

## **Titanate-Zircon-Apatite Bearing Diorite-Monzodiorites and their Resource Potentiality**

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### ***Abstract***

*Placer beach sand deposits are considered as the reserve for ilmenite, rutile, zircon, monazite, xenotime. The global reserve for titanium, zirconium and rare earth metals is accounted from the distribution of these minerals in the beach sand. It is proposed to look into Archean diorites and monzodiorites as the potential resource for these minerals. These rocks contain sphene, ilmenite, zircon and apatite in trace amount but account for about 3 wt% of TiO<sub>2</sub>, 700 ppm of Zr, and about 500-800 ppm of rare earth in bulk. The mineralogical and geochemical characteristic of such rocks is discussed. The potentiality of sphene as a resource for titanium is highlighted*

### **INTRODUCTION**

Titanium, zirconium and rare earth metals are gaining significance for the demand of advanced materials for potential applications in aerospace-, nuclear-, thermal power-, pigments industries and others such as chlor-alkali, metallurgical, paper and pulp, fertilizer, automobile, ceramic, electro-ceramic industries (Bradley and Sabol, 1996; Nair and Subramanyam, 1998; Roskill, 1990). These metals are in demand due to their corrosion resistance, high specific strength, heat transfer properties etc. They have a strategic value due to the lack of deposit of suitable grade. Though all these elements are abundant in the crust, they occur in the rock forming silicate minerals but do not form a deposit of economic grade. Ilmenite, rutile, leucosene, zircon, monazite and xenotime are the minerals in placer beach sand and are the main resource of present day need (Roskill, 1990). Carbonatites are also explored and exploited for rare metals and radioactive metals (Krishnamurthy, 1988). However, the global reserve for titanium, zirconium and rare earth metals is accounted by the distribution of these minerals in the beach sand (Driessen, 1992). The present work proposes titanate-zircon-apatite bearing Archean diorites and monzodiorites as the potential resource for these minerals.

### **ARCHEAN DIORITES AND MONZODIORITES**

Archean terrain exposed on the earth is a portion of deep continental crust down below 30 kilometers from mean sea level in the Archean age. It is a representative of magma, melts at that depth. The granitoids (tonalite-trondhjemite-granodiorite, TTG; or tonalite-trondhjemite-diorite, TTD) of Archean and Precambrian were generated by the partial melting of oceanic crust, sediments, sedimentary rocks and continental crust, whereas the Archean oceanic crustal rocks were evolved from the partly melted primitive mantle, mantle and Komatiites. However, the crustal rocks of andesitic, dacitic, dioritic and sanukitoid type are derived from metasomatised mantle (Shirey and Hanson, 1984; Stern et al., 1989; Stern and Hanson, 1991; Evans and Hanson, 1995; Jayananda et al., 1995) or by magma mixing (Mohanta, 1998). The understanding on the granite petrogenesis has drawn attention towards the Archean sanukitoids with geochemical characteristics hybrid between granites and basalt. The monzodioritic rocks derived from sanukitoid type source materials carry

exotic chemistry with anomalously high content of Ti, Zr, Ba, Sr and rare earth elements (REE) in comparison to the associated granite-granodioritic rocks (Mohanta, 1998).

### ARCHEAN SANUKITOID TYPE ROCKS AND THEIR DERIVATIVES

Archean 'sanukitoids' were reported from southwestern Superior Province by G. N. Hanson and his group, and were characterized through mineralogy, geochemistry, trace element geochemistry and isotope geochemistry, and their petrogenetic modeling. Similar types of rocks were also reported as Dod gneiss at the western part of Kolar Schist Belt in the eastern Dharwar craton (Balakrishnan and Rajamani, 1987). These rocks were characterized by a chemistry : 55-60 wt.%  $\text{SiO}_2$ ,  $\text{MgO} > 6$  wt.%,  $\text{Mg\#} > 0.6$ , Ni and Cr both  $> 100$  ppm,  $\text{Na}_2\text{O} + \text{K}_2\text{O} = 6$  wt.%, Sr and Ba both 600-1800 ppm and rare-earth-element (REE) pattern that are strongly light rare-earth-element (LREE) enriched ( $\text{Ce}_N = 80-250$ ,  $\text{Yb}_N = 4-10$ ) and show no Eu anomaly. This suite shows synkinematic to early postkinematic intrusive complexes consisting of monzodiorite and spatially and temporally related diorite, monzonite and granodiorite. The rocks of this suite contain quartz, alkali feldspar and plagioclase feldspar and distinctive mafic minerals of clinopyroxene (salite to augite), amphibole, (edenite, magnesio hornblende, actinolitic hornblende), and biotite with accessory sphene, apatite and epidote.

Ganga quartz-monzodiorite (GMD) of Gangam Complex (Mohanta, 1998; Zachaiah et al., 1996) at the western part of Ramagiri Schist Belt in the eastern Dharwar craton is derived from the sanukitoids as suggested by geochemical modeling (Mohanta, 1998). It has a characteristic geochemistry of silica undersaturation to nearly saturation with 55-65 wt.% of  $\text{SiO}_2$ , metaluminous, high FeO (5.5-9 wt%) and low  $\text{MgO}$  (1.5-2.5 wt%), low Ni and Cr content (50 ppm each), high concentration of other trace elements like Ba (430-1380 ppm), Sr (330-500 ppm), Zr (300-770 ppm) and light rare-earth-elements (Ce in the range of 240-428 ppm, total REE about 490-720 ppm) as detailed in the Table-1, and LREE-enriched REE-pattern (Fig.1). The exotic chemistry of this rock type suggests the possibility of heavy minerals as the host of Ti, Zr and REE.

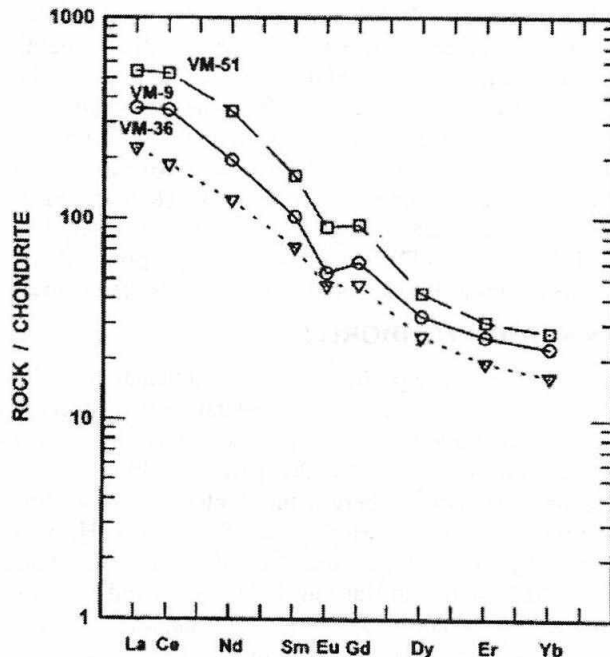
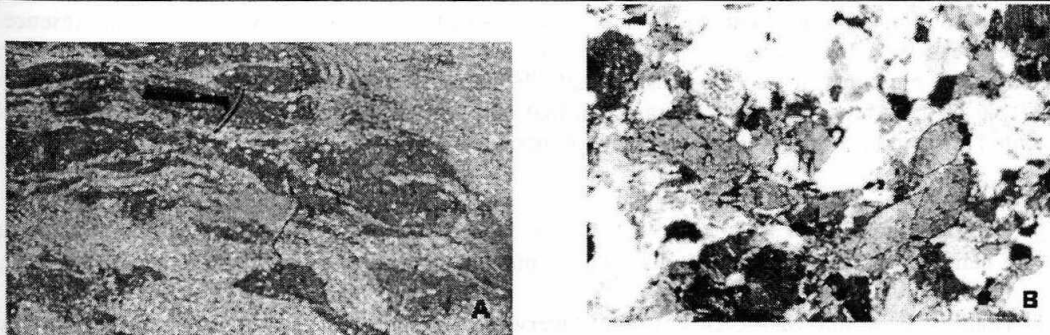


Fig. 1: Chondrite Normalised REE Pattern of Ganga Quartz-Monzodiorites (GMD) and Mafic Variants of Ganga Quartz-Monzodiorite (Mafic GMD, Square Symbol) in Gangam Complex

**Table 1: Geochemical Data of Ganga Diorites-Monzodiorites-Quartz Monzodiorites Compared with Reported Dod Gneiss and Sanukitoids**

	GMD				Dod Gneiss	Sanukitoids	
	mafic GMD	mafic GMD					
Wt% / No.	VM-51	VM-36	VM-9			# 5-80	# 41-66
SiO <sub>2</sub>	50.15	55.6	60.04		64.69	54.55	58
TiO <sub>2</sub>	2.31	2.2	1.29		14.48	0.72	0.71
Al <sub>2</sub> O <sub>3</sub>	17.33	14.13	14.92		0.49	14.38	14.3
Fe <sub>2</sub> O <sub>3</sub> (T)	11.06	9.95	7.67		4.85	8.56	7.74
MnO	0.13	0.12	0.08		2.97	0.12	0.11
MgO	2.95	2.46	1.77		0.09	7.98	5.99
CaO	7.18	4.97	4.55		3.7	8.71	5.96
Na <sub>2</sub> O	4.62	3.95	4.37		3.9	2.87	3.61
K <sub>2</sub> O	3.52	2.5	3.16		2.79	1.34	2.43
P <sub>2</sub> O <sub>5</sub>	0.68	0.45	0.41		0.27	0.36	0.35
TOTAL	98.82	95.34	97.49		98.24	99.59	99.2
Mg#	0.35	0.33	0.31		0.55	0.69	0.64
Ni	41	55	32		72	188	159
Cr	37	54	36		100	469	291
Ba	1502	429	1134		819		
Sr	960	408	511		574	650	1164
Zr	274	393	766		150	138	140
La	171.2	70.67	111.4			28.4	
Ce	428.3	150.8	280.5		112.88	64.7	86.4
Nd	204.2	73.65	116.5		47.43	33.4	42.4
Sm	31.36	13.83	19.62		7.94	6.39	7.23
Eu	6.54	3.36	3.88		1.73	1.64	1.77
Gd	24.07	12.18	15.72		5.41	5.1	4.85
Dy	13.86	8.48	10.65		3.9	4.44	3.47
Er	6.54	4.09	5.49		1.92	2.5	1.79
Yb	5.63	3.41	4.7		1.64	2.31	1.64



**Fig. 2: [A] Occurrence of gangainonzodiorite-quartz monzodiorite and its variants (Inesocratic to melanocratic colour) in the field. [B] Photomicrograph of lozenge shaped sphene and ilmenite associated with biotite and feldspars in Ganga quartz monzodiorite, under transmitted light and crossed nicols, 625X**

## **GEOLOGICAL OCCURRENCE AND MINERALOGY OF GMD**

GMD occurs as synkinematic to early postkinematic intrusives and enclaves associated with a spectrum of co-magmatic porphyritic granodiorites with several transitional units in the area adjacent to the village Gangampalli. It is massive, mesocratic to melanocratic, medium grained, equigranular rock comprised of feldspar, biotite, hornblende and quartz with occasional laths of feldspars, and characteristically significant amount of accessory phases. The accessory phases are sphene, zircon, apatite, ilmenite and magnetite. Hornblende and biotite occur in the intergranular space between feldspars and quartz with their abundance increasing in the mafic variants. The modal distribution of minerals is about trace to 23 % of quartz, 47-58 % of plagioclase, 1% of perthite, 15-23% of biotite, 16-24% of hornblende. Apatite, zircon, sphene, ilmenite and magnetite comprise 1-4% of modal mineralogy. It is comparable to Dod gneiss and sanukitoids by the mineral abundance of these accessory phases. GMD and its variants are grouped as granodiorite, quartzmonzodiorite and diorite based on QAPF modal classification. The abundance of titanates (ilmenite, sphene), zircon and apatite possibly corroborates the exotic concentration of Ti, REE and Zr in these rocks.

## **HEAVY MINERALS**

Sphene, ilmenite, zircon and, apatite are usually associated with biotite and hornblende, occasionally grown at the intergranular space between feldspars. Their grain size varies proportionally with the grain size of the matrix minerals and is the smaller towards the mafic variants. Ilmenite proportion also increases towards the mafic variants. Sphene in mafic variants are fine grained with irregular shape whereas those in the felsic variants are larger in size with lozenge shape, overgrown around precursor minerals like ilmenite and make direct contact to the feldspars. The electron-probe micro-analysis shows that  $\text{TiO}_2$  content of sphene is about 37-43 wt.% and that of ilmenite is in the range of 49-51 wt.%. The larger grains of sphene in felsic variants contain ~37 wt% of  $\text{TiO}_2$ , ~26.7 wt% of CaO, and 29.8 wt% of  $\text{SiO}_2$  is comparable to reported value of natural ones. Sphenes juxtaposed with ilmenite contain higher amount of  $\text{TiO}_2$  about 41-43 wt% much above reported value. The fine grained sphene in mafic GMD are of Ti-enriched ones with lower amount of  $\text{SiO}_2$  (~29 wt%) and higher amount of CaO (~29 wt%). The distribution of Ti is variable grain-to-grain and within grain of sphene. Considering the  $\text{TiO}_2$ -content, sphene can also be considered as a potential heavy mineral resource for titanium.  $\text{TiO}_2$ -content in ilmenites is about 49.5% comparable to the chemistry of natural ilmenites reported elsewhere.

## **CONCLUSION**

Amongst the titanates, the most recognized resource is ilmenite and rutile. However, sphene can also be a resource for titanium if explored for and reserves estimated. The study indicates the presence of silicate rocks with high content of Ti, Zr, REE and mineralogical attributes with heavy minerals hosting these elements. It may be possible that silicate rocks with more exotic geochemistry may be available in the Archean gneissic terrains. In that case, the drainage basins of such terrains may be potential areas to be explored for these heavy minerals.

## **REFERENCES**

- [1] Balakrishnan, S. and Rajamani, V. (1987) Geochemistry and petrogenesis of granitoids around Kolar Schist Belt, southern India: constraints for the evolution of crust in the Kolar area, *J. Geology*, V-95, pp.219-240.
- [2] Bradley, E. R. and Sabol, G. P. (1996) Overview, Zirconium in the Nuclear Industry, American Society for Testing and Materials, USA.
- [3] Driessen, A. (1992) Australia's resources of rare earths, In: R. G. Bautista and N. Jackson (Eds.) Rare Earths Resources, Science, Technology and Applications, The Minerals, Metals & Materials Society, Warrendel, USA, pp.3-14.

- [4] Evans, O. C. and Hanson, G. N. (1995) Late- to post-kinematic Archean granitoids of the S.W. Superior Province: derivation through direct mantle melting, In: L. Ashwal and M. de Witt (Eds.), *Tectonic Evolution of Greenstone Belts*, Oxford University Press.
- [5] Jayananda, M., Martin, H., Peucat, J-J. and Mahabaleswar, B. (1995) Late Archean crust-mantle interactions: geochemistry of LREE-enriched mantle derived magmas. Example of the Closepet batholith, southern India, *Contributions to Mineralogy and Petrology*, V-119, pp. 314-329.
- [6] Krishnamurthy, P. (1988) Carbonatites of India, *Exploration and Research for Atomic Minerals*, V-1, pp.81-115.
- [7] Mohanta, M. K. (1998) Geochemistry and nuclear energy potential of the granitic gneisses around Ramagiri Gold Fields, Unpublished Ph.D. Thesis, Jawaharlal Nehru University, New Delhi, India, p.319.
- [8] Nair, C. G. K. and Subramanyam, R. B. (1998) Titanium, Nonferrous Metals Strategy cum Source Book, Book-5, Indian Institute of Metals and Technology Forecasting Assessment Council, New Delhi.
- [9] Roskill (1990) *The Economics of Zirconium*, Roskill Information Services Ltd., London, p.213
- [10] Shirey, S. B. and Hanson, G. N. (1984) Mantle derived Archean monzodiorites and trachyandesites, *Nature*, V-310, pp.222-224
- [11] Stern, R. A., and Hanson, G. N., (1991) Archean high-Mg granodiorite: a derivative of light rare earth element- enriched monzodiorite of mantle origin, *J. Petrology*, V-32, part-1, pp.201-238.
- [12] Stern, R. A., Hanson, G. N., and Shirey, S. B. (1989) Petrogenesis of mantle derived , LILE-enriched Archean monzodiorite and trachyandesites (sanukitoids) in southwestern Superior Province, *Can. J. Earth Science*, V-26, pp.1688-1712.
- [13] Zachariah, J. K., Mohanta, M. K. and Rajamani, V. (1996) Accretionary evolution of the Ramagiri Schist Belt, eastern Dharwar craton, *J. Geol. Soc. India*, V-47, pp.279-291.