PGE, Au AND Ag DISTRIBUTION IN THE PRECAMBRIAN NIQUELÂNDIA COMPLEX, CENTRAL GOIÁS, BRAZIL

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ABSTRACT Precious metals distribution in the Precambrian mafic-ultramafic layered complex of Niquelândia, central Goiás, Brazil, has been investigated by flameless Atomic Absorption Spectroscopy. The contents of Ag, Au, Pd, Pt, Rh and Ru were determined in the different units of the complex, mainly in the basal peridotite and the layered ultramafic zone constituting the ultramafic portion. In the latter zone (27 analyzed samples) average contents for Ag, Au and Pd are 70, 30 and 15 ppb, respectively. In most samples Pt, Rh and Ru are below 10 ppb. The precious metals are very unevenly distributed and their concentrations in individual samples appear controlled by the amount of sulphides. The variations in average composition appear to be related to stratigraphic position and/or rock composition. Ag and Au tend to concentrate in sulphide-bearing pyroxenitic horizons of the upper gabbroic zone. The Pt-group elements mainly concentrate in peridotitic layers within the ultramafic portion. Factors affecting the geochemistry of the precious metals during the fractionation of mafic magmas are discussed. The influence of structural features (*i.e.* the polymerization state) of the silicate liquids in equilibrium with the sulphide phase is emphasized.

INTRODUCTION A vast amount of data is now available on the distribution of the precious metals in major stratiform mafic intrusions. Most data, however, refer to a single or few elements, or are restricted to a specific section (*e.g.* the sulphide-bearing layers) of a given complex. Gold and silver distributions have been extensively described in a number of complexes. The geochemistry of the platinum group elements (PGE) is much less known in spite of some excellent studies (see *e.g.* Crocket *et al.*, 1976; Page *et al.*, 1972, 1976, 1980; Gibjels *et al.*, 1974, 1976) on different layered complexes. Apart from some analyses of Pt and PGE on a chromite horizon published by White *et al.* (1971), data on precious elements in the mafic-ultramafic Niquelândia complex in Goiás State, Brazil, are virtually absent.

The present data represent the initial part of a comprehensive study on the precious element distribution in layered complexes of Precambrian age of Brazil. The aim of this study is to give a preliminary evaluation of the concentration of precious metals and of their distribution in the Niquelândia Complex.

THE NIQUELÂNDIA COMPLEX The Niquelândia complex is a mafic-ultramafic body of presumably Archean or Early Proterozoic age occurring within metamorphic terrains in central Goiás, Brazil.

Data on general geology, petrology and chemistry of the complex are reported in a number of papers (see references in the recent comprehensive papers of Danni *et al.*, 1982, and of Rivalenti *et al.*, 1982). The complex consists of a 2-4 km wide ultramafic portion, considered as the stratigraphic lower zone, overlain by an upper sequence of gabbroic rocks. In the uppermost portion, anorthosites and olivine-gabbros occur, but their relationship to the layered complex is problematic.

The genesis of the complex is still rather controversial. Almeida (1968) and Angeiras (1968) interpreted Niquelândia as a "serpentine belt". Other authors recognize strong affinities with Alpine-type suites (Da Costa and Angeiras, 1971) and with proto-ophiolite suites (Danni and Leonardos, 1981; Danni *et al.*, 1982). Finally, other authors (*e.g.* Barbosa, 1968; Motta *et al.*, 1972; Rivalenti *et al.*, 1982) conclude that the complex was derived by fractional crystallization processes of basaltic magmas.

A recent paper by Rivalenti *et al.* (1982) has shown that mantle tectonites do not occur at Niquelândia and that, therefore, the hypothesis that the complex represents a proto-ophiolite suite can no longer be held. Niquelândia is nothing more than a stratiform complex.

According to the same paper the studied portion of the complex can be subdivided in the following units or zones:

a) basal gabbroic zone (BGZ)
b) basal peridotite zone (BPZ)
c) layered ultramafic zone (LUZ)
d) layered gabbroic zone (LGZ)

A schematic stratigraphic column is given in Fig. 2.

The BGZ begins with a fine-grained gabbro and continues upwards with a centimetric to decimetric alternance of gabbros, pyroxenites and peridotites. BGZ gradually passes into BPZ (considered by Danni *et al.*, 1981, as mantle tectonite) by increasing the number and thickness of the peridotitic layers. BPZ (800-1,500 m thick) is mainly composed of dunites and harzburgites, with minor pyroxenite veins and layers. The top of BPZ is marked by an increase of the pyroxenite layers and by the appearance of a chromitite horizon. LUZ is composed of peridotitic (dunite, harzburgite and lherzolite) and pyroxenitic (bronzitite and websterite) layers from a few cm to 60 cm thick. Two gabbro layers occur near the base of the LUZ. Pyroxenites (and sometimes peridotites) are sulphide-bearing and become coarse-grained in contact with LGZ. This unit is formed of gabbro and norite layers. Peridotite and pyroxenite layers occur but are very rare.

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Bulk rock and phase geochemistry are reported in Rivalenti *et al.* (1982). The examined section of the complex is characterized by a moderate upwards iron enrichment with frequent reversals. A discussion of the fractionation pattern is found in the above mentioned paper.

In the present study, the distribution of the precious metals has been determined in the ultramafic rocks of BPZ, LUZ and LGZ, and in a few gabbro samples of LGZ.

NOTES ON ANALYSES Silver, gold and platinum-group elements have been determined by flameless Atomic Absorption Spectroscopy, using a Perkin-Elmer Model 603 spectrophotometer and a Model 500 Graphite Furnace. The method is based on the procedure described by Fryer and Kerrich (1978). A preconcentration of noble metals was obtained by coprecipitation on metallic tellurium. Five-gram samples have been usually taken for analysis. Solubilization of the sample was achieved by treatment with combined HNO_3-HF followed by an acqua regia attack. Details on procedure and analytical perfomances will be reported elsewhere (Sighinolfi *et al.*, in prep.). Analytical errors for the various elements range between 10% and 60% commonly.

ANALYTICAL RESULTS A total of 40 samples have been analyzed for Ag, Au and PGE. Fig. 1 shows the collection localities, while Table 1 sets forth the analytical results. Most samples present Rh and Ru below the detection limits (1 and 5 ppb, respectively). This happens for Pt as well (detection limit 10 ppb). Precious metals appear unevenly distributed: Ag varies from 10 to 600 ppb, Au from 1 to 700, Pd from 1 to 63 ppb, and Pt from 10 to 77 ppb. Qualitative observations on the rock mineralogy indicate a close relationship between the amount of sulphides and Ag and Au contents.

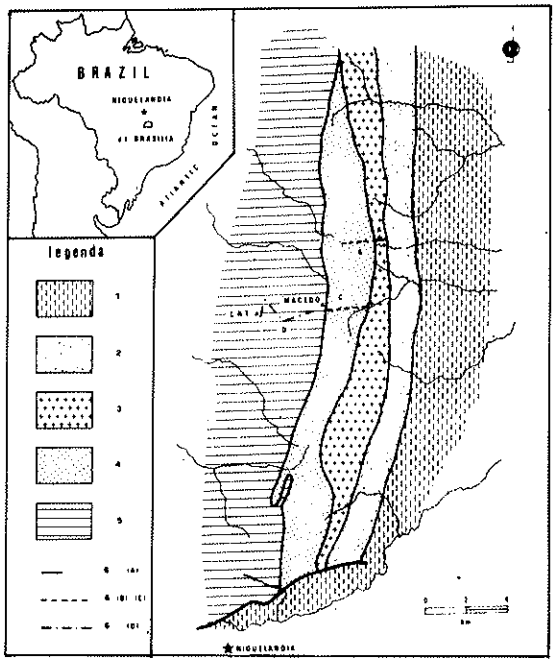

Figure 1 — Schematic geological map of the Niquelandia Complex in the area of the Serra da Mantiqueira (modified after Danni and Leonardos, 1981). 1: Gneisses; 2: basal gabbro zone (BGZ); 3: basal peridotite zone (BPZ); 4: layered ultramafic zone (LUZ); 5: layered gabbroic zone (LGZ); 6: sample collection profiles. a: BPZ (Corrego Forquilha de Baixo); b: LUZ (Corrego Forquilha de Baixo); c: LUZ (east of Macedo); d: LGZ (between Macedo and Cia. Niquel-Tocantins)

Table 1

Sample	Ag	Au	Pd	Pt	Rh	Ru
	BPZ	Dunites				
192	nd	200	7	15	< 1	6
193	45	37	7	< 10	nd	< 5
197	< 10	30	30	12	2.1	5
			Harzburgites			
205	10	23	14.5	22	1.2	15
207	< 10	16	10	10	< 1	< 5
211	15	10	21	10	< 1	20
			Pyroxenites			
191	14	30	14	12	< 1	< 5
200	12	2	4.5	< 10	< 1	< 5
208	36	2	8	13	3	nd
	LUZ	Dunites				
223	15	7	18	26	2.5	< 5
164	5	2	1.5	nd	nd	nd
165	60	2	3.5	< 10	1	< 5
121	15	55	63	50	1.6	11
			Harburgites			
220	63	6	30	15	3.2	< 5
225	92	30	77	60	6.2	11
232	< 5	9	2.5	< 10	< 1	< 5
144	24	17	26	20	2.8	< 5
153	50	3	8	< 10	< 1	< 5
			Lherzolites			
216	50	25	5.5	10	nd	< 5
219	30	7	10	48	1	6
149	600	24	25	15	< 1	< 5
			Bronzitites			
161	75	20	29	35	2.2	6
125	20	14	4	< 10	< 1	< 5
126	10	56	15	15	< 1	< 5
145	14	53	20	20	1.4	< 5
150	120	3	7.4	20	1.7	< 5
156	30	52	16	< 10	1	< 5
157	165	18	3.5	< 10	2.5	< 5
158	70	7	7	20	1.1	< 5
150	30	16	12	10	< 1	< 5
			Websterites			
215	78	1	3	< 10	< 1	< 5
218	80	10	8	< 10	< 1	< 5
224	nd	15	10	< 10	< 1	< 5
166	22	7	6	< 10	< 1	nd
131	86	16	1	<10	<1	<5
			Gabbro			
233	< 5	1	< 1	< 10	< 1	< 5
	LGZ	Pyroxenites				
109	152	27	2	< 10	< 1	< 5
112	180	700	5.6	< 10	< 1	< 5
			Gabbros			
111	24	15	2.5	< 10	< 1	< 5
115	12	12	1	< 10	< 1	< 5

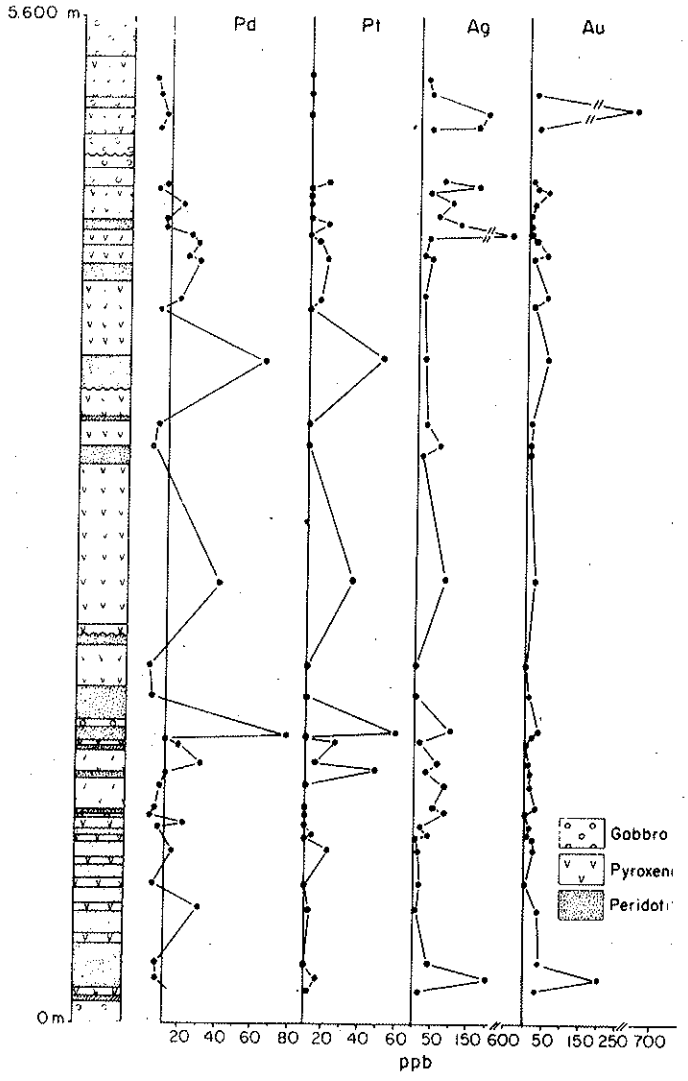

Figure 2 — Stratigraphic variation of Pd, Pt, Au and Ag in the Niquelandia Complex

Although very low, the concentration of Pt and Pd in the BPZ peridotites is distinctly higher than that of mantle tectonites (Paul and Crocket, 1979; Arculus and Delano, 1981). This gives additional support to the finding of Rivalenti *et al.* (1982) that mantle tectonites do not occur at Niquelândia.

The variation of Ag, Au, Pd and Pt content with stratigraphy is show in Fig. 2. In general Pd is enriched with respect to Pt, and both elements are higher in peridotites than in pyroxenites and gabbros. Only one pyroxenite layer, bearing sulphides and coarse grained, has appreciable amounts of Pt and Pd. A higher PGE content has been found in two stratigraphically controlled ultramafic layers of LUZ, as is common in layered complexes (*e.g.* Page *et al.*, 1980). These are peridotites interlayered with pyroxenites that occur shortly after the appearance of chromitite layers. They occur also near the first appearance of gabbroic layers. A similar distribution has also been observed in other layered complexes, such as that of Stillwater (Naldrett and Cabri, 1976).

A plot of FeO/(FeO + MgO) ratio against Pd (Fig. 3) or Pt shows that there is a positive relationship between iron enrichment and PGE. The higher iron enrichment of the rocks having higher PGE is partly due to a slightly higher concentration of Fe-bearing sulphides (as confirmed also by higher Ag and Au content), but also corresponds to iron rich composition of the silicate phases.

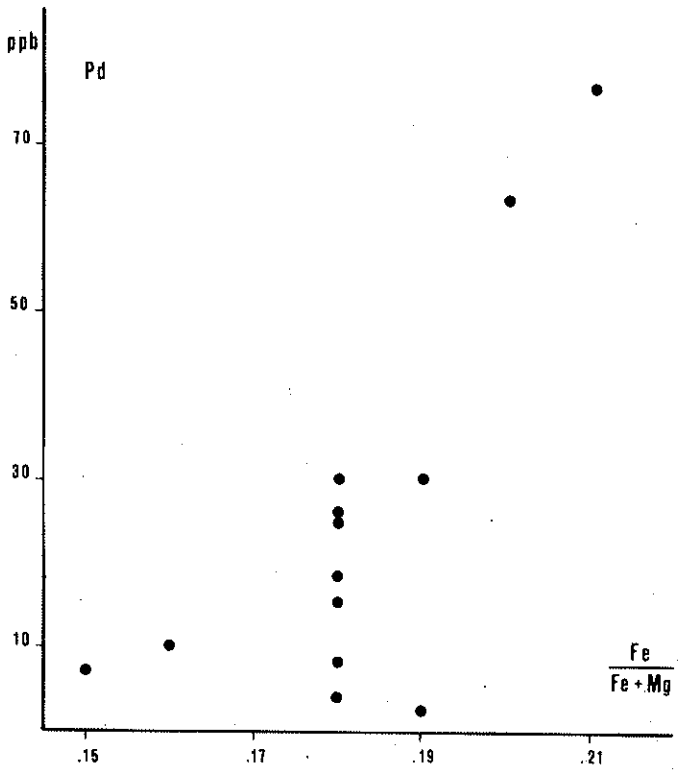

Figure 3 — Palladium vs. the Fe/Fe+Mg ratio in peridotite layers of the Niquelandia Complex

Ag and Au show a tendency to increase with increasing stratigraphic height: the highest Au content (700 ppb) is found in a pyroxenite horizon within the LGZ.

PRELIMINARY INTERPRETATION AND CONCLUSIONS A number of studies dealing with the distribution of precious metals in layered intrusions have put forward hypotheses on the mechanism that leads to the concentration of these elements in specific horizons. The main results are:

a) most of the precious metals tend strongly to partition in sulphide phases (Keays and Campbell, 1981);

b) the platinum group elements in economic deposits are frequently connected with high activities of fluid phases (Stumpfl, 1974);

c) peculiar compositional features (*i.e.* high Fe/Mg ratios; Stillwater, Niquelândia) and liquid fractionation stages (*e.g.* apearance of plagioclase in the liquidus, Bushveld) seem to coincide with maximum PGE precipitation in specific horizons.

As for Niquelândia, definite conclusions and interpretations are strongly hampered by the limited number of available data and by the little information regarding sulphide mineralogy and trace element geochemistry. However, it has been shown that at Niquelândia precious metal distribution follows trends that are common to other layered complexes. Silver and gold, elements that are strongly partitioned into sulphide phases, concentrate in the upper sulphide-bearing pyroxenite layers. PGE are concentrated in stratigraphically controlled, sulphide-bearing peridotitic layers displaying a

high Fe/Mg ratio and occurring near chromititic and gabbroic layers, or, to a lesser extent, in sulphide-bearing pyroxenitic layers formed under a relatively high fluid activity (as suggested by the coarse grain size).

From the findings in other layered intrusions, it is apparent that precious metal distribution depends on the peculiar fractionation path and the physico-chemical properties of the liquid. Keays and Campbell (1981) have shown that Pd content of sulphides in equilibrium with silicate melt increases when the volume of the silicate melt is very large with respect to that of the sulphide. In other words precious metals concentrate in the unmixed liquid or in the crystallizing phase only when this represents a small percent of the total liquid volume, thus leading to the extracting of precious metals from a very large volume of liquid. This also corresponds to a peculiar polymerisation state of the silicate melt, and polymerisation is in turn influenced by the fluid phase content, pressure (Kushiro, 1976, 1978; Mysen *et al.*, 1980), iron content and other physical and chemical variables.

Rivalenti *et al.* (1982) have proposed a mechanism for fractionation at Niquelândia that essentially relates the percent of crystallization and formation of layering to the variations of pressure acting on the liquid, as well as to a T gradient. The liquid path moves away from the olivine field so that, in general, successive peridotitic layers from BPZ to LUZ represent decreasing percent of fractionation, while pressure variations determined the layered structure by influencing the phase (and its composition) that appears on the liquidus. A minimum of crystallization occurs at the stratigraphic height where chromite layers (and associated peridotites) occur. The fact that PGE are concentrated at this stratigraphic height is in agreement with what is found in other occurences. The polymerisation state of the liquid is undoubtedly here increased with respect to that at the moment of BPZ fractionation, and this permits the first separation of a sulphide liquid that in turn concentrates PGE. The reason why sulphide-bearing peridotites are enriched in PGE with respect to sulphide-bearing pyroxenites is still unknown. Speculatively, it may be proposed that polymerisation needs to be high enough to permit the separation of a sulphide-bearing phase, but not so high as to determine extensive sulphide separation. These conditions may be reached in the iron-enriched peridotitic layers, with respect to the pyroxenitic ones.

Lack of data on the distribution and behaviour at Niquelândia of elements such as As, Te and Sb, that are likely related to PGE, prohibits further speculation.

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