Cryptic Mantle Metasomatism: Evidences from Spinel Lherzolite Xenoliths/Al-Harida Volcano in Harrat Al-Shaam, Jordan

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Abstract: Problem statement: Al-Harida volcano is located in the Jordanian parts of the Harrat Al-Shaam plateau and contains considerable amounts of mantle xenoliths within its pyroclastic successions. Approach: These xenoliths are reported for the first time for this area. Mineralogical investigations show that they are composed of olivine, orthopyroxene, clinopyroxene, spinel and phlogopite. Results: The xenoliths range in size from 5-30 cm with an average of 10 cm. They are classified as Type I and belong to the Cr-diopside group and are characterized by high contents of MgO, Cr and Ni. The occurrence of hydrous mineral phases and the enrichment of incompatible elements such as Sr, Rb and Ba indicate a considerable mantle metasomatism. Conclusion/Recommendations: Thermobarometry of the studied xenoliths indicates a temperature ranging from 960-1040°C and pressure ranging from 11-13 Kbar which corresponds to a depth of origin of about 43 km.

Key words: Mantle metasomatism, xenoliths, spinel lherzolite, Harrat Al-Shaam, Al-Harida, Jordan

INTRODUCTION

The term metasomatism usually refers to a solid-state transformation without or only marginal melting[1]. Metasomatic xenoliths are mostly found in host magmas of mantle origin that are enriched in incompatible elements[2] and other magmas like highly potassic mafic volcanoic[3]; basanites and alkali olivine basalts[4]. In the last three decades, mantle metasomatism has been increasingly recognized as an important process[5-7]. However, metasomatism has been described by[8] as the change in rock chemistry caused by the passage of hydrothermal fluids. Mantle metasomatism was at the center of the discussion in the First International Kimberlite Conference held in Capetown in 1973[9]. Three main types of metasomatism are discerned[10]: Modal metasomatism, enrichment in major and trace elements in the absence of modal metasomatism and isolated trace element enrichment.

Experimental constrains of solubility of major and trace elements in the mantle metasomatic fluids were established by[11]. The system C-O-H-S is proposed to exist the others in the mantle volatile-bearing minerals, dissolved in silicate- or carbonate-rich melts. Fluid inclusions in mantle-derived minerals are typically found to be CO2[12,13]. However, CO2-CO inclusions have also been reported by Bergman and[14]. At the pressure of the upper mantle, a metasomatic fluid can consist of a carbonate-rich melt; of a silicate melt, or of a low density, volatile-rich fluid[9].

Spinel lherzolite is considered to form the major part of the upper mantle[15,18] occurring at depths of 40-60 km[17,18]. The existence of such xenoliths offers a direct insight into the lithosphere and the asthenosphere. Moreover, xenoliths helps in reconstructing the petrogenesis of the magma and its thermobarometric conditions. They are relevant to the understanding of the process that gives rise to the magma and the nature of the mantle[19]. Textures of xenoliths provide the crystallization or deformation histories of these rocks within the mantle[20].

The Tertiary-Quaternary basaltic Harrats of the Arabian plate (Fig. 1) contain several xenolith assemblages as far south as Yemen[21,22]. The Harrat Al-Shaam (or Ash shaam) covers an area of 45 000 km2 and is the most northwestern basalt plateau of the Arabian plate. This plateau extends from Syria to Saudi Arabia through Jordan. It is considered to be one of the largest alkali olivine basalt plateaus globally. The Harrat contains a large diversity of xenolith assemblages in different localities[23-28].

In this research, spinel lherzolite xenoliths from the Jabal Al-Harida volcano in the NE of the plateau were investigated for their chemical characteristics. The present research reports also the discovery of new xenolith occurrences in the Jordanian part of Harrat Al-Shaam.
Fig. 1: Map of the Arabian plate and its basaltic Harrats (modified after Al-Malabeh\textsuperscript{29}).

Geologic setting: The Jordanian part of the Harra Al-Shaam plateau is geomorphologically known as the Jordanian Harrat or Harrat El-Jabban\textsuperscript{29,30}. The former name will be used in this study. It covers 11 400 km\textsuperscript{2}, i.e., one tenth of Jordan area (Fig. 1). The Jordanian Harrat has about 80 volcanic cones with more than 200 eruptive centers that are aligned mostly in NNW-SSE or NW-SE directions. The volcanoes cluster in three volcanic fields, those of Remah, Ashqaf and Al-Dhirwa (Fig. 2), which are located in the western, eastern and southern parts of the Harrat, respectively\textsuperscript{29,31}.

The Ashqaf volcanic field lies in the eastern part of the Harrat (Fig. 2). It begins in the west with the Qitar Al-Abed volcanic chains and the Suwaied Volcano and ends with the Al-Harida Volcano in the east. More than 15 volcanoes are counted in this field, including more than 35 volcanic centers distributed over ca. 70 km\textsuperscript{2}\textsuperscript{32}. The distances between the volcanic centers exceed mostly 2-5 km.

The Jabal Al-Harida Volcano is located about 40 km East of Al-Safawi about 15 km south of the Mafraq-Baghdad road at 32°11’32” N and 37°40’65” E. The volcano has a height of 70 m and covers an area of about 3 km\textsuperscript{2}. The volcano shows an elliptical overall shape with a NW-SE striking long axis.

Fig. 2: Location map of Jabal Al-Harida Volcano. Data of volcanic fields are modified after Al-Malabeh\textsuperscript{29,31}

MATERIALS AND METHODS

Analytical methods: Geochemical investigation was carried out on selected xenoliths and scoria samples. Whole rock samples were analyzed for major oxides of Si, Ti, Al, Fe, Mg, Mn, Ca, Na, K and P as well as selected trace elements using X-Ray Fluorescence (XRF) in the Department of Mineralogy, Würzburg University, Germany. Measurements were calibrated against international standards (e.g., GR1, EF1 and HW2). Loss On Ignition (LOI) was determined by weight loss after drying at 1000°C.

Selected samples were also analyzed using an ARL-GMX electron microprobe. The analytical conditions were 1×10\textsuperscript{-8} mA, 25-50 nA specimen current potential, 10 sec integration time and 20 kV acceleration potential, the SPI mineral standards were used for the calibration process. An integration time of 10 sec and an On-line-Data reduction was done on a computer using the Bence Albee matrix at the University of Tübingen, Germany. At least three determinations were averaged for each quoted analysis.

RESULTS

Volcanology: The Jabal Al-Harida Volcano consists of scoria-fall pyroclastic rocks that are arranged in beds and form two distinct horizons. The xenoliths were mainly collected from the upper horizon. It is xenolith-rich, particularly in spinel peridotites. These xenoliths intercalate with the pyroclastic rocks and occur as cored bombs.
The xenoliths range in size from 2-10 cm with an average diameter of 5 cm. The xenoliths are mostly light to dark green in color and spherical in shape. Some of them exhibit red to orange color.

These pyroclastic deposits show a high degree of fragmentation and are dominated by lapilli-sized ejecta. The lower horizon is composed of material mainly <2.5 cm in size, which can be classified as cinder. The upper horizon is composed of two members. The lower member is composed of agglutinated pyroclastics of angular to sub-angular blocks and spherical, oval and elliptical bombs. The clasts are gray to violet in color and range in size from 10 cm up to 1 m in diameter with 30 cm on average. Bombs and blocks are sintered together to form agglomerates. The upper member of this horizon is gray and brown in color and 15 m thick and characterized by planar stratification. It consists mainly of lapilli-sized pyroclastics intercalated with blocks and bombs. This is the horizon where most of spinel lherzolites were collected.

Overall the Jabal Al-Harida Volcano can be classified as a blocky-lapilli scoria cone. The volcano appears to have resulted from multiple, explosive eruptions, separated by quite periods. The low degree of fragmentation, the basaltic affinity and the small eruptions, classified as a blocky-lapilli scoria cone. The volcano

**Petrography and mineral chemistry:** The ultramafic xenoliths of Jabal Al-Harida are peridotites dominated by spinel lherzolite. The lherzolites are composed of olivine, orthopyroxene, clinopyroxene, spinel, magnetite and phlogopite. They have a protogranular texture similar to those defined by[33]. The samples are classified as Type I following the classification of[35], while the geochemical composition classifies them as Cr-diopside peridotite following the classification of[36].

**Olivine:** Olivine is the main mineral phases and forms about 25-35 vol%. It occurs as subhedral to anhedral, medium to coarse-grained (up to 7 mm) crystals. Some olivines show wavy extinction, which indicates that they were strained. Metamorphic triple junctions are also recorded in olivine denoting annealing recrystallization. Another distinguishing feature of olivine is the presence of deformation lamellae. Preferred orientation is occasionally recorded in some samples. Idioblastic olivine is prevalent. Chemical analyses (Table 1) show that they are Mg-rich olivines and show limited normal zoning, ranging from Fo 87 to Fo 90 (i.e., forsterite-chrysotile composition). The NiO content is varying between 0.23 and 0.34 wt%, which is within the range of olivine peridotite reported by[37] and close to the value of about 0.4 reported by[38] for olivine of primary magmas. The chemical composition is that of the olivine of spinel lherzolite reported from Saudi Arabia given by[32] and from Jordan by[39].

**Enstatite:** Enstatite is the second most abundant mineral phase and forms up to 15% of the xenoliths. The crystals are subhedral to anhedral and coarse-grained (up to 3 mm). Preferred orientation of olivine and enstatite is recorded. Furthermore, kinkband structure, deformation lamellae and exsolution lamellae of clinopyroxene are observed in the same crystals. The chemical analysis (Table 2) shows that the enstatites have the following composition Fe: 7.76-8.68; Ca 0.76-1.04; Mg: 90.01-91.20. They are close to enstatite composition given by[40].

**Diopside:** Diopside crystals are subhedral in shape and the grain size varies from 3-6 mm. They compose up to 12% of the volume. Chemical analysis shows that the composition of the clinopyroxene is similar to diopside according to the classification of[36]. Diopside-endmember composition is: Fe: 4.11-5.50; Ca: 42.57-50.96; Mg: 44.17-52.03 (Table 3). They are characterized by a high Al2O3 content (1.73-2.95 wt%) and a low TiO2 content ranging from 0.09-0.33 wt%. The Cr2O3 content ranges from 1.09-2.47 wt%. They resemble the composition of chromium-diopside[41]. Similar geochemical trends are reported by[42] for spinel lherzolite in Jordan from the volcano Jabal Aritain-South.

**Table 1: Electron microprobe analysis of olivine**

|           | Hr1   | Hr1   | Hr4   | Hr4   | Hr5   |
|-----------|-------|-------|-------|-------|-------|
| SiO2      | 40.41 | 41.14 | 42.40 | 39.47 | 39.69 |
| TiO2      | 0.03  | 0.01  | 0.04  | 0.04  | 0.02  |
| FeO       | 10.05 | 9.10  | 8.80  | 12.00 | 9.61  |
| MnO       | 0.08  | 0.05  | 0.10  | 0.11  | 0.08  |
| MgO       | 49.44 | 51.08 | 50.01 | 47.61 | 50.34 |
| CaO       | 0.04  | 0.00  | 0.01  | 0.00  | 0.00  |
| NiO       | 0.23  | 0.25  | 0.24  | 0.23  | 0.34  |
| Sum       | 100.11| 101.40| 101.37| 99.34 | 100.08|

**End members**

|     | Fo   | Fa   |
|-----|------|------|
| Fo  | 89.760| 10.240|
| Fa  | 90.090| 9.900|

The ultramafic xenoliths of Jabal Al-Harida are peridotites dominated by spinel lherzolite. The lherzolites are composed of olivine, orthopyroxene, clinopyroxene, spinel, magnetite and phlogopite. They have a protogranular texture similar to those defined by[33]. The samples are classified as Type I following the classification of[35], while the geochemical composition classifies them as Cr-diopside peridotite following the classification of[36].
Spinel: Spinel is ubiquitous in all the samples collected. The crystals are anhedral in shape and occur interstitially between the olivine and enstatite crystals, occupying from 3-7 vol.%. Crystals are green in color and vary in grain size from 0.3-5 mm. Some crystals show a marked wavy extinction due to strain. Glomeroporphyritic spinel crystals as many as three to five crystals are occasionally observed. The spinels (Table 4) are aluminum-rich. The Al₂O₃ ranges from 52.25-53.90 wt%. The spinel is Fe-rich with FeO content ranging from 11.08-14.06 wt%. They are also Cr-rich (0.25-0.41 wt% Cr₂O₃) and colorless to light yellow. They are characterized by one set of cleavage and have a parallel extinction. The spinels are 0.2-5 mm in diameter. The Cr/(Cr+Al) ratio match the Cr-spinel given by[43].

**Phlogopite:** Phlogopite form about 3-5 vol% of the studied rocks. They dominating habitus is tabular and prismatic. They have a slight pleochroism from colorless to light yellow. They are characterized by one set of cleavage and have a parallel extinction. The phlogopite crystals are 0.2-5 mm in diameter. Phlogopites (Table 5) are moderately chromium-rich (0.25-0.41 wt% Cr₂O₃), sodium-rich (2.11-2.31 wt% Na₂O), aluminum rich (16.18-18.57 wt% Al₂O₃) and moderately titaniferous (6.52-7.06 wt% TiO₂). These phlogopites lie in the “secondary phlogopite” field associated with spinel peridotite[43].

### Table 2: Electron microprobe analysis of enstatite

|         | Hr1 | Hr1 | Hr4 | Hr4 | Hr5 |
|---------|-----|-----|-----|-----|-----|
| SiO₂    | 56.63 | 56.36 | 57.36 | 57.08 | 56.61 |
| TiO₂    | 0.06 | 0.11 | 0.06 | 0.00 | 0.01 |
| Al₂O₃   | 1.58 | 1.73 | 1.07 | 1.01 | 2.00 |
| Cr₂O₃   | 0.38 | 0.48 | 0.35 | 0.46 | 0.49 |
| FeO     | 5.69 | 5.20 | 5.45 | 5.59 | 5.45 |
| MnO     | 0.08 | 0.11 | 0.12 | 0.10 | 0.09 |
| MgO     | 34.20 | 34.19 | 34.11 | 35.33 | 34.56 |
| CaO     | 0.49 | 0.52 | 0.43 | 0.46 | 0.49 |
| Na₂O    | 0.29 | 0.06 | 0.10 | 0.11 | 0.04 |
| Sum     | 99.52 | 99.29 | 99.08 | 100.13 | 99.74 |

### Table 3: Electron microprobe analysis of diopside

|         | Hr1 | Hr1 | Hr4 | Hr4 | Hr5 |
|---------|-----|-----|-----|-----|-----|
| SiO₂    | 54.68 | 54.18 | 52.53 | 51.85 | 52.61 |
| TiO₂    | 0.09 | 0.10 | 0.07 | 0.11 | 0.33 |
| Al₂O₃   | 2.95 | 2.94 | 1.73 | 2.93 | 2.22 |
| Cr₂O₃   | 1.41 | 1.44 | 2.47 | 1.45 | 1.09 |
| FeO     | 2.76 | 3.05 | 2.54 | 2.85 | 2.50 |
| MnO     | 0.04 | 0.05 | 0.09 | 0.07 | 0.05 |
| MgO     | 16.27 | 16.24 | 17.43 | 16.45 | 16.51 |
| CaO     | 19.62 | 18.53 | 20.87 | 21.82 | 22.38 |
| Na₂O    | 1.71 | 1.74 | 0.93 | 0.90 | 0.56 |
| Sum     | 99.56 | 98.31 | 98.68 | 98.00 | 99.33 |

### Table 4: Electron microprobe analysis of spinel

|         | Hr1 | Hr2 | Hr3 | Hr4 |
|---------|-----|-----|-----|-----|
| SiO₂    | 0.030 | 0.040 | 0.010 | 0.040 |
| TiO₂    | 0.010 | 0.010 | 0.090 | 0.040 |
| Al₂O₃   | 52.550 | 53.900 | 52.250 | 53.040 |
| Cr₂O₃   | 17.300 | 17.210 | 14.640 | 13.780 |
| FeO'    | 11.290 | 11.080 | 13.790 | 14.060 |
| MnO     | 0.050 | 0.100 | 0.100 | 0.130 |
| MgO     | 20.410 | 20.100 | 18.670 | 18.940 |
| CaO     | 0.000 | 0.000 | 0.000 | 0.000 |
| NiO     | 0.260 | 0.260 | 0.170 | 0.160 |
| Sum     | 101.920 | 102.740 | 99.840 | 100.230 |

### Table 5: Electron microprobe analysis of phlogopite

|         | Hr1 | Hr2 | Hr3 | Hr4 |
|---------|-----|-----|-----|-----|
| SiO₂    | 38.69 | 39.42 | 38.33 | 39.44 |
| TiO₂    | 6.82 | 6.52 | 6.37 | 7.06 |
| Al₂O₃   | 17.13 | 17.82 | 18.57 | 16.18 |
| Cr₂O₃   | 0.37 | 0.41 | 0.25 | 0.34 |
| FeO'    | 8.04 | 8.23 | 7.43 | 8.58 |
| MgO     | 17.14 | 16.52 | 17.41 | 18.23 |
| CaO     | 0.04 | 0.05 | 0.05 | 0.06 |
| Na₂O    | 2.11 | 2.14 | 2.15 | 2.31 |
| K₂O     | 9.33 | 8.52 | 9.35 | 10.42 |
| Sum     | 99.67 | 99.63 | 99.90 | 100.62 |

52.25-53.90 wt%. The spinel is Fe-rich with FeO content ranging from 11.08-14.06 wt%. They are also Cr-rich with Cr₂O₃ ranging between 13.78 and 17.30 wt%. The Cr/(Cr+Al) ratio match the Cr-spinel given by[43].
Table 6: Whole rock chemical analyses of spinel lherzolite xenoliths from Jabal Al-Harida.

| Major oxides | Hr1   | Hr2   | Hr3   | Hr4   |
|--------------|-------|-------|-------|-------|
| SiO₂         | 44.17 | 43.14 | 42.31 | 42.48 |
| TiO₂         | 0.22  | 0.15  | 0.10  | 0.21  |
| Al₂O₃        | 1.53  | 1.54  | 1.79  | 1.44  |
| FeO          | 8.01  | 8.18  | 8.86  | 9.24  |
| MnO          | 0.11  | 0.11  | 0.12  | 0.12  |
| MgO          | 43.11 | 44.23 | 44.28 | 44.13 |
| CaO          | 1.86  | 1.42  | 1.78  | 1.63  |
| Na₂O         | 0.13  | 0.23  | 0.12  | 0.17  |
| K₂O          | 0.03  | 0.05  | 0.04  | 0.04  |
| P₂O₅         | 0.04  | 0.04  | 0.02  | 0.05  |
| LOI          | 0.63  | 0.35  | 0.49  | 0.73  |
| Sum          | 99.84 | 99.44 | 99.92 | 100.07|

| Trace elements (ppm) | Hr1  | Hr2  | Hr3  | Hr4  |
|----------------------|------|------|------|------|
| Sc                   | 8.00 | 7.00 | 8.00 | 9.00 |
| V                    | 62.00| 39.00| 41.00| 52.00|
| Rb                   | 13.00| 15.00| 15.00| 17.00|
| Ba                   | 32.00| 22.00| 26.00| 31.00|
| Co                   | 120.00| 117.00| 121.00| 132.00|
| Cr                   | 2619.00| 2631.00| 2563.00| 2552.00|
| Ni                   | 2891.00| 2731.00| 2288.00| 2214.00|
| Y                    | 6.00 | 6.00 | 7.00 | 8.00 |
| Sr                   | 32.00| 27.00| 32.00| 35.00|
| Zn                   | 80.00| 62.00| 54.00| 60.00|
| Zr                   | 18.00| 16.00| 17.00| 19.00|

Opaque minerals: Opaque minerals (1-3%) are mainly euhedral to subhedral in shape. Most of them are magnetite grains. Their petrographical characteristics show that they are of the chromium type.

Bulk geochemistry: Bulk chemistry of four representative samples show that the xenoliths have comparable amounts of major oxides (Table 6). They have a low silica content that ranges from 42.31-44.17 wt% allowing them to be classified as ultramafic rather than mafic. They are characterized by high MgO, Cr, Ni content and relatively low contents of Al₂O₃, FeO, CaO and K₂O. However, their range of chemical composition is similar to the average of lherzolite of upper mantle origin reported by [44].

**CONCLUSION**

The petrographical characteristics, textures and chemistry of the studied xenoliths suggest that they are pieces of upper mantle material brought up by the host magma during the ascent (Fig. 3). The xenoliths of the Jabal Al-Harida volcano have a mineralogical composition similar to the other occurrences in Jordan [45,27] and in Saudi Arabia [20,46].

Thermometry estimation of the Jabal Al-Harida xenoliths are calculated by using a BASIC computer program based on the two-pyroxene method of [47] and was applied to co-existing pyroxenes and tested against experimental data on the delegate xenoliths [46].

For Jabal Al-Harida xenoliths, the Herzberg method gave temperatures ranging from 960-1040°C. Barometry estimates for spinel lherzolite are inherently difficult, since no accurate barometer exists for spinel bearing xenoliths. Approximate minimum and maximum pressure equilibration estimates are obtained from the observed mineral assemblage, particularly from the presence or absence of spinel or garnet and by looking at the mole fraction of Cr₂O₃ in the spinel [48] and correlate it to CMAS (CaO-MgO-Al₂O₃-SiO₂) [49]. The pressure estimate of the studied samples yields ranges between 11-13 Kb. The estimated values compare well with estimates for spinel lherzolite xenoliths 12-15 Kb, 925-1025°C [30], 12-18 Kb [50] and 13-19 Kb and 990-1070°C [27]. However, the depth of the host magma must exceed the source of the highest-pressure xenoliths (Fig. 3).

The presence of phlogopite in the studied xenoliths makes an argument and represents convincing evidence for a metasomatism in the mantle at the depth where the xenoliths were extracted [50]. It reflects a modal evidence for the replacement of primary minerals by hydrous minerals and is indicative of metasomatism. Phlogopite is stable at temperatures of 900-1300°C [51] and indicates the presence of water in the upper mantle. However, metasomatism is a mechanism for promoting chemical change in the upper mantle in a solid-state transformation without melting [50]. The most metasomatizing fugitive constituents are H₂O, CO₂ among other fluids. The limited occurrence of
metasomatized minerals (hydrous minerals compared with the volume of MARID minerals. (mica- amphibole-rutile-ilmenite-diopside) are similiar to xenoliths associated with kimberlites.[52]. This may reflect that the metasomatism degree in Jabal Al-Harida was not high. The slight selective enrichments of some incompatible elements such as Sr, Rb and Ba may be due to cryptic metasomatism as defined by[9] and coincides with the latter results.

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