Open System Condition Serpentinization of Host-rock Magnesite in Süleymaniye, Tutluca and Margı Region of Eskişehir, NW Turkey

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Abstract  Host rock of magnesite occurrences in three areas (Süleymaniye, Margı, Tutluca) are the altered peridotite which on the northernmost outcrops of the İzmir-Ankra suture zone. Magnesite is formed in the cracks and fractures of highly altered harzburgite in these three areas. Chrysotile and lizardite are the abundant serpentinite mineral and orthopyroxene, olivine, magnetite, talc, brucite and chromite consist of these rocks which have mesh to hourglass texture. Source of Mg2+ for magnesite formation is coming from serpentinite. During serpentinization processes H2O and CO2 input mineralogic structure and form mineral transform. H2O content in system increases, MgO, CaO and SiO2 content decreases because of remove the systems. According to mineralogic association serpentinization of harzburgite occurs low temperature below 350°C and represents the open system serpentinization condition. These rocks show positive La, Nd, Eu, Ho, Tm, Lu anomalies but negative Ce, Pr, Sm, Gd, Er, Yb anomalies to chondrite/normalize diagram. REE content of serpentinite are consumed according to chondrite. According to mineralogical and geochemical properties is these rock related to the SSZ type ophiolites.

Keywords  Host-rock Magnesite, Serpentinite, Geochemistry, Eskişehir

1. Introduction

Study areas are located in the SSZ-type ophiolites in the İzmir-Ankara suture zone (Figure 1). Suture zones are mostly characterized by outcrop of ophiolite complexes, their fragments and the serpentinite melanges. Since the description of the formation of the supra-subduction zone (SSZ) type oceanic crust at the eastern part of İzmir-Ankara Suture Belt [1,2], İzmir-Ankara oceanic basin is considered to begin to close with an intra-oceanic subduction [1,3,4,5]. One of the most important parameters that control the types of ophiolite which formation in different environments such as mid-ocean ridge, back-arc spreading center and supra-subduction zone (SSZ) ophiolites is the rate of spreading center [6]. Ophiolites which form at fast spreading centers have a strongly depleted residue harzburgite [7], whereas those that form in slow spreading center and continental ridge environments have a weakly depleted residual herzolite [7]. Harzburgites of MORB types ophiolities generally less depleted than harzburgites of SSZ-type ophiolities and contain more than the average of Al, Ca and Ti [8]. [9] indicated that meteoric groundwater is the main factor in serpentinization and lizardite-chrysotile serpentinite minerals formed at lower temperatures than antigorite minerals. Again same researchers stated that ocean-floor serpentinites have a uniform isotopic ratio and ocean water also plays a role in the process of formation of it. [10,11] marked that serpentinites can be formed also hydrotation of mantle peridotites which rising under ridge with juvenil water. Chrysotile, antigorite and lizardite are primary serpentine minerals. Other secondary minerals are magnesite, talc, tremolite-actinolite, chlorite and magnetite. Serpentine minerals occur due to metasomatism of Mg-silicate in particular olivine and pyroxene minerals. $4\text{Mg}_2\text{SiO}_4+4\text{H}_2\text{O}+2\text{CO}_2\rightarrow 2\text{Mg}_3\text{SiO}_5(\text{OH}) + 2\text{MgCO}_3$

Olivine Serpentine

With this change rock receive water and volume increases in closed system. Volume increase due to the replacement of bulk (massive) cause a brigh appearance of crack surface. Serpentinization occurs in relation to the conditions of strong reduction, H2 leads to the formation of it, fluid pH varies between 3 (high temperature) and 12.5 (low temperature) and it is the lowest of SiO2 among terrestrial silicate systems. [12-25] Effective physical condation, formation of minerals and these minerals are represented by P/T ranges during the
2. Material and Method

During field studies, 30 samples from the host rock of magnesite in the Sülaymaniye, Margi and Tutluca areas of them were collected. Thin section was made all of the harzburgite sample. Mineralogical determination of harzburgites was done by transmitted and reflected-light microscope and X-Ray diffraction in General Directorate of Mineral Research and Exploration (Turkey). XRD analysis was performed with Philips PW 3710/1830 in Mineralogical Researches Laboratories in General Directorate of Mineral Research and Exploration. 15 samples were chosen for analysis of major, trace and rare earth element content (Table 1) and samples were conducted at the ACME Analytical Laboratories Ltd., Canada, using ICP-MS, Fire Assay and ICP-ES methods.

2.1. Regional Geology

Study areas are located in the province of Eskişehir in Northwest Anatolia Region. Tavşanlı Zone which study area is located in the northern edge of the Anatolide-Tauride Platform in Western Anatolia and, in the north contact with Pontides along the İzmir-Ankara suture; in the south is located on the tectonically metamorphic rocks of the Afyon Zone (Figure 1). The study areas are situated within the belt stretching from İzmir to Ankara which is called İzmir-Ankara suture by [29]. This belt consists of ophiolitic melanges and ophiolitic rocks of widely spread. The study areas are located on the ultramafic units which host rock of cryptocrystalline magnesite formation studied by [30] around Sülaymaniye (Mihallıccık), Margi (Dağ köprü) and Tutluca. According to the evidence all radiolaria Triassic age reflects the age of the İzmir-Ankara branch of Neotethys and the İzmir-Ankara oceanic plate rifting not subducted until Cenomanian [31]. After the definitions the formation of supra-subduction zone SSZ type oceanic crust in the east part the İzmir-Ankara suture zone [1, 2], it is agreed that İzmir-Ankara oceanic basin began to close by intra oceanic subduction [1,3,4,5,31]. Amphibolities in the İzmir-Ankara Suture (IAE) Zone have the oldest radiometric ages between 101 Ma [31,32] ve 90 Ma [31,33] and indicate that intra-oceanic subduction started in the Albian [31] and this data is compatible with the Late Santonian-Campanian age which stated by [5]. Spreading is last until the beginning of the Late Cretaceous according to the age data obtained from fragments of SSZ-type oceanic crust, MORB-type and related to the spreading within the İzmir-Ankara Sutur Zone; SSZ-type oceanic crust started to formation probably in the Late-Early Cretaceous but definitively lasted until early Santonian [31]. Occurrences of ophiolitic melange in the trench of dipping north of IAE may be starting in early Cretaceous time, the collision with before the Campanian continued until late of Middle Lutetian [34, 35].

2.2. Geology

In Süleymaniye area, the geological units are the Karkin Formation, ultramafic unit, the Porsuk Formation. The Karkin Formation is composed of metaconglomerate, metasandstone and phyllite of the Triassic age. The formation includes a recrystallized Lower Carboniferous-Upper Permian limestone block [30, 36]. An ultramafic unit consisting of serpentinized peridotite and listvenite, overlies the tectonically metadetritic unit of the Karkin Formation. Ultramafic unit is a host rock of magnesite deposits. The Middle-Upper Miocene Porsuk Formation rests unconformably on the ultramafic unit and is composed of a conglomerate-limestone unit, limestone and marl-clay units. Silicified serpentine (listvenite) is located at the top, and usually surface along of fractures and part of the high area. This unit is massive and rigid structures observed in tile-red, burgundy, brown color (Figure 2). Ophiolitic rocks are mainly serpentinized peridotites and listvenite [30, 36]. Serpentinized peridotites outcrop mainly in the 1-2 km south of Doğray, Süleymaniye, Yahmil villages. Listvenite take place especially at the top of the small topographic highs (namely in the west of the Bükadası, Hamam, Kızıl, Karakaya, Sarıkaya, Kışlaçlık hills and around Süleymaniye village). Serpentinized peridotites are mainly sheared at the lowermost part of the ultramafic bodies. Listvenite occurrences in brown, reddish brown, violet colors are observed to the upwards, especially along fracture zones (Figure 2).

Margi is located in the north-east of Eskişehir, between Margi-Taycılar-Sepetci. Triassic aged Sömdiken Metamorrites forming the basement of the region composed of Sömdiken gneiss and Sömdiken marble [30, 36]. Gündüzler Melange overlies tectonically Sömdiken...
metamorphites. These formations from bottom to top are mudstone-radiolarite, metadetritic and crystallized limestone and each unite has tectonic contact with each other. Ophiolites (Karabayar ophiolite) comprise peridotites, diabase and listvenite. This unit is called Dağköy Complex around Gündüzler-Yakayıklı village in North of Eskişehir [30, 37]. Middle-Upper Miocene Porsuk Formation rest unconformably on the former units and consist of conglomerate-sandstone (Np1), marl-clay (Np2), limestone (Np5) members. Karabayar ophiolite outcropping around Margi-Taycılar- Başören villages include mainly peridotites, diabase, listvenite. Peridotites are mainly in harzburgitic composition. This serpentinized peridotite is a host rock of magnesite deposits and chromite deposits. Magnesite deposits previously exploited but chromite is run as open and closed pit (Figure 3).

Tutluca area is located at the south-west of Eskişehir. Triassic aged Inonu metamorfoites consisting mainly of blueschist facies metamorphic rocks and marble form the basement in the study. Ophiolitic Complex rest on tectonically Inonu metamorphite and represented by peridotite and meta-gabbros. This peridotite is a host rock of magnesite and magnesite deposits is run as open pit. Pliocene aged İlica formation overlies unconformity former units and is composed of conglomerate-sandstone (ph), basalt (PIB), andesite (ő). All of these units cover unconformably by alluvial deposits [30, 37]. (Figure 4).

3. Petrography

Host rock of magnesite is harzburgite which consist of serpentine, olivine, orthopyroxene, brucite, chromite and magnetite-chlorite minerals and effected serpentinization process. Harzburgites are generally show a brown in colour because of serpentinization. Serpentine crystallized in veins, at olivine-orthopyroxene grain boundaries, and expense of olivine (mesh texture). The mineral nomenclature used here according to [38]. Abundant serpentinite mineral are chrysotile, lizardite and very lesser amount of antigorite mineral by XRD analysis. Rock become a mesh texture because of extensive serpentinization. Chrysotile form below 250°C and product of alteration and degradation of ultramafic rocks [26]. Olivines form anhedral crystals and have variable sizes (from 0.5 mm-2 mm), showing very crack and serpentinizations occur in this cracks and olivines lost primary future also magnetites which is opaque minerals occur in cracks of some samples in orthopyroxene and olivine (Figure 5a, c). Olivines show triple-junction grain boundaries. Some of the olivine have kink-band geometry. [39] explained that the microstructure and kink-band geometry of olivine indicates that these minerals exposed to the high-temperature plastic deformation. Relict olivine which represent the interaction between olivine and magma is in orthopyroxene. Secondary talk and Mg-clorite occur in fracture within olivine. Orthopyroxenes are euhedral-subhedral minerals found in porphyroclasts, the average grain sizes range from 1-2 mm. Bending of cleavages because of deformation are apparent. Most of orthopyroxene minerals have diopside (clinopyroxene) exsolutions which form along cleavages like a thin lamellae were observed (Figure 5a). This clinopyroxene exsolutions lamellae which in orthopyroxene indicate that formation of these minerals under high pressure. Magnetites decomposition form in cracks of these minerals (Figure 5b, c). In addition, transitions to talc minerals in some cracks of orthopyroxenes minerals were observed. Chromite crystals form euhedral to subhedral minerals and mostly grain size 0.5mm-1mm, brown-black, generally show a pull-apart fracture. Some of these are rounded or elongate due to development of foliation and show a orientation some sample have orientation. Assemblage of chrysotile and brucite occur from Fe-poor Fo80 composition olivine and after reaction Fe show dispersion as magnetite [40]. It is stated that upper temperature limit of this mineralogic assemblage approximately 390 C (± C and 100). Most of the serpentinite contain magnetite. Ferroan magnetite occur exchange of Fe-Mg between olivine and serpentine during the serpentinization in low SiO2 [25,40]. Magnetite not important only understand the geochemistry of serpentinite it is important to understand the magnetization of serpentinite (Example; formation of magnetite relate to reduction condation and characterize the active serpentinizing condition). In particular, [41] argued that between the beginning of serpentinization (shown by a decrease in density) and occurring the modal of the magnetite (demonstration of the sensitivity of magnetic with susceptibility) is a stop, this situation delayed the formation of magnetite and a result of multi-stage serpentinization. [42] stated that in their study magnetites in serpentinites occur two-stage process as oxidation-silification of brucite and oxidation-desilification of Fe-serpentine. [43], defined that his study in Guleman serpentinites, some of the magnetites occur with iron ions released from the structure of silicate minerals during serpentinization and then entering the structure of chormite, some of magnetites also occur with oxidation of iron ions and this stated along the line of cracks in developed serpentinization like anhedral grain. The formation of magnetite is formed by release of silica from serpentine (Fe3Si2O5 (OH)) composition and product of reduction environment. [44] stated that in their study weak serpentinized harzburgite which opx rich in New Caledonya, formation of magnetite related to the gradual change at silica activity during serpentinization process. Opx-rich serpentinite has richer silica than serpentinite related to serpentinization of olivine. [43] indicate that in their analyses the Opx was hydrated by a reaction in which the Fe and Mg were transferred directly to the serpentine. All the iron is the accepted ferrous and the reaction can be modeled as follow [44].

\[
1.5 \text{Fe}_{0.26}\text{Mg}_{0.74}\text{Si}_2\text{O}_6 + 2 \text{H}_2\text{O} = \\
\text{Fe}_{0.39}\text{Mg}_{2.61}\text{Si}_2\text{O}_5(\text{OH})_4 + \text{SiO}_2
\]

If some of the Fe was ferric, very low silica derived from

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this reaction. Silica which derived from this reaction is consumed by serpentinization with olivine. Here as reaction. 

\[
3.084 \text{Mg}_{3.8} \text{Fe}_{0.2} \text{SiO}_4 + 0.916 \text{SiO}_2 + 5.89 \text{H}_2\text{O} = \\
2 \text{Mg}_{2.775} \text{Fe}_{0.225} \text{Si}_2\text{O}_5(\text{OH})_4 + 0.056 \text{Fe}_2\text{O}_4 + 1.89 \text{H}_2
\]

Fe is dissolved serpentinites in high silica activity environment, but in with low silica activity environment silica is release from serpentine and Fe leaves to form a magnetite in. [44], ssimultaneous formation of olivine which dissolved temperatures above 330°C, serpentine, magnetite and dihydrogen depends on the silica source of external. 

<330°C at low temperatures, the formation of hydrogen which is simplifying by brucite, serpentine which form olivine dissolution, magnetite and brucite does not require additional silica. Temperature range of the observed iron distribution in serpentine and brucite is compatible with the formation temperature <150 to 250°C [45]. In the study area harzburgites are subject to serpentinization, so the rock is rich in terms of the content of orthopyroxene, Fe and Mg directly enter into the serpentinite which hydration with orthopyroxene. Silica released this process consumed with the serpentinization of olivine and Fe forms the magnetite.

4. Geochemistry

Whole rock chemical analysis of serpentinitized harzburgite in the study area are given in Table 1. Los ignation LOI values 23.2-6.5 wt% and higher water contents of the investigated rocks shows extensive serpentinization of olivine and orthopyroxene. SiO₂ and MgO are high and variable (32.76-52.08 and 29.59-38.13 wt%, respectively). Al₂O₃ content (0.11-0.92 wt%) and CaO (0.10-7.58 wt%) content of host rock is low and indicate that a felspar and clinopyroxene are absent in it. Na₂O (0.01-0.05 wt%) and TiO₂ (<0.01 wt%) are very low. MgO, CaO and SiO₂ content of serpentinitized harzburgites in study areas show a clear negative correlation with H₂O content (Figure 6a, b, c). As shown in Figure 6b, there are weak negative correlations of CaO with H₂O. Such a characteristic is common to serpentinitized harzburgites. In the system, H₂O increases, whereas MgO, CaO, SiO₂ content decreases. In the study area, harzburgites are mainly altered to serpentine. For this reason rocks are enriched in orthopyroxene intern alorthopyroxene. By hydration of orthopyroxene, Fe and Mg enter structure of serpentine. The silica released from orthopyroxene is used in serpentinization of olivine. The average composition of Ni is 2110 ppm in ultramafic rocks representing the oceanic crust [46] and the average of Cr is 3140 ppm in it [47]. Ni values of serpentinites are in the range of 2781-1041 ppm, suggesting a small amount of enrichment. According to the chondrite normalized REE diagram Ce, Pr, Sm, Gd, Er, Yb showed a slight negative anomaly while La, Nd, Eu, Ho, Tm, Lu showed a slight positive anomaly (Figure 7a). [47] stated that positive Eu anomaly of Pindos dunite and Troodos harzburgite, Eu²⁺ preferential mobility of the process of serpentinization, shows a lack of plagioclase. Primitive mantle show the same abundance chondrite meteorite [48]. In Chondrite and N-type MORB normalized diagram (Figure 7a, b [49]), the serpentinites of the Süleymaniye, Margi and Tutluca areas show very depleted according to REE quantities. Rare earth element contents of ultramafic rocks are very low in ordinary conditions and it is under-chondrite values. At the same time, heavy rare elements (HREE) values in these rocks are evident relative the high values according to the light rare earth element (LREE) values and has a connection of LREE/HREE <1 [50]. Serpentinites in the study areas are LREE/HREE <1 ratio. Enrichment of the HREE elements is observed as a result of alteration and metamorphism of ultramafic rocks, this event as a mobilization of this elements. This situation is acceptable of serpentinitizations. MORB-type ophiolites generally less consumed then SSZ-type ophiolite and contain more Al, Ca and Ti [8, 51]. Study area serpentinites showed a similar feature of SSZ-type ophiolites according to Cr-TiO₂ diagram (Figure 8, [52]).

5. Discussion and Conclusions

Serpentinized harzburgite is a magnesite host rock which samples were taken from them to study petrographic and mineralogical characteristics, geochemical properties. Harzburgites has turned into serpentine mineral with 80-90% volume because of extensive serpentinization. Rock has transform to 70% serpentine mineral in volume is sufficient for naming the serpentine [53]. Serpentinization, initially like that fine-reticulate veins of minerals by the edges and cracks starts from the cleavage of minerals and gradually changes the whole texture of the rock. In harzburgites (study areas) which commonly composed of orthopyroxene and olivine, olivine beginning to serpentinization from edges and cracks then developed extensively sieve texture while same sample has an hour glass texture. Residue olivine minerals found in the center of sieve texture in progressive serpentinized sample. Orthopyroxenes are generally protected the crystal form and the boundaries and transform serpentine mineral by substitution in cleavage and cracks. The presence of primary mineral like a residual minerals expression us essential water to complete the transformation of mineral in not adequate for this part but formation mineral give us a information about metamorfism efect. Identification of primary rock can be done with the help of the residue minerals. By means of antigorite mineral commonly found in serpentine, these rocks has been exposed to the effects of hydrothermal metamorphism in some places up to 500°C [54,55]. At the same time the presence of antigorite minerals and rock has dump texture like a needle shape show the rock exposed to the effects of regional metamorphism in greenschist facies metamorphism [56]. The antigorit mineral is not common is very small amouth in the study areas. Presence of antigorite represent
the early serpentinization temperature $T > 300 \, ^\circ C$ and reflect a rock-dominant serpentinization (closed system serpentinization) [57], [58] and [59] explained that depleted REE contents of serpentinite and listvenites is associated with alteration product of depleted MORB. REE content of the serpentinitized harzburgites in the study area are depleted so we say that alteration of marine and the atmosphere water is exist. [59] show that negative Ce anomaly is evidence of the balance between REE and the sea water samples and similar to the sea water. The negative Ce anomaly in the serpentinitized harzburgite of the study area has demonstrated that serpentinization is associated with meteoric and hydrothermal solution and also sea water in light. Petrographic features, Al, Ca and Ti contents, the REE content of the study area is similar future of SSZ tectonic features of region. According to the mineralogical composition of chrysotile/lizardite are common serpentine mineral and antigorite mineral is very little minerals, magnetite presence can we said that during serpentinization temperature lower than $350 \, ^\circ C$ and rise in places. We can say that in the beginning serpentinization process initially closed system environment serpentinization conditions is current, then changing the system condition and then open system environment serpentinization is dominate. We can say that effective CO$_2$ of magnesite occurrences in the fractures and cracks of the ultramafic rocks enter into the system from the atmosphere and the surrounding carbonate rock is the evidence of the open system conditions of serpentinization.

Figure 1. Tectonic map of Tavsanlı Zone [5, 30]
Figure 2. Geologic map of Süleymaniye area [30, 36].
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Figure 3. Geologic map of Margi area [30, 36]
Figure 4. Geologic map of Tutluca area [30, 36]
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Figure 5. 4 photomicrographs of serpentized harzburgite.

(mt: magnetite, crz: chrysotile, olv: olivine, opx: orthopyroxene, cr: chromite, cpx: clinopyroxene)

a) Exsolution lamelle of orthopyroxene and iddingisite of olivine (Süleymaniye, crossed polars)
b) Chromite minerals of serpentinized dunite, cr: chromite, mt: magnetite (Tutluca, crossed polars)
c) Chrysotile and magnetite in olivine of serpentized harzburgite (crz: chrysotile, mt: magnetite, Margı, crossed polars)
d) Harzburgite of Tutluca cr: chromite, olv: olivine, opx: orthopyroxene (Tutluca, crossed polars)
Figure 6. Relationship diagram between MgO, CaO, SiO₂ with H₂O
Figure 7. a) Chondrite normalized REE diagram pattern of the harzburgites, b) sample-N type MORB normalized REE of the harzburgites in the study area [49].
Figure 8. Cr versus TiO$_2$, tectonic discrimination diagram [52].

Table 1. Major, trace and rare earth element data of serpentinites from the study areas (S: Süleymaniye köyü, M: Margı-Taycılar-Sepetci, T: Tutluca)

| Sample | SY1 | SY2 | SY3 | SY  | M1Y | M4 | M6Y |
|--------|-----|-----|-----|-----|-----|----|-----|
| **Major oxide elements (wt %)** |     |     |     |     |     |    |     |
| SiO$_2$ | 38.18 | 39.74 | 32.76 | 40.01 | 38.93 | 32.17 | 29.80 |
| Al$_2$O$_3$ | 0.11 | 2.00 | 1.04 | 1.83 | 0.35 | 3.05 | 0.21 |
| Fe$_2$O$_3$ | 9.65 | 9.60 | 7.64 | 7.27 | 8.14 | 8.71 | 6.82 |
| MgO | 33.76 | 29.59 | 30.89 | 35.62 | 35.20 | 30.38 | 31.55 |
| CaO | 0.43 | 0.66 | 5.36 | 0.27 | 0.08 | 0.10 | 7.58 |
| Na$_2$O | 0.01 | 0.05 | 0.04 | 0.01 | 0.02 | 0.01 | 0.02 |
| K$_2$O | 0.04 | 0.08 | 0.06 | <0.04 | <0.04 | <0.04 | <0.04 |
| TiO$_2$ | 0.01 | 0.03 | 0.02 | 0.03 | <0.01 | 0.05 | <0.01 |
| P$_2$O$_5$ | 0.03 | 0.02 | 0.02 | 0.02 | <0.01 | <0.01 | <0.01 |
| MnO | 0.11 | 0.07 | 0.10 | 0.08 | 0.08 | 0.10 | 0.08 |
| Cr$_2$O$_3$ | 0.361 | 0.516 | 0.300 | 0.425 | 0.369 | 12.001 | 0.347 |
| LOI | 16.9 | 17.3 | 21.4 | 14.1 | 16.4 | 13.0 | 23.2 |
| **Trace elements (ppm)** |     |     |     |     |     |    |     |
| Ni | 2735 | 2157 | 1865 | 1944 | 2392 | 2454 | 2214 |
| Sc | 4 | 12 | 9 | 11 | 7 | 8 | 6 |
| Ba | 11.7 | 18.3 | 29.9 | 12.1 | 4.6 | 3.4 | 3.5 |
| Be | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Co | 105.2 | 87.5 | 86.8 | 83.8 | 106.4 | 103.7 | 95.8 |
| Cs | 0.2 | 13.2 | 0.2 | 0.9 | <0.1 | <0.1 | <0.1 |
| Ga | 0.5 | 1.5 | 1.1 | 1.5 | <0.5 | 4.1 | <0.5 |
| Hf | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| Nb | <0.5 | 0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| Rb | 0.5 | 3.8 | 2.0 | 0.6 | <0.5 | 0.8 | <0.5 |
| Sn | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Sr | 30.4 | 20.6 | 499.9 | 19.7 | 1.7 | 2.0 | 27.4 |
| Ta | <0.1 | 0.1 | 0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
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|     | Sample M17Y | Sample M18Y | Sample T4Y | Sample T1Y | Sample T2Y | Sample T3Y | Sample T3Y1 | Sample T2Y1 |
|-----|--------------|--------------|------------|------------|------------|------------|-------------|-------------|
|     | Major oxide elements (wt %) | | | | | | | |
| SiO₂ | 41.82 | 52.18 | 37.79 | 39.93 | 40.11 | 38.95 | 37.50 | 40.19 |
| Al₂O₃ | 0.53 | 1.12 | 0.35 | 0.61 | 0.92 | 0.40 | 0.59 | 0.30 |
| Fe₂O₃tot | 8.22 | 7.25 | 8.05 | 8.53 | 8.98 | 7.86 | 7.78 | 6.82 |
| MgO | 38.13 | 30.71 | 34.00 | 33.79 | 33.33 | 34.61 | 33.05 | 36.88 |
| CaO | 0.68 | 1.34 | 0.65 | 0.50 | 0.44 | 0.91 | 2.39 | 0.15 |
| Na₂O | 0.01 | <0.01 | 0.01 | 0.02 | 0.05 | 0.01 | 0.01 | 0.01 |
| K₂O | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 |
| TiO₂ | <0.01 | 0.02 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| P₂O₅ | <0.01 | <0.01 | 0.02 | 0.01 | 0.03 | 0.03 | 0.03 | 0.02 |
| MnO | 0.11 | 0.14 | 0.10 | 0.11 | 0.12 | 0.10 | 0.10 | 0.09 |
| Cr₂O₃ | 0.402 | 0.498 | 1.553 | 0.413 | 0.428 | 0.382 | 0.312 | 0.258 |
| LOI | 9.7 | 6.5 | 17.0 | 15.7 | 15.2 | 16.4 | 17.9 | 14.9 |

|     | Trace elements (ppm) | | | | | | | |
| Ni | 2364 | 1014 | 2781 | 2259 | 2344 | 2186 | 2049 | 2356 |
| Sc | 11 | 18 | 5 | 9 | 11 | 7 | 9 | 3 |
| Ba | 7.2 | 6.6 | 24.6 | 9.5 | 9.7 | 5.1 | 9.1 | 4.9 |
| Be | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Co | 107.6 | 69.6 | 114.1 | 110.8 | 115.6 | 100.9 | 103.0 | 103.8 |
| Cs | <0.1 | <0.1 | <0.1 | 0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Ga | 0.6 | 1.1 | 0.5 | 0.6 | 0.9 | 0.5 | 0.8 | 0.5 |
| Hf | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| Nb | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |

### Rare earth elements (ppm)

|     | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| M17Y | 0.3 | 0.3 | 0.3 | 0.1 | <0.5 | <0.5 | <0.5 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| M18Y | 0.3 | 0.4 | 0.3 | 0.2 | <0.5 | <0.5 | <0.5 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| T4Y | 0.05 | 0.05 | 0.05 | 0.05 | <0.02 | <0.02 | <0.02 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| T1Y | <0.3 | <0.3 | <0.3 | <0.3 | <0.4 | <0.4 | <0.4 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| T2Y | <0.05 | 0.09 | <0.05 | 0.09 | <0.1 | <0.1 | <0.1 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| T3Y | <0.02 | 0.03 | 0.03 | 0.03 | <0.05 | <0.05 | <0.05 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 |
| T3Y1 | 0.01 | 0.01 | 0.01 | 0.01 | <0.01 | <0.01 | <0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| T2Y1 | 0.01 | 0.02 | 0.01 | 0.03 | <0.01 | <0.01 | <0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Rb   | <0.5 | <0.5 | <0.5 | 0.5  | <0.5 | <0.5 | <0.5 | <0.5 |
|------|------|------|------|------|------|------|------|------|
| Sn   | <1   | <1   | <1   | <1   | <1   | <1   | <1   | <1   |
| Sr   | 1.5  | 2.8  | 5.6  | 2.5  | 3.5  | 6.4  | 20.5 | 1.6  |
| Ta   | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Th   | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| U    | <0.1 | <0.1 | <0.1 | 0.1  | 0.9  | 0.7  | 0.3  | <0.1 |
| V    | 43   | 59   | 35   | 34   | 47   | 25   | 27   | 14   |
| W    | 0.2  | <0.1 | 0.1  | 0.1  | 0.1  | 0.1  | <0.1 | <0.1 |
| Zr   | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | 0.5  |
| Y    | <0.1 | 0.2  | <0.1 | 0.1  | 0.1  | 0.1  | 0.4  | 0.2  |

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