SHORT COMMUNICATION

SEM-EDS STUDY OF THE PLATINUM-GROUP MINERALS IN THE PGE MINERALIZED HANUMALAPURA SEGMENT OF THE LAYERED MAFIC-ULTRAMAFIC COMPLEX OF CHANNAGIRI, DAVANGERE DISTRICT, KARNATAKA

T.C. DEVARAJU¹, T.T. ALAPIETI² and R.J. KAUKONEN² ¹Department of Applied Geology, Kuvempu University, Jnanasahyadri, Shankaraghatta, Shimoga – 577 451 **Email**: devaraj63@sancharnet.in ²Institute of Geosciences, University of Oulu, P.O.Box 3000, Oulu, Finland

SEM-EDS study of outcrop samples from the PGE mineralized, layered Hanumalapura segment of the Channagiri mafic-ultramafic complex, has revealed that they contain a variety of platinum-group mineral inclusions. Among more than 25 different PGM's distinguished, *sperrylite, stibiopalladinite, hollingworthite, keithconnite, mertieite II, laurite, ruarsite* together with a suite of *Pt* and *Pd alloys,* constitute the more important carriers of PGE in the ore reefs. From the close association of PGM's with chromite-bearing host rocks, it is inferred that crystallization of chromite had the governing control over the concentration of PGE.

Introduction

Encouraged by the discovery of definite evidence of PGE mineralization in the nintees (Devaraju et al. 1994; Alapieti et al. 1994), the authors have mapped the 3.5 x 0.3 km Hanumalapura segment of the Channagiri layered complex, hosting the mineralization, on a scale of 1:2000 (Fig.1) and have studied in detail its lithogeochemistry as well as mineralogy. This publication, however, selectively presents an account of the distribution and paragenesis of platinum-group minerals based on scanning electron microprobe analytical data obtained for the minerals noted in a set of outcrop samples, collected over the length and breadth of the segment.

Geological Setting

The Channagiri layered complex is made up of several tectonically segmented blocks together stretching in a NE-SW direction over a strike length of more than 40 km. The segment hosting the PGE mineralization, which is located just ½ km west of Hanumalapura (recently renamed as Jayapura), however, measures a little more than 3 km in length and about 300 m in width.

The Channagiri layered complex is located near the southeastern boundary of the Shimoga Greenstone Belt. It is predominantly an ultramafic complex. While a large part



Fig.1. Geological map of a part of the PGE mineralized layered Hanumalapura segment with locations of key samples studied.

of the complex is surrounded by Archaean tonalitic gneiss, on the N-NE and S-SW it lies in juxtaposition with the Kurgudda and Tuppadahalli Formations of the sequence. Chadwick et al. (1988) have classified the complex as a part of the Hedale Gudda Formation, comprising the lowermost sequence of the Shimoga Greenstone Belt stratigraphy. The contacts of the complex with both the tonalite and the Shimoga Greenstone Belt are not usually exposed to enable an assessment to be made of the age relationship and when exposed they coincide with a shear zone.

Lithogeochemistry of the PGE Mineralized Hanumalapura Segment

Detailed 1:2000 scale mapping (Fig.1) and lithogeochemical study of the segment has yielded the following information:

- 1. NS to NNW strike, 55° to 70° easterly dip and evidence of penetrative deformation and greenschist-low amphibolite facies of metamorphism which were so strong as to almost destroy completely the original cumulate textures and primary minerals of the layered complex, excluding chromite.
- Layering consists of a central 100-150 m ultramafic zone and a narrow outer gabbroic zone, the interface between the two being occupied by almost massive titaniferrous magnetite seams and small disconnected pods of anorthositic rocks.
- The presence of a complex mixture of the fine-grained chromite-chlorite rock (metadunite-chromitite) and a coarse-grained pegmatitic hornblendite (metapyroxenite) constituting the central ultramafic zone.
- 4. Localization of zones enriched in PGE to the central fine-grained ultramafite containing chromite and chlorite and to the chromiferrous magnetite forming a part of the eastern magnetite seam of the complex (*see* Table 1 for whole rock analysis of Pt, Pd and Au in these litho units).
- Absence of PGM and evidence of PGE mineralization in the coarse-grained ultramafite, western V-Ti magnetite seam, gabbroic anorthosite and outer gabbroic zones.

Table 1. Whole rock analyses of Pt, Pd and Au	ı
in some of the samples studied (values in ppb))

Sample	Pt	Pd	Au
2-IND	1090	3050	49
3-IND	4000	1700	29
M 93	639	1000	4
M 98	2296	881	65

6. Existence of both Pt- and Pd-enriched reefs, the latter dominating the former.

PGM Analytical Techniques

Analysis of the platinum minerals presented here was carried out at the Institute of Electron Optics, University of Oulu, Finland. A JEOL Super Probe JCXA-733 fitted with a Link A10000 Energy Depressive Spectrometer (EDS) was employed for the analysis. The analytical facilities of the lab have proved to be adequate for obtaining acceptable analyses of platinum-mineral grains as small as 1.5 microns in diameter.

The standard analytical conditions included an acceleration voltage of 15 kV and sample current of 1.5 nA. The standards used were pyrite for S, haematite for Fe, synthetic InAs for As, PbTe for Te and Pb and pure metallic standards for other elements reported here. Due to the very small size of most of the platinum-group minerals, a focused beam with a diameter of about one micrometer was used in most analyses.

About 75% of the PGM analyses reported here have been performed by the third author. The remaining analyses were done by Dr. Tapio Halkoaho, a former associate of TTA.

PGE Mineralogy

15 samples from fine-grained ultramafite, 4 from chromiferrous magnetite (the two main lithologies hosting PGE mineralization), one from schistose metagabbro and 3 from coarse grained ultramafite, collected from isolated spots, located over a 3.5 km strike length of the segment, have been examined. Of the 23 samples examined, 14 of fine-grained ultramafite and all four of chromiferous magnetite, were noted to contain variable numbers of PGM inclusions. These inclusions were almost missing in the other five samples. The following is a summary of the PGE mineralogical information gathered during the present study:

- The individual PGMs identified in the samples occur as minute inclusions (range in size from less than 2-3 microns to more than 10-15 microns) within the main minerals viz., chromite and chlorite and also occupying the boundaries between these two minerals (Figs.2 to 7).
- 2. About 60% of the PGM inclusions were found enclosed in chromite.
- The frequency of PGM inclusions vary greatly; while samples M93:97 and M98:97 (both of chromiferrous magnetite) contain, within the limits of a single section of 2.5 cm x 3 cm, over 100 inclusions each, similar sections of samples M1:96, M2:96, M7:96, M11:96







Figs.6 to 8. Backscattered electron images of PGM inclusions (bright white looking). 6. Inclusions A to F in sample M 93. (Λ) Unnamed Pd-Cu alloy (hydroxide?) in chlorite (10x11µm). (B) Sperrylite in Cr-rich magnetite (1.5x2µm). (C & F) Hollingworthite in altered chromite (2.5x5.5µm). (D) Palladoarsenide in Cr-rich magnetite (2x6µm). (E) Mertiete II in Cr-rich magnetite (2.5x3.5µm).
7. Laurite in zoned chromite (3x1.5µm) (JS 159). 8. Rare evidence of hydrothermal alteration of PGM. The large core area (bright white) corresponds to sperrylite whereas the altered border zone (light grey) is Pt-Fe hydroxide (M98).

contain less than ten inclusions and in M5:96 and M104:97 there are more than 30.

- In all, over 400 PGM inclusions have been identified and analyzed and more than 25 different PGM elements have been distinguished on the basis of chemical data.
- 5. Among the more than 25 different PGM's

distinguished, sperrylite, stibiopalladinite, hollingworthite, keithconite, laurite, mertieite-II, ruarsite together with a suite of alloys of Pt-Pd, Pd-Sb, Au-Ag-Pd, Pd-Bi-Sb-Te, Pd-Sb-Au and Pd-Cu constitute the most important carriers of PGE in the complex. The other PGM inclusions of sporadic and

SHORT COMMUNICATION

		18	ible 2. Sele	cied SEM-	EDS analy	ses of POM	I S HOM PC	c mineraliz	zed zones c	n Hanumai	apura segn	ient	
St.N	No. nple	1 1-IND	2 3-IND	3 M93	4 1-IND	5 M93	6 M93	7 3-IND	8 1-IND	9 3-IND	10 M93	11 3-IND	12 1-IND
Pt		57.70	53.30	48.33	30.22	25.73	11.45		30.19	17 45	14 85	85 33	5.05
Pd			0.56	1.06	_	1 21		— .			2 68	14 67	
Rh		0.36	3.47	4.72	12.01	15.28	38.18	41 10		26 31	8 99		45 65
Ru			_		10.28	2.20	1.11	2.65	10.28	4 06	1.87		
Ir		_			213	9 59	••••	2 10	213	5 77	14.81	_	
Os		_			4.00		4.94	2.10	4	5.11	17.44		_
Ni						_		1.22			_		_
Co		_						0.77				_	
S		· ·	1.81	2.07	11.71	8.06	13.13	16.53	11.7	13 44	11 64	_	13.98
As		41.92	41.40	42.55	31.06	36.21	33.81	35.61	31.06	32.96	28.08	_	35.52
											20.00		
SI.N	lo.	13	14	15	16	17	18	19	20	21	22	23	24
Sam	ple	2-IND	I-IND	3-IND	3-IND	3-IND	2-IND	M104	M98	M104	2-IND	M98	M99
		74.00		<u> </u>	<u> </u>								
Pa		14.28	12.57	/0.59	54.57	/0.59	64.79	70.15	69.52	65.53	53.95	62.15	71.27
50		15.20	24.24	4.53	16.20	4.53	2.70	26.91	30.67	1.66	0.47	27.36	27.67
Au		—							_	_	·	9.59	
Bi		—	—			_	16.48	- ,	_	6.03	9.63	—	_
Te			_		<u> </u>	—	16.03		<u> </u>	25.19	10.08	-	
Cu		-	_		-	_				1.58	17.64		_
N1 È		.	_	3.45		3.45	—	_		—		· ,	
re		-	`				_	·	<u> </u>	— .	7.95		
AS		10.48	3.20	21.43	29.23	21.43		2.30	0.48			0.90	·
SIN		25	26	27	20	20	20	21	20		24	25.	26
51.1V Sam	nla	2.J 2. INID	20 M2	27	40	29	30 M02	31 MIA.06	32	33 M2	34	30°	20 M09
	ipie	3-IND		M96	13-139	IVI 2	M95	MTA:90	12-129	M2	M93	/-IND	M98
Pt	•	13.38				· ·	_		—		20.66		
Pd		86.62	67.96	67.59		—	_		-	1.51	45.92	16.32	14.49
Rh			—	—		—	—	*	1.58	2.36		—	—
Ru				—	35.33	42.13	29.74	20.22	18.72	5.97		—	
lr		<u> </u>	—		6.04	·	2.99	6.48	26.06	50.75			<u> </u>
Os			<u> </u>	_	26.38	22.55	21.18	42.61	12.50	_		-	-
Sb				5.37					—	—			5.22
Au						—	—					83.68	52.45
Ag			-	-			—						26.15
Bi				22.10		· · ·			—	—			<u> </u>
Te		·	_	4.99	-	—				—	_	 .	
Cu			32.05	—	_	-	—	_	—	-	12.04		
S			_		32.25	34.45	12.18	27.40	22.79	12.30	·	´	
As				—			33.02		18.37	27.26	_		

1-3: Sperrylite; 4: Platarsite; 5-9: Hollingworthite; 10: Osarsite; 11: Pt-Pd Alloy; 12: Cherepanovite;

13-14:Stibiopalladinite; 15-17:Arsenopalladinite; 18:Michenerite; 19-20:Merticite-II; 21:Keithconnite; 22:Testibiopalladite;

23: Pd-Sb-Au Alloy; 24:Pd-Sb Alloy; 25:Pt-Pd Alloy; 26:Pd-Cu Alloy; 27: Pd-Bi-Te-Sb-Cu alloy; 28-29: Laurite; 30: Ruarsite;

31: Erlichmanite; 32: Irarsite-laurite; 33: Irarsite; 34:Pd-Cu-Pt Hydroxide; 35:Au-Pd Alloy; 36:Au-Ag-Pd Alloy

localized occurrence include isomertiete, michenerite, kotulskite, irarsite, irarsite-laurite, osarsite, platarsite, testibiopalladinite, rustenburgite, erlichmanite, Pd-Cu hydroxide, Pt-Fe hydroxide (see Cabri, 1981; Daltry and Wilson, 1997 for nomenclature and definition of PGM; see Table 2 for analyses of selected PGM's).

6. Of the 400 PGM grains analyzed, 24% were accounted for by Pd-Sb minerals (mainly in the range of

stibiopalladinite-metieite II-kotulskite), 23% by sperrylite, 17% by Pd-Te-Be alloys, 14% by other Pd minerals, 10% by hollingworthite, 9% by Ru-Os-Ir minerals (e.g., laurite, irarsite, ruarsite) and 3% by other Pt minerals.

7. The PGM inclusions are not found selectively occupying any of the weak planes of the host minerals nor do they show evidence of replacement.

8. Compositionally related minerals like laurite and

IOUR.GEOL.SOC.INDIA, VOL.65, JUNE 2005

irarsite, and hollingworthite and sperrylite may form composite grains.

- 9. The PGM inclusions are typically fresh being apparently unaffected by the very penetrative hydrothermal alteration and low-grade metamorphism to which the host rocks have been subjected, at places, however, corrosive alteration of PGM related to hydrothermal activity is noted (Fig.8).
- 10. The compositions and frequency of occurrence of the PGM's are directly linked to the concentration of the individual PGE's in the bulk composition of the sample; concentrations in excess of 100 ppb of an individual PGE is associated with the appearence of PGM inclusions corresponding to such PGE elements.
- 11. An association of two or more PGM's in a single sample is normal (Fig.6); in some of the samples e.g., M93:97, an association of as many as 12 different mineral phases is recorded.
- 12. In samples like JS159, 8-IND-93 and M7-96, with

relatively high concentration of IPGE viz., Ru, Ir and Os, and depleted PPGE viz., Pt, Pd, and Rh, the PGM's exist mainly in the range of laurite-irarsite.

- 13. Compositional variation recorded among 107 of the analysed PGM inclusions are shown by plotting related mineral compositions on four ternary diagrams (Figs. 9 to 12).
- 14. In respect of an Fe-Cr oxide association and absence of a Ni-base metal sulphide association, the PGE mineralization in the Hanumalapura segment closely compares with that of the Penikat, Koitelainen and Keivitsa-Satovaara mafic-ultramafic intrusions in northern Finland (Alapieti, 1986; Mutanen, 1989; Halkoaho, 1994).

Comments on the Paragenesis of Hanumalapura PGM

The occurrence of PGM as minute inclusions within chromite and silicate, usually without any preference for planes of weakness in the host minerals, is thought to indicate



Figs.9 to 12. Compositional variations recorded among Pt (Rh), Pd (Sb+Bi+Te) and Ru-Ir-Os mineral inclusions illustrated with the aid of trilinear plottings. 9. Variation in compositions of sperrylite-hollingworthite inclusions. 10. & 11. Variation in compositions of assenopalladinite-keithconnite-merteite inclusions. 12. Variation in composition of laurite-irarsite-osarsite inclusions.

JOUR GEOL SOC INDIA, VOL 65, JUNE 2005

their early crystallization and entrapment in the later formed chromite and silicates. Alteration of original silicate, olivine (and pyroxene) to chlorite, under hydrothermal and lowgrade metamorphic conditions was apparently not associated with the dissolution and migration of PGM's.

Absence of obvious replacement features do not permit interlinking of the PGM inclusions with the extensive penetrative hydrothermal activity, shearing and low-grade metamorphism, which has affected the host rock.

The PGE mineralogy of the Hanumalapura complex is very variable. The variation is largely the result of reequilibrium during slow cooling (Merkle, 1992; Coghill and Wilson, 1993). The present mineralogy and mineral composition probably represent equilibrium assemblages at only a few hundred degrees centigrade thus triggering crystallization of PGM (Naldrett and Laehmann, 1988; Scoon and Teigler, 1994) and should not be construed to indicate variations in the primary mineralogy (Cawthorn, 1999).

The extremely low-sulphide but high PGE content of the PGE mineralized chromite-bearing units, as suggested by some workers (e.g., von Gruenewaldt et al. 1989; Naldrett et al. 1988), could be explained by invoking the presence, initially of more abundant sulphide in the system which has been oxidized by reaction with chromite. In addition, the close association of PGM's with chromite-bearing host rocks further suggests that chromite had governing control over the concentration of PGE. Nucleation of chromite presumably changed the solubility of sulphur at the locus of chromite formation.

The discrete PGM's are too small to accumulate in significant amounts and require some additional factor(s) in order to concentrate them into economically viable reefs, be they sulphide-bearing or chromite bearing. Direct precipitation of PGM's as discrete phases from the magma relatively enriched in PGE is proposed by Hiemstra, (1985), Merkle (1992) and Tredoux et al. (1995). Hiemstra (1995) suggested entrapment of PGE through adherence to chromite grains whereas Merkle (1992) proposed the encapsulation of PGM's in silicate minerals as well. Tredoux et al. (1995) postulated the presence of 50-100 atom sized clusters of PGE atoms in magmas and visualized stabilization of such clusters by the presence of soft ligands of S, Se, Te, As, Sb and Fe atoms.

Acknowledgements: This publication is a part of the study accomplished by TCD under the research project "Investigation of Archaean layered mafic-ultramafic complexes of the Shimoga belt of Karnataka with special reference to evidence of platinum mineralization" sponsored by the Dept. of Science & Technology, Govt. of India. TTA and RJK have participated in this study when TTA held research grants of the Finnish Academy during the years 1994-1998. Dr. R.C. Nymati, former associate of TCD, assisted in the compilation of the data, and Sri. T.L. Sudhakara, present associate, has rendered valuable help in the final processing, compilation and preparation of the electronic version of this paper. We are indebted to Prof. R.P. Viljoen for reviewing the paper and offering many valuable suggestions.

References

- ALAPIETI, T.T., HALKOAHO, T.A.A., DEVARAJU, T.C. and JAYARAJ, K.R. (1994) Chromitite-hosted PGE mineralization in the Channagiri area, Karnataka State, India. VII International Platinum Symposium, 1-4 August, Moscow (Abstract), pp.3-4.
- ALAPIETI, T.T. and LAHTINEN (1986) Stratigraphy, petrology and platinum-group element mineralization of the early Proterozoic Penikat layered intrusion, Northern Finland. Econ. Geol. v.81, pp.1126-1136.
- CABRI, L.J. (1981) The platinum-group minerals. In: L.J. Cabri (Ed.), Platinum-group elements: Mineralogy, Geology and Recovery. Canadian Institute of Mining and Metallurgy Montreal, CIM Spec. Publ., v.23, pp.83-150.
- CAWTHORN, R.G. (1999) Platinum-group element mineralization in the Bushveld complex: A critical reassessment of geochemical models. South African Jour. Geol., v.102(3), pp.268-281.
- CHADWICK, B., VASUDEV, V.N. and JAYARAM, S. (1988) Stratigraphy and structure of Late Archaean Dharwar volcanic and sedimentary rocks and their basement in a part of the Shimoga

JOUR GEOL SOC INDIA, VOL 65, JUNE 2005

Basin, East of Bhadravathi, Karnataka. Jour. Geol. Soc. India, v.32 pp.1-19.

- COGHILL, B.M. and WILSON, A.H. (1993) Platinum-group minerals in the Selukwe subchamber, Great Dyke, Zimbabwe: Implications for PGE collection mechanisms and postformational redistribution. Mineral. Mag., v.57 pp.613-633.
- DALTRY, V.D.C. and WILSON, A.H. (1997) Review of platinumgroup mineralogy: compositions and elemental associations of the PG-minerals and unidentified PGE-phases. Mineral. Petrol., v.60, pp.185-229.
- DEVARAJU, T.C., ALAPIETI, T.T., HALKOAHO, T.A.A., JAYARAJ, K.R. and KHANADALI, S.D. (1994) Evidence of PGE mineralization in the Channagiri mafic complex, Shimoga district, Karnataka, Jour. Geol. Soc. India, v.43, pp.317-318.
- HALKOAHO, T. (1994) The Sompujarvi and Ala-Penikka PGE reefs in the Penikat layered intrusion, Northern Finland: Implications for PGE reef-forming processes. Doctoral dissertation submitted to Faculty of Sci., Univ. Oulu, Finland, pp.115.

SHORT COMMUNICATION

- HIEMSTRA, S.A. (1985) The distribution of some platinum-group elements in the UG2 chromite layer of the Bushveld complex. Econ. Geol. v.80, pp.944-957.
- MERKLE, R.K.W. (1992) Platinum-group minerals in the middle group of chromitite layers at Marikana, western Bushveld complex: indications for collection mechanisms and post magmatic modification. Can. Jour. Earth Sci. v.29, pp.209-221.
- MUTANEN, T. (989) Koitelainen intrusion and Keivista-Satovaara complex. Excursion Guide 5th International Platinum Symposium. Geol. Surv. Finland, Guide 28, pp.1-49.
- NALDRETT, A.J. and LEHMANN, J. (1988) Spinel non-stoichiometry as the explanation for Ni, Cu- and PGE-enriched sulphides in chromites. *In:* H.M. Prichard, P.J.Potts, J.F.N. Bowles and

S.J. Cribb (Eds.), Geoplatinum 87 Symposium, London, Elsevier, pp.93-109.

- SCOON, R.N. and TEIGLER, B. (1994) Platinum-group element mineralization in the critical zone of the western Bushveld Complex: I Sulphide-poor chromitites below the UG2. Econ. Geol. v.89, pp.1094-1121.
- TREDOUX, M., LINDSAY, N.M., DAVIES, G. and MACDONALD, I. (1995) The fractionation of platinum-group elements in magmatic systems with the suggestion of a novel causal mechanism. South African Jour. Geol, v.98, pp.157-167.
- VON GRUENEWALDT, G., HULBERT, J. and NALDRETT, A.J. (1989) Contrasting platinum-group element concentration patterns in cumulates of the Bushveld Complex. Mineralium Deposita, v.24, pp.219-229.

(Received: 23 October 2004; Revised form accepted: 20 January 2005)

752