



Field Occurrences of Lithium and Its' Associated Minerals from Kariya and Environs, Ganjuwa L.G.A., Bauchi State, NE Nigeria

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ABSTRACT

The energy transition challenges faced by modern civilization have significantly enhanced the demand for critical metals like lithium resulting in improved methods to explore, extract, and utilize these metals. In this research work, we aim to provide an updated global perspective on various aspects of lithium including its occurrence, mineralogy and different types of deposits. In this research work, we discussed the different types of lithium resources, field occurrences and host rocks of lithium enrichment in various geological settings. The field method was done through systematic mapping and sampling of suspected ore rocks. Hand specimen and petrographic studies were carried out minerals were identified based on petrographic characteristics and relate them to lithium ore. The study area was found viable to host rocks that are associated with lithium ore occurrences most especially the pegmatite, paragneisses and granodiorite rocks.

1. Introduction

The study of lithium and its associate mineral is of prime importance looking at Lithium as a critical element in modern technology and lithium minerals will play a key role in the fight against climate change. Lithium occurs in limited amounts on the Earth in a surprising diversity of mineral species, from pyroxenes to amphiboles, phyllosilicates to phosphates. Lithium was first identified as a component of the mineral petalite and was discovered in 1817 by the Swedish chemist, Johan August Arfwedson. W.T. Brande and Sir Humphry Davy isolated lithium from its mineral for the first time. The name lithium comes from the Greek word 'lithos', meaning stone (Bolewski et al., 1976).

Lithium has an atomic mass of 6.941 g/mol, meaning it has 3 protons, 3 electrons, and 4 neutrons. Lithium is the lightest

metal with a density of 0.534 g/cm³. It is highly reactive and flammable and tends to form hydroxides. It reacts with nitrogen, oxygen, and water vapor in the air, and has never been found in its pure form in nature. For this reason, Li is stored in an inert atmosphere such as pure kerosene or mineral oil, or under a vacuum (Szlugaj and Bak, 2022). With an average crustal abundance of 25 ppm, lithium (Li) is the 25th most abundant element in the Earth's crust (Taylor and McLennan, 1985). Lithium is found in a variety of rocks, clays and brines.

Global climate change has emerged as a major threat to mankind with a substantial focus on the reduction of anthropogenic greenhouse gas emissions. Transportation and power generation sectors are the two largest sources of greenhouse gas emissions (Rogelj et al., 2021; Balaram,



2023a). Crucial and innovative technologies are being developed and effectively applied to mitigate carbon emissions by replacing non-renewable energy resources with renewable energy technologies. In this context, lithium-ion energy storage systems are currently playing a pivotal role in reducing carbon emissions over the world due to their long cycle life and high efficiency (Zubi et al., 2018).

In addition, lithium finds extensive applications in ceramic, glass, steel, nuclear, chemical industries, medicine as well as in several other important areas. The major application of lithium has been in transportation (e.g., hybrid and electric vehicles, electric scooters, e-bikes), and stationary power storage systems for intermittent energy sources (e.g., solar or wind) (Michelini et al., 2023; Ralls et al., 2023). As the world

is going through a major era of energy transition, a significant increase in the global lithium demand is expected.

Economically viable deposits of lithium occur in three major categories: in pegmatites typically as the minerals spodumene and lepidolite; in volcanic clays as hectorite, montmorillonite and bentonite; and from brine and geothermal deposits which includes solar evaporates, playa lakes, and extracted subsurface brines from petroleum and geothermal production. Lithium, the lightest of metals, is a widely used critical industrial mineral. The USGS has classified Lithium as a critical mineral on the last several Critical Minerals lists (USGS, 2023a; USGS, 2023b). The crustal abundance of Lithium is 20-70 ppm by weight. It is usually found in granites, typically granitic pegmatites.

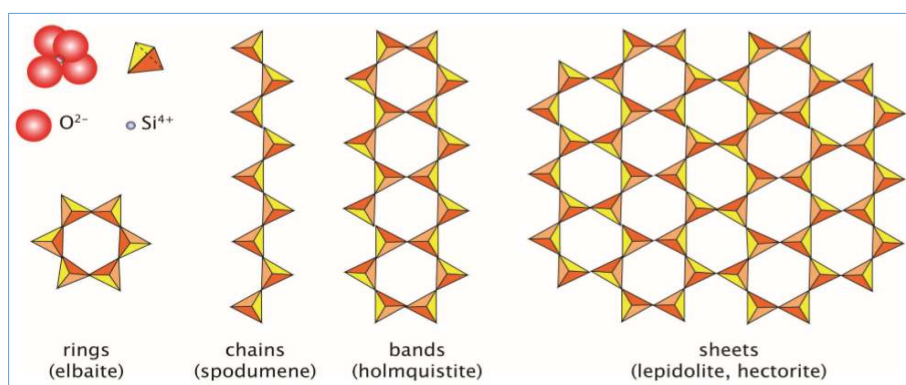


Fig. 1. Arrangements of SiO₄ tetrahedral as found in common rock forming silicates, emphasizing the lithium mineral in each group. These units are held together by other cations: Fe₂⁺, Mg₂⁺, Al₃⁺ or in this case Li⁺

Table 1. Main lithium minerals

Mineral	Formula	Remarks
Spodumene	LiAlSi ₂ O ₆	A number of the pyroxene group
Holmquistite	Li ₂ (Mg,Fe) ₃ Al ₂ Si ₈ O ₂₂ (OH) ₂	A number of the amphibole group
Lepidolite	K(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (Fe,OH) ₂	A number of the mica group (phyllosilicate)
Polyolithionite	KLi ₂ AlSi ₄ O ₁₀ (Fe,OH) ₂	Another member of the mica group
Zinnwaldite	-	No longer recognized as a distinct mineral (see text)
Hectorite	Na _{0.3} (Mg,Li) ₃ Si ₄ O ₁₀ (OH) ₂	Chlorite group
Cookeite	(LiAl ₂)Al ₂ (AlSi ₃ O ₁₀ (OH) ₈	Another phyllosilicate (sheet silicate)
Eucryptite	Li(AlSiO ₄)	A nesosilicate (like olivine) but related to phenakite (Be ₂ SiO ₄)
Amblygonite	(LiNa)Al(PO ₄)(Fe,OH)	Phosphate
Lithiophilite	LiMn(PO ₄)	Phosphate
Triphylite	LiFe(PO ₄)	Phosphate
Elbaite	Na(Li _{1.5} Al _{1.5})Al ₆ Si ₆ O ₁₈ (BO ₃) ₃ (OH) ₄	Tourmaline group
Jadarite	NaSiB ₃ O ₇ OH	A recently discovered Li mineral

2. Regional Geologic Settings

Lithium is associated with many minerals in various igneous rocks such as granite, and pegmatites, spodumene and petalite being the most common minerals. Over 124 lithium mineral species have been recognized mainly in four geologic environments:

- Lithium-Cesium-Tantalum (LCT) granitic pegmatites and associated metasomatic rocks,
- Highly peralkaline pegmatites,
- Metasomatic rocks not directly associated with pegmatites, and
- Manganese deposits.

The LCT pegmatites are associated with the geologically oldest lithium minerals (3,000–3,100 Ma) (Grew, 2020). Though, Li is found in a large number of minerals, it is extracted only from spodumene, lepidolite, amblygonite, petalite and eucryptite.

Lithium a highly reactive metal, only occurs in nature combined with other elements in a variety of minerals. Of these, an important group mimic the common rock forming minerals, being in the form of polymerized SiO₄⁴⁻ groups: rings, chains, bands and sheets which are held together by interstitial lithium and aluminium ions. Thus, enstatite is a form of pyroxene (a common rock forming mineral) and has

the formula MgSiO_3 ($= \text{Mg}_2\text{Si}_2\text{O}_6$), while spodumene has $\text{Li}^+ + \text{Al}_3^+$ in place of the 2Mg_2^+ ($\text{LiAlSi}_2\text{O}_6$).

3. Occurrences of Lithium Ore

Australia, the USA, Canada, Nigeria and the Democratic Republic of Congo are known to host large pegmatite lithium deposits. Several smaller to medium-sized lithium-bearing pegmatites occur in China, Russia, Brazil, India, Mali, and Namibia. There is prominent pegmatite deposits scattered across Europe which are found in Austria (e.g., Wolfsberg lithium deposit), Portugal (e.g., Sepeda deposit), Ireland (e.g., pegmatite deposit of Carlow County), and Finland

(e.g., Lantta deposit), (Gourcerol et al., 2019; Keyser et al., 2023). The bulk compositions of pegmatites are poorly understood because of their highly heterogeneous occurrence. Pegmatites associated with felsic intrusions are texturally complex igneous rocks showing a very coarse texture, with large interlocking crystals. Pegmatites are formed when mineral-rich magma intrudes from magma chambers into the crust. The source granitic magma must be rich in lithium and undergo extreme fractional crystallisation to form pegmatite deposits (London, 2018; Sykes and Schodde, 2019). There is no universally accepted model for the formation of pegmatites.

Table 2. Lithium concentrations in different types of rocks, ores, water, and other geological materials (modified after Balaram et al., 2023)

Type of geological material	Concentration	Reference
Upper continental crust	35 ± 11 ppm	Tang et al., 2004
Continental crust	17 ppm	Rudnick and Gao, 2005
Igneous rocks	29 ppm	Horstman, 1957
Sedimentary rocks	53-60 ppm	Evans, 2014
Hydrothermal water (general)	8.2 ppm	Shaw et al., 1977
Petroleum water	2.0 - 2.7 µg/ml	Shaw et al., 1977
Formation water, Oil wells, British Colombia, Canada	50 ppm	Simandl et al., 2018
Marine sediments (manganese nodules)	139 ppm	Heller et al., 2018
Deep sea sediments (central Pacific)	30.50 ppm	Sreekumaran et al., 1968
Marine sediments (ferromanganese Crusts)	294.3 ppm	Zawadzki et al., 2022
A typical lithium mine ore (~20% spodumene)	1% - 2% Li_2O	Warren, 2021
Brines	200 - 1400 ppm	Gruber et al., 2011
Sea water	0.1 - 0.7 ppb	Li et al., 2021a; Li et al., 2021b
Groundwater	0.9 - 161 ppb (average 13.9)	Sharma et al., 2022
Surface water	<0.5 to 130 ppb (average 3.9)	Sharma et al., 2022
Public supply wells in the U.S.	<1 ppb to 396 ppb with a median of 8.1 ppb	AWWA, 2022
Geothermal water	77.31 - 99.40 ppm	Suud et al., 2023
Brines associated with oilfield	7.56 - 150 ppm	Yu et al., 2023a; Yu et al., 2023b

A basic requirement of pegmatite formation is the initial composition of the pegmatite-forming melt and constraints on the pressure and temperature conditions. During magmatic differentiation, owing to the small value of the coefficient of distribution, the migration routes of Mg and Li are decoupled.

Lithium accumulates in the latest differentiates of granitic complexes at their final stage of consolidation and thus gets concentrated in significant amounts in pegmatites. The final exotic mineral assemblages contain an abundance of lithium in spodumene, petalite, and lepidolite in addition to several others (London, 2018).

Table 3. Lithium Ore Deposits in Nigeria (MMSD, 2022)

Deposits	State	Associated minerals
Panda	Nasarawa	Pegmatite
Wamba	Nasarawa	Quartzite
Kabba	Kogi	Quartzite
Kushaka, Birnin Gwari	Niger	Pegmatite/Petalite
Isanlu Egbe	Kogi	Pegmatite
Ilesha	Osun	Pegmatite
Ijero Aramoko	Ekiti	Pegmatite
Arikya Tsauni	Nasarawa	Pegmatite and Quartzite
Kafin Maiyarki	Nasarawa	Granite
Itakpe Area	Kogi	Quartzite and Pegmatite
Oke Ogun	Oyo	Quartzite
Ago Iwoye	Ogun	Pegmatite
Hong	Adamawa	Lepidolite/Kunzite
Zuru	Zamfara	Petalite
Kafanchan	Kaduna	Spodumene/Kunzite
Lere	Kaduna	Petalite
Jos- South	Plateau	Quartzite/Lapidolite
Ganjuwa	Bauchi	Lithium Oxide/ Lithia
Gidan Boda, Baruten	Kwara	Spodumene
Keffi	Nasarawa	Lepidolite

There are two types of pegmatite deposits: (i) LCT pegmatites, and (ii) other pegmatites associated with magmatic and metasomatic rocks. LCT pegmatites show strong enrichment in Li, Cs, and Ta with the most abundant minerals such as spodumene, petalite, and lepidolite, in subduction and continental collision tectonic settings. Most LCT pegmatites are hosted in metamorphosed supracrustal rocks in the upper green schist to lower amphibolite facies and are mainly associated with Precambrian rocks. For example, the Greenbush pegmatite deposit in Australia was developed in 1983 and accounted for nearly 40% of the output of hard rock lithium in 2021 was formed about 2.5 billion years ago. This deposit is hosted by a giant (2,500 m long and 60-250 m width) pegmatite dyke intruding into amphibolite. It is a complex of tin, tantalum, lithium, and kaolin-bearing pegmatites, with extensive weathered and alluvial material at the surface (Sykes and Schodde, 2019). This deposit has the highest lithium grade (up to 5 wt.% Li_2O). Here spodumene containing lithium ore is mined from the fresh unweathered zones in the open pits. Recently, due to intense exploration for LCT pegmatites to supplement

lithium production from the giant Greenbushes LCT pegmatite deposit, several new pegmatite-hosted spodumene deposits were discovered in the Yilgarn and Pilbara Cratons,

and most of them anomalously enriched in Li with an extensive pegmatite geometry most suitable for open pit mining (Barber et al., 2022).

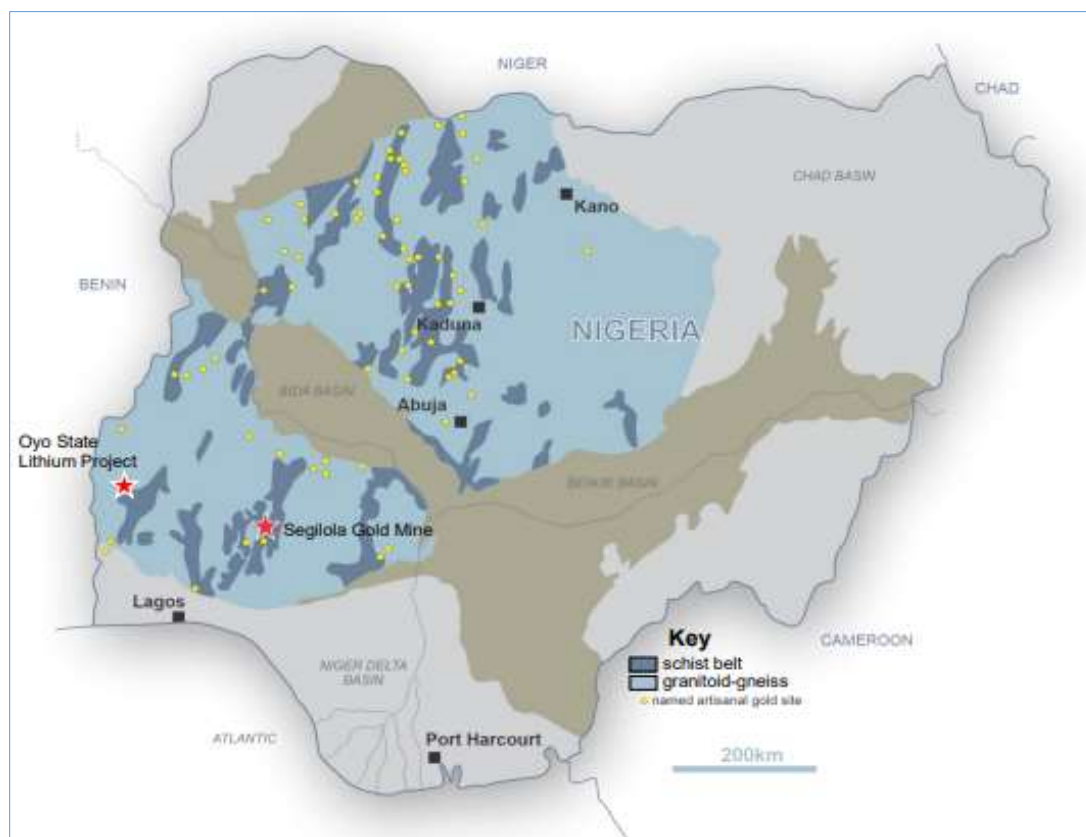


Fig. 2. Map of Nigeria showing areas with Lithium ores

Lithium occurs in three (3) major categories:

- Pegmatites typically as the minerals spodumene and lepidolite.
- Volcanic clays as hectorite, montmorillonite and bentonite (sedimentary rocks).
- Brine and geothermal deposits which includes solar evaporates, playa lakes, and extracted subsurface brines from petroleum and geothermal production.

Spodumene: The name is from Greek meaning 'burnt to ashes', a reference to its most common colour: grey, although other striking colours occurred. Originally spodumene and the related minerals of granite pegmatites (eucryptite, lepidolite and petalite) were the main source of lithium but this position became eclipsed by lithium from brines, which is much cheaper to extract. However, spodumene still has considerable importance as a source of lithium. Pure spodumene ideally contains 8 percent (8%) Li_2O . Spodumene is a type of pyroxene, whose basic structure consists of chains of SiO_4 tetrahedral. Each tetrahedron shares an oxygen ion with its neighbour building up these chains, which are then held together by interstitial Li^+ and Al_3^+ ions. This structure gives an orthorhombic or monoclinic crystal symmetry and two perfect cleavages at almost right angles to each other, which is a disadvantage when the mineral is used as a

gemstone as it is easily broken along these cleavages. Spodumene is normally monoclinic (α -spodumene), but inverts to a tetragonal form Fig. 1 (β -spodumene above 900°C).

4. Gem Quality Types

Gem quality spodumene comes in three varieties:

- Kunzite shows a range of colours from pink to purple,
- Green spodumene is known as hiddenite and
- Yellow varieties are called triphane

These colours are caused by traces of transition metals such as chromium and manganese. Some varieties are quite rare and the striking colours mean they can command high prices for either cutting as gemstones or for sale to mineral collectors.

Granitic pegmatites are the latest products of magmatic crystallization. They consist of large, sometimes gigantic, crystals, whose growth is facilitated by the high content of water and other volatile species (also incompatible components). Such late melts contain high concentrations of the incompatible elements: lithium and other alkali metals, along with metals having highly charged ions, such as tin (Sn_4^+), thorium (Th_4^+), zirconium (Zr_4^+) and niobium (Nb_5^+).

5. Materials and Methods

Various materials were used during the research work such as: Topo Map of the study area was used to demarcate the area of interest and all possible features were noted on it. Relevant field materials (Fig. 3) were used in collecting the samples and measurement were taken for structure observed during the field work.

5.1. Field Method

Traversing method was used at the beginning of the field work to identify the area of study and compare with the information acquired from Topo-map as reconnaissance. Thirty-five (35) different samples at different locations were collected from the field for laboratory studies and hand specimen descriptions.

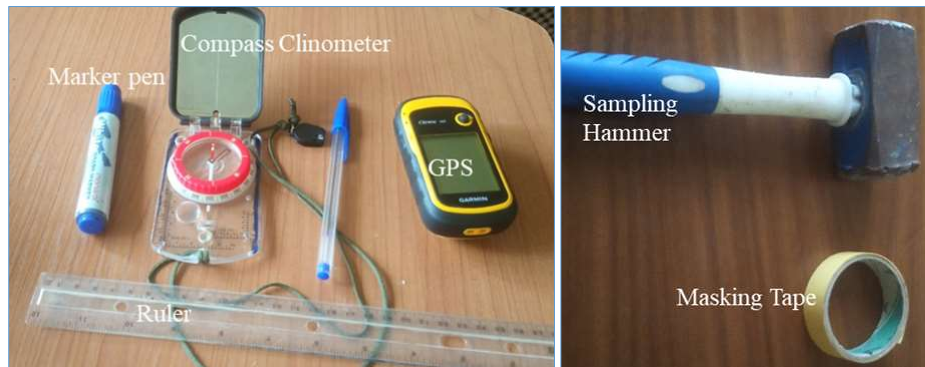


Fig. 3 Materials used in field study

6. Results and Discussions

The study area consists of migmatite and pegmatite rocks. The field work carried out showed that the studied rocks grades from low grade migmatite from western part into medium to high grade migmatites to the central and eastern part.

The occurrence and associations of the various rock types observed in the field are signatures of their genesis. Hand specimen of various rock types sampled at different locations were observed in the field and interpreted based on major rock forming minerals (mineralogy), colour, structures and textural characteristics.



Fig. 4. Field views of Lithium occurrences

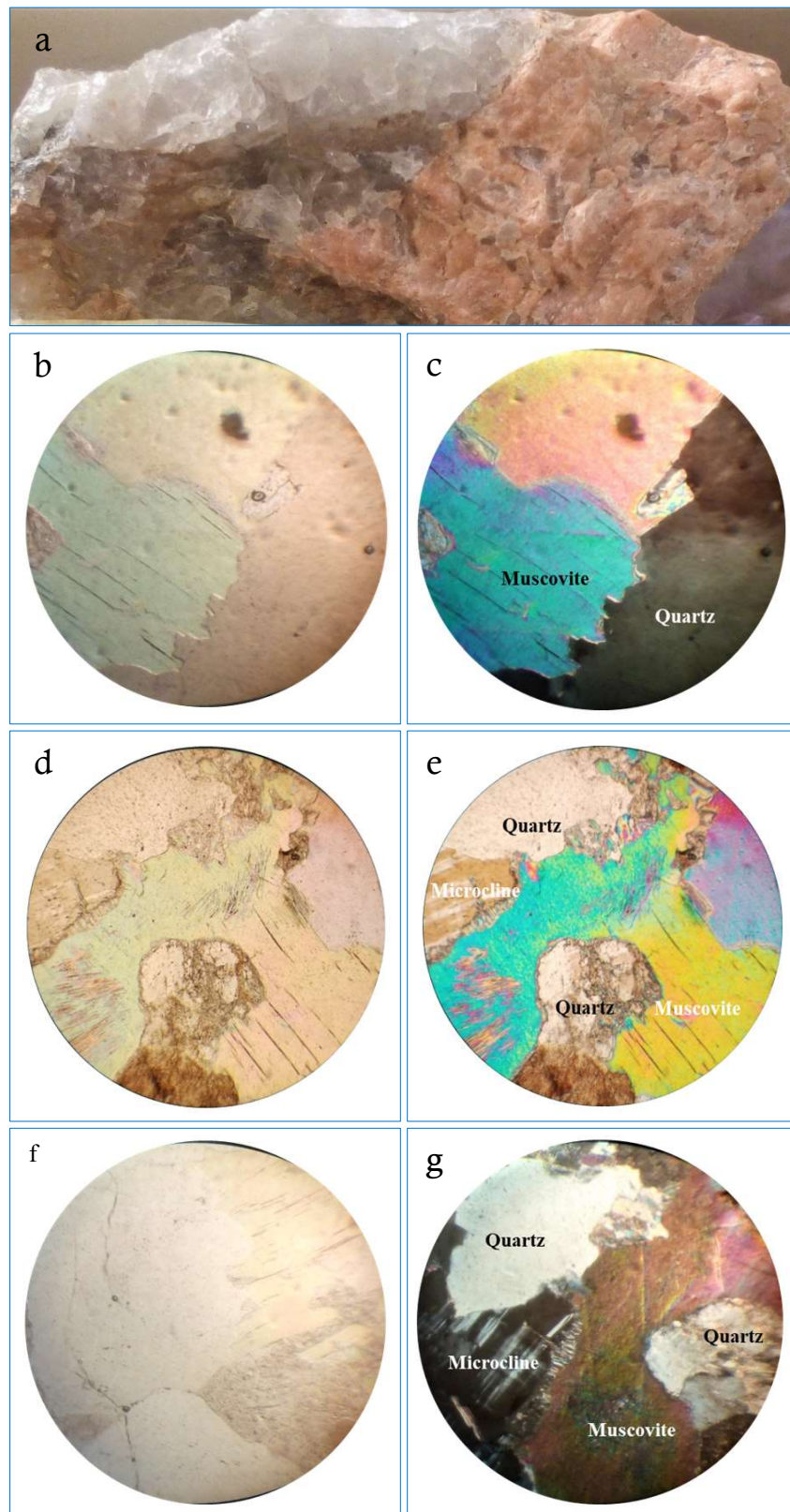


Fig. 5. Hand specimen (a) and photomicrograph of pegmatite (b, c, d, e, f and g)

6.1. Field Relationship

It is observed that the rocks in the study area hosted variable forms of lithium ores. The lithium ore ranges from pegmatite hosted ores and to some extent some occurred as sills those formed within the migmatite rocks. During the field work, various samples were collected at different locations within

the study area. The rocks were found to be migmatite occurring with pegmatites. Some of the migmatite have leucosomes that occurred as sills which were found valuable in lithium ore mineralizations. The migmatites in some areas where paragneisses predominate form the mica lithium bearing whereas areas with fractionated (segregated) into

diatexite to form quartz diorite and granodiorite form the lepidolite to amblygonite lithium ore varieties. Figs. 4a, 4b, 4c and 4d are the various field views of location where lithium ore were suspected and sampled. In Fig. 4a, is a dug pit where artisanal miners started exploiting lithium and its associated minerals (lepidolite) at Gadar Maiwa area, whereas in Fig. 4b is a picture of field occurrence of lithium ore (amblygonite) at around Rakajuwa village along Gadar Maiwa-Ningi road, Bauchi state. The areas where lithium ore (mica bearing and spodumene) were also seen and sampled were areas around Jangu, Natsira, Wushi and Filin Shagari towns all in Kariya area, Ganjuwa LGA, Bauchi state (Figs. 4a, 4b, and 4c).

6.2. Petrographic Studies

Optical studies revealed that the migmatite rock units from the study area are medium to fine grained with the exception of pegmatite which is coarse grained. The main mineral

assemblage include quartz, K-feldspar, plagioclase, biotite, orthopyroxene, serpentinites, cordierite, sillimanite, garnet and opaque. Under hand specimen examination the weakly foliated rock (stromatic migmatite) contains melanocratic and leucocratic minerals in almost equal proportions whereas the isotropic rocks have leucocratic minerals as dominant if compared with melanocratic minerals.

Petrographic investigation indicates that biotite, orthopyroxene, cordierite and opaque minerals constitute the mafic aggregates while quartz and feldspar dominate the felsic assemblage. Quartz contents range from 42 to 57%, feldspar (20-26%), cordierite (3-6%), biotite (9-18%), muscovite (2-4%) while opaque varies between 3 and 8% of the rocks mass. Fig. 5A shows a hand specimen and Figs. 5B-5G photomicrograph of a pegmatite rocks from the research area where quartz in gray, muscovite in blue-green to yellow, microcline with cross hatched twinning were seen and noted.

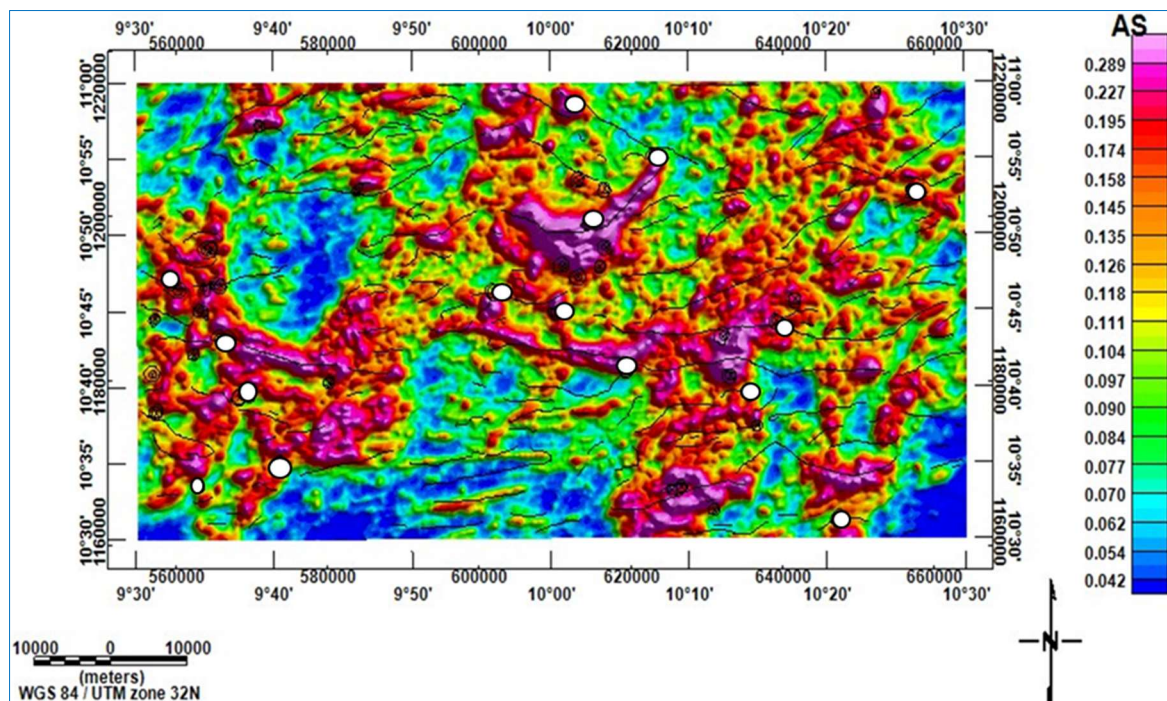


Fig. 6. Magnetic imagery of the research area

6.3. Aeromagnetic Imagery and Lineament Map

The magnetic image of the study area was gotten from NGS Abuja central office. The image was used to have an idea on the effects of rocks in relation to magnetic susceptibility and relate it to economic potentials of the area. The imagery was also used to come up with areas that have anomaly and were marked as hotspots areas for further exploration of economic minerals and hydrogeological search. The magnetic image was superimposed with sample locations and mark them as hotspot areas Fig. 6.

7. Conclusions

This research work based on field work and laboratory analysis (petrographic studies and software interpretations) the following suggestive conclusions were made.

1. The study area was found to be migmatite terrain with paragneisses, diatexite, quartz diorite and pegmatite dykes and sills,
2. The some paragneisses were found to host mica bearing lithium,
3. The pegmatite dykes and sills were seen to be productive in terms of lithium ore mineralizations and
4. The aeromagnetic map superimposed with lineament map showed some hotspots within the sample locations.

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