

## Redox Reactions in Antigorite Serpentinities

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**Abstract** – We investigated serpentinites that contain a significant amount of magnetite, originating from ophiolites and tectonic melanges. Variations in the amount of magnetite were observed in serpentinites dominated by antigorite. While some samples exhibited a prevalence of iron oxides, others contained almost none. The Mg# [ $100 \times \text{Mg}/(\text{Mg}+\text{Fe})$  atomic] values of the studied samples were found to range from 79 to 88. However, for antigorite, the Mg# value can reach up to 92 in magnetite-rich rocks. In samples devoid of iron oxides, this value decreases, indicating the preservation of relic protolith textures.

Serpentinites, despite having different formation mechanisms, typically result from the hydration of peridotite. Hydration involves redox reactions, which yield brucite and magnetite. The formation of magnetite occurs primarily due to the preferential partitioning of Mg over  $\text{Fe}^{2+}$  in serpentine compared to olivine or orthopyroxene. Consequently, the excess iron, mainly derived from olivine, predominantly generates magnetite through redox reactions involving iron-rich brucite ( $\text{Fe}^{2+}(\text{OH})_2$ ) or reacting with available oxygen or product  $\text{H}_2$  (or  $\text{CH}_4$ ). The presence of magnesite and dolomite has been identified in the samples. Based on the obtained findings, it can be inferred that rocks devoid of magnetite indeed contain magnetite produced by serpentinization, but ongoing reactions with fluid allowing iron back-reaction serve to re-equilibrate  $f\text{O}_2$  to preserve the entire rock's Mg#. Although this process may be challenged by the extended storage of antigorites at high P - T conditions, it appears to be a relatively closed system for oxides.

*Key Words – Dolomite, Fluid-Rock Interactions, Oxidation State, Peridotite, Hydration*

### I. INTRODUCTION

Serpentinites are hydrated fragments of the mantle layer and are typically found in subduction zones. They play a significant role in the global cycling of water, carbon, nitrogen, fluid-mobile elements, and halogens. These elements are released at depth during prograde hydration as part of the subduction process [1,2,3,4]. Serpentinities and metamorphic slices formed at depth in subduction zones play a crucial role in generating the characteristic chemical composition of arc magmas [5,6,7,8]. Subducting oceanic plates significantly contribute to the net redox and oxidation state of dehydration fluids infiltrating the overlying mantle [9,10]. Within serpentinized rocks comprising chrysotile, antigorite, and lizardite, the extensive stability field

of antigorite allows for the possibility of these chemical components to be transported deeper into the mantle [6].

The presence of serpentinized rocks in paleo-subduction complexes, along with associated metasomatic rocks, provides information about subduction processes, including the transport and chemical evolution of fluids during subduction and exhumation. The aim of this study is to examine how rocks containing magnetite, as well as those lacking it, actually produce magnetite through serpentinization via redox reactions and provide an insight into the petrographic characteristics of magnetites.

## II. MATERIALS AND METODS

Mineralogical identification of total of 22 selected serpentinite samples from the study area were conducted through XRD (X-Ray Diffraction) analyses. The analyses were carried out using an INEL model 1000 XRD instrument at Ankara University's YEBIM laboratory. Once the samples were ground to clay size, XRD measurements were performed on the entire rock.

## III. RESULTS

### A. Petrography

Serpentinites are primarily composed of antigorite, talc, and magnetite, constituting more than 90% of the rock, with occasional remnants of chromian spinel, olivine and clinopyroxene. Antigorite typically serves as the predominant matrix phase, forming interlocking crystals with varying degrees of preserved evidence of mesh texture (Figure). In certain samples, anhedral fine-grained ( $<10\mu\text{m}$ ) recrystallized antigorite is found in association with talc. Furthermore, magnetite is present as a matrix phase, appearing as individual subhedral grains with an approximate size of 1 mm (Fig. 1). In exceptional instances, residual chromite can be observed in the central part of these grains, surrounded by chromite and enclosed by a magnetite rim.

Serpentinites exhibit the presence of remnants of orthopyroxene and olivine, and their degree of serpentinization ranges from approximately 50% to 90%. Notably, samples from this location do not contain talc, and among them, four samples have distinct characteristics. Oxide textures display a spectrum of retrogression, ranging from chromite with magnetite rims (Fig. 1) to chromian magnetite cores that have undergone complex replacement by magnetite (Fig. 1).

Mesh textures exhibit a less pronounced development when contrasted with the comprehensive pseudo-morphism observed in specific samples. In cases where serpentinization and replacement processes are more extensive (Fig. 1), it becomes apparent that samples that are more than 90% serpentinized feature a common assemblage of antigorite + talc + magnetite, along with lower and more heterogeneous MgO contents. Conversely, in samples with a serpentinization

range of approximately 50% to 90%, there is a noticeable preservation of orthopyroxene and olivine, coupled with the distinct presence of awaruite and elevated MgO contents. Cluzel et al. (2020) suggests that the development of chromium-rich magnetite around chromite grains within tremolite veins originating from subduction slabs necessitates the presence of oxidizing fluids.

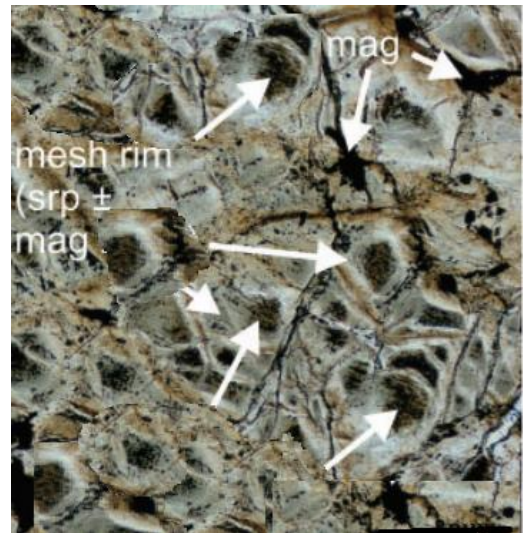


Figure 1. View of mesh-textured serpentinites and magnetites

Magnetites, subhedral, fine-grained and cataclastic in texture. They are occasionally found in primitive formations and emerge through serpentinization, appearing as pseudomorphs of olivine and orthopyroxene. These which can sometimes be veined or occur as veinlets, can have grain sizes of up to approximately 0.3 - 0.5 mm. Along the edges and fractures of magnetite grains, very weak levels of martitisations are observed (Figure).

### B. Geochemistry

The XRF data of serpentinites indicate high concentrations of  $\text{K}_2\text{O}$  (0.96%),  $\text{SiO}_2$  (35.36%),  $\text{Al}_2\text{O}_3$  (5.09%),  $\text{CaO}$  (14.45%),  $\text{TiO}_2$  (0.34%), Ba (317.1 ppm), La (398 ppm), Rb (104 ppm), Sn (35.2 ppm), Ce (350 ppm), Y (15.4 ppm), and Zr (43.8 ppm), with low contents of MgO (22.70%) and  $\text{Fe}_2\text{O}_3$  (10.80%). The geochemistry represented by these values, which display the average composition, is characteristic of silicification, carbonatization, and clay-rich serpentinites. In these

samples, where hydrothermal alteration is pronounced, magnetite spots are observed.

### C. Redox Reactions and magnetite

Redox reactions are chemical reactions involving reduction and oxidation. In such reactions, one component gains electrons (reduced), while the other component loses electrons (oxidized). These two processes are interconnected and occur on both sides of the same reaction. The fundamental characteristics of redox reactions.;

Electron transfer (the transfer of electrons from one compound to another), oxidation numbers, Redox reactions, and the most significant example of these reactions, is magnetite ( $\text{Fe}_3\text{O}_4$ ). In this reaction, iron is initially oxidized by oxygen (loses electrons), and then oxygen accepts electrons (is reduced)[3,6]. Magnetite, a natural magnetic mineral, can form particularly during the serpentinization process of basic/mafic igneous rocks. In this process, redox conditions are crucial, and a series of chemical reactions occur in the formation of magnetite.

The primary redox reactions involved in the formation of magnetite:

At the onset of the serpentinization process, olivine mineral reacts with water. During this reaction, olivine forms a series of minerals known as serpentine minerals. This reaction traces the beginning of a series of chemical reactions and serves as a fundamental step in the formation of magnetite [12,13]. Serpentine minerals contain a range of elements that are prone to redox reactions. In particular, Mg and Fe elements play a significant role in these reactions [9,10,11]. These minerals have a specific crystal chemistry that allows the substitution of Mg with  $\text{Fe}^{2+}$ . The formation of magnetite occurs due to the specific crystal structure and chemical composition of serpentine minerals [11,12]. Serpentine minerals preferentially partition  $\text{Fe}^{2+}$  over Mg, which can lead to the utilization of excess iron in the formation of magnetite. The formation of magnetite, which occurs during the serpentinization process and is based on redox reactions, involves the chemical evolution of serpentine minerals, especially in the presence of water and oxygen, facilitating the formation of magnetite.

## IV. CONCLUSION

In conclusion, our study revealed that most of the investigated serpentinites, predominantly dominated by antigorite, contain a significant amount of magnetite, while some samples showed almost no magnetite presence. The magnetite-rich rocks with antigorite, the Mg# value could reach up to 92. Serpentinites, despite having different formation mechanisms, typically result from the hydration of peridotite. Hydration involves redox reactions that yield brucite and magnetite.

The formation of magnetite occurs primarily due to the preferential partitioning of Mg over  $\text{Fe}^{2+}$  in serpentine compared to olivine or orthopyroxene. The excess iron, mainly derived from olivine, predominantly generates magnetite through redox reactions involving iron-rich brucite or reacting with available oxygen or product  $\text{H}_2$ .

The presence of magnesite and dolomite can be inferred that rocks devoid of magnetite indeed contain magnetite produced by serpentinization, but ongoing reactions with fluid allowing iron back-reaction serve to re-equilibrate  $f\text{O}_2$  to preserve the entire rock's Mg# and it appears to be a relatively closed system for oxides.

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