# Noble metals, u, Pb and HREE bearing baddeleyite from placer sands of Manavalakurichi, Tamil Nadu, India

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**Abstract:** Heavy mineral placer sands were collected from Manavalakurichi, Tamil Nadu. A broken piece of a euhedral grain of dark brown placer sand grain was examined under High Resolution Scanning Electron microscope attached with EDAX probe analyzer. The grain is enriched with zirconium oxide but it is greatly impoverished in silica to form zircon. From normative calculation, it is known that $ZrO_2$ remains as 47% wt% as baddeleyite after saturating 36% of zircon with all available cations to fill tetrahedral sites. The mineral is enriched with heavy rare earth elements, dense platinum group of elements and gold. LREE, PGE of lower atomic numbers and Ag are characteristically absent in this mineral. The numbers of ions calculated on the basis of 2(O) ions for baddeleyite ($Zr_{0.662}$ $P_{0.065}$ $Fe_{0.029}$ $Y_{0.029}$ $U_{0.028}Dy_{0.014}Si_{0.111}Hf_{0.008}Al_{0.008}$ $Os_{0.008}Ir_{0.008}Pt_{0.007}Pb_{0.007}Ta_{0.006}Au_{0.006}Ti_{0.005}Lu_{0.005}Na_{0.004}Yb_{0.004}$) structure indicating deficiency of 0.105 metallic ions after entering all the metallic ions into the mineral structure. The high Zr/Hf, ratio of 45.9 indicates that early crystallization of baddeleyite. Therefore, it might be related to the provenance of either silica undersaturated ultrabasic rocks or volcanic rocks derived from mantle horizon probably crystallized at temperature below $1170^{\circ}C$.
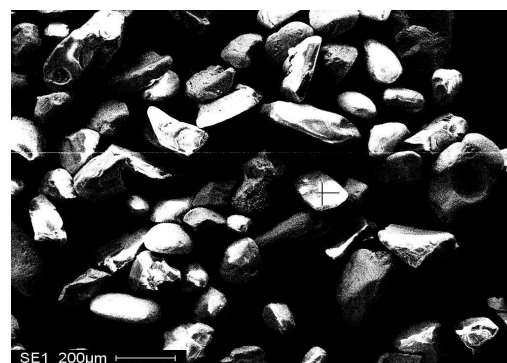
**Keywords:** Baddeleyite, Zircon, Platinum Group of Elements, Heavy Rare Earth Elements, Gold, U-Pb, Beach Placers

## 1. Introduction

Garnet, ilmenite, rutile, zircon and monazite concentrated placer sands were collected from Manavalakurichi, Tamil Nadu for geochemical studies of these minerals. Energy dispersive X-ray microanalyses (EDAX) showed that one of the grains studied was enriched with $ZrO_2$. Its geochemical properties were studied and reported it as a rare mineral of baddeleyite in this short communication. It is dark brown square shaped grain and occurs as a broken piece of a euhedral grain (Fig. 1) showing distinct (001) cleavages and striations. It has tabular form with pyramidal faces at its corners. The length (150μm) and breadth (120μm) ratio is 5:4 and almost equidimension in nature.
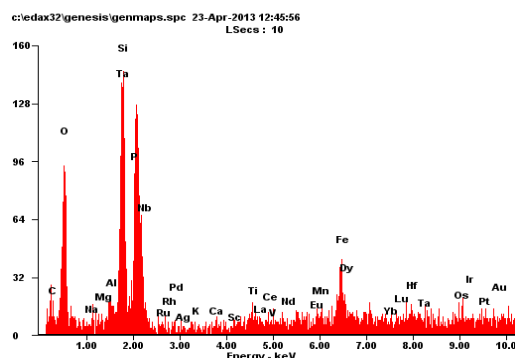
## 2. Methodology

Before examination under High resolution Scanning Microscope sand grains were strewn on a carbonated adhesive tape and subjected to coating of thin film of gold for 90 seconds for better clarity under higher magnification and to avoid charging of the mineral grains. It was verified



*Figure 1. Baddeleyite is indicated by the cursor point at which the mineral is analyzed.*

that the gold coating did not have any added effect on the trace element of gold content in the mineral investigated. The analyses were carried out using Micronsperpixy-0031 attached with an EDAX probe high resolution SEM in the Metallurgical Engineering and material Science Laboratory, Indian Institute of Technology Madras (IITM), Chennai-36. Energy Dispersive X-ray micro-spot analysis of the individual grain (Fig. 1) was made. Counts versus electron

volts keV were measured for various elements present in the mineral in Fig. 2.



**Figure 2.** *The peaks of elements analyzed plotted counts frequencies against electron energy in keV.*

The figure 2 represents the chemical composition at the site of cursor position where the EDAX analysis was made. The elements were recalculated into their oxide contents. Only total iron is reported in the form of FeO. $H_2O$ and other volatiles like F, Cl, $CO_2$ $CH_4$, and $SO_3$ were not determined. Further, some suspected presence of V, Nb, Th, Sb, Te, Bi, As, Cu, Cr, Ni, F and Cl are also not detected for better reliability and noise reduction. The quantitative oxidation states of some trivalent and divalent transition elements including REE were not known. Therefore, distributions oxygen atoms in normal oxidized state in the mineral were not calculated. The contents of moisture and loss of ignition are not included. The limitation of error do not exceed over $\pm 2\%$.

# 3. Results and Discussion

The elemental analyses carried out by the probe (Fig. 2) were recalculated into their oxide contents.  A heavy mineral characteristically was represented a high content of ZrO2 with relative impoverishment of $SiO_2$ to form zircon was studied and reported as baddeleyite. The chemical composition of the mineral in weight percentage is given as follows; $SiO_2$ 5.489, $Al_2O_3$ 0.342, FeO 1.534, MnO 0.160, $Na_2O$ 0.103, $TiO_2$ 0.334, $P_2O_5$ 3.824, $Dy_2O_3$ 1.269, $Yb_2O_3$ 0.597, $Lu_2O_3$ 0.748. $Y_2O_3$ 2.677, $ZrO_2$ 67.102, $HfO_2$ 1.462, PbO 1.377, $UO_2$ 6.134, $Ta_2O_5$ 1.176, $OsO_4$ 1.746, $IrO_2$ 1.535, PtO 1.354, and $Au_2O_3$ 1.038. The structural formula on the basis of 2(O) atoms is ($Zr_{0.662}$ $P_{0.065}$ $Fe_{0.029}$ $Y_{0.029}$ $U_{0.028}Dy_{0.014}Si_{0.111}Hf_{0.008}Al_{0.008}$ $Os_{0.008}Ir_{0.008}Pt_{0.007}$ $Pb_{0.007}$ $Ta_{0.006}$ $Au_{0.006}Ti_{0.005}Lu_{0.005}Na_{0.004}Yb_{0.004}$)    The weight percent of oxygen element is only 16.315%. However, to form oxides of respective elements analyzed is 20.775% considering all Fe element in the form of reduced state as FeO. Some REE elements belonging to the group of transition elements have low degree of oxidation states as that of iron as in the state of FeO as well as $Fe_2O_3$. In order to meet oxygen deficiency some rare earth elements may be in the reduced state and the presence of noble metals of Os (0.008 ions), Ir (0.008 ions), Pt (0.007 ions) and Au (0.006

ions) on the basis of 2(O) ions may be present in the form of metals without forming their oxide components. Heavy rare earth elements of Dy 0.014 ions, Yb 0.004 ions 0.005 ions are present in their structural formula. Again, it reveals that almost all required elements have been detected.   The chemical composition of baddeleyite was re-calculated on the basis of 2 (O), as it is belonging to rutile group to derive their structural formula. The metal ions are slightly lesser than 1. The significant amount of U 0.028 ions and Pb 0.007 ions are characteristic of the mineral. Hence, it is considered to be raw a material for nuclear fuel ($UO_2$ 0.08% $ZrO_2$ 92% wt.% ). Baddeleyites in many occurrences are used for geo-chronologic studies to determine age of layered ultramafic complexes [1, 2]. The Rittmann's normative mineral proportions are as follow: zircon 35.69, baddeleyite 47.43, xenotime 12.93, ilmenite 0.96, platinum group of metals 2.40, and gold & silver 0.60    in weight percentages. P (0.065 ions) and Y (0.029 ions) together form xenotime of 12.93 wt%. Dissolution of significant amount of xenotime may be possible by the enrichment of $P_2O_5$ and $Y_2O_3$. Zircon of 36% is dissolved into the 47% of baddeleyite with dissolution of 1% of ilmenite [3].

The P-T phase diagram for $ZrO_2$ ($ZrO_2$ 92% $SiO_2$ 8% wt. %) shows that baddeleyite [4] is monoclinic under igneous crystallization conditions (T<1000°C, P < 4 GPa). Zr/Hf ratio is 45.9 indicating its early magmatic crystallization of silica undersaturated ultramafic rocks, carbonatites, anorthosites or volcanic basalts derived from mantle source [5, 6]. The absence of LREE, platinum group of elements having lower atomic numbers and the absence of Ag lying adjacent to Pd are the characteristic of the baddeleyite mineral. On the other hand enrichments of HREE, Os, Ir, Pt and Au indicate the early crystallization of baddeleyite (density~5.6gm/cc) before the crystallization of zircon (density~4.6gm/cc) in alkaline environment. Baddeleyite is mostly found in silica undersaturated ultramafic rocks and volcanic rocks derived from mantle horizon. The occurrence of noble metals might be formed at interstitial grain boundaries as micro-platelets and this should be confirmed by future studies under higher magnifications. The presence of significant amounts of Os, Ir, P and Au, the exploration of such minerals and metals in carbonatite, anorthosite and ultramafic complexes will improve the economy of the country. The intimate relationships of REE between PGE, silver and gold opens new avenues for geochemical explorations in these rock types and in coastal placer deposits.

# 4. Conclusion

The high contents HREE, Au and dense PGE indicate that the mineral might be formed from deep-mantle source.  The beach placers associated with baddeleyite, zircon, ilmenite, rutile, garnet and monazite might be looked for Ag, Au and PGE contents and possible evaluation of processing techniques should be evolved to separate these precious metals and rare earth elements economically.

# Acknowledgement

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