# TITANITE-ILMENITE ASSEMBLAGE IN GRANODIORITE OF WASIMI, SOUTHWESTERN NIGERIA

Ehitua Julius Oziegbe<sup>1</sup>, Olubukola Oziegbe<sup>2</sup> and Olusola Titilope Kayode<sup>3</sup>

- Department of Geosciences, Faculty of Science, University of Lagos, Nigeria (eoziegbe@unilag.edu.ng)
- Department of Biological Sciences, College of Science and Technology Covenant University, Nigeria
- 3. Department of Physics, College of Science and Technology, Covenant University, Nigeria

## Abstract

Mineral assemblage observed is amphibole + biotite + plagioclase + quartz + titanite + ilmenite + apatite. Titanite occur as anhedral grains interstitial between biotite and plagioclase feldspars, intergrown with amphibole (or as inclusion) and biotite (or replacing it). Also, anhedral titanite forms reaction rim around ilmenite. Amphiboles have sieve textures with inclusions of plagioclase, titanite, ilmenite and quartz. In addition, amphibole forms reaction rim around biotite, plagioclase and quartz. Two sets of plagioclase were identified, Plagioclase 1 occur as inclusion in biotite and amphibole, while Plagioclase 2 mantles both amphibole and biotite. Anhedral quartz occur as interstitial grains in contact with amphibole and plagioclase, and in some cases mantles plagioclase feldspar. Textural observations made on the rock strongly suggest that Plagioclase 1 could have supplied Ca, while ilmenite loses its FeO to the formation of titanite rims and subsequent formation of biotite. Biotite could have taken K<sub>2</sub>O and FeO and Plagioclase 2 enriched in albitic component. The reaction rim of amphibole on most of the other minerals is an indication that amphibole formed in the late stage of crystallization.

Key words: Anhedral titanite, ilmenite, reaction rim, magmatic phases, sieve texture

## 1. Introduction

Titanite which commonly occur as accessory mineral can crystallize in both igneous and metamorphic rocks (Franz and Spear, 1985; Lucassen et al., 2003; Pan et al., 2018), and can have magmatic, metamorphic and hydrothermal origins (Mazdab et al., 2007). Igneous titanite occurs mostly as a late-stage mineral in felsic calcalkaline plutons (Kohn, 2017). Titanite are common accessory mineral in granodiorites (Carcangiu et al., 1997; Uher et al., 2019). Accessory titanite has the capability to record formation ages as well as crystallization conditions of magmatic process (Jiang et al., 2016). The iron in titanite is Fe<sup>3+</sup> and occupies the Ti site (Seifert and Kramer, 2003). Titanite can thus be considered an important store or repository for Rare Earth Elements (REE) and High Field Strength Elements (HFSE) in metamorphic and igneous rocks (Tiepolo et al., 2008), oxygen and water fugacity, and fluid composition (Manning and Bohlen, 1991; Cao et al., 2015). Previous study has described granodiorite of Wasimi as dark-spotted, coarse-grained, lightcoloured rock which comprises low-lying outcrops and boulders (Oziegbe et al., 2020a). This study uses the textural relationship to determine the origin of titanite in granodiorite and to interpret the coexistence of titanite with ilmenite and biotite.

# 2. Geological setting

The Nigerian basement complex is part of the Pan-African mobile belt which lies between the West African and Congo Cratons (Figure 1). Wasimi which is the area of study is 12.4 km NE of Ikire. Charnockite, early granitic phases of Older Granite Cycle, and younger granitic phases of Older Granite Cycle, migmatite and amphibolite are the prominent rock units at Wasimi (Figure 2). The units can best be described as Migmatite-Gniess-Granite-Complex (Hubbard, 1975). Early tonalitic and syenitic diapirs and late magmatic, granitic, pegmatitic and aplitic intrusions have been reported within Iwo-Ikire complex of southwestern Nigeria (Hubbard, 1975). 'Older Granite' which is now very common of literature of granite in Nigeria was brought in by Falconer (1911) to differntite the concordant or semi-concordant granites (or deep-seated) of the Basement Complex from the highly discordant (or high-level) tin-bearing granites found in Northern Nigeria.

# 3. Methodology

Thin sections of granodiorite from Wasimi (7° 26' 7.35"N 4° 15' 53.586"E) were prepared and the labouratory of the Depatment of Geology, Obafemi Awolowo University, Nigeria.



**Figure 1**: Location Map showing position of Nigerian sector of the Pan-African Province of West Africa (Turner, 1983).



**Figure 2:** Geologic map of Iwo region of which Ikire-Wasinmi complex is part (Hubbard, 1975). Detailed petrography of the thin sections was done at the labouratory of the Department of Geosciences, University of Lagos, Nigeria using a polarizing microscope. Photomicrographs of areas of interest were taken with the aid of a digital camera.

## 4. Results

## Petrography

The following minerals were observed, amphibole, biotite, plagioclase, titanite, quartz, ilmenite and apatite. Amphibole is light green to brownish in colour having inclusions of titanite, plagioclase, apatite and ilmenite (Figures 3a - 3d) and can be described to have sieve texture. The

inclusions are more concentrated in the cores of amphibole grains. Biotite grains and brown, green in colour and in close contact with amphibole and in some cases rimmed by amphibole (Figures 3e, 3f, 4a & 4b). Also, deep-brown biotite (altered biotite) were observed, most of which have inclusions of titanite. Amphibole and biotite are both mantled by plagioclase feldspar (Figure 4c & 4d). Titanite are anhedral and forms reaction rim on ilmenite (Figures 4a & 4b). Also, titanite occur at the edges of biotite in the proximity of plagioclase (Figure 4e & 4f), and as inclusions in amphibole (Figure 4a). Two generations of plagioclase feldspars were observed, the first generation (Plagioclase 1) which occur as inclusions in biotite and second generation (Plagioclase 2) which mantles both amphibole and biotite (Figure 4d). Anhderal to subehdral quartz occur as interstitial grains in contact with amphibole, biotite and plagioclase (Figure 5). In some cases, anhedral quartz mantles plagioclase feldspars (Figure 5d). Euhedral apatite occur as inclusions mainly in biotite and amphibole, while some grains occur within the matrix (Figures 3c & 3d).

#### 5. Discussion

The textural feature in which titanite reaction rims surround ilmenite has been reported from amphibolite-facies terranes (Harlov and Forster, 2002; Harlov and Hansen, 2005). This texture can be formed from the destruction of minerals such as pyroxenes and hornblende and leaving quartz (Drakoulis et al., 2013). Seive-textured amphibole may be the result of bulk assimilation of xenoliths from the magma during crust-mantle mixing (Beard et al., 2005). Sieve-textured amphibole with inclusions of pyroxene, plagioclase and quartz has previously been described in granodiorite of Wasimi (Oziegbe et al., 2020a). The texture can be used to describe the late-stage formation of biotite and amphibole at expense of orthopyroxene, clinopyroxene, and ilmenite (Beard and Day, 1988; Beard et al., 2005).

**Figure 3:** Photomicrographs of granodiorite showing a) Sieve-textured greenish amphibole (Am), PPL b) sieve-textured amphibole (Am) surrounded by plagioclase feldspar (Pl). XPL c) amphibole (Am) in contact with biotite (Bt), amphiboles and biotite both having inclusions of apatite (Ap), PPL d) amphibole (Am) and biotite (Bt) surrounded by plagioclase feldspar (Pl), XPL e) amphibole (Am) forms reaction rim on both biotite (Bt) and titanite (Ttn), while titanite (Ttn) forms reaction rim on ilmenite (ilm), PPL. f) amphibole (Am) forms reaction rim round biotite (Bt), plagioclase feldspar (Pl) and titanite (Ttn), XPL.



**Figure 4:** Photomicrographs of granodiorite showing a) sieve-textured amphibole (Am) with inclusions titanite (Ttn) and ilmemite (Ilm), take note of reaction rim of titanite (Ttn) on ilmenite (Ilm), biotite (Bt) in contact with amphibole (Am), PPL b) sieve-textured amphibole (Am) with inclusion of tiranite (Ttn) and ilmenite, XPL c) brownish amphibole (Am) in contact with biotite (Bt), PPL d) amphibole (Am) and biotite (Bt) mantled by plagioclase feldspar, XPL, e) titanite (Ttn) along the edges of biotite (Bt), PPL f) titanite (Ttn) between biotite (Bt) and plagioclase feldspar (Pl), XPL.



**Figure 5:** Photomicrographs of granodiorite showing a) reaction rim of titanite (Ttn) on deepbrown biotite (Bt). PPL b) biotite (Bt) surrounded by plagioclase feldspar (Pl) and quartz (Qtz), XPL c) titanite (Ttn) enclosed within biotite (Bt), biotite surrounded by plagioclase feldspar (Pl) and quartz (Qtz), XPL d) plagioclase feldspar (Pl) mantled by quartz (Qtz), XPL.

Such hornblende texture has been ascribed to K- and Si-metasomatism after solidification of the plutonic rocks (Collins, 2003).

Studies have observed that the Ca/Al ratio of a melt influences the presence or absence of titanite in igneous rocks (Frost et al., 2001). Based on the fact that clinopyroxene is absent, the reaction can be represented by Equation (1) (Harlov and Hansen, 2005):

$$Amphibole + Ilmenite + O_2 \implies Titanite + Magnetite + Quartz + H_2O$$
(1)

This implies that  $TiO_2$  is extracted from ilmenite was used in the formation of titanite. Such reactions have been reported in orthogneisses of the amphibolite facies (Harlov. and Förster, 2002). Titanite forming reaction rim on opaque (ilmenite) has been reported in the tonalitic

samples of Iwo region (Oziegbe et al., 2020b). A study on amphibole-orthogneiss has reported a similar texture (Gutiérrez-Aguilar et al., 2021). Also, study on amphibolites has reported a similar texture (Rene, 2008). Clinopyroxene + ilmenite-bearing assemblages have been reported to transform into amphibole + titanite-bearing assemblages (Frost et al. 2001). Titanite has been reported to commonly form with amphibole in the late stage of crystallization (Xirouchakis et al., 2001).

Titanite along biotite grains (Figures 4e & 4f) is an indication that titanite is a by-product of the reaction in which plagioclase replaces biotite (Wintsch et al 2015). Plagioclase could be the source of Ca for titanite (Imon et al., 2002), while silica could be from the dissolution of quartz. Textural feature show plagioclase feldspar mantled by quartz (Figure 5d). Anhedral titanite has been described as secondary titanite forming as reaction rim around primary magmatic phases (Piccoli et al., 2000). The replacement of ilmenite by titanite in the absence of magnetite is indicative of relatively low oxygen fugacity (Cao et al., 2015). Texture of reaction rim on ilmenite is suggestive of reducing environment for hydrothermal fluid (Cao et al., 2015). Magmatic titanite in interstices/cleavages and enclosed within primary biotite (Figures 4a, 4e, 5a & 5b) can be described as magmatic titanite based on the fact that it was formed before biotite and because the grains occur in the late stage of magmatic process (Cao et al., 2015). The reaction texture in Figures 3a & 4e can be best represented by Equation (2), (Harlov et al., 2006):

$$[XCaAl_2Si_2O_8 + YKAlSi_3O_8 + ZNaAlSi_3O_8] + 3AlFeTiO_3 + AH_2O = Plagioclase 1 Ilmenite [(X-3A)CaAl_2Si_2O_8 + (Y-A)KAlSi_3O_8 + (Z+4A)NaAlSi_3O_8] + 3ACaTiSiO_5 + Plagioclase 2 Titanite AKFe_3Si_3AlO_{10}(OH)_2 (2) Biotite$$

Plagioclase 1 (Ca-rich plagioclase) supplies Ca, while ilmenite loses its FeO to the formation of titanite rims as well as the formation of biotite (Harlov et al., 2006). Biotite takes  $K_2O$  and FeO and Plagioclase 2 is enriched in albitic component. Textures of inclusion of titanite in biotite (Figures 4a, 4b, 5b, 5c & 5d) with the absent of ilmenite in the core can be represented by the reaction in Equation (3), (René, 2019):

Andesine + Ti-rich annite = Titanite + Oligoclase + Quartz (3) This chemical reaction has been proposed for the titanite of late-magmatic origin in I-type granite and spotted granodiorite (Broska et al., 2007; René, 2019).

## 6. Conclusion

As shown in the petrography, straight edges of some mineral grains (amphibole, biotite and plagioclase feldspar), coupled with reaction rim of late amphibole on biotite, plagioclase feldspar and quartz are suggestive of igneous origin. Textural observations made on the rock strongly suggest two origins for titanite: 1) reaction of Ca-rich plagioclase with ilmenite to produce titanite, Na-rich plagioclase (albitic plagioclase) and biotite, and 2) Ca-rich plagioclase (andesine) reacting with biotite (Ti-rich annite) to give titanite, albite-rich plagioclase (oligoclase) and quartz. Amphibole can be interpreted as a product of late stage magmatic crystallization.

## References

Beard, J.S., Day, H.W. 1988. Petrology and emplacement of reversely zoned gabbro-diorite plutons in the Smartville Complex, northern California. Journal of Petrology, 29(5), pp.965-995. Doi.org/10.1093/petrology/29.5.965

Beard, J.S., Ragland, P.C., Crawford, M.L. 2005. Reactive bulk assimilation: A model for crustmantle mixing in silicic magmas. Geology, 33(8), pp.681-684. Doi.org/10.1130/G21470AR.1

Broska, I., Harlov, D., Tropper, P., Siman, P. 2007. Formation of magmatic titanite and titanite– ilmenite phase relations during granite alteration in the Tribeč Mountains, Western Carpathians, Slovakia. Lithos, 95(1-2), pp.58-71. Doi.org/10.1016/j.lithos.2006.07.012

Cao, M., Qin, K., Li, G., Evans, N.J., Jin, L. 2015. In situ LA-(MC)-ICP-MS trace element and Nd isotopic compositions and genesis of polygenetic titanite from the Baogutu reduced porphyry Cu deposit, Western Junggar, NW China. Ore Geology Reviews, 65, pp.940-954. Doi.org/10.1016/j.oregeorev.2014.07.014

Carcangiu, G., Palomba, M., Tamanini, M. 1997. REE-bearing minerals in the albitites of central Sardinia, Italy. Mineralogical Magazine, 61(405), pp.271-283. Doi.org/10.1180/minmag.1997.061.405.10

Collins, L.G. 2003. Transition from magmatic to K-metasomatic processes in granodiorites and Pyramid Peak granite, Fallen Leaf Lake 15-Minute Quadrangle, California.

Drakoulis, A., Koroneos, A., Soldatos, T., Papadopoulou, L. 2013. Mineralogy and chemistry of amphiboles and thermobarometry of Papikion Mt pluton, Rhodope, Northern Greece. Bulletin of the Geological Society of Greece, 47(1), pp.373-382. Doi.org/10.12681/bgsg.11012

Falconer, J.D. 1911. The geology and geography of Northern Nigeria. Macmillan, London. 295 pp.

Franz, G., Spear, F.S. 1985. Aluminous titanite (sphene) from the eclogite zone, south-central Tauern Window, Austria. Chemical Geology, 50(1-3), pp.33-46. Doi.org/10.1016/0009-2541(85)90110-X

Frost, B.R., Chamberlain, K.R., Schumacher, J.C. 2001. Sphene (titanite): phase relations and role as a geochronometer. Chemical geology, 172(1-2), pp.131-148. Doi.org/10.1016/S0009-2541(00)00240-0

Gutiérrez-Aguilar, F., Schaaf, P., Solís-Pichardo, G., Arrieta-García, G.F., Hernández-Treviño, T., Linares-López, C. 2021. Phase equilibrium modelling of the amphibolite facies metamorphism in the Yelapa-Chimo Metamorphic Complex, Mexico. Geoscience Frontiers, 12(1), pp.293-312. Doi.org/10.1016/j.gsf.2020.05.001

Harlov, D.E., Förster, H.J. 2002. High-grade fluid metasomatism on both a local and a regional scale: the Seward peninsula, Alaska, and the Val Strona di Omegna, Ivrea–Verbano Zone, Northern Italy. Part I: petrography and silicate mineral chemistry. Journal of Petrology, 43(5), pp.769-799. Doi.org/10.1093/petrology/43.5.769

Harlov, D. E., Hansen, E. C. 2005. Oxide and sulphide isograds along a Late Archean, deepcrustal profile in Tamil Nadu, south India. Journal of Metamorphic Geology, 23(4), 241–259. Doi:10.1111/j.1525-1314.2005.00574.x

Harlov, D., Tropper, P., Seifert, W., Nijland, T., Förster, H.J. 2006. Formation of Al-rich titanite (CaTiSiO4O–CaAlSiO4OH) reaction rims on ilmenite in metamorphic rocks as a function of fH2O and fO2. Lithos, 88(1-4), pp.72-84. Doi.org/10.1016/j.lithos.2005.08.005

Hayden, L.A., Watson, E.B., Wark, D.A. 2008. A thermobarometer for sphene (titanite). Contributions to Mineralogy and Petrology, 155(4), pp.529-540. Doi.org/10.1007/s00410-007-0256-y

Hubbard, F.H. 1975. Precambrian crustal development in western Nigeria: indications from the Iwo region. Geological Society of America Bulletin, 86(4), pp.548-554. Doi.org/10.1130/0016-7606(1975)86%3C548:PCDIWN%3E2.0.CO;2

Imon, R., Okudaira, T., Fujimoto, A. 2002. Dissolution and precipitation processes in deformed amphibolites: an example from the ductile shear zone of the Ryoke metamorphic belt, SW Japan. Journal of metamorphic Geology, 20(3), pp.297-308. Doi.org/10.1046/j.1525-1314.2002.00367.x

Jiang, P., Yang, K.F., Fan, H.R., Liu, X., Cai, Y.C., Yang, Y.H. 2016. Titanite-scale insights into multi-stage magma mixing in Early Cretaceous of NW Jiaodong terrane, North China Craton. Lithos, 258, pp.197-214. Doi.org/10.1016/j.lithos.2016.04.028

Kohn, M.J. 2017. Titanite petrochronology. Reviews in Mineralogy and Geochemistry, 83(1), pp.419-441. Doi.org/10.2138/rmg.2017.83.13

Lucassen, F., Becchio, R. 2003. Timing of high-grade metamorphism: Early Palaeozoic U–Pb formation ages of titanite indicate long-standing high-T conditions at the western margin of Gondwana (Argentina, 26–29 S). Journal of Metamorphic Geology, 21(7), pp.649-662. Doi.org/10.1046/j.1525-1314.2003.00471.x

Manning, C.F., Bohlen, S.R. 1991. The reaction titanite+ kyanite= anorthite+ rutile and titaniterutile barometry in eclogites. Contributions to Mineralogy and Petrology, 109(1), pp.1-9. Doi.org/10.1007/BF00687196

Mazdab, F.K., Wooden, J.L., Barth, A.P. 2007. Trace element variability in titanite from diverse geologic environments. In Geological Society of America, Abstracts with Programs (Vol. 39, p. 406).

Oziegbe, E.J., Ocan, O.O., Adebisi, A.P. 2020a. Petrography and Microtextural Characteristics of Granodiorite from Wasimi, Southwestern Nigeria. Earth Sciences Malaysia, 4(2): 82-89. DOI: Doi.org/10.26480/esmy.02.2020.51.58

Oziegbe, E.J., Ocan, O.O., Buraimoh, A.O. 2020b. Petrography of Allanite-bearing Tonalite from Iwo Region, Osun State, Nigeria. Materials and Geoenvironment, 67(2), pp.79-89. Doi.org/10.2478/rmzmag-2020-0006

Pan, L.C., Hu, R.Z., Bi, X.W., Li, C., Wang, X.S., Zhu, J.J. 2018. Titanite major and trace element compositions as petrogenetic and metallogenic indicators of Mo ore deposits: Examples from four granite plutons in the southern Yidun arc, SW China. American Mineralogist: Journal of Earth and Planetary Materials, 103(9), pp.1417-1434. Ddoi.org/10.2138/am-2018-6224

Piccoli, P., Candela, P., Rivers, M. 2000. Interpreting magmatic processes from accessory phases: titanite—a small-scale recorder of large-scale processes. Earth and Environmental Science Transactions of the Royal Society of Edinburgh, 91(1-2), pp.257-267. Doi.org/10.1017/S0263593300007422

Rene, M. 2008. Titanite-ilmenite-magnetite phase relations in amphibolites of the Chynov area (Bohemian massif, Czech Republic). Acta Geodynamica et Geromaterialia, 5(3), pp.239-247.

René, M. 2019. Titanite from Titanite-Spots Granodiorites of the Moldanubian Batholith (Central European Variscan Belt). In Mineralogy-Significance and Applications (p. 41). IntechOpen.

Seifert, W., Kramer, W. 2003. Accessory titanite: an important carrier of zirconium in lamprophyres. Lithos, 71(1), pp.81-98. Doi.org/10.1016/j.lithos.2003.07.002

Tiepolo, M., Oberti, R., Vannucci, R. 2002. Trace-element incorporation in titanite: constraints from experimentally determined solid/liquid partition coefficients. Chemical Geology, 191(1-3), pp.105-119. Doi.org/10.1016/S0009-2541(02)00151-1

Turner, D.C. 1983. Upper Proterozoic schist belts in the Nigerian sector of the Pan-African province of West Africa. Precambrian research, 21(1-2), pp.55-79. Doi.org/10.1016/0301-9268(83)90005-0

Uher, P., Broska, I., Krzemińska, E., Ondrejka, M., Mikuš, T., Vaculovič, T. 2019. Titanite composition and SHRIMP U–Pb dating as indicators of post-magmatic tectono-thermal activity: Variscan I-type tonalites to granodiorites, the Western Carpathians. Geologica Carpathica, 70(6). Doi: 10.2478/geoca-2019-0026

Wintsch, R.P., Aleinikoff, J.N., Yi, K. 2005. Foliation development and reaction softening by dissolution and precipitation in the transformation of granodiorite to orthogneiss, Glastonbury Complex, Connecticut, USA. The Canadian Mineralogist, 43(1), pp.327-347. Doi.org/10.2113/gscanmin.43.1.327

Xirouchakis, D., Lindsley, D.H., Frost, B.R. 2001. Assemblages with titanite (CaTiOSiO4), Ca-Mg-Fe olivine and pyroxenes, Fe-Mg-Ti oxides, and quartz: part II. Application. American Mineralogist, 86(3), pp.254-264. Doi.org/10.2138/am-2001-2-307

Zhou, K., Chen, Y.X., Zheng, Y.F. 2021. Geochemistry of polygenetic titanite traces metamorphic and anatectic processes during the exhumation of deeply subducted continental crust. Lithos, 398, p.106314. Doi.org/10.1016/j.lithos.2021.106314