Hydrogeochemistry of mine, surface and groundwaters from the Sanggok mine creek in the upper Chungju Lake, Republic of Korea

C.H. Lee · H.K. Lee · J.C. Lee

Abstract The Sanggok mine used to be one of the largest lead-zinc mines in the Hwanggangri mining district, Republic of Korea. The present study characterizes the heavy metal contamination in the abandoned Sanggok mine creek on the basis of physico-chemical properties of various kinds of water samples (mine, surface and groundwater). Hydrochemistry of the water samples is characterized by the relatively significant enrichment of Ca^{2+}, HCO_3^-, NO_3^- and Cl^- in the surface and groundwaters, whereas the mine water is relatively enriched in Ca^{2+}, Mg^{2+}, heavy metals, and HCO_3^- and SO_4^{2-}. The more polluted mine water has a lower pH and higher Eh, conductivity and TDS values. The concentrations of some toxic elements (Al, As, Cd, Cu, Fe, Mn, Pb, Se, Sr, Pb and Zn) are tens to hundreds of times higher in the mine water than in the unpolluted surface and groundwaters. However, most immobile toxic pollutants from the mine drainage were quickly removed from the surface water by the precipitation of Al and Fe oxyhydroxides. Geochemical modeling showed that potentially toxic heavy metals might exist largely in the forms of MSO_4^{2-} and M^{2+} in the mine water. These metals in the surface and groundwaters could form M^{2+}, CO_3^{2-} and OH^- complex ions. Computer simulation indicates that the saturation indices of albite, alunite, anhydrite, chlorite, fluorite, gypsum, halloysite and strontianite in the water samples are undersaturated and have progressively evolved toward the saturation condition. However, barite, calcite, chalcedony, dolomite, gibbsite, illite and quartz were in equilibrium, and only clay minerals were supersaturated. Ground and mine waters seemed to be in equilibrium with kaolinite field, but some surface water were in equilibrium with gibbsite and seceded from the stability field of quartz. This indicates that surface water samples in reaction with carbonate rocks would first equilibrate with carbonate minerals, then gibbsite to kaolinite. Investigations on water quality and environmental improvement of the severely polluted Sanggok creek, as well as remediation methods on the possible future pollution of the groundwater by the acid mine drainage from the abandoned metal mines, are urgently required.

Keywords Geochemical modeling · Physicochemical property · Sanggok mine · Water

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Introduction

In southern Korea, poly-metallic base metal mines producing W, Mo, Fe, Sn, Cu, Fe, Pb, Zn and precious ores are distributed almost all over the country and were actively developed until the early 1970s. However, most metal production has declined and most of the mines have closed and/or been abandoned for economic reasons. Upon the closure of the mines, leakage of improperly disposed mineral waste piles and untreated mine drainage have become the most important sources of heavy metals in the nearby environments. Environmental surveys of soil, sediment and various kinds of water (precipitation, mine, surface and groundwater) in the mining district have been recently undertaken.

The Sanggok mine is located ~135 km east-southeast of Seoul within the Hwanggangri mining district in the Ogcheon belt. This belt extends for 350 km across the central part of the southern Korean peninsula as a narrow (40–60 km wide) northeast to southwest sedimentary basin. The basin contains pelitic metasedimentary and carbonate rocks of Paleozoic age that are intruded through Mesozoic igneous rocks. The Hwanggangri mining district contains numerous mineral deposits including at least 60 W-Mo, Cu-Pb-Zn, Au-Ag bearing metallic ores and lesser fluorite and talc deposits.

Previous studies of the Hwanggangri mining district were mostly concerned with petrology, stratigraphy, geological structure and ore mineralization. However, all mines in the district have been closed and abandoned. The Sanggok mine was one of the largest Pb-Zn mines in the belt. The mine had a managed dressing plant, several cross adits, drifts, shafts, an ore dump and a tailing pond. After closure, the mining company left all facilities for mining activities. Therefore, the secondary contaminants have dispersed into the nearby ecosystem.

The Sanggok mine is located at the upper part of Chungju Lake which is the main water source for domestic, agricultural and industrial use. At the upper part of Chungju Lake, about 100 metal mines that once operated in the area have been closed, and a few mines remain in operation. After closure, the mine creeks are exposed to potentially severe pollution from abandoned mine drainage. Acid mine water generated by the oxidation of sulfide minerals reacts with the country rock, resulting in the leaching of many toxic elements (Sullivan and Yelton 1988). Mine drainage contains a relatively high content of Al and heavy metals as well as Fe and SO_4.

This study was set up to characterize the environmental geochemistry and heavy metal contamination at Sanggok mine creek on the basis of physico-chemical properties of mine, surface and groundwaters along the mine drainage. The results of the study will help identify the pollutants from the abandoned metal mine drainage and assess the degree of pollution along the stream pathways. The results can also be used to help improve the ecosystem of the polluted mine creeks, prepare a treatment program for polluted water and prevent the streams from further pollution in the future, and investigate the environmental impact.

Regional and local geology

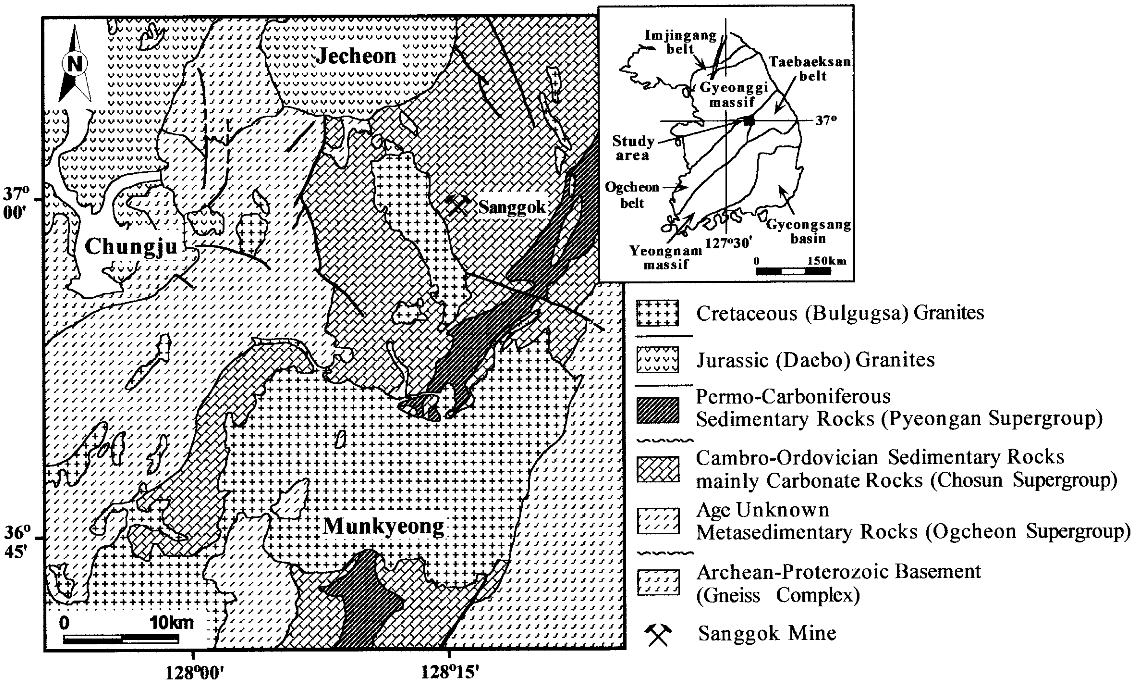
Geological setting

Regional geology and the geological setting of the Hwanggangri mining district within the Ogcheon belt are shown on the simplified geological map in Fig. 1. Three main lithostratigraphic sedimentary units are recognized in the district: the Ogcheon Supergroup, the Chosun Supergroup and the Pyeongan Supergroup. Theses units unconformably overlie Precambrian gneiss complexes of the Gyeonggi and Youngnam massifs, which form the basements of the southern Korean peninsula.

The NE-SW trending Ogcheon belt is divided into two zones: the south-western metamorphic Ogcheon zone and the northeastern non-metamorphic Taebaeksan zone (Fig. 1). The Ogcheon zone is composed of the metasedimentary Ogcheon Supergroup. Its age is unknown. The Taebaeksan zone is composed of the Chosun Supergroup of calcareous sedimentary rocks of Cambro-Ordovician age, and the Pyeongan Supergroup of clastic and coal-type sedimentary rocks of upper Carboniferous to Triassic age.

The geological age of the Ogcheon Supergroup and the stratigraphic relationships between the Ogcheon and Chosun Supergroups are very important for understand-

Fig. 1
Tectonic setting, geology and location in the Hwanggangri mining district, Republic of Korea



ing the tectonic evolution of the Korean Peninsula. The Ogcheon belt is believed to be one of the possible suture zones between the Sino-Korea and Yangtz plates. The age and stratigraphy of the Ogcheon Supergroup still remains unresolved because of the paucity of fossils and the lack of primary structures. Some researchers have considered its age to be late Proterozoic on the basis of tillite occurrence (Reedman and Fletcher 1976; Lee and others 1998). Others have interpreted it to be the lateral equivalent of the Cambro-Ordovician of the Chosun Supergroup based on field evidence and a few fossils (Cluzel and others 1990; Koh and Kim 1995).

The Pyeongan Supergroup of middle Carboniferous to early Triassic age occurs largely in the north-east portion of the Ogcheon belt and was deposited unconformably on pre-Silurian strata after a long hiatus. The Supergroup is mainly composed of terrigenous coal-bearing formations deposited in a cratonic dominant environment with intermittent communication with the oceanic domain. The Pyeongan Supergroup in the Hwanggangri district, however, represents predominantly terrigenous clastic formations.

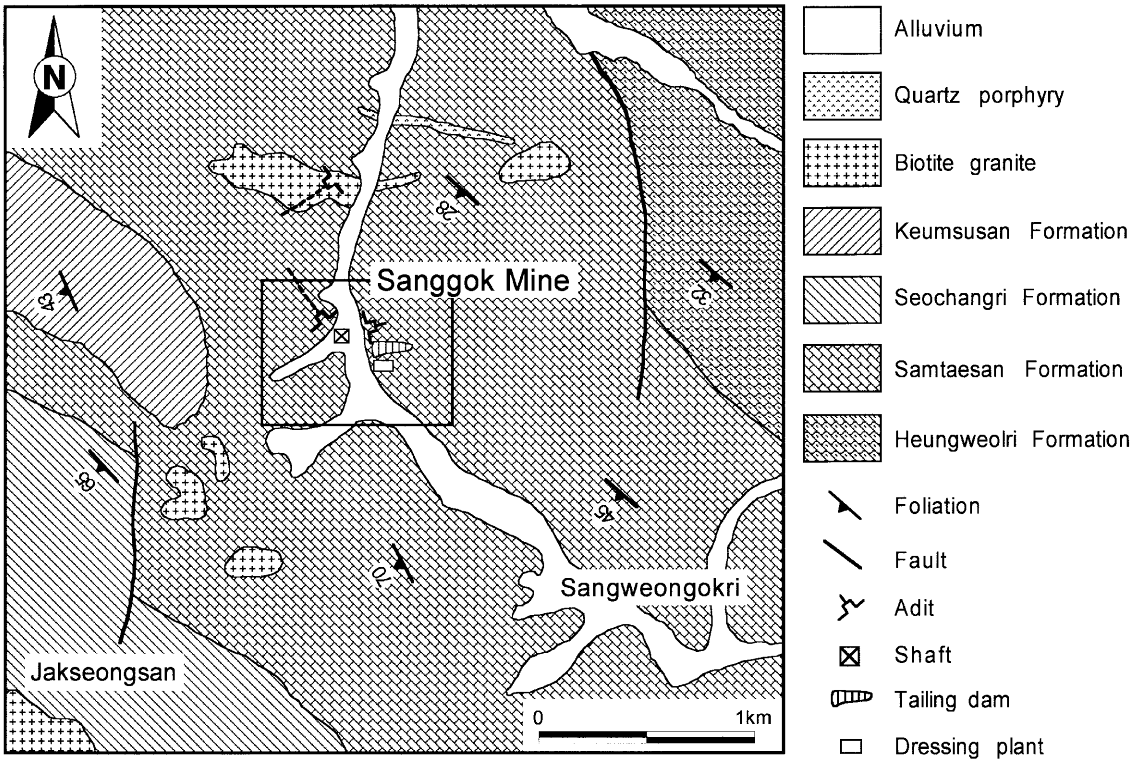
Granitic rocks in the Hwanggangri district intruded all previously described bedrocks that originated from the Jurassic (the Daebo) granites and Cretaceous to early Tertiary (the Bulgugsa) granites (Fig. 1). The Daebo granites in Korea have been considered deeper level intrusions than the Bulgugsa granite. The granites in the Hwanggangri district are the Chungju and Jecheon granites, which form the northeast-trending batholiths. The Wolagsan, Sogrisan, Muamsa and Susan granite and ubiquitous small granitic bodies and dykes belong to the Bulguksa granites. The Muamsa, Susan and Wolagsan granites show a close spatial relationship to metallic mineralization in the Hwanggangri mining district.

Local geology

The geology of the mine area is composed of Cambro-Ordovician sedimentary rocks of the Chosun Supergroup, the clastic metasedimentary rocks of the Ogcheon Supergroup and the late Cretaceous Muamsa granite, as shown in Fig. 2. The sedimentary rocks of the Chosun Supergroup are mainly composed of limestones, lime-silicates and hornfels, which belong to the Samtaesan Formation. The limestones generally strike 10°NW to 50°NW and dip 40 to 80°SW, and have a pale to dark gray color. Silicified limestones occur along the contact with the granite, and are composed of calcite and quartz with minor amounts of sericite, muscovite, biotite and magnetite.

The metasedimentary rocks of an unknown age in the mine area are composed of the Keumsusan Formation and the Seochangri Formation. The Keumsusan Formation (mainly quartzite) disconformably overlies the Samtaesan Formation rocks and was intruded by the Muamsa granite. The Seochangri Formation overlies the Samtaesan Formation rocks and consists of chlorite schist and phyllite. The Muamsa granite forms a small cupola that intrudes the Samtaesan Formation. The granite is typically medium-grained, but its marginal phases are fine-grained with feldspar phenocrysts displaying myrmekitic and per-

Fig. 2
Local geologic map of the Sanggok mine area in the Hwanggangri mining district. The area in the *box* is presented in Fig. 3



thitic textures. More than 60 mineral deposits, including W-Mo, Pb-Zn, Cu, Au-Ag, F and talc ores, are mostly distributed around the Muamsa granite. The granite body has a petrochemical characteristic of a K-rich magnetite series, and I-type granitoids that were highly evolved through fractional crystallization of calc-alkaline magma (So and Yun 1992). The Rb-Sr age of the granite is 83.0 ± 5.0 Ma. Acidic dykes of aplite and quartz porphyry ubiquitously intruded into the Samtaesan Formation. The Sanggok mine extracted minerals from the hydrothermal quartz and carbonate veins that filled the fault-related fissures in the limestone-rich Samtaesan Formation and phyllite-rich Seochangri Formation. The veins are commonly parallel to the strike direction of host rocks and generally strike 30°NW to 40°NW with a nearly vertical dip. Ore bodies occur as pockets and lenses that are 10–15 m wide and 50 m long, and up to 250 m below the land surface. Studies for the mineral deposition of the mine including mineralization, fluid inclusion and stable isotope were reported by Choi and others (1997).

Results and discussions

Occurrence and physico-chemical properties

The Sanggok Pb-Zn mine started operation in the 1920s. It processed up to 200 tons of ore daily from the 1940s to 1950s. The mine ceased operation in 1962 because of destruction by typhoon Sara. The mine had managed several tailing ponds on site without bottom linings during its 40 years of operation. After closing, the mining company left all the tailings in the ponds. A nearby small valley was filled with tailings as well. The tailings consist of fine sand to silty-clays. They have dispersed around the nearby ecosystem in the air as dust particles, along the stream with surface runoff and possibly through the groundwater.

Various kinds of Fe and/or Al compounds have been reported to precipitate from the mine drainage and the stream waters polluted by mining activities. In the mining area and in the vicinity of the tailing ponds, most of the precipitates form very fine particles and amorphous soup in white, yellowish-brown and reddish-brown. They can continuously coat bottom rock, gravel and other sediments, destroy benthic organisms, and can be easily suspended to block the sunlight and interfere with aquatic organic production. The Sanggok mine drainage flows into Chungju Lake ~1.5 km downstream from the mining area.

The acid mine drainage contains relatively high contents of Al and heavy metals as well as Fe and SO_4^{2-}. Some of the elements in mine drainage may be transported as dissolved ions or complexes downstream. Others, especially Fe and Al, may be quickly removed from the water by precipitation as solid phases, depending on the physico-chemical conditions along their migration path (Bigham and others 1990). These precipitates play an important role in the removal of heavy metals by adsorption and coprecipitation (Stumm and Sulzberger 1992).

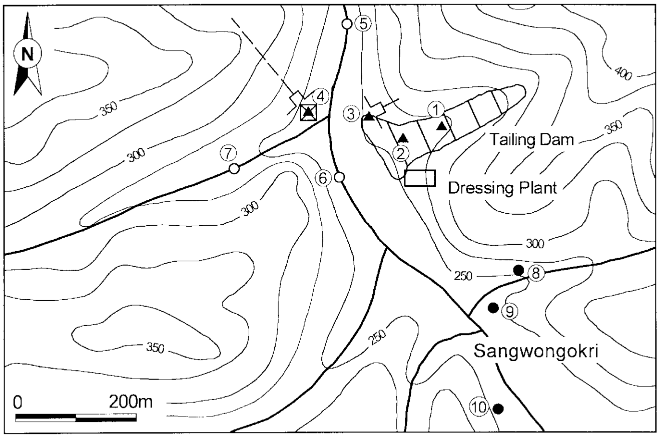


Fig. 3
Sample locations of mine, surface and groundwaters from the Sanggok mine area

Twenty-five samples representing mine, surface and groundwater were collected in 10 locations between February and December in 1998. The sampling locations are shown in Fig. 3. Physical properties of the water samples, such as pH, redox potential (Eh; mV), temperature (T; °C) and electrical conductivity (EC; µS/cm) were measured in situ with portable devices (HANNA Instruments, HI-8314 and HI-8633), which were calibrated by standard solutions.

Measured physicochemical data of the water samples from the Sanggok mine creek are summarized in Tables 1 and 2. Because the depth to groundwater ranges from 15 to 60 m, the groundwater samples represent the shallowly circulated water, which is similar to the local surface waters. The water samples do not show any recognizable physico-chemical change with their sampling time at the same site.

Water samples can be distinctly divided into two main groups based on the pH, Eh and EC conditions: the mine water with pH values between 6.70 to 8.45, and the surface and groundwaters with high pH values between 7.68 to 9.07. These two types of water represent different hydrological and hydrogeochemical processes. The Eh values of the water samples also varied systematically with the water groups, in a general decreasing order from the mine water (–30 mV), through to groundwater (–55 mV) to the surface water (–77 mV). The mine water shows a higher oxidation state.

Figure 4 shows the relationships between the T, EC and Eh against pH for all three types of water. The mine water has the lowest pH, and the highest Eh and EC values. The surface water has the highest pH and the lowest Eh and EC values. Some mine water samples have very-high EC values ranging from 20,200 to 35,300 µS/cm. The pH-T relationships of water samples show a very heterogeneous pattern. The pH and Eh of the mine water samples are nearly neutral to slightly alkaline. However, their average EC (12,170 µS/cm) is very high compared with that of surface water (368 µS/cm) and groundwater (257 µS/cm).

Table 1
Selected physical and anion constituents of mine, surface and groundwaters from the Sanggok mine creek area. *nd* Not detected; *na* not analyzed

No.	Sample descriptions	Sampling date	pH	T (°C)	Eh (mV)	EC (μS/cm)	HCO_3^- (mg/l)	NO_2^- (mg/l)	NO_3^- (mg/l)	PO_4^{3-} (mg/l)	SO_4^{2-} (mg/l)	Br^- (mg/l)	Cl^- (mg/l)	F^- (mg/l)	TDS[a] (mg/l)
SG-1	Mine water from the tailing dam	30/5/98	6.70	23.7	5	35,300	205.943	nd	0.308	nd	1713.900	0.033	2.316	0.120	2579.777
		21/8/98	7.16	20.7	–5	25,200	51.867	nd	0.918	nd	1377.070	0.023	1.488	0.166	2032.219
SG-2	Mine water near the dressing plant	21/8/98	6.95	19.8	9	20,200	259.335	0.021	0.144	nd	968.936	nd	1.847	0.058	1696.499
SG-3	Mine water from the old adit	23/2/98	7.84	6.3	–48	1060	171.472	nd	0.621	nd	409.160	nd	0.015	0.050	859.260
		30/5/98	8.49	13.1	–78	1692	244.080	nd	1.228	nd	534.600	0.017	2.097	0.154	1088.748
		21/8/98	7.87	15.0	–50	967	210.519	nd	0.771	nd	309.390	0.016	1.777	0.074	721.333
		7/12/98	8.04	7.2	–47	773	225.774	nd	2.202	nd	495.969	na	2.236	0.222	967.398
SG-4	Surface water near the main shaft and adit	23/2/98	7.91	6.9	–49	473	146.580	nd	2.280	nd	84.324	nd	1.495	0.051	349.732
		30/5/98	8.42	19.1	–77	451	189.111	0.024	5.452	nd	18.539	nd	1.560	0.034	290.698
		21/8/98	8.10	21.3	–61	340	167.703	0.024	2.258	nd	26.959	nd	1.202	0.043	261.098
SG-5	Surface water of the mining creek	23/2/98	8.16	7.3	–86	370	274.592	nd	9.470	nd	14.220	nd	4.235	0.049	374.954
		30/5/98	9.07	19.7	–108	410	279.167	nd	10.865	nd	12.879	0.012	5.809	0.024	381.735
		21/8/98	8.30	22.1	–80	375	211.739	0.064	7.191	nd	9.502	nd	2.518	0.056	302.689
		7/12/98	8.64	5.7	–74	300	243.470	nd	9.039	nd	10.329	na	2.067	0.070	345.003
SG-6	Surface water of the mining creek	23/2/98	8.72	7.5	–87	373	177.333	nd	9.106	nd	19.426	nd	3.719	0.028	280.539
		30/5/98	8.69	19.5	–90	439	216.621	0.041	7.360	nd	26.322	nd	4.654	0.077	333.578
		21/8/98	8.20	21.2	–73	389	206.858	0.020	6.785	nd	21.015	nd	2.359	0.063	313.362
		7/12/98	8.54	5.7	–69	320	241.639	nd	7.886	nd	20.656	na	3.978	0.086	355.739
SG-7	Surface water from the mountain valley	23/2/98	8.61	7.2	–81	325	149.479	nd	11.651	nd	11.295	nd	11.651	0.034	258.525
		30/5/98	8.34	19.0	–74	376	192.213	0.115	10.656	nd	20.969	nd	3.460	0.101	304.997
		21/8/98	8.10	18.4	–72	333	189.772	nd	4.605	nd	10.311	nd	1.309	0.053	277.582
		7/12/98	8.71	6.1	–77	263	202.892	nd	8.285	nd	12.025	na	4.114	0.078	299.745
SG-8	Groundwater near the mining area	7/12/98	8.45	6.4	–65	240	181.229	nd	6.234	nd	14.022	na	1.902	0.053	270.302
SG-9	Groundwater near the mining area	7/12/98	7.68	12.8	–31	425	259.335	nd	13.875	nd	176.970	na	9.171	0.128	585.850
SG-10	Groundwater of the non-mining area	7/12/98	8.52	9.4	–69	106	68.648	nd	4.741	nd	4.434	na	1.753	0.067	109.388
Mean-1 (mean value of the mine waters)			7.58	15.1	–30	12,170	159.570	0.003	0.885	nd	829.861	0.013	1.682	0.121	1406.551
Mean-2 (mean value of the surface waters)			8.43	13.8	–77	369	205.945	0.019	7.526	nd	21.251	0.001	3.690	0.056	315.416
Mean-3 (mean value of the groundwaters)			8.22	9.5	–55	257	169.737	nd	8.283	nd	65.142	na	4.275	0.083	321.846

[a] Total dissolved solids

The relationship between Eh and pH data showed that Eh decreases with an increase in pH. Although it is intrinsically difficult to measure accurate redox potential in the field (Stumm and Morgan 1981), this relationship may indicate the progressive reduction of Fe^{2+} with deeper circulation and an associated pH increase. Because there is no clear relationship between redox potential and iron concentration, the iron contents in the waters are possibly controlled by organic compounds.

As indicated by the Sanggok mine, the observed pH-Eh, pH-EC values of the mine water are likely to reflect the effects of mixing of acid-sulfate mine water with general carbonate-type water. Oxidation of sulfide minerals in the sulfide ores of the Sanggok mine formed the low-pH, high-Eh and high-EC mine water with rich dissolved solids (Bass Becking and others 1960; Xian and Shokohifard 1989). This concept is further supported by the fact that typical carbonate type water occurs at distant sites from the mines.

Hydrogeochemistry

Samples for chemical analyses were filtered through a 0.45-μm pore-size nitrate cellulose membrane filter by a hand-vacuum pump. Alkalinity of the water was measured in situ using a standard titration method immediately after sampling. Samples for cation analyses were acidified to $pH < 2.0$ by adding a few drops of 50% ultrapure HNO_3. Collected water samples were transferred to the laboratories in high-density 500-ml polypropylene bottles, and tightly sealed with a double cap, and then stored in a refrigerator.

Major dissolved ionic constituents in the waters were analyzed at the Center for Mineral Resources Research in Korea University, and Central Research Facilities of Chungnam National University in Korea. Concentrations of major cations were measured with an inductively coupled plasma atomic emission spectrometer (ICP-AES; Perkin Elmer, Optima 3000) and mass spectrometer (ICP-MS; Perkin Elmer, Elan 6000). Major anions were measured using ion chromatography (IC; Dionex 120). A rigorous quality control was implemented, which included reagent blank, duplicate samples and certified reference materials (Ramsey and others 1987).

Hydrochemical compositions of the water samples were plotted in trilinear equivalence diagrams (Fig. 5). Cation contents in the samples were similar. Generally, the mine water was characterized by rich Mg^{2+}, whereas the surface and groundwaters were enriched in Ca^{2+}. In terms

Table 2
Selected cation constituents (mg/l) of mine, surface and groundwaters from the Sanggok mine creek area. *nd* Not detected; *na* not analyzed; *Mean-1* mean value of the mine waters; *Mean-2* mean value of the surface waters; *Mean-3* mean value of the groundwaters

No.	Sampling date	Al	As	Ba^{2+}	Ca^{2+}	Cd	Co	Cr	Cu	Fe	K^+	Li	Mg^{2+}	Mn	Na^+	Ni	Pb	Se	Si	Sr	U	Zn
SG-1	30/5/98	0.167	0.021	1.258	474.851	nd	nd	nd	0.037	nd	10.942	0.002	148.454	9.919	5.778	nd	0.019	0.001	3.825	1.655	0.004	0.224
	21/8/98	0.082	0.025	0.708	348.461	0.024	0.016	nd	0.014	nd	5.088	0.012	84.866	145.855	3.188	0.104	0.023	0.204	6.446	0.854	0.041	6.676
SG-2	21/8/98	0.010	0.133	nd	366.983	0.001	0.005	nd	nd	7.282	6.192	0.006	53.217	23.534	4.251	nd	0.013	0.092	3.605	0.754	0.052	0.028
SG-3	23/2/98	0.001	nd	na	236.176	0.001	0.001	nd	0.011	0.007	2.200	na	26.510	0.049	4.846	0.005	nd	0.100	5.022	na	Nd	0.013
	30/5/98	0.186	0.016	2.537	246.721	nd	nd	nd	0.007	0.154	3.305	0.002	42.486	0.048	4.946	nd	0.029	0.001	5.139	0.828	0.003	0.164
	21/8/98	0.012	0.008	nd	165.372	nd	nd	nd	nd	nd	1.897	0.007	22.722	0.037	3.787	nd	0.005	0.043	4.333	0.494	0.045	0.024
	7/12/98	0.004	0.011	0.041	197.711	nd	nd	nd	nd	nd	2.442	nd	29.561	nd	5.306	nd	nd	nd	5.127	0.783	0.009	nd
SG-4	23/2/98	0.003	nd	na	102.335	0.001	nd	0.001	0.004	0.010	0.953	na	6.622	0.027	2.183	0.004	nd	0.024	2.630	na	nd	0.205
	30/5/98	3.215	0.031	2.589	60.898	nd	nd	nd	0.013	0.144	0.562	0.001	4.156	0.239	0.281	nd	0.024	0.001	3.436	0.147	0.001	0.240
	21/8/98	0.019	0.003	0.113	53.372	nd	nd	nd	nd	nd	0.291	0.006	4.142	0.612	1.543	nd	nd	0.007	2.443	0.122	0.042	0.194
SG-5	23/2/98	0.010	nd	na	56.137	0.001	0.001	nd	0.003	0.013	1.061	na	11.486	0.004	1.831	0.004	nd	0.044	1.772	na	nd	0.021
	30/5/98	0.178	0.018	2.547	52.513	nd	nd	nd	0.003	0.007	1.589	0.001	12.241	0.010	2.131	nd	0.019	0.001	1.448	0.121	0.001	0.151
	21/8/98	0.016	nd	1.059	53.143	nd	nd	nd	nd	nd	1.080	0.006	11.406	0.001	1.803	nd	0.002	0.019	2.920	0.110	0.013	0.041
	7/12/98	0.006	nd	0.013	61.069	nd	nd	nd	nd	nd	1.334	nd	13.513	nd	2.559	nd	nd	nd	1.588	0.122	0.004	nd
SG-6	23/2/98	0.007	nd	na	62.725	0.001	nd	0.001	0.003	0.006	0.695	na	2.062	0.002	1.757	0.005	0.001	0.006	3.646	na	nd	0.010
	30/5/98	0.949	0.019	2.438	60.646	nd	nd	nd	0.004	0.056	1.268	0.001	8.057	0.083	2.540	nd	0.024	0.001	2.216	0.144	0.001	0.056
	21/8/98	0.019	0.002	1.099	58.934	nd	nd	nd	nd	nd	1.067	0.006	10.603	0.078	1.804	nd	0.002	0.016	2.860	0.119	0.001	0.016
	7/12/98	nd	nd	0.013	63.117	nd	nd	nd	nd	nd	1.280	nd	12.793	nd	2.483	nd	nd	nd	1.659	0.131	nd	0.018
SG-7	23/2/98	0.004	nd	na	58.953	0.001	nd	nd	0.001	0.008	1.025	na	10.761	0.004	1.829	0.005	nd	0.040	1.772	na	nd	0.012
	30/5/98	0.204	0.021	3.095	64.780	nd	nd	nd	0.003	nd	1.024	0.001	2.133	0.001	2.459	nd	0.020	0.001	3.476	0.144	0.001	0.120
	21/8/98	0.015	nd	0.850	62.578	nd	nd	nd	nd	nd	0.636	0.006	1.981	nd	1.809	nd	0.002	nd	3.477	0.122	0.031	0.025
	7/12/98	nd	nd	0.010	64.644	nd	nd	nd	nd	nd	0.739	nd	2.142	nd	1.805	nd	nd	nd	2.880	0.131	nd	nd
SG-8	7/12/98	0.003	0.004	0.003	58.872	nd	nd	nd	nd	nd	0.315	nd	2.512	nd	2.009	nd	nd	nd	2.962	0.177	0.005	nd
SG-9	7/12/98	0.002	0.001	0.021	95.327	nd	nd	nd	nd	nd	7.966	nd	11.486	nd	7.425	nd	nd	nd	3.927	0.205	0.011	nd
SG-10	7/12/98	nd	nd	0.003	21.154	nd	nd	nd	nd	nd	0.608	nd	1.744	nd	1.516	nd	nd	nd	4.650	0.043	nd	0.027
Mean-1		0.066	0.031	0.649	290.869	0.004	0.003	nd	0.010	1.063	4.581	0.004	58.259	25.635	4.586	0.016	0.013	0.050	4.785	0.767	0.022	1.018
Mean-2		0.310	0.006	0.922	62.390	0.001	nd	nd	0.002	0.016	0.974	0.002	7.606	0.071	1.921	0.001	0.006	0.011	2.548	0.141	0.007	0.074
Mean-3		0.002	0.002	0.009	58.451	nd	nd	nd	nd	nd	2.963	nd	5.247	nd	3.650	nd	nd	nd	3.846	0.142	0.005	0.009

of anion content, the mine water was typically enriched in SO_4^{2-}, whereas the surface and groundwaters were enriched in carbonates ion (HCO_3^-). Some surface and groundwaters showed the transitional area having intermediate anion compositions between the two groups of water. Typical mine water belongs to the ($Mg^{2+}+Ca^{2+}$)-SO_4^{2-} type, whereas the peripheral surface and groundwaters have the characteristics of the ($Ca^{2+}+Mg^{2+}$)-HCO_3^- type.

Chemical composition and total dissolved solids (TDS) data of the water samples are also shown in Tables 1 and 2. The TDS values of the mine water ranged widely from 721.333 to 2579.777 mg/l (mean = 1406.551). The groundwater showed higher degrees of TDS (mean = 321.846 mg/l) than the surface water TDS (mean = 315.416 mg/l), whereas their ranges are similar. This also indicates that these three types of water have undergone different geochemical evolutionary paths during their circulation.

All of the water samples have high alkalinity. The HCO_3^- content of mine water is 159.570 mg/l, surface water 205.945 mg/l and groundwater 169.737 mg/l. However, they show different hydrochemical features. The decreasing orders of the absolute abundances of major ions in mine water are $SO_4^{2-}>HCO_3^->Cl^->NO_3^->F^-$ and $Ca^{2+}>Mg^{2+}>Mn^{2+}>Si>Na^+=K^+$. The surface and groundwaters have similar patterns and they are $HCO_3^->SO_4^{2-}>NO_3^->F^-$ and $Ca^{2+}>Mg^{2+}>Si>Na^+>K^+$.

The concentrations of typical major ions in waters are plotted with respect to pH conditions (Fig. 6). Major ion contents tend to increase with the decrease of pH, whereas $HCO_3^-+Cl^-$ showed nearly positive correlations with increase of pH, indicating progressively larger degrees of dissolution of the host rock compositions. In Fig. 7, the correlation between HCO_3^-/Σ anions and pH is positive, and the values of K^+/Na^+ follow the same pattern with the increase in TDS contents. However, the relationships between HCO_3^-/SiO_2 and EC, Na^+/Na^++Ca^{2+} and TDS are negative. This is because of the continuous dilution effects of the surface waters by the addition of sporadic precipitation waters (Gibbs 1970).

Based on these observed hydrochemical characteristics, along with major mineral constituents in rocks and ores, it is suggested that the mine water evolved largely through preferential dissolution of sulfide and carbonate minerals with a lesser degrees of silicate minerals. Because of the very high alkalinity, white- and brown-colored materials caused by Al and/or Fe oxyhydroxide minerals were precipitated. A simple comparison between the chemical compositions of the surface and groundwaters and their catchment rocks indicate that the bedrock types control the chemical characteristics of the surface waters. However, more objective and convincing evidence to relate water chemistry to geology are needed for geostatistical analyses.

Water-rock interaction and saturation index

The mine waters are typically enriched not only in sulfate and carbonate anions, but also in most cations, as shown in Tables 1 and 2. With reference to the present situation, the probable sources of sulfate and heavy metals are the oxidation of sulfide minerals (mainly pyrite) in the sur-

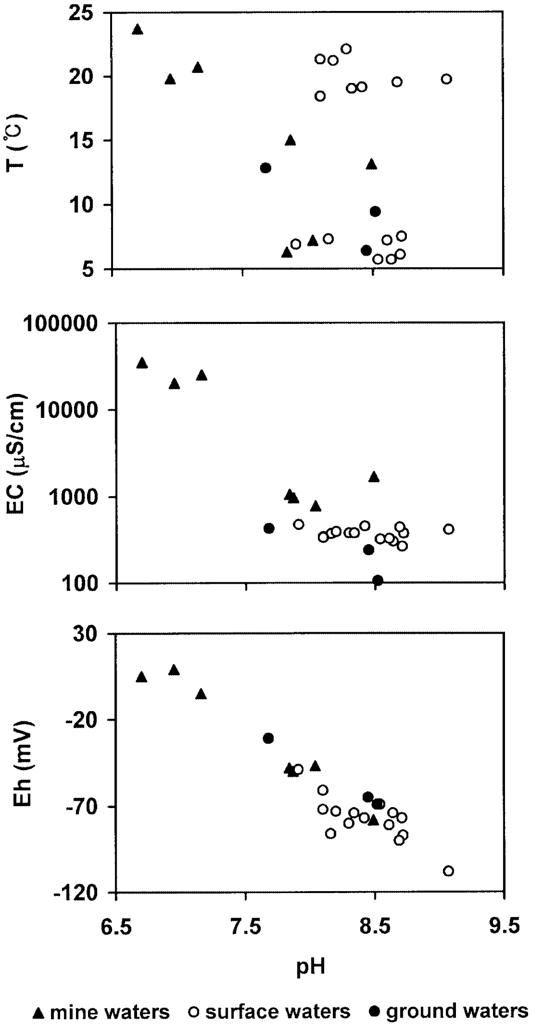


Fig. 4
Plot of correlation between temperature, electrical conductivity (EC) and redox potential (Eh) versus pH mine, surface and groundwaters from the Sanggok mine area

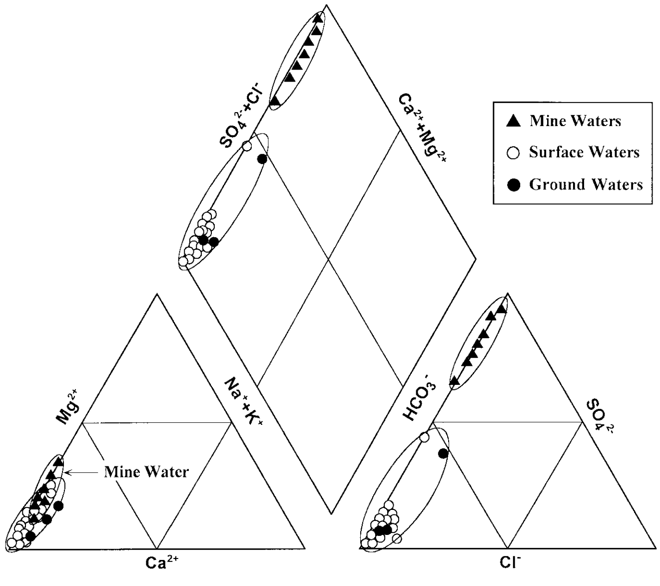


Fig. 5
Trilinear diagram showing some major chemical compositions of mine, surface and groundwaters from the Sanggok mine area

rounding ore veins and tailing piles. These cases and solutions prepare the latter explanation because pyrite oxidation would effectively form sulfate-rich acidic water that would be subsequently capable of reacting intensively with carbonates and silicates.

The measured major concentrations of Ca^{2+} and Mg^{2+} are relatively high in mine water in comparison with the surface and groundwater. At high pH, Ca^{2+} and Mg^{2+} are usually transferred to a solid phase, therefore, their concentrations are controlled by mineral precipitation. It is interesting that the contents of the dissolved carbonates in the mine waters are relatively high, regardless of the pH and concentration of sulfates. This indicates the saturation state of the waters with respect to each of the mineral species.

Hydrochemical modeling of the water samples was performed using the aqueous speciation program WATEQ4F (Ball and Nordstrom 1991) to eliminate the reactions that are thermodynamically invalid. Table 3 shows the calculations for the degree on the saturation index (SI) of the water with respect to various specified minerals. Within uncertainties of ±1 in log K values, it is clear that the water samples in the Sanggok area are undersaturated with respect to most silicate minerals. The SI calculation of the representative minerals in waters (Fig. 8) show that mine waters are under and/or supersaturated, whereas most carbonate and clay minerals are nearly in an equilibrium state. The saturation state was retarded with the decrease of TDS caused by the increase in surface water interaction.

The increase in Ca^{2+} and Mg^{2+} concentrations from surface and/or groundwater to mine water may be a result of the dissolution of calcite and dolomite, which is the main composition of the bedrocks. Saturation indices of these minerals show the nearly equilibria states. However, water samples in the area are undersaturated with albite, which implies that albite is not the source of Ca^{2+} and Na^+. The increase in K^+ and Na^+ concentration in mine water can be explained mostly by the enrichment of mine materials contained in the bedrocks. The stability diagram (Fig. 9) indicate that kaolinite can be a stable source of K and Na minerals.

The concentrations of Si and Al decrease with an increase in pH. The dissolved Si^{4+} and Al^{3+} that originate from the hydrolysis of alumino-silicate minerals are derived from the bedrocks and the vein materials. Therefore, chalcedony might control Si^{4+} concentrations of the waters because the saturation index of chalcedony and quartz are in a equilibrium state in all the samples. Saturation indices of alunite, anhydrite, chlorite and halloysite in the water samples are undersaturated, but have evolved towards an equilibrium because of the fresh sur-

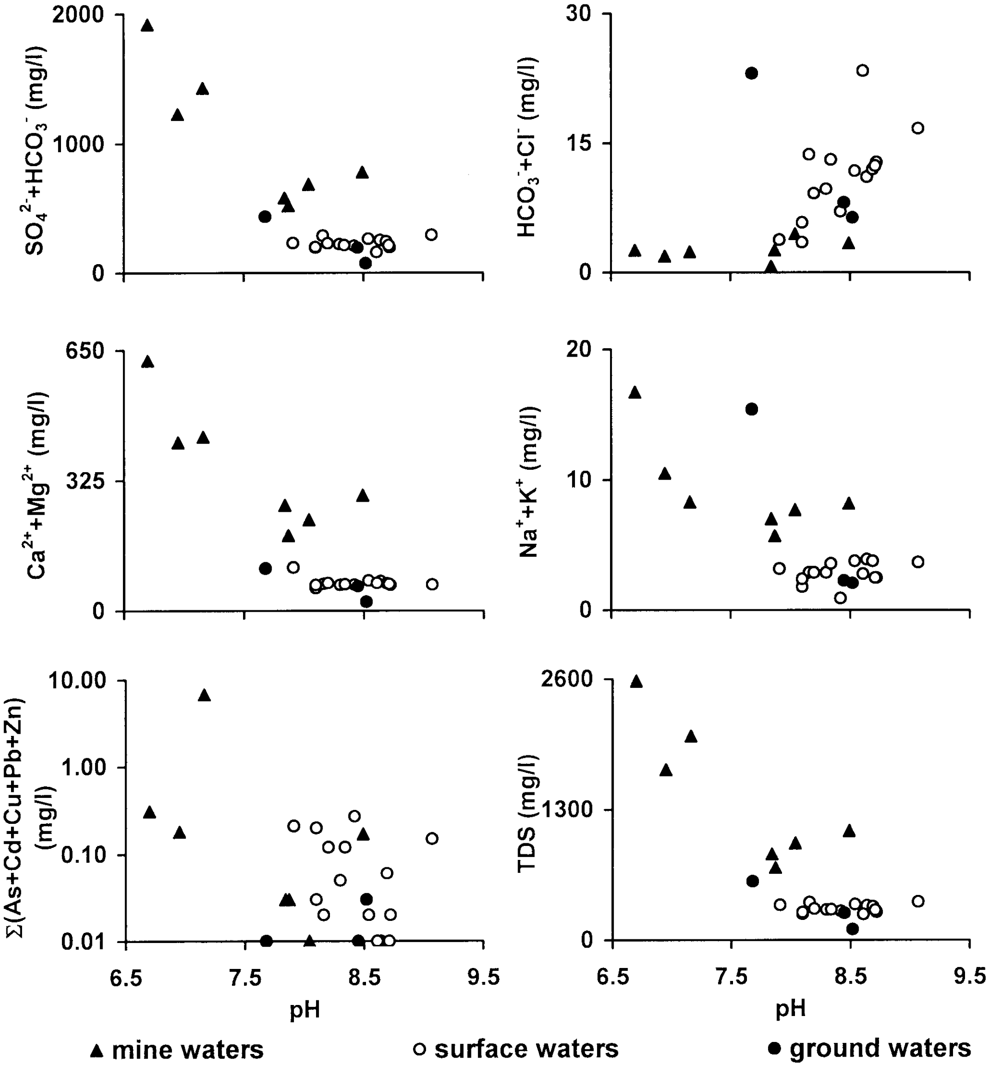


Fig. 6
Plot of correlation between contents of some major elements versus pH for mine, surface and groundwaters from the Sanggok mine area

face water mixing. Barite, gibbsite and illite are nearly in equilibrium. Most clay minerals are supersaturated.

The chemical compositions of the water samples in the Sanggok area are plotted in the mineral stability diagram for the systems of CaO-, K_2O-, MgO- and $Na_2O–Al_2O_3–SiO_2–H_2O$ at 25 °C (Fig. 9). Groundwater and mine water seem to be equilibrated with the kaolinite field, indicating that silica and aluminum are largely conserved by the formation of kaolinite through incongruent dissolution of silicate minerals. However, some samples of the surface water are equilibrated with gibbsite and seceded from the stability field of quartz and amorphous silica.

Surface water in a reaction path with carbonate rocks would first equilibrate with carbonate minerals, then with gibbsite and finally with kaolinite. In the kaolinite field, the evolutionary path is accompanied with an increasing silica concentration. Figure 9 shows that the simulation of the evolutionary path of the water samples is valid and reasonable, even though the complexities of natural processes in the mine area could not be duplicated.

Assessment of contamination

The surface water and groundwater are a major source of agricultural irrigation, domestic and/or drinking waters in this area. Some trace elements in water samples were analyzed to identify the existing contaminants. Tables 1 and 2 show the concentrations of potentially contaminants such as SO_4^{2-}, NO_3^-, Cl^- and total ions of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, U and Zn. The concentrations of the most toxic elements were below the detection limits. All mine water, and some surface and groundwater that are polluted by mining activities have concentrations higher than fresh water standards. However, toxic heavy metals (As, Cd, Cu, Pb and Zn) seem to be similar. Arsenic is likely to be controlled by a different chemistry from Cd, Mn and Zn (Pierce and Moore 1980). Multiple correlation study of the elements shows that most toxic metals are correlated with each other within 92% of the confidence level, implying that their occurrences are closely related. Several researchers have also reported that heavy metals might be in very low concentrations in waters because of the adsorption

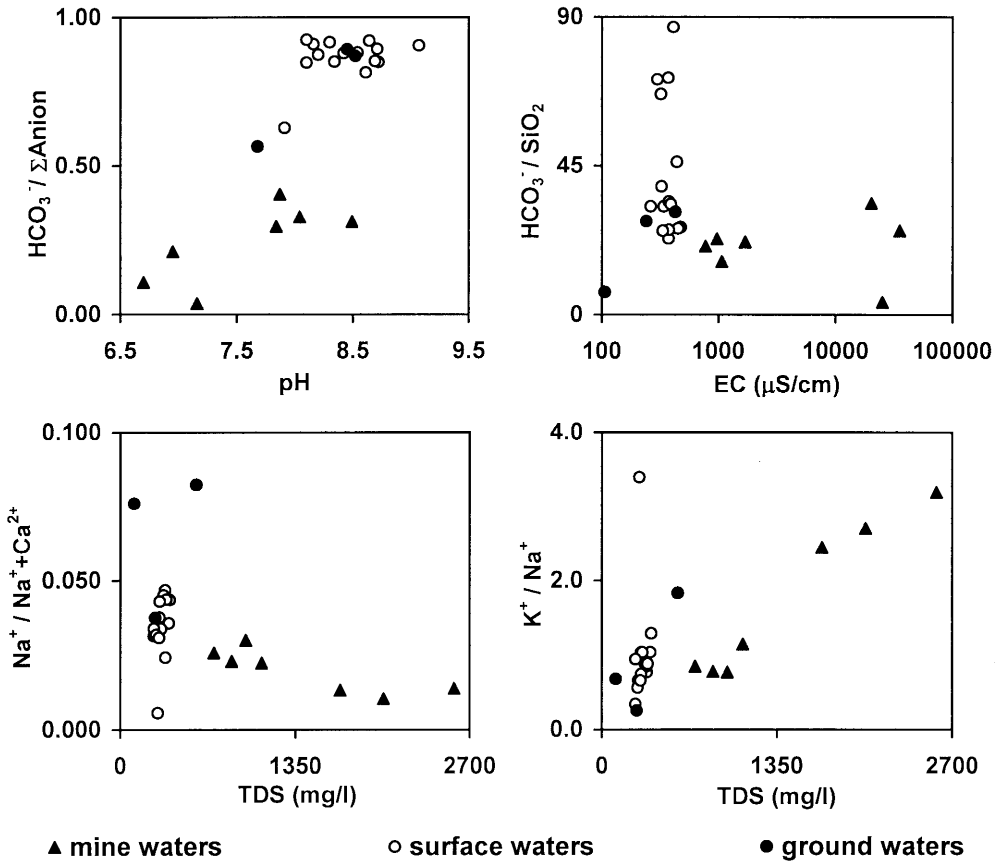


Fig. 7
Plot of correlation between some ratios of major elements versus pH, electrical conductivity (*EC*) and total dissolved solids (*TDS*) for mine, surface and groundwaters from the Sanggok mine area

Table 3
Selected saturation indices of mineral species for mine, surface and groundwaters from the Sanggok mine creek area. *nc* Not calculated; *Mean-1* mean value of the mine waters; *Mean-2* mean value of the surface waters; *Mean-3* mean value of the groundwaters

No.	Sampling date	Albite	Alunite	Anhydrite	Barite	Calcite	Chalcedony	Chlorite	Dolomite	Fluorite	Gibbsite	Gypsum	Halloysite	Illite	Kaolinite	Mica	Pyrophyllite	Quartz	Smectite	Strontianite	Zeolite
SG-1	30/5/98	–2.584	5.063	–0.338	1.999	–0.179	–0.293	–5.701	–0.547	–2.522	2.519	–0.114	1.060	3.604	6.138	10.680	8.682	0.140	4.669	–2.176	2.242
	21/8/98	–2.185	1.851	–0.471	1.804	–0.448	–0.033	–3.288	–1.224	–2.223	1.987	–0.236	0.487	3.501	5.600	9.962	8.221	0.410	4.484	–2.580	3.083
SG-2	21/8/98	–3.689	0.273	–0.549	nc	0.103	–0.274	–8.506	–0.355	–3.034	1.303	–0.311	–1.371	0.856	3.752	7.059	5.765	0.171	1.938	–2.102	0.395
SG-3	23/2/98	–3.200	–6.084	–0.911	nc	0.541	0.036	nc	0.193	–2.980	0.191	–0.655	–3.112	nc	2.177	nc	nc	0.527	nc	nc	0.394
	30/5/98	–1.414	–4.269	–0.851	2.345	1.383	–0.053	5.680	2.188	–2.156	1.440	–0.601	–0.722	3.353	4.482	9.325	5.893	0.414	3.471	–0.562	4.168
	21/8/98	–3.026	–5.083	–1.144	nc	0.669	–0.142	–2.586	0.686	–2.902	0.776	–0.895	–2.208	0.679	2.972	6.243	4.505	0.391	1.401	–1.346	1.230
	7/12/98	–2.600	–5.426	–0.914	0.694	0.773	0.031	–2.946	0.802	–1.808	0.544	–0.658	–2.404	0.862	2.874	6.233	3.497	0.519	1.448	–1.062	1.434
SG-4	23/2/98	–3.922	–6.635	–1.733	nc	0.332	–0.255	–7.730	–0.461	–3.171	0.583	–1.476	–2.902	–0.563	2.380	4.969	2.379	0.234	0.414	nc	–0.057
	30/5/98	–2.297	–4.565	–2.584	1.270	0.917	–0.305	4.032	0.945	–3.879	2.466	–2.308	0.887	4.224	6.019	10.925	7.859	0.134	4.925	–1.211	4.951
	21/8/98	–4.359	–9.701	–2.420	0.041	0.559	–0.473	–3.032	0.311	–3.751	0.448	–2.187	–3.465	–1.492	1.640	3.788	3.470	–0.033	–0.484	–1.609	–0.347
SG-5	23/8/98	–4.016	–8.051	–2.704	nc	0.628	–0.435	–3.811	0.637	–3.442	0.840	–2.447	–2.743	–0.219	2.534	5.510	2.241	0.053	0.404	nc	8.387
	30/5/98	–3.987	–12.138	–2.368	1.069	1.558	–0.735	7.681	2.790	–4.330	0.528	–2.599	–3.844	–0.584	1.280	5.019	2.346	–0.290	–0.971	–0.599	0.551
	21/8/98	–4.197	–11.658	–2.901	0.534	0.849	–0.409	0.945	1.348	–3.558	0.133	–2.670	–3.960	–1.309	1.136	3.814	3.213	0.029	–0.910	–1.363	–0.295
	7/12/98	–4.289	–11.430	–2.813	–1.017	1.039	–0.518	–0.679	1.466	–3.079	0.229	–2.557	–4.149	–1.348	1.148	3.982	0.421	–0.025	–1.188	–1.076	–0.628
SG-6	23/2/98	–3.291	–11.780	–2.500	nc	1.033	–0.136	–2.372	0.662	–3.861	0.119	–2.243	–3.587	–0.504	1.687	4.627	2.024	0.351	0.015	nc	0.959
	30/5/98	–2.507	–7.217	–2.429	1.361	1.216	–0.512	5.933	1.842	–3.208	1.645	–2.190	–1.166	2.192	3.960	8.467	5.443	–0.066	2.340	–0.914	3.012
	21/8/98	–4.086	–10.049	–2.523	0.892	0.779	–0.405	0.012	1.118	–3.404	0.341	–2.290	–3.545	–0.944	1.562	4.343	3.513	0.036	–0.444	–1.440	–0.044
	7/12/98	nc	nc	–2.502	–0.730	0.954	–0.448	nc	1.256	–2.888	nc	–2.246	nc	nc	nc	nc	nc	0.045	nc	–1.148	nc
SG-7	23/2/98	–4.427	–12.110	–2.764	nc	0.830	–0.442	–1.111	0.992	–3.719	0.002	–2.508	–4.436	–1.691	0.842	3.410	0.517	0.046	–1.425	nc	–0.755
	30/5/98	–2.523	–7.296	–2.472	1.392	0.887	–0.296	–0.467	0.565	–2.906	1.353	–2.232	–1.322	1.688	3.810	7.792	5.651	0.153	2.341	–1.278	2.620
	21/8/98	–3.681	–9.945	–2.778	0.562	0.642	–0.266	–4.791	0.048	–3.458	0.490	–2.536	–2.995	–0.595	2.145	4.841	3.953	0.184	0.351	–1.579	0.502
	7/12/98	nc	nc	–2.696	–1.048	1.071	–0.219	nc	0.714	–2.939	nc	–2.439	nc	nc	nc	nc	nc	0.272	nc	–1.041	nc
SG-8	7/12/98	–3.770	–11.640	–2.653	–1.501	0.757	–0.204	–5.221	0.205	–3.306	0.082	–2.396	–3.808	–1.327	1.480	3.687	1.498	0.286	–0.430	–1.192	–0.003
SG-9	7/12/98	–3.472	–5.535	–1.515	0.070	0.360	–0.156	–7.412	–0.026	–2.558	0.308	–1.262	–3.194	–0.381	2.013	5.210	3.172	0.313	0.135	–1.784	–0.444
SG-10	7/12/98	nc	nc	–3.480	–1.941	0.074	–0.050	nc	–0.826	–3.515	nc	–3.224	nc	nc	nc	nc	nc	0.430	nc	–2.071	nc
Mean-1		–2.671	–1.954	–0.610	1.583	0.406	–0.104	–2.893	0.252	–2.375	1.251	–0.496	–1.181	2.143	3.999	8.250	6.094	0.367	2.902	–1.638	1.849
Mean-2		–3.660	–8.550	–2.546	–0.393	0.886	–0.390	–0.415	0.950	–3.440	0.706	–2.328	–2.864	–0.088	2.319	5.499	3.310	0.097	0.450	–1.102	1.450
Mean-3		–3.621	–8.588	–2.549	–1.124	0.397	–0.137	–6.317	–0.216	–3.126	0.195	–2.294	–3.501	–0.854	1.747	4.449	2.335	0.343	–0.148	–1.682	–0.224

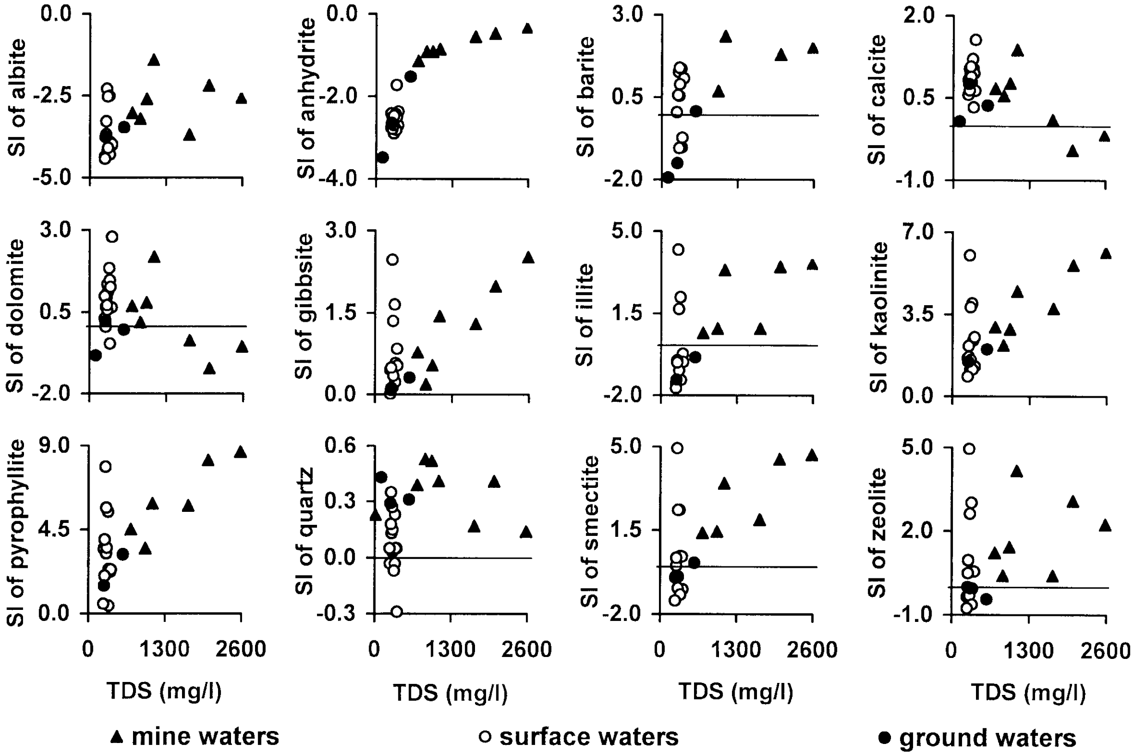


Fig. 8
Plot of calculated saturation indices (*SI*) of some minerals species versus total dissolved solids (*TDS*) for mine, surface and groundwaters from the Sanggok mine area

by iron hydroxide or coprecipitation and combination with sulfide in reduced bottom mud (Pierce and Moore 1980; Masscheleyen and others 1991).

Other contaminants of surface and groundwater in the Sanggok creek were NO_3^- and Cl^-. As shown in Table 1, the NO_3^- concentrations of the water samples were mostly below the drinking water standard of 10 mg/l, except for some samples with ~11 mg/l. These waters varied with seasonal change and random distribution. This implies that nitrates are different from the metal contaminants in their sources, such as domestic sewage, agricultural chemicals, fertilizer and/or livestock manure.

Geochemical modeling (Ball and Nordstrom 1991) showed that potentially toxic heavy metals might exist largely in the form of MSO_4^{2-} and M^{2+} in the mine water. These metals could be formed from M^{2+}, CO_3^{2-} and OH^- complex ions. Arsenic may exist as aqueous anions of H_3AsO_3 and/or H_2AsO_4 species in the mine water. And, Al exists as species of Al, AlF, AlF_2, $AlSO_4$ and $Al(SO_4)_2$, which are evolved from forms of $Al(OH)_2$ and $Al(OH)_4$ in the surface and groundwater because of fresh water mixing.

Water types can be grouped according to the shape of Stiff diagrams. This pattern is useful in making a rapid visual comparison between waters from different sources. Hounslow (1995) showed various Stiff's patterns in which the water originated from various rocks. In the Sanggok area, waters could be identified as mine, surface and groundwaters (Fig. 10). The larger the area of the polygonal shapes, the greater the concentrations of the various ions. Therefore, the waters in the area are significantly affected by the local conditions. Some water samples exhibit seasonal variations with similar compositions, indicating the origin of induced recharge of precipitation waters.

Figure 11 schematically shows the variations of representative physicochemical properties (Σ anion, TDS, pH and EC) in the water samples. The value of EC, Σ anion and TDS contents in the mine water are extremely high, compared with the surface and groundwater. They increased significantly at the influx points of the abandoned mine drainage, and gently decrease as the water moves out of the downstream area. However, they do not reduce to the local background values.

This indicates that most of the toxic heavy metals have relatively low mobilities and are quickly removed with total toxic elements from the water. The neutral to slightly alkaline pH and relatively high contents of $Ca^{2+} + Mg^{2+}$ in the mine drainage is probably the result of neutralization of the water with carbonate minerals, mainly comprising the limestone in the basement rocks. Wiggering (1993), and Webb and Sasowsky (1994) have discussed the importance of carbonate minerals in buffering acid mine drainage and the control over pH.

Although dilution by fresh water inflow from the tributaries contributes to the decrease in the pollutant contents in the Sanggok creek, the abrupt decrease in total dissolved ions may be a result of their removal through

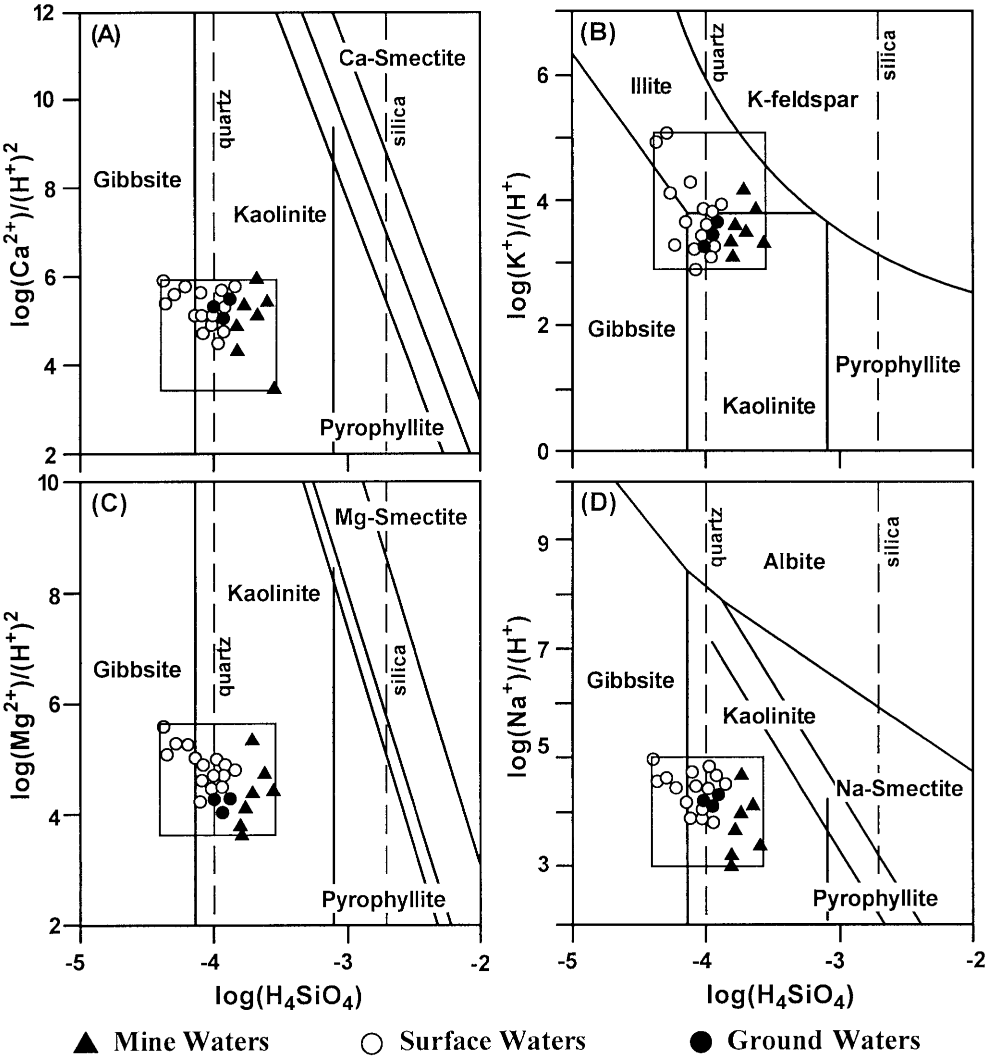


Fig. 9
Diagrams showing stability fields in the systems **A** CaO- , **B** K_2O- , **C** MgO- and **D** Na_2O-Al_2O_3-SiO_2-H_2O for mine, surface and groundwaters from the Sanggok mine area. The boundaries between kaolinite, smectite, quartz and amorphous silica saturation lines are from Helgeson (1969) and Nesbitt (1977)

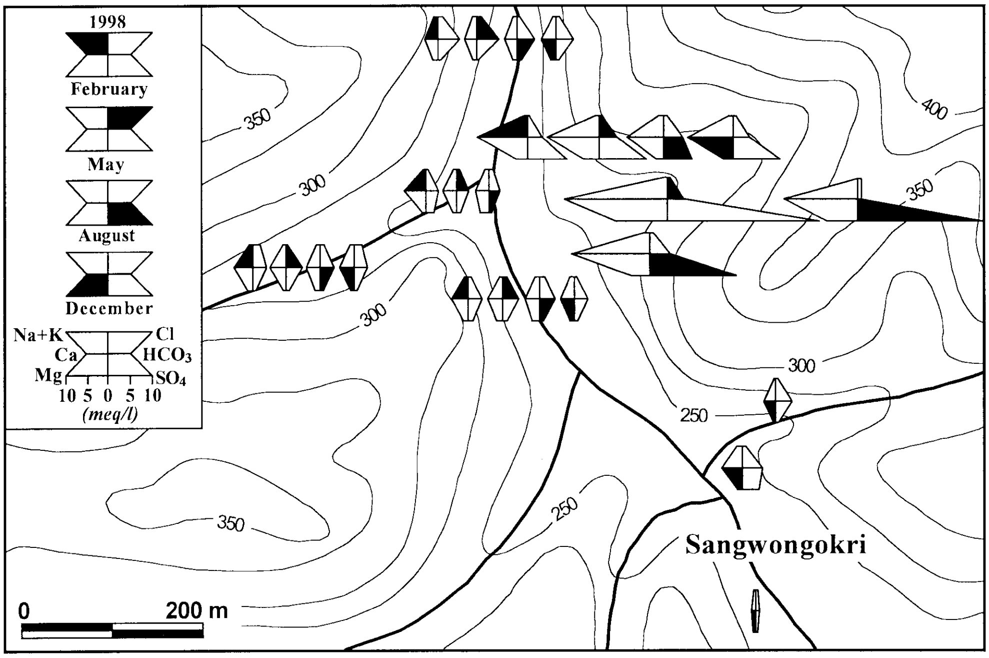


Fig. 10
Map showing Stiff's patterns of major chemical compositions for mine, surface and groundwaters from the Sanggok mine creek

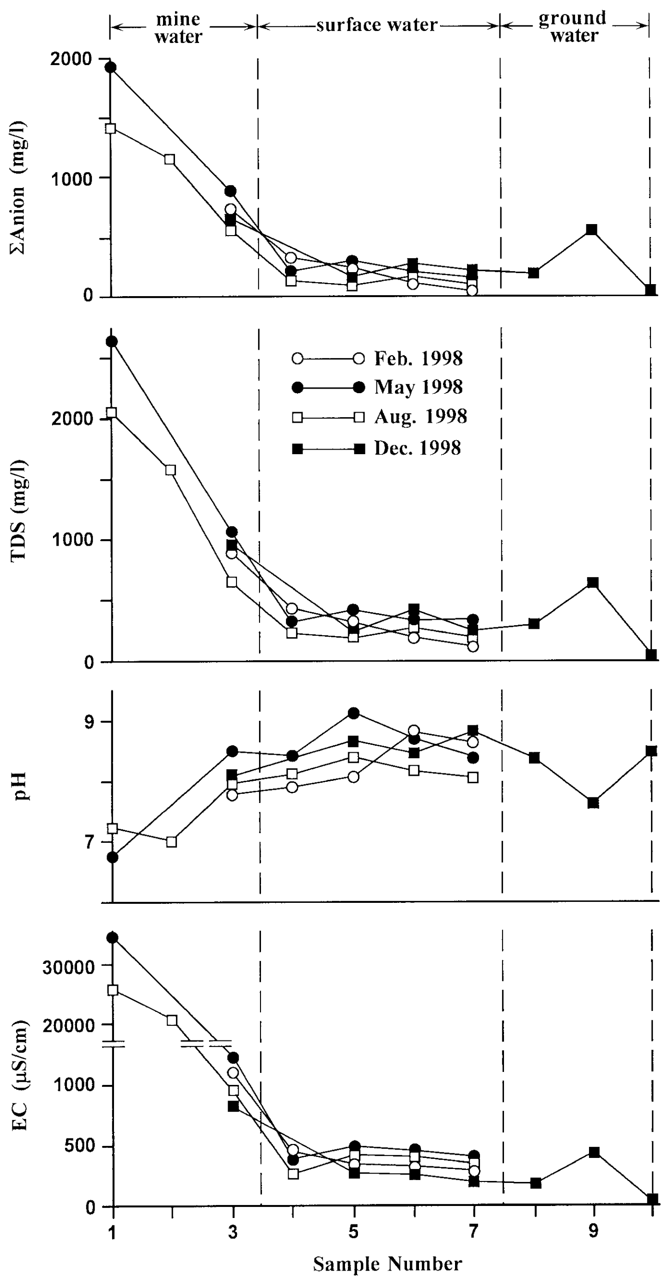


Fig. 11
Variations of the major physicochemical properties for mine, surface and groundwaters from the Sanggok mine creek

the fast precipitation of Al and/or Fe compounds (Anderson and Benjamin 1985; Nordstrom and Ball 1986). The brown to reddish-brown and sometimes white precipitates are easily observed on the Sanggok creek, especially around the influx points of the abandoned mine drainage. The forms of fixed and mobile species of heavy metal contamination, the controlling factor of those speciation in terms of pH and redox condition, and suggestions for the proper management of contamination materials in the area need to be studied.

Conclusions

The hydrochemistry of the water samples are characterized by the relatively significant enrichment of Ca^{2+}, alkaline ions, HCO$_3^-$, NO$_3^-$ and Cl$^-$ in ground and surface water, whereas the mine water is relatively enriched in Ca^{2+}, Mg^{2+}, heavy metals, and HCO$_3^-$ and SO$_4^{2-}$. The typical mine waters belong to the (Mg^{2+}+Ca^{2+})-SO$_4^{2-}$ type, whereas the peripheral surface and groundwaters have the characteristics of the (Ca^{2+}+Mg^{2+})-HCO$_3^-$ type. The pH and Eh of the water samples are nearly neutral to slightly alkaline. The average EC (12,170 μS/cm) and TDS (1406.551 mg/l) of the mine water are very high, compared with those of surface water (369 μS/cm, 315.416 mg/l) and groundwater (257 μS/cm, 321.846 mg/l). Computer simulation indicates that albite, alunite, anhydrite, chlorite, fluorite, gypsum, halloysite and strontianite in the waters are undersaturated and progressively evolving towards the saturation condition. Barite, calcite, chalcedony, dolomite, gibbsite, illite and quartz are near equilibrium, and mostly clay minerals are supersaturated. Groundwater and mine water seem to be equilibrated with the kaolinite field. Some surface water are equilibrated with gibbsite and seceded from the stability field of quartz. This suggests that surface water in a reaction path with carbonate rocks would first equilibrate with carbonate minerals, then with gibbsite and kaolinite.
The concentrations of some toxic elements (Al, As, Cd, Cu, Fe, Mn, Pb, Se, Sr, Pb and Zn) are tens to hundreds of times higher in the mine water than in the unpolluted surface and groundwaters. However, most immobile toxic pollutants from the mine drainage are quickly removed from the surface water by the precipitation of Al and Fe oxyhydroxides. Geochemical modeling showed that potential toxic heavy metals might exist largely in the forms of MSO$_4^{2-}$ and M^{2+} in mine water. These metals of the ground and surface water could be formed of M^{2+}, CO$_3^{2-}$ and OH$^-$ complex ions.

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