3-6 Metallic Minerals in the Paraná Flood Basalts

A trace of native copper is often found in the Paraná basin flood basalts. Particularly, Paranapanema-Ribeira frequently forms amygdaloidal texture, and flaky native copper often exists in pore-space and fracture. Although quite rare, native copper has been found in other types of rocks in the lava group. Native copper is considered to be a secondary mineral because of its shape. It is very difficult to identify sulfide minerals in the lavas with the naked eye. On the other hand, many samples attest to the existence of pyrite in intrusions.

In this survey, we examined some representative samples (Table II-3-6-1) that contained native copper and pyrite under a microscope and conducted EPMA test in order to identify sulfide minerals contained and their chemical compositions.

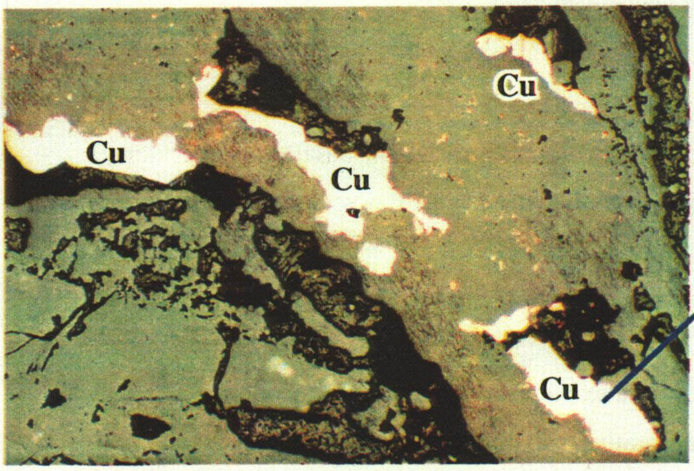
Table II-3-6-1 Samples for microscopic observation and EPMA test

Sample No.	Sample description
KN22C	Paranapanema-Ribeira type basalt, native copper visible
KN033	Paranapanema-Ribeira type basalt, native copper visible
KN35B	Gabbroic sill from the Ponta Grossa Arch, pyrite dissemination
NK047	Pitanga type basalt, small native copper visible
AT03-486 (2 samples)	Hanging wall black shale of the northeast sill of Lomba Grande, native copper visible

The microscopic images and back scattered electron images are shown in Fig. II-3-6-1 to Fig. II-3-6-4. Examination of all samples with microscope has found that the metallic minerals contained were native copper, pyrite, pyrrhotite, chalcopyrite, and iron titanium oxide minerals such as magnetite. Any minerals containing nickel or cobalt could not be found. Observation of back scattered electron images was done for the entire surface of all samples. The observation did not find any other minerals besides the ones that had been identified. Under ordinary circumstances, the heavier the contained element, the brighter the images become. The brightest image was one of barite.

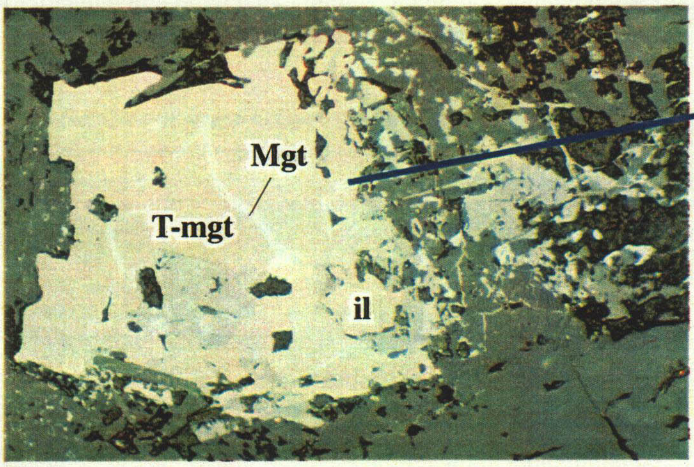
We made chemical analysis on native copper and sulfide minerals identified under the microscope. The instruments used for the measurement were an electron microscope, JEOL5400, and Link System model, QX2000 (energy dispersion system). The acceleration voltage was 15kV and the electrical current for irradiation was 1nA. The diameter of the beam

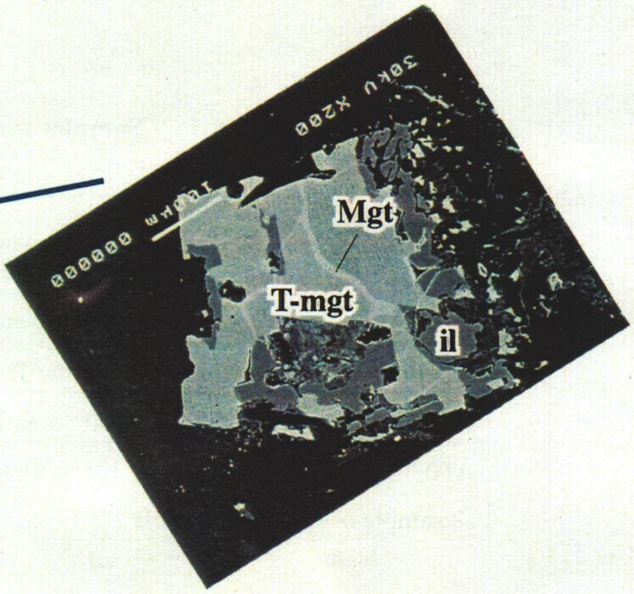
KN022C



Cu:native copper

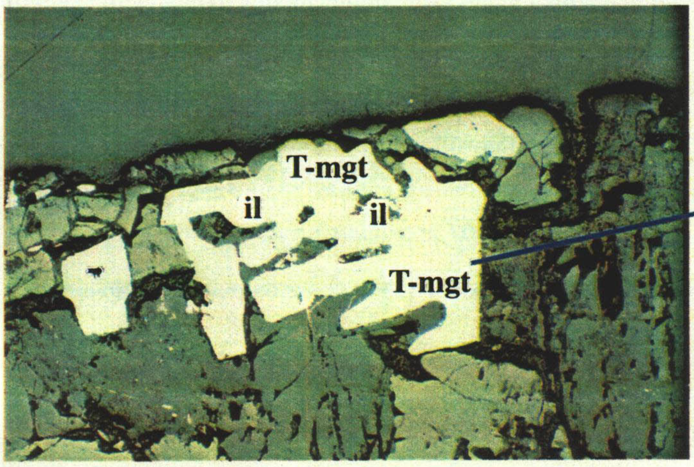
KN022C

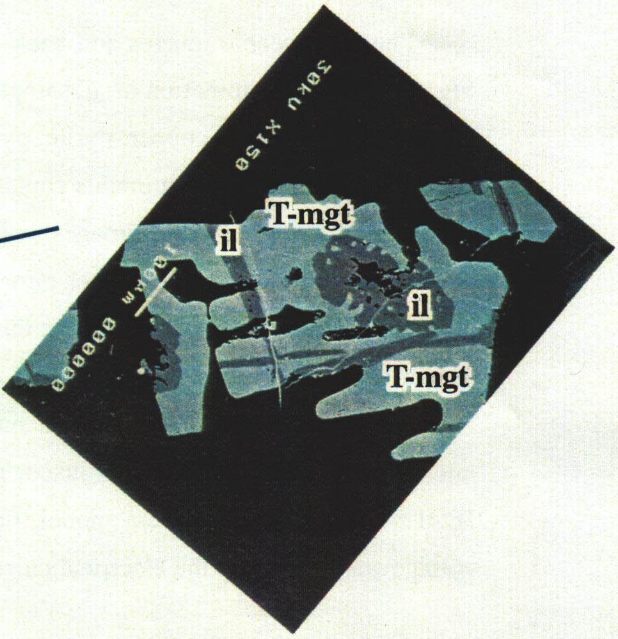




Mgt:magnetite, T-mgt: Ti rich magnetite, il:ilmenite

KN022C

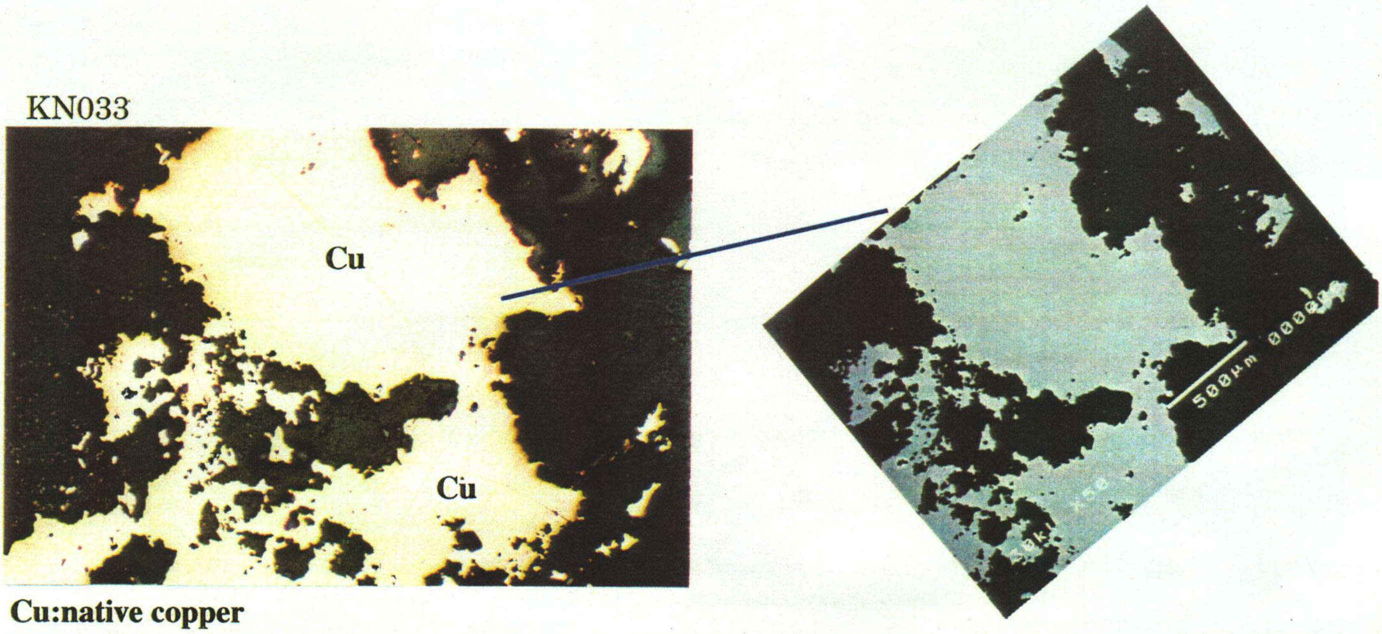




T-mgt: Ti rich magnetite, il:ilmenite

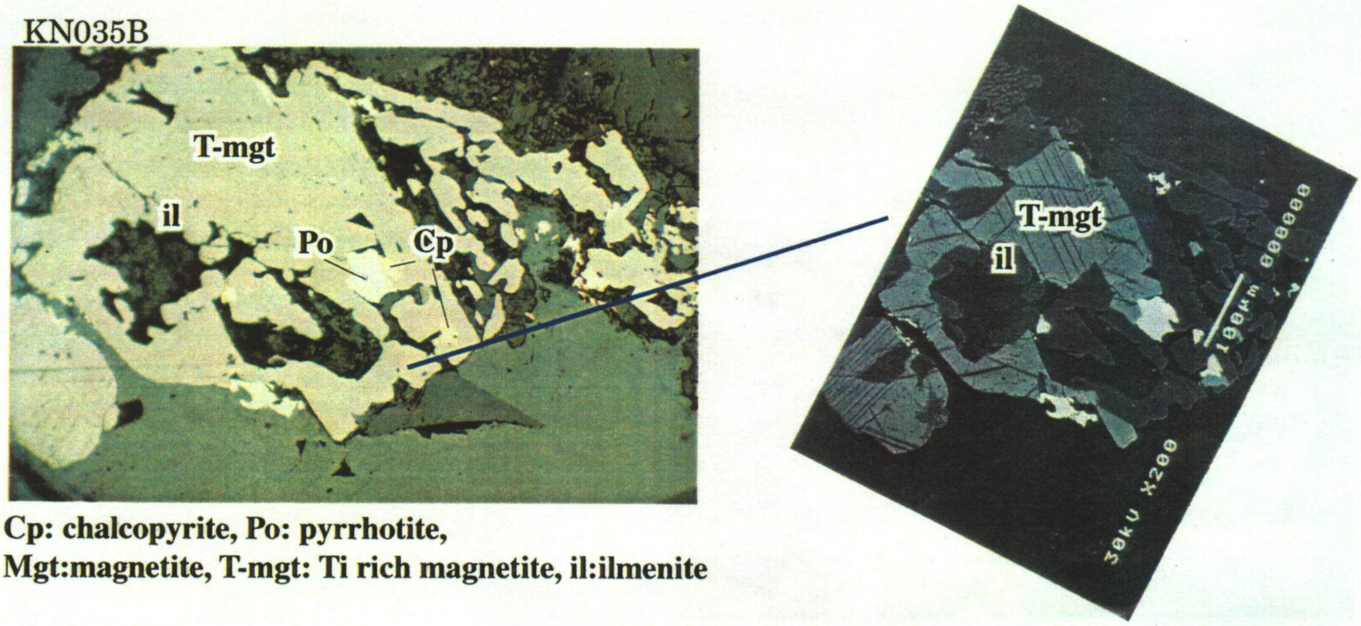
Fig. II-3-6-1 Microscopic and backscattered electron images (KN022C)

KN033



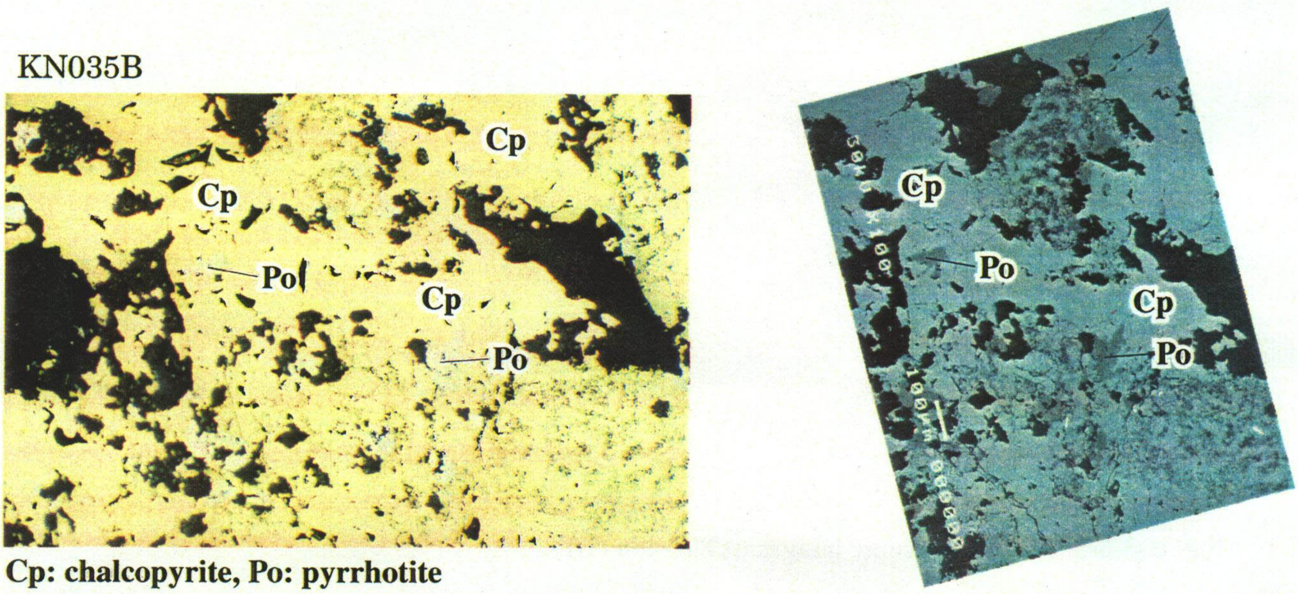
Cu:native copper

KN035B



Cp: chalcopyrite, Po: pyrrhotite,
Mgt:magnetite, T-mgt: Ti rich magnetite, il:ilmenite

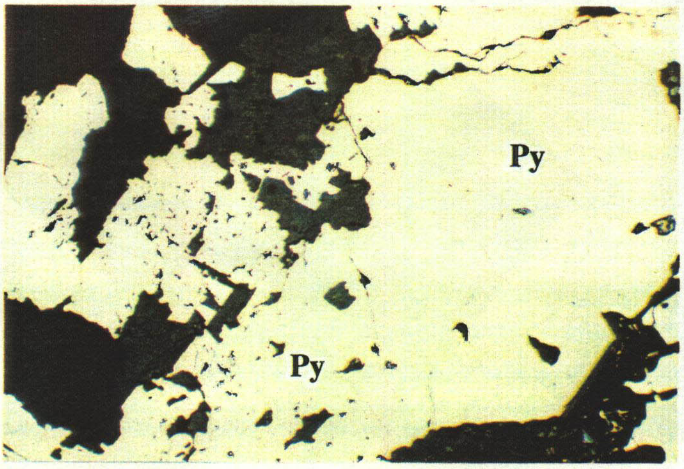
KN035B



Cp: chalcopyrite, Po: pyrrhotite

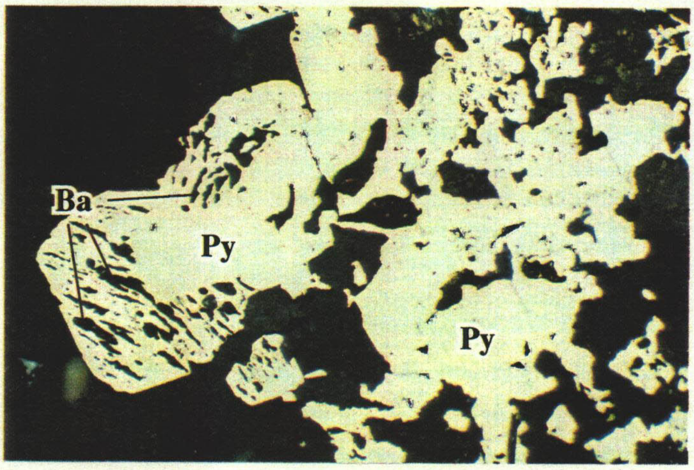
Fig. II-3-6-2 Microscopic and backscattered electron images (KN033, KN035B)

AT03-486



Py: pyrite

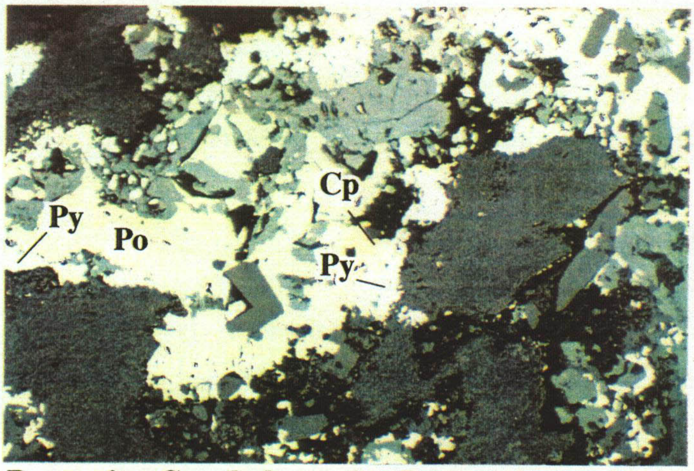
AT03-486



Py: pyrite, Ba: barite

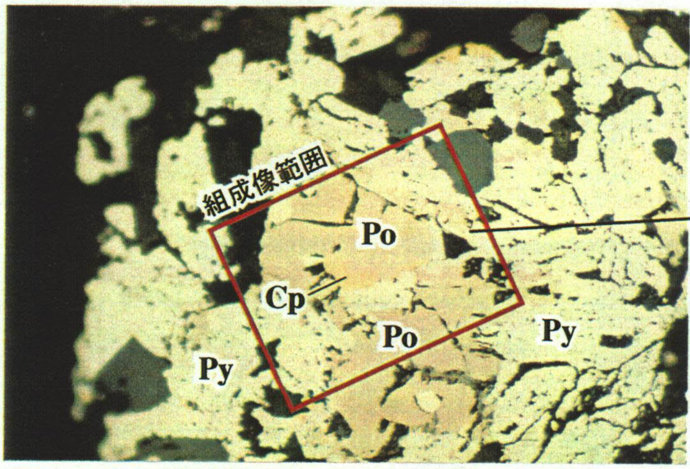
Fig. II-3-6-3 Microscopic images (AT03-486 (1))

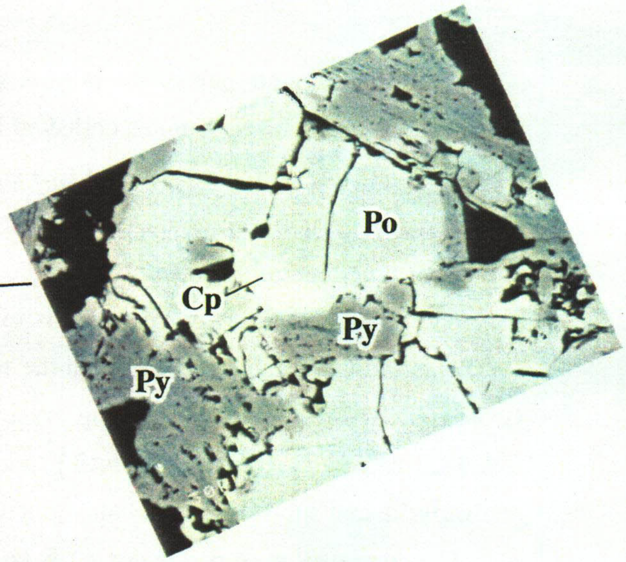
AT03-486



Py: pyrite, Cp: chalcopyrite, Po: pyrrhotite

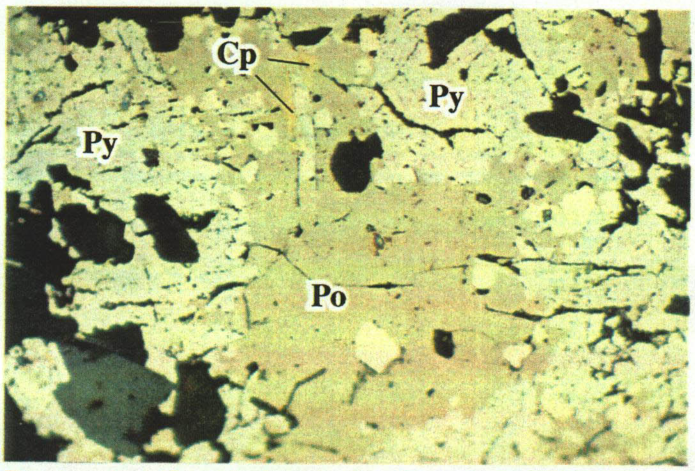
AT03-486

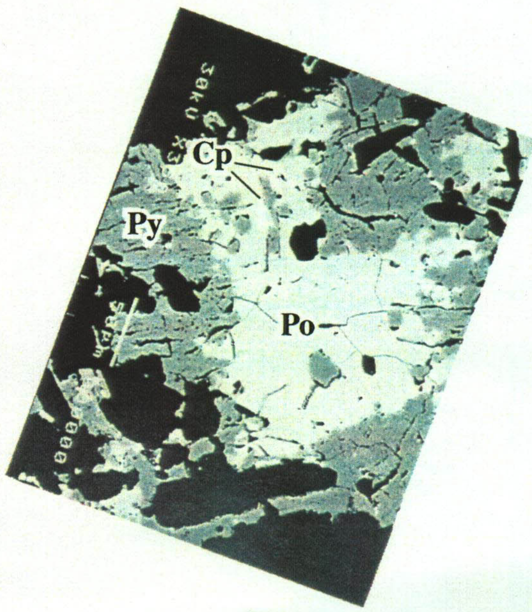




Py: pyrite, Cp: chalcopyrite, Po: pyrrhotite

AT03-486





Py: pyrite, Cp: chalcopyrite, Po: pyrrhotite

Fig. II-3-6-4 Microscopic and backscattered electron images (AT03-486 (2))

was 3-4 nm, and the duration of the measurement was 80 seconds. We conducted a quantitative analysis on native copper and sulfide minerals for the following 10 elements: Fe, Cu, Cr, Ni, Au, Pt, Pd, Zn, Mn, and S. The analytical value thus derived was revised using ZAF correction. The result of the analysis is shown in Table II-3-6-2.

The back scattered electron images of native copper and its quantitative analysis found that it had homogeneous composition and that it had a trace of Ni, Fe and S on the rim of its crystal.

Sulfide minerals (pyrite, chalcopyrite, and pyrrhotite) do not contain impurities and their composition is extremely homogeneous. AS for AT03-486, chalcopyrite, pyrite, and pyrrhotite were found. Also in this sample, a trace of Au was found in the chalcopyrite and barite was found in a worm-eaten manner in the pyrite.

CPRM, the counterpart of the present survey, conducted the observation of back scattered electron images on seven samples collected in the present survey. Sample KN038 of the Ponta Grossa Arch detected the presence of two gold fragments of 10 to 60 microns. Up to now, the presence of gold in the flood basalts has been reported only in pan concentrated sample. This is the first time that gold fragments could be confirmed in rock sample.

The result of the chemical analysis on native copper and sulfide minerals using EPMA (WDS) is shown in Table II-3-6-3. In the samples AS010 and KN038 collected from the Ponta Grossa Arch, chalcopyrite containing crystal inclusion of Co-As mineral (As: 40.3-42.1 wt%, Co: 13.5-23.5 wt%, Ni: 5.6-8.9 wt%), and sphalerite were found. Furthermore in AS010, chalcopyrite and spots of Pb (probably galena) were found by EDS spectrum.

The composition of native copper is homogeneous with no impurities. However, some of these have a cuprite (Cu_2O) and a tenorite (CuO) rim, as an oxidation product.

Table II-3-6-2 EPMA test for intrusive rocks

Sample No.	Mineral	weight % element Fe	Cu	Cr	Ni	Au	Pt	Pd	Zn	Mn	S	Total	number of atoms per formula unit Fe	Cu	Cr	Ni	Au	Pt	Pd	Zn	Mn	S	TOTAL
KN022C	native copper		99.90									99.90		1.000									1.0000
	native copper		100.10									100.10		1.000									1.0000
	native copper		99.49		0.47							99.96		0.995		0.005							1.0000
	native copper		99.22									99.22		1.000									1.0000
	native copper		99.55									99.55		1.000									1.0000
	native copper	0.59	98.81								0.14	99.54	0.007	0.990								0.003	1.0000
	native copper		99.51									99.51		1.000									1.0000
	native copper	1.60	97.91								0.16	99.67	0.018	0.979								0.003	1.0000
	native copper		100.04									100.04		1.000									1.0000
	native copper		100.12									100.12		1.000									1.0000
	native copper		99.92									99.92		1.000									1.0000
	native copper	0.26	99.47								0.21	99.95	0.003	0.993								0.004	1.0000
	native copper		100.29									100.29		1.000									1.000
	native copper		99.46								0.23	99.69		0.995								0.005	1.000
	native copper		100.37									100.37		1.000									1.000
	native copper		98.94								0.23	99.17		0.995								0.005	1.000
KN033	native copper		100.03									100.03		1.000									1.000
	native copper		98.95		0.41							99.37		0.996		0.004							1.000
	native copper		100.02									100.02		1.000									1.000
	native copper		99.93									99.93		1.000									1.000
	native copper		100.15									100.15		1.000									1.000
	native copper		99.86									99.86		1.000									1.000
KN035B	chalcopyrite	31.43	33.79								35.19	100.41	0.257	0.243								0.501	1.000
	chalcopyrite	31.59	33.58								34.96	100.13	0.259	0.242								0.499	1.000
	chalcopyrite	30.46	33.40								35.17	99.02	0.252	0.242								0.506	1.000
	chalcopyrite	30.90	33.94								35.09	99.93	0.254	0.245								0.502	1.000
	chalcopyrite	30.70	33.87								35.39	99.95	0.251	0.244								0.505	1.000
	chalcopyrite	30.45	34.55								34.93	99.93	0.250	0.250								0.500	1.000
	chalcopyrite	30.81	33.82								35.09	99.72	0.253	0.244								0.502	1.000
	pyrrhotite(5C:Fe_9S_{10})	61.33									38.88	100.21	0.475									0.525	1.000
	chalcopyrite+pyrrhotite	33.75	28.87								35.69	98.31	0.278	0.209								0.513	1.000
	pyrrhotite(4C:Fe_7S_8)	60.08									39.22	99.30	0.468									0.532	1.000
	chalcopyrite	31.20	32.70								34.90	98.80	0.258	0.238								0.504	1.000
	chalcopyrite	30.90	34.04								34.57	99.51	0.255	0.247								0.498	1.000
	pyrrhotite(5C:Fe_9S_{10})	60.85									39.44	100.29	0.470									0.530	1.000
	pyrrhotite(5C:Fe_9S_{10})	61.04									39.39	100.43	0.471									0.529	1.000
	chalcopyrite	31.15	33.40								34.82	99.37	0.257	0.242								0.501	1.000
	pyrrhotite(5C:Fe_9S_{10})	60.97									39.10	100.07	0.472									0.528	1.000
	pyrrhotite(5C:Fe_9S_{10})	60.67									39.10	99.77	0.471									0.529	1.000
	chalcopyrite	30.66	33.64								34.92	99.21	0.253	0.244								0.502	1.000
AT03-486(1)	pyrite	45.94									53.41	99.35	0.331									0.669	1.000
	pyrite	46.77									53.58	100.35	0.334									0.666	1.000
	pyrite	46.60									53.50	100.10	0.333									0.667	1.000
	pyrite	46.49									53.55	100.04	0.333									0.667	1.000
AT03-486(2)	pyrite	47.51									55.46	102.97	0.330									0.670	1.000
	pyrrhotite(4C:Fe_7S_8)	60.17									40.09	100.26	0.463									0.537	1.000
	pyrite	47.03									53.56	100.59	0.335									0.665	1.000
	chalcopyrite	30.62	34.11								35.07	99.80	0.252	0.246								0.502	1.000
	pyrite	46.72									53.44	100.15	0.334									0.666	1.000
	pyrrhotite(4C:Fe_7S_8)	60.61									39.70	100.31	0.467									0.533	1.000
	pyrite	46.11									54.16	100.27	0.328									0.672	1.000
	pyrrhotite(5C:Fe_9S_{10})	60.53									39.16	99.69	0.470									0.530	1.000
	pyrrhotite(4C:Fe_7S_8)	59.85									39.66	99.50	0.464									0.536	1.000
	chalcopyrite	30.78	33.42								34.56	98.76	0.256	0.244								0.500	1.000
	pyrite	46.60									53.66	100.26	0.333									0.667	1.000
	pyrite	46.55									54.14	100.70	0.330									0.670	1.000
	pyrrhotite(5C:Fe_9S_{10})	60.82									39.43	100.25	0.470									0.530	1.000
	pyrite	46.34									53.62	99.96	0.332									0.668	1.000
	chalcopyrite	31.30	32.53			0.65					35.52	100.00	0.257	0.234			0.002					0.507	1.000

Table II-3-6-3 Metal mineral analysis from Serra Geral basalt flows by CPRM (1/3)

Calcopyrite

Sample	KN-38/1	KN-32/2	KN-38/4	KN-38/6	KN-38/8	KN-38/9	KN-38/12	KN-38/13	KN-38/14	KN-38/15	AS-10/4	AS-10/5	AS-10/6
Fe	28.963	28.827	29.321	29.88	30.091	30.204	30.417	30.243	28.245	29.625	30.396	30.408	30.802
Co	0	0	0	0	0	0	0.008	0	0	0	0	0	0.002
Ni	0.018	0.007	0.006	0.008	0	0.017	0.022	0	0	0.015	0.018	0.014	0.004
Au	0	0	0	0	0	0.113	0.102	0.137	0	0	0.067	0.032	0
Cu	31.32	32.931	33.323	32.596	33.948	33.783	33.947	33.58	31.796	34.119	33.956	34.413	33.63
Zn	0.988	0	0.085	0.385	0.092	0.074	0.3	0.07	2.031	0.092	0.034	0.018	0.038
As	0	0.03	0	0.004	0.014	0	0	0.063	0	0.003	0	0	0.027
S	34.183	34.197	33.12	35.494	34.562	34.162	34.373	35.558	34.848	34.698	34.916	34.931	35.153
Ag	0	0.023	0	0	0	0.058	0	0.044	0.068	0.006	0.036	0	0
Total	95.472	96.015	95.855	98.367	98.707	98.411	99.169	99.695	96.988	98.558	99.423	99.816	99.656

Sample	AS-10/9	AS-10/10	AS-10/11	AS-10/12	AS-10/15	AS-10/16	AS-10/23	AS-10/24	KN-24/1	AS-10/1
Fe	30.546	30.715	30.972	30.325	30.758	30.485	30.767	30.788	14.45	29.828
Co	0	0	0	0	0.008	0	0	0.039	0.004	0
Ni	0	0	0.003	0	0.016	0.004	0.002	0	0.003	0.004
Au	0.029	0	0	0.07	0	0	0	0	0.27	0
Cu	33.888	34.261	34.011	34.276	34.527	34.28	34.332	33.88	56.752	34.07
Zn	0.02	0.115	0.011	0.07	0.059	0.029	0.13	0.038	0	0.107
As	0.077	0	0.023	0.075	0	0	0	0.048	0.014	0.024
S	34.495	35.073	34.697	35.72	34.73	35.344	34.576	34.946	26.885	34.325
Ag	0	0	0	0	0.065	0.042	0	0.056	0	0.036
Total	99.055	100.164	99.717	100.536	100.163	100.184	99.807	99.795	98.378	98.394

Table II-3-6-3 Metal mineral analysis from Serra Geral basalt flows by CPRM (2/3)

Native copper

Sample	KN-24/4	KN-24/5	KN-24/6	KN-24/7	KN-24/8	KN-24/2	KN-24/3
Fe	0.127	0.046	0.131	0.006	0.546	0.057	0.011
Co	0	0.015	0.023	0	0	0.007	0.009
Ni	0.016	0.004	0.012	0	0	0	0
Au	0.043	0	0	0	0	0.219	0.066
Cu	101.178	101.934	101.572	101.451	99.466	102.603	101.506
Zn	0.02	0	0	0	0	0.011	0
As	0.031	0	0.036	0.028	0.051	0.047	0
S	0.029	0.015	0.034	0.023	0.011	0.009	0.004
Ag	0.06	0	0.021	0	0.019	0	0
Total	101.504	102.014	101.829	101.508	100.093	102.953	101.596

Cobalt-Arsenic mineral(escuterrudite)

Sample	AS-10/26	AS-10/X	AS-10/8
Fe	7.113	11.587	32.237
Co	23.527	13.547	13.089
Ni	5.566	8.99	9.184
Au	0.257	0	0.019
Cu	0.013	0.548	5.675
Zn	0	0.076	0.011
As	40.33	42.089	0.105
S	17.421	17.156	39.54
Ag	0	0.013	0.01
Total	94.227	94.006	99.87

Table II-3-6-3 Metal mineral analysis from Serra Geral basalt flows by CPRM (3/3)

Spharelite

Sample	KN-38/3	KN-38/5	KN-38/11	KN-38/16	KN-38/17	AS-10/3	AS-10/13	AS-10/18	AS-10/19	AS-10/20	AS-10/21	AS-10/22
Fe	10.505	1.661	14.666	14.677	14.199	14.305	12.263	14.014	12.958	14.294	15.026	14.588
Co	0.135	0.019	0.089	0.022	0.082	0.056	0.06	0.125	0.011	0.024	0.103	0.006
Ni	0.026	6.957	0	0.022	0.004	0.006	0.018	0.005	0.027	0	0.028	0
Au	0	0	0	0	0	0	0	0	0	0	0	0
Cu	2.427	37.138	5.606	4.694	0.283	4.923	0.11	0.334	0.341	0.418	0.153	0.054
Zn	49.869	19.028	44.791	45.852	49.101	46.104	52.151	50.425	51.419	49.772	50.299	50.322
As	0.026	0.009	0.003	0	0	0.007	0.089	0	0.026	0	0.034	0.082
S	33.498	0.014	32.9	34.147	34.911	33.657	33.911	35.59	33.952	33.155	34.016	33.589
Ag	0.071	0	0.039	0	0	0	0.018	0	0.033	0	0	0
Total	96.557	64.826	98.094	99.414	98.58	99.058	98.62	100.493	98.767	97.663	99.659	98.641

Pyrite

Sample	KN-38/7	KN-38/10	AS-10/7	AS-10/14	AS-10/17	AS-10/2
Fe	47.684	46.868	47.718	60.428	60.308	48.123
Co	0	0	0	0.004	0.041	0
Ni	0	0	0.017	0.068	0.045	0.01
Au	0.006	0.096	0	0	0	0
Cu	0	0.024	0	0.023	0	0.013
Zn	0	0.007	0.031	0	0.008	0
As	0.026	0	0	0.085	0	0
S	53.572	53.309	53.46	39.445	39.477	53.773
Ag	0.016	0	0.026	0	0	0.028
Total	101.304	100.304	101.252	100.053	99.879	101.947

3-7 Geochemical Survey with Stream Sediments and Stream Water

3-7-1 Introduction

The geology of the southern part in the Lomba Grade district is characterized by the sedimentary rocks and basic sills and dykes of 180 meters or more in thickness. We carried out the experimental geochemical survey using stream sediments and water was carried out to check the mineralization of Cu-Ni and PGE in these intrusive rocks distributed in the Lomba Grande district.

The geochemical survey of stream water is based on chemical and physical reactions between rocks, metallic elements and water. Some underground data getting on the surface are related to infiltration and melting of sulfates (Dekkers et al., 1989: Ren et al., 1989: Miller et al., 1992).

Metallic elements cause precipitation as a metallic ion and a manganese oxcide by chemical and physical conditions of stream water such as pH, Eh and others. Therefore, analytical results of the stream sediments are supposed to supplement the results of geochemical survey using stream water.

3-7-2 Collecting and Treatment Samples

We collected stream water and sediments at 182 points in the southern part of the Lomba Grande district. Sampling area is covered about 660 km^2 with a density of 3.2 km^2/sample, mainly over the sills detected by drilling in the Lomba Grande district. Collecting of samples was conducted during a rainy season. And, we collected 100 ml/ample of stream water, which were filtered to extract the solid contain, and acidified with neutral acid to pH<2 to prevent ion precipitation from the solution. Also, on the each sampling points, the temperature, pH, turbidity and ion solubility were measured.

We also collected the samples of stream sediments at the same points where the samples of stream water were collected. The samples of stream sediments were dried, and prepared as -80 mesh samples. Analysis of samples was done on Activation Laboratories Ltd in Canada. The water samples were analyzed to 68 elements by ICP-MS, and sulfate ion was analyzed by ionic chromatography. Meanwhile, The stream sediments were analyzed to 31 elements by ICP-OES. The results of analysis are included in appendices of this report.