# THE EXISTANCE OF HERCYNITE IN METAPELITES FROM MOGOK METAMORPHIC BELT

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# Abstract

Hercynite observed in the metapelitic rocks; sillimanite-garnet-biotite gneiss and felsic granulite rocks from Mogok and Momeik area. It is one of the spinel group minerals with the formula  $FeAl_2O_4$ . The present contribution provided and confirmed the presence of hercynite in pelitic rocks (gneiss and granulite) and pair essential assemblage of [Spinel (Hercynite)+Quartz)] in Mogok Metamorphic Belt indicate that these rocks were experienced in/ developed under UHT metamorphism.

Keywords: Hercynite, Metapelitic, Granulite, Spinels, UHT metamorphism

### Introduction

**Hercynite** is one of the end-members of the spinel group in the spinel mineral series with the formula FeAl<sub>2</sub>O<sub>4</sub>. Chemical formula of common spinel is MgAl<sub>2</sub>O<sub>4</sub> and it is a Magnesium (Mg) spinel though hercynite is Iron (Fe) spinel. The Mg may be partially or fully replaced by Fe, Zn, and/or Mn. This leads to a mineral series with the formula (Mg,Fe,Zn,Mn) Al<sub>2</sub>O<sub>4</sub>. It was first described in 1847 and its name originates from the Latin name for the Harz, Silva Hercynia, where the species was first found (Anthony, 1990), is a spinel of regular symmetry and normal cation distribution, but some disorder occurs in its structure. It consists of ferrous (Fe<sup>2+</sup>) ions and aluminium ions (Al<sup>3+</sup>), however some ferric ions (Fe<sup>3+</sup>) may be located in the structure of hercynite (Jastrzębska, 2015). General information of spinel mineral series is described in Table 1. Hercynite occurs in high-grade metamorphosed iron argillaceous sediments as well as in mafic and ultramafic igneous rocks (Anthony, 2001). The purpose of this paper is to provide and confirm the determination of metamorphic grade and facies and estimating *P-T* conditions of hercynite bearing pelitic rocks of Mogok Metamorphic Belt on the basis of mineral assemblages.

### Table 1 General information of the spinel mineral series (www.mineral.net)

### **The Spinel Mineral Series**

Chemical Formula : MgAl<sub>2</sub>O<sub>4</sub>

The Mg may be partially or fully replaced by Fe, Zn, and/or Mn. This leads to a mineral series with the formula (Mg,Fe,Zn,Mn) Al<sub>2</sub>O<sub>4</sub>.

| The end-members of the Spinel group   |                                    |  |  |  |  |  |
|---|------------------------------------|--|--|--|--|--|
| Spinel (or Magnesium Spinel)  | - MgAl <sub>2</sub> O <sub>4</sub> |  |  |  |  |  |
| Gahnite (Zinc Spinel)   | - ZnAl <sub>2</sub> O <sub>4</sub> |  |  |  |  |  |
| Hercynite (Iron Spinel)   | - FeAl <sub>2</sub> O <sub>4</sub> |  |  |  |  |  |
| Galaxite (Manganese Spinel)   | - MnAl <sub>2</sub> O <sub>4</sub> |  |  |  |  |  |
| Composition : Series of magnesium, iron, zinc, and/or manganese aluminum oxide. |                                    |  |  |  |  |  |

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### **Materials and Methods**

Although spinels are widely distributed in nature, hercynite was analyzed by electron probe as a Fe Spinel and identified with the aid of petrological microscope. Minerals were analysed using the Electron Probe Micro Analyser (EPMA) Jeol, JXA 8200, equipped with SE- and a BSEdetector, 5 WDS crystal spectrometer and an EDS-analyser at Swiss Federal Institute of Technology (ETH) in Zurich, Switzerland. Operation conditions were: 15.0 kV applied accelerating voltage, 100  $\mu$ m beam size and 10 or 20 nA depending on the stability of the analyzed minerals under the electron beam. Hercynite bearing thin sections of different rock units exposed in the research area were analysed by means of polarizing microscope. Determination of metamorphic grade and facies and estimating *P-T* conditions of hercynite bearing pelitic rocks of Mogok Metamorphic rocks based on mineral assemblages and comparison is carried out on the literature and previous works of the area.

### Geology

The research area is situated within the northern part of Mogok Metamorphic Belt (MMB) of Searle and Haq, 1964 and Searle et. al., 2017. With reference to provided regional geological map (Myanmar Geosciences Society, 2014) (Fig. 1), rocks in the investigated area are categorized into medium-to-high grade metamorphic rock units and younger igneous intrusion. In metamorphic units, medium-to-high grade rocks consisting of marble, calc-silicate rocks, gneiss and granulite are exposed (Wai Yan Lai Aung, 2016) in the research area. Among them, hercynite can be noted from argillaceous pelitic rocks such as sillimanite-garnet-biotite±ilmenite gneisses and felsic granulite. Location map is shown in (Fig. 2).



Figure 1 Regional geological map of the research area and its environs (AfterGeological Map of Myanmar Geosciences Society, 2014).



Figure 2 Location map of the research and surrounding areas.

# Results

# Mineralogy

Hercynite is the predominant mineral of the sillimanite-garnet-biotite gneiss and felsic granulite units within the research area. In hand specimen, it is not distinct. Under the microscope, hercynite is characterized by its colour (greenish and black), medium- to coarse-grained subhedral to euhedral form, no cleavage and high relief in PPL. Isotropic nature is pronounced between XN (Kerr, 1977). In sillimanite-garnet-biotite gneiss, spinels (hercynite) show green and euhedral form (Fig. 3), which may probably formed by the releasing of alumina.

Mineral assemblages recognized in the sillimanite-garnet-biotite±ilmenite gneiss are (Fig. 4) :

Quartz + orthoclase + biotite + plagioclase + almandine + sillimanite + diopside + ilmenite + spinel + zircon + apatite + sphene + hypersthene

Quartz + orthoclase + plagioclase + biotite + almandine + sillimanite + ilmenite + spinel

Quartz + orthoclase + plagioclase + biotite + almandine + sillimanite + spinel + opaque + sphene

In some xenoblastic garnets, hercynites are observed as inclusions associated with small anhedral quartz grains, tabular biotite flakes and sillimanite as inclusions (Fig. 5)

Mineral assemblages of granulite rocks in the study area are:

orthopyroxene + alkali feldspar + biotite + plagioclase + chlorite + garnet + quartz + rutile + sapphirine + ilmenite + **hercynite** + sillimanite + zircon.

Hercynites, iron alumina spinels, are found as equant grains (Fig. 6). They show high relief, pale green under plane-polarized light and isotropic between cross nicols.



Figure 3 Euhedral spinel (hercynite) in sillimanite-garnet-biotite gneiss



Figure 4 Mineral assemblages of sillimanite, hercynite, quartz and feldspars in sillimanitegarnet-biotite-ilmenite gneiss



Figure 5 Coarse-grained xenoblastic garnet with various inclusions (sillimanite trails, hercynite, quartz and biotite).



Figure 6 Grains of hercynite in felsic granulite.

# Geochemistry

Ilmenite and hercynite are diagnostic minerals of some acid granulitic assemblages. Electron microprobe analyses of spinel and ilmenite in sillimanite-garnet-biotite gneisses (Fig. 7) are shown in Table 2. Spinels in research area are ferroan aluminium spinel, hercynite. Deer, Howie & Zussman, 1992, explained that the experimental investigation on the system FeAl<sub>2</sub>O<sub>4</sub> (hercynite) – Fe<sub>3</sub>O<sub>4</sub> (magnetite) shows there has complete solid solution above 858°C, but below this temperature, the two-phase region of exsolution widens with decreasing temperature. Hercynite forms complete solid solution with chromite and spinel but only limited solid solution with magnetite (Rutley, 1991). Hercynite of spinel series and ilmenite from the microprobe data are plotted as colourful dots on ternary diagrams of Butler, 1998 (Fig. 8).



Figure 7 Electron microprobe analyses of spinel and ilmenite in sillimanite- garnet- biotite gneisses

| Name   | 1A-sp1 | 1A-sp2 | 1A-sp3 | 1A-sp4 | 1A-ilm1 | 1A-ilm2 |
|--|--------|--------|--------|--------|---------|---------|
| Symbol                                       | •      |        | •      |        | •       | •       |
| SiO <sub>2</sub>                             | 0.030  | 0.030  | 0.071  | 0.022  | 0.023   | 0.082   |
| TiO1   | 0.093  | 0      | 19.300 | 0.154  | 46.410  | 43.740  |
| Cr <sub>2</sub> O <sub>3</sub>               | 0      | 0      | 0      | 0.552  | 0       | 0       |
| Al <sub>2</sub> O <sub>3</sub>               | 59.500 | 59.61  | 0.377  | 0      | 0.090   | 0.079   |
| Fe <sub>2</sub> O <sub>3</sub>               | 2.407  | 2.291  | 28.527 | 67.986 | 0       | 0       |
| FeO  | 27.844 | 27.648 | 46.879 | 30.992 | 50.120  | 52.600  |
| MnO  | 0.265  | 0.264  | 0.122  | 0.014  | 0.653   | 0.482   |
| NiO  | 0      | 0      | 0      | 0      | 0       | 0       |
| MgO  | 8.43   | 8.48   | 0,422  | 0.037  | 1.065   | 0.938   |
| CaO  | 0.039  | 0.008  | 0.002  | 0.019  | 0.010   | 0.024   |
| Na <sub>2</sub> O                            | 0      | 0      | 0.020  | 0.006  | 0       | 0       |
| K20  | 0.018  | 0.02   | 0.028  | 0.013  | 0.028   | 0.030   |
| Total  | 98.626 | 98.352 | 95.748 | 99.794 | 98.398  | 97.975  |
| FeAl <sub>2</sub> O <sub>4</sub> (Hercynite) | 0.627  | 0.627  | 0.009  | 0      | -1.524  | -1.613  |
| MgAl <sub>2</sub> O <sub>4</sub> (Spinel)    | 0.338  | 0.343  | 0      | 0      | -0.058  | -0.051  |
| MnAl <sub>2</sub> O <sub>4</sub> (Galxite)   | 0.006  | 0.006  | 2.247  | 0      | -0.020  | -0.015  |
| FeFe <sub>2</sub> O <sub>4</sub> (Magnetite) | 0.016  | 0.015  | 0.411  | 0.983  | 0       | 0       |
| MgFe2O4 (Mg-Ferrite)                         | 0.009  | 0.008  | 0.007  | 0.002  | 0       | 0       |
| MnFe <sub>2</sub> O <sub>4</sub> (Jacobsite) | 0      | 0      | 0.001  | 0      | 0       | 0       |

 Table 2 Analytical data of spinel and ilmenite in sillimanite-garnet biotite gneiss



**Figure 8** The system FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> showing the major high-temperature solid solution series magnetite-ulvospinel, hematite-ilmenite, pseudobrookite-FeTi<sub>2</sub>O<sub>5</sub> plotted on a mol per cent basis (After Butler, 1998).

# Discussion

#### Occurrences

Protolith of spinel-bearing rocks were clayey limestones and calcic limestones, which may become dolomitic limestone by metamorphism (Gübelin & Koivula, 2005). Spinel was formed both mafic igneous rock and metamorphic rock which found in carbonate series underwent high temperature amphibolite to lower granulite grade regional metamorphism (Malsy & Klemm, 2010). At Mogok, spinel was formed as a result of contact metamorphism or skarn metasomatism within regionally metamorphosed basement rocks where the presence of fluids played an important role (Iyer, 1953; Themelis, 2009), where, high temperature regional metamorphism and then larger - scale transformation of carbonate rocks, high mobilization and migration of many chemical elements and containing Al and Cr in the dynamothermal metamorphism of carbonate rocks (Kisin et al., 2016). Wai Yan Lai Aung, 2016, reported that, in Loi-Sau and its environs, sillimanite-garnet-biotite±ilmenite gneiss including spinel are high-grade gneiss and they are included in granulite facies. Moreover, she also contributed on granulite in Mogok and Momeik area.

In Mogok, Jedi spinel (Hot spinel) occurs as bright neon red spinel crystals and found in both Mogok Valley and the Namya area (Pardieu, 2014). Moreover, Man Sin Hot spinel in Mogok occurs as porphyroblast in marble and due to the presence of Cr (Thet Tin Nyunt and Phyu Phyu Win, 2018).

Ternary spinels in the system (Fe, Zn, Mg) Al<sub>2</sub>O<sub>4</sub> are apparently relatively common and widespread constituents of some metamorphic rocks in the amphibolite and granulite facies (Stoddard, 1979). High-grade metamorphic rocks of upper-amphibolite and granulite facies were reported in the Mogok metamorphic belt, central Myanmar (Yonemura et al., 2013; Maw Maw Win et al., and Wai Yan Lai Aung, 2016).

### **P-T** Condition

The temperature of spinel is about from 600°C and depending on the amount of magnesium which played an important factor during the genesis of spinel (Widmer, 2014). In Mogok Metamorphic Belt, Mitchell et. al., (2006) constrain that the K-feldsapr augen gneisses represents at 4.9 ±1.7 kbar and about 680 °C and Searle et. al., (2017) imply high-temperature sillimanite+muscovite metamorphism peak at  $4.9 \pm 1.7$  kbar and 680°C, and based on the result of EPMA. Yonemura et. al., (2013) found Grt-Opx granulite in the Mogok area, which was formed under pressure-temperature (P-T) conditions estimated as being 6.5-8.7 kbar and 800-950 °C with the aid of EPMA. Wai Yan Lai Aung and Maw Maw Win, et al., (2016) estimated petrologically and mineralogically that the metamorphic P-T conditions of pelitic gneisses in regional Mogok metamorphic belt with garnet-biotite-plagioclase-sillimanite-quartz assemblage and its peak metamorphic stage is 6-10 kbar and 780-850 °C. Ye Kyaw Thu, et al., (2016) reported a paragenesis with a spinel + quartz assemblage coexisting with Ti-rich biotite (up to 6.9 wt% TiO<sub>2</sub>) that formed under granulite facies conditions. They also suggest in (2017) that the P-T conditions of granulite facies paragenesis with Grt-Bt-Pl-Sil-Qtz and Grt+Crd+Sil+Bt+Qtz from the middle segment of the Mogok metamorphic belt is 6 – 7.9 kbar/ 800 – 860 °C and 6.5 kbar/ 820 °C, resprctively. Wai Yan Lai Aung, (2017) calculated two occurrences of sillimanite-garnet-biotite gneiss with and without of pyroxene and hercynite minerals by using normalized composition of garnet, biotite and plagioclase from X-ray Fluorescence and Electron Microprobe analyses with Pseudosection and Perple\_X software. The P-T equilibration of hercynite bearing gneiss is higher than that of without; 6.5-9.3 kbar, 740-810 °C. In (2018), She also contributed the possible P-T condition of granulite rocks in Mogok and its environs, and the presence of spinel relics in sapphirine are shown in symplecitic intergrowths of the two minerals. Its development can be explained by the simple reaction: Spinel + Silica = Sapphirine (Deer, Howie & Zussman, 1992).

Schollenbruch, et al., (2010) investigated experimentally the stability of hercynite (FeAl<sub>2</sub>O<sub>4</sub>) at high pressure and temperature between 7-24 GPa and 900-1700 °C. Hercynite breaks down to its constituent oxides at 7-8.5 GPa and temperatures > 1000 °C. Zn-rich spinel is associated with quartz in the Al-rich metapelites of the Mashan complex, NE china and Al-rich metapelites from Mashan khondalite series are characterized by the assemblage Spl+Grt+Sil+Crd+Bt+Pl(An<sub>72</sub>)+Kfs+Quartz+graphite peak P-T condition is 820 °C and 8.0 kb (Guo, 2008). Spl + Otz assemblage requires at least 840 °C (Bucher & Frey, 1994) and stated that hercynite spinel is present in metapelites with high X<sub>Fe</sub> at 860 °C (Bucher, 2010). The rocks loose quartz between 620 °C (Mg-rich) and 670 °C (Fe-rich). At about 700 °C (at 600 °C), upper amphibolite facies, spinel appears at medium  $X_{Fe}$  in assemblages such as Spl + Grt + Crd. Spinel appears at a temperature 250 °C lower than in Qtz-saturated rocks. The assemblage Grt + Crd + Opx + Spl is characteristic for ultra-high grade metamorphism in Qtz-bearing rocks. In contrast, the temperature of Qtz-free rocks is as low as 700 °C. This shows that the pair Spl + Qtz is the essential assemblage for UHT metamorphism (Bucher, 2010). Hercynite from research area is associated with quartz and analysed by EPMA. Comparison of P-T analytical data and possible P-T condition in Mogok Metamorphic Belt (MMB) are shown in Table 3 and (Fig 9).

The spinels observed in the metapelitic rocks; sillimanite-garnet-biotite gneiss and felsic granulite of Mogok and Momeik area were identified as hercynite. A study of the chemical composition confirmed that it is iron aluminium spinel and the colour due to the Fe. In research area, hercynite bearing high-grade gneiss and felsic granulite indicate granulite facies and high-grade metamorphosed iron rich argillaceous sediments. The present study proved that hercynite in pelitic rocks (gneiss and granulite) and pair essential assemblage of [Spinel (Hercynite)+Quartz)] in Mogok Metamorphic Belt were experienced in/ developed under UHT metamorphism.

| Reference                   | Rock Units of MMB                              | Analytical<br>Methods    | Calculated<br>mineral assemblages                 | P/T                             |  |
|-----------------------------|--|--------------------------|---|---------------------------------|--|
| Mitchell et al.,<br>2006    | K-spar augen gneiss                            | EPMA                     | Bt-Sil-Pl-Kfs-Qtz                                 | 4.9 ±1.7 kbar/<br>& 680 ℃       |  |
| Searle et al.,<br>2007      | Sillimanite gneiss                             | EPMA                     | Sil-Mus   | 4.9 ± 1.7 kbar/<br>680 °C       |  |
| Yonemura et al.,<br>2013    | Granulite                                      | EPMA                     | Grt-Opx   | 6.5 – 8.7 kbar/<br>800 – 950 °C |  |
| Maw Maw Win et al.,<br>2016 | Pelitic gneisses                               | Petrology/<br>Mineralogy | Grt-Bt-Pl-Sil-Qtz                                 | 6 – 10 kbar/<br>780 – 850 °C    |  |
| Wai Yan Lai Aung,<br>2016   | Sillimanite-garnet-biotite-<br>ilmenite gneiss | EPMA                     | Grt-Sil-Bt-Pl-Kfs-Qtz                             | 6.5 - 9.3 kbar/<br>740 - 810 °C |  |
| Wai Yan Lai Aung,<br>2017   | Sillimanite-garnet-biotite<br>gneiss           | EPMA                     | Grt-Sil-Bt-Pl-Kfs-Qtz                             | 6.2 - 8 kbar/<br>750 - 790 °C   |  |
| Ye Kyaw Thu et al.,<br>2017 | Metasedimentary rocks                          | EPMA                     | Grt-Bt-Pl-Sil-Qtz                                 | 6 – 7.9 kbar/<br>800 – 860 °C   |  |
| Ye Kyaw Thu et al.,<br>2017 | Metasedimentary rocks                          | EPMA                     | Grt-Crd-Sil-Bt-Qtz                                | 6.5 kbar/<br>820 °C             |  |
| Wai Yan Lai Aung,<br>2018   | Felsic granulite                               | Petrology/<br>Mineralogy | Opx-Grt-Bt-Rt-Sil-Plg-Kfs-<br>Spr-Spl-Qtz-Zir-Ilm | P-T is greater<br>than gneisses |  |
| Wai Yan Lai Aung,<br>2018   | Mafic granulite                                | Petrology/<br>Mineralogy | Cpx-Ca-Plg-Kfs-Qtz-Bt-<br>Opx-Sp-Opq              | P-T is greater<br>than gneisses |  |

 Table 3 Comparison of P-T analytical condition and mineral assemblages in Mogok Metamorphic Belt (MMB)



**Figure 9** *P-T* diagram showing the comparison of analytical data and possible *P-T* condition in Mogok Metamorphic Belt (After Liau et al., 1998, Harley, 1998, Okamoto and Maruyama,1999, and Harley, 2004) UHP – ultrahigh pressure; UHT – ultrahigh temperature; VLT – very low temperature; AM – amphibolite; Amp-EC – amphibolite– eclogite; BS – blueschist; EA – epidote amphibolite; EC – eclogite; Ep-EC – epidote-eclogite; GR – granulite; GS – greenschist; HGR – high-grade granulite; Lw-EC – lawsonite-eclogite.

#### Conclusion

The spinels observed in the metapelitic rocks; sillimanite-garnet-biotite gneiss and felsic granulite of Mogok and Momeik area were identified as hercynite. A study of the chemical composition confirmed that it is iron aluminium spinel and the colour due to the Fe. In research area, hercynite bearing high-grade gneiss and felsic granulite indicate granulite facies and high-grade metamorphosed iron rich argillaceous sediments. The present study proved that hercynite in pelitic rocks (gneiss and granulite) and pair essential assemblage of [Spinel (Hercynite)+Quartz)] in Mogok Metamorphic Belt were experienced in/ developed under UHT metamorphism.

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