.17	70.11
Cr	1610	4367	15.8	71.9
Mn	770	573	1518	6937
Co	115.0	125.7	42.58	28.63
Ni	2500.1	3679.4	32.9	147.3
Cu	53.9	134.7	115.7	1082.4
Zn	56.42	163.02	250.18	511.46
Ga	1.552	5.508	3.359	0.346
Ge	1.321	0.053	0.775	0.107
As	34.611	-	16.177	12.914
Rb	0.359	0.544	0.328	0.172
Sr	8.9	6.3	65.0	1644
Y	0.250	0.473	13.169	46.115
Zr	2.064	0.799	104.74	441.59
Nb	0.270	0.619	9.879	25.469
Mo	н.о.	0.197	0.223	0.347
Hg	1.704	0.754	н.о.	0.246
Cd	1.062	0.552	0.414	7.937
Sb	5.399	2.319	0.763	0.965
Cs	0.059	0.263	0.387	0.085
Ba	7.65	13.24	6.11	53.10
Hf	0.053	0.022	2.914	11.452
Ta	0.008	0.468	0.915	2.923
Pb	8.523	51.539	18.992	3.480
Bi	0.991	0.148	0.069	0.301
Th	0.078	0.098	6.412	58.233
U	0.027	0.096	3.660	19.596
Sum REE	1.92	1.61	231.72	304.31

Note. Samples: 1512, antigorite serpentinite; 1422, chloritolite with scarce magnetite dissemination; 1410, chloritolite with ilmenite and apatite phenocrysts; 1421, magnetite–chlorite–carbonate rock (with ilmenite and apatite). The trace-element composition of rocks was determined by ICP MS on an ELAN 9000 Perkin Elmer mass spectrometer at the Institute of Geology and Geochemistry, Yekaterinburg (analyst D.V. Kiseleva) [1].

Table S2. Components of aqueous solution and gases taken into account in thermodynamic models.

Aqueous Solution							
Component	**Ref.**	**Component**	**Ref.**	**Component**	**Ref.**	**Component**	**Ref.**
$Ag(CO_3)^{-}$	2	$CaHCO_3^{+}$	4	Fe^{+2}	6	K^{+}	6
$Ag(CO_3)_2^{-3}$	2	$CaHSiO_3^{+}$	2	Fe^{+3}	6	KCl^{0}	2
$Ag(OH)_2^{-}$	4	$CaOH^{+}$	6	$FeCl^{+}$	2	$KHSO_4^{0}$	2
Ag^{+}	3	$CaSO_4^{0}$	2	$FeCl^{+2}$	2	KOH^{0}	6
Ag^{+2}	3	Cl^{-}	6	$FeCl_2^{0}$	2	$KSO4^{-}$	2
$AgCl^{0}$	4	$Cu(HS)_2^{-}$	5	FeO^{0}	6	$CH4^{0}$	7
$AgCl_2^{-}$	4	$Cu(OH)_2^{-}$	4	FeO^{+}	6	Mg^{+2}	6
$AgHS^{0}$	5	Cu^{+}	6	FeO_2^{-}	6	$MgCO_3^{0}$	3
AgO^{-}	6	Cu^{+2}	3	$FeOH^{+}$	6	$MgCl^{+}$	2
$AgOH^{0}$	4	$CuCl^{0}$	4	$FeOH^{+2}$	6	$MgHSiO_3^{+}$	6
$Al(OH)^{+2}$	7	$CuCl^{+}$	2	HCO_3^{-}	6	$MgOH^{+}$	7
$Al(OH)_2^{+}$	8	$CuCl_2^{0}$	2	HCl^{0}	7	$MgSO_4^{0}$	6
$Al(OH)_3^{0}$	9	$CuCl_2^{-}$	4	$HFeO_2^{0}$	6	Na^{+}	2
$Al(OH)_4^{-}$	9	$CuCl_3^{-}$	2	$HFeO_2^{-}$	6	$NaCl^{0}$	2
Al^{+3}	7	$CuCl_4^{-2}$	2	$HHgO_2^{-}$	6	$NaHSiO_3^{0}$	6
$Au(HS)_2^{-}$	5	$CuHS^{0}$	4	H_2S^{0}	10	$NaOH^{0}$	7
$Au(OH)_2^{-}$	4	CuO^{0}	6	HS^{-}	10	$NaSO_4^{-}$	6
Au^{+}	4	CuO_2^{-2}	6	HSO_4^{-}	6	SO_4^{-2}	2
Au^{+3}	6	$CuOH^{0}$	4	$Hg(HS)_2^{0}$	10	$HSiO_3$	7
$AuCl^{0}$	4	$CuOH^{+}$	6	$Hg(OH)_2^{0}$	10	SiO_2^{0}	11
$AuCl_2^{-}$	4	Mn^{+2}	6	Hg^{0}	10	$H_2PO_4^{-}$	11
$AuHS^{0}$	5	Mn^{+3}	6	Hg^{+2}	3	HPO_4^{-2}	2
$AuOH^{0}$	4	MnO_4^{-}	6	Hg_2^{+2}	6	PO_4^{-3}	2
CO^{0}	7	MnO_4^{-2}	6	$HgCl^{+}$	2	$P_2O_7^{-4}$	2
CO_2^{0}	7	$MnOH^{+}$	6	$HgCl_2^{0}$	2	$HP_2O_7^{-3}$	2
CO_3^{-2}	6	MnO^{0}	6	$HgCl_3^{-}$	2	$H_2P_2O_7^{-2}$	2
Ca^{+2}	6	$HMnO_2^{-}$	6	$HgCl_4^{-2}$	2	HPO_3^{-2}	2
$CaCO_3^{0}$	2	MnO_2^{-2}	6	HgO^{0}	6	$H_2PO_3^{-}$	3
$CaCl^{+}$	2	$MnCl^{+}$	6	$HgOH^{+}$	6	H_2^{0}	3
$CaCl_2^{0}$	2	$MnSO_4^{0}$	6	$HgS(HS)^{-}$	10	O_2^{0}	
Gases							
Component	**Ref.**	**Component**	**Ref.**	**Component**	**Ref.**	**Component**	**Ref.**
HCl	12	H_2S	12	H_2	12	S_2	12
SO_2	12	O_2	12	CO_2	12	CO	12
CH_4	12	Hg	13				

Table S3. Solid phases components used in thermodynamic models.

Mineral	**Formula**	**Ref.**	**Mineral**	**Formula**	**Ref.**
Ag-Au-Cu-Hg	Au	18	Ilmenite	$MgTiO_3$	14
	Ag	18		Fe_2O_3	14
	Cu	18		$FeTiO_3$	14
	Hg	18		$MnTiO_3$	14
Chlorites	$Mg_6Si_4O_{10}(OH)_8$	14	Cuprite	Cu_2O	15
	$Mg_4Al_4Si_2O_{10}(OH)_8$	14	Tenorite	CuO	15
	$Mg_5Al_2Si_3O_{10}(OH)_8$	14	Diopside	$CaMg(SiO_3)_2$	15
	$Fe_5Al_2Si_3O_{10}(OH)_8$	14	Montroydite	HgO	16
Pyroxenes	$CaMgSi_2O_6$	14	Akermanite	$Ca_2MgSi_2O_7$	15
	$CaFeSi_2O_6$	14	Albite	$NaAlSi3O_8$	14
	$NaAlSi_2O_6$	14	K-feldspar	$KAlSi3O_8$	14
Carbonates	$CaCO_3$	14	Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	15
	$MgCO_3$	14	Anhydrite	$CaSO_4$	15
	$MnCO_3$	14	Plagoiclase	$NaAlSi_3O_8$	14
	$FeCO_3$	14		$CaAl_2Si_2O_8$	14
	$CaMg(CO_3)_2$	14	Ferrosilite	$FeSiO_3$	15
Garnets	$Fe_3Al_2Si_3O_{12}$	14	Ferrous-oxide	FeO	15
	$Ca_3Fe_2Si_3O_{12}$	14	Graphite	C	14
	$Ca_3Al_2Si_3O_{12}$	14	Halite	NaCl	15
	$Mg_3Al_2Si_3O_{12}$	14	Hematite	Fe_2O_3	14
	$Mn_3Al_2Si_3O_{12}$	15	Magnetite	Fe_3O_4	14
Chalcocite	Cu_2S	15	Pyrite	FeS_2	15
Chalcopyrite	$CuFeS_2$	16	Troilite	FeS	17
Silver (I) oxide	Ag_2O	17	Quartz	SiO_2	14
Chlorargyrite	AgCl	18	Rutile	TiO_2	14
Argentite(acanth	Ag_2S	18	Sphene	$CaTiSiO_5$	14
ite)	Ag_3AuS_2	18	Mercury	Hg	15
Uytenbogaardtit	AgAuS	18	Sulfur	S	16
e	$Mg_3Si_2O_5(OH)_4$	15	Talc	$Mg_3Si_4O_{10}(OH)_2$	14
Petrovskaite	α-HgS	15	Olivine	Fe_2SiO_4	14
Chrysotile	β-HgS	15		Mg_2SiO_4	14
Cinnabar	Cu	15	Hydroxyapatite	$Ca_5(PO_4)_3OH$	20
Metacinnabar	CuS	15	Serpentine	$Mg_3Si_2O_5(OH)_4$	19
Copper	Cu_5FeS_4	15		$Mg_{5.5}AlSi_{3.5}O_{10}(OH)_8$	19
Covellite					
Bornite					

References

1. Murzin, V.V.; Varlamov, D.A.; Palyanova, G.A. Conditions of formation of gold-bearing magnetite–chlorite–carbonate rocks of the Karabash ultrabasic massif (South Urals). *Russian Geol. and Geophys.* **2017**, *58*, 803–814, DOI 10.1016/j.rgg.2017.06.003

2. Sverjensky, D.A.; Shock, E.L.; Helgeson, H.C. Prediction of the thermodynamic properties of aqueous metal complexes to 1000°C and 5 kb. *Geochim. Cosmochim. Acta* **1997**, *61*, 1359–1412. DOI:10.1016/S0016-7037(97)00009-4.
3. Shock, E.L.; Helgeson, H.C.; Sverjensky, D.A. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species. *Geochim. Cosmochim. Acta* **1989**, *53*, 2157–2183. DOI:10.1016/0016-7037(89)90341-4.
4. Akinfiev, N.N.; Zotov, A.V. Thermodynamic description of chloride, hydrosulfide, and hydroxo complexes of Ag(I), Cu(I), and Au(I) at temperatures of 25–500°C and pressures of 1–2000 bars. *Geochem. Int*. **2001**, *39*, 990–1006.
5. Akinfiev, N.N.; Zotov, A.V. Thermodynamic description of aqueous species in the system Cu-Ag-Au-S-O-H at temperatures of 0–600°C and pressures of 1–3000 bar. *Geochem. Int.* **2010**, *48 (7)*, 714–720, DOI: 10.1134/S0016702910070074.
6. Shock, E.L.; Sassani, D.C.; Willis, M.; Sverjensky, D.A. Inorganic species in geologic fluids: Correlation among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. *Geochim. Cosmochim. Acta* **1997**, *61*, 907–950. DOI: 10.1016/S0016-7037(96)00339-0.
7. Johnson, J.W.; Oelkers, E.H.; Helgeson, H.C. SUPCRT92: software package for calculating the standard molal thermodynamic properties of mineral, gases, aqueous species, and reactions from 1 to 5000 bars and 0 to 1000°C. *Comput. Geosci.* **1992**, *18*, 899–947. DOI: 10.1016/0098-3004(92)90029-Q.
8. Pokrovskii, V.A.; Helgeson, H.C. Thermodynamic properties of aqueous species and the solubilities of minerals at high pressures and temperatures: the system Al_2O_3-H_2O-NaCl. *Am. J. Sci.* **1995**, *295*, 1255–1342. DOI: 10.2475/ajs.295.10.1255.
9. Diakonov, I.; Pokrovski, G.; Schott, J.; Castet, S.; Gout, R. An experimental and computational study of sodium-aluminum complexing in crustal fluids. *Geochim. Cosmochim. Acta* **1996**, *60*, 197–211. DOI: 10.1016/0016-7037(95)00403-3.
10. Bessinger, B.; Apps, J.A., The hydrothermal chemistry of gold, arsenic, antimony, mercury and silver. Report Number: LBNL-57395. 2003. DOI: 10.2172/840338
11. Shock, E.L.; Helgeson, H. C. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C, *Geochim. Cosmochim. Acta* **1988**, *52*, 2009-2036. DOI: 10.1016/0016-7037(88)90181-0.
12. Reid, R.C.; Prausnitz, J.M.; Sherwood, T.K. *The Properties of Gases and Liquids*. McGraw-Hill Book Company: New York, USA, 1977; pp. 688
13. Yokokawa, H. Tables of thermodynamic properties of inorganic compounds. *J. Nat. Chem. Lab. Indus. Tsukuba Ibaraki., Jap.* **1988**, *83*, 27-118.
14. Holland, T.J.B.; Powell, R. An internally consistent thermodynamic data set for phases of petrological interest. *J. Metamorph. Geol.* **1998**, *16*, 309–343. DOI: 10.1111/j.1525-1314.1998.00140.x.
15. Helgeson, H.C.; Delany, J.M.; Nesbitt, H.W.; Bird, D.K. Summary and critique of the thermodynamic properties of rock-forming minerals. *Am. J. Sci* **1978**, *278A*, 1–229.
16. Naumov, G.B.; Ryzhenko, B.N.; Khodakovsky, I.L. *Handbook of Thermodynamic Data.* U.S. Geol. Surv.WRD-74-001, 1974, pp. 240 (In Russian).
17. Robie, R.A.; Hemingway, B.S. Thermodynamic Properties of Minerals and related Substances at 298.15 K and 1 bar (10^5Pascals) Pressure and at Higher Temperatures. U.S. Geol. Survey Bull. 2131. United States government printing office, Washington, 1995; pp. 456.
18. Tagirov, B.R.; Baranova, N.N.; Zotov, A.V.; Schott, J.; Bannykh, L.N. Experimental determination of the stabilities of Au_2S(cr) at 25°C and $Au(HS)_2^-$ at 25–250°C. *Geochim. Cosmochim. Acta* **2006**, *70*, 3689–3701. DOI: 10.1016/j.gca.2006.05.006.
19. Stefansson, A. Dissolution of primary minerals of basalt in natural waters. I. Calculation of mineral solubilities from 0°C to 350°C, *Chem. Geol*. **2001**, *172*, 225-250. DOI:10.1016/S0009-2541(00)00263-1.
20. Dorogokupets, P.I.; Karpov, I.K. *Thermodynamics of Minerals and Mineral Equilibria*. Novosibirsk: Nauka, Russia, 1984; pp.185 (In Russian).