New Orthorhombic Phases on the Join \( \text{NiAl}_2\text{O}_4 \) (Spinel Analog)-\( \text{Ni}_2\text{SiO}_4 \) (Olivine Analog): Stability and Implications to Mantle Mineralogy

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Abstract. Three new crystalline phases differing in Si/Al ratio have been synthesized from compositions along the join \( \text{NiAl}_2\text{O}_4-\text{Ni}_2\text{SiO}_4 \). Four reversible univariant equilibria involving these new phases plus \( \text{Ni}_2\text{SiO}_4 \) (olivine) have been located within the \( P-T \) region studied (1 atm-40 kb, 1000-1700 °C); an invariant point occurs near 22 kb, 1150°C.

All three new phases are orthorhombic. Precession photographs and electron microprobe analyses yield the following information:

Phase I: \( 5\text{NiO}-3\text{Al}_2\text{O}_3-\text{SiO}_2 = 3\text{NiAl}_2\text{O}_4-\text{Ni}_2\text{SiO}_4 \),

\[ \text{Pm} \text{ma}, a = 5.67, b = 11.51, c = 8.10 \ (\text{Å}) \]

Phase II: \( 7\text{NiO}-3\text{Al}_2\text{O}_3-2\text{SiO}_2 = 3\text{NiAl}_2\text{O}_4-2\text{Ni}_2\text{SiO}_4 \),

\[ \text{Im} \text{ma}, a = 5.66, b = 17.32, c = 8.11 \]

Phase III: \( 3\text{NiO}-\text{Al}_2\text{O}_3-\text{SiO}_2 = \text{NiAl}_2\text{O}_4-\text{Ni}_2\text{SiO}_4 \),

\[ \text{Im} \text{ma}, a = 5.68, b = 11.49, c = 8.12 \]

Comparison with known structures suggests that these three phases plus \( \text{NiAl}_2\text{O}_4 \) spinel and high pressure \( \text{Ni}_2\text{SiO}_4 \) spinel belong to a homologous series based on a cubic close oxygen packing of the formula: \( M_{n\omega}O_{n-1}(T_03n_{\omega}+1) \) where \( M \) and \( T \) are octahedrally and tetrahedrally coordinated cations, respectively. When \( n = 1 \) the formula for spinel is obtained; \( n = 2 \) for phase I and phase III, both similar to the beta-phase of orthosilicates; and \( n = 3 \) for phase II which is related to the manganostibite structure.

Similar phase equilibria and structural relations may occur on other joins of the aluminate-orthosilicate type. Furthermore, the occurrence of such structural modifications between the spinel (aluminate) and olivine (orthosilicate) compositions suggests that there could be a corresponding polymorphic series between the olivine and spinel forms of orthosilicates.

1. Introduction

Silica (SiO\(_2\)), magnesium oxide (MgO), ferrous oxide (FeO), and alumina (Al\(_2\)O\(_3\)) are possibly the four most abundant oxide components in the earth’s mantle. The mineral olivine, a compound of the first three oxides above, is generally believed to be the major mineral in the upper mantle. Studies of phase equilibria among olivine and aluminous minerals (such as pyroxene, garnet, and spinel) at \( P-T \) conditions comparable to those in the earth’s mantle is therefore essential if we are to understand the mineralogy and petrology of the mantle.

Although numerous studies have been carried out on upper-mantle mineral assemblages at high pressures and high temperatures, no such studies have ever involved joins of the type aluminate (spinel)-orthosilicate (olivine). Such joins are, in my opinion, particularly interesting for the following reasons:

1. Olivine transforms to a spinel form at high pressures. It is therefore reasonable to assume that at high pressures something other than a simple eutectic relation must occur between the usual aluminate spinels and the olivine and spinel orthosilicates.
2. At intermediate pressures, other polymorphs exist between the olivine and spinel forms of orthosilicates. A study of joins of the type aluminate-orthosilicate might offer some insight into the crystallochemical nature of possible intermediate phases between the olivine and spinel forms of orthosilicate composition.

The join nickel aluminate, NiAl_2O_4 (spinel analog)-nickel orthosilicate, Ni_2SiO_4 (olivine analog) within the system SiO_2-NiO-NiAl_2O_4 was chosen for this study mainly because the olivine-spinel transformation of Ni_2SiO_4 occurs at pressure conditions attainable with the piston-cylinder apparatus available at Harvard University. In addition, this chemical system had the following advantages:

1. Nickel (unlike iron) remains divalent under the subsolidus experimental conditions in this study without specifically controlling the oxidation state.

2. Except for three new phases found on the join NiAl_2O_4-Ni_2SiO_4, no other ternary phases have been encountered in the system SiO_2-NiO-NiAl_2O_4 in this study. The nickel system thus appears to be the simplest ternary system for characterizing the aluminate-orthosilicate type of join.

1.1. Previous Work

The join NiAl_2O_4-Ni_2SiO_4 and the system SiO_2-NiO-NiAl_2O_4 are part of the ternary system NiO-Al_2O_3-SiO_2 which was the subject of an extensive study at atmospheric pressure by Phillips et al. (1963). They proposed a ternary liquidus diagram as well as T-X diagrams of several joins including the join NiAl_2O_4-Ni_2SiO_4. Except for confirming the existence of two previously known compounds, NiAl_2O_4 spinel and Ni_2SiO_4 olivine, they did not detect any other nickel compounds.

Previous work at high pressures involves the study of olivine-spinel transformation in Ni_2SiO_4 (e.g., Ringwood, 1962; Akimoto et al., 1965) and the doubtful synthesis of NiSiO_3 pyroxene. Hayashi et al. (1966) claimed to have successfully synthesized a monoclinic NiSiO_3 pyroxene at about 50 kb and 900-1500°C, and a rhombic NiSiO_3 pyroxene at 37-50 kb and 1600-2000°C, although other workers (e.g., Akimoto et al., 1965) have failed to synthesize any NiSiO_3 pyroxene.

1.2. This Study

This study began with a reconnaissance study based on runs made on mixtures of NiAl_2O_4 spinel and Ni_2SiO_4 olivine phases at 35-40 kb and 800-1000°C, conditions under which both end members have the spinel structure. Although a continuous simple spinel solid solution was expected, new crystalline phases appeared. Further study revealed that one of the new phases even forms at atmospheric pressure, contrary to the available phase diagram (see Phillips et al., 1963) in which a simple two phase region (olivine plus spinel) is implied between NiAl_2O_4 and Ni_2SiO_4.

To characterize these new phases, the ternary system SiO_2-NiO-NiAl_2O_4 was investigated over a wide range of P-T conditions (1 atm-40 kb, 1000-1700°C). Except for the highest pressure applied, the P-T conditions studied were in the stability field of the olivine-form of Ni_2SiO_4. The use of the mixture of NiAl_2O_4 spinel plus Ni_2SiO_4 olivine phases as the starting material was discontinued, because such a mixture is not an equilibrium phase assemblage even