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Revision 1

HIGHLIGHTS AND BREAKTHROUGHS

Making a fine-scale ruler for oxide inclusions

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Constraining the phase relations and valence state of iron-bearing oxides is crucial to understanding the chemistry of earth's mantle. In this issue of *American Mineralogist*, Uenver-Thiele et al. present an experimental study on the phase diagrams of magnesioferrite-magnetite solid solutions at high pressures and high temperatures. By analyzing the compositions of the quenched products, Uenver-Thiele et al. were able to constrain the phase diagram of the (Mg, Fe^{2+})$Fe^{3+}_2O_4$ series, and they identified several new phases with non-conventional stoichiometry. From the phase diagrams of (Mg, Fe^{2+})$Fe^{3+}_2O_4$ spinels determined in this study and the stability fields of the new phases, the authors proposed an empirical method to recover the petrological history of magnesium-iron oxide inclusions in natural diamonds.

Oxygen and iron are the two most abundant elements in the earth, and their compounds, the iron oxides, are common in the crust and the mantle. Iron is the most important multivalent transitional metal in the mantle, and the stability fields of different iron oxides covers the mantle conditions in the P-T-fO_2 space. Certain iron oxides, such as magnetite (Fe_3O_4) and wüstite ($Fe_{1-x}O$) and their solid solutions with periclase (MgO), have been used as scales to constrain the P-T-

fO_2 history of petrological assemblages. One application of such an "oxide scale" is to determine the petrological history of diamonds with inclusions. For example, diamonds with ferropericlase ((Mg, Fe)O) inclusions are usually associated with a lower mantle origin (Wirth et al., 2014), whereas magnesioferrite ($MgFe_2O_4$) inclusions have a maximum formation pressure (Uenver-Thiele et al., 2017b). The oxygen fugacity of petrological experiment is usually associated with a certain redox reaction, and redox reactions between iron oxides, such as wüstite, magnetite and hematite, have been established as standard oxygen fugacity buffers (Myers and Eugster, 1983).

In the past few years, several non-conventional iron oxides, including Fe_4O_5, Fe_5O_6, Fe_5O_7, Fe_7O_9, $Fe_{13}O_{19}$, $Fe_{25}O_{32}$ and FeO_2 have been identified experimentally (Bykova et al., 2016; Hu et al., 2016; Lavina et al., 2011; Lavina and Meng, 2015; Merlini et al., 2015; Sinmyo et al., 2016). These non-conventional iron oxides form homologous series from several fundamental iron-oxygen polyhedral blocks (Bykova et al., 2016; Guignard and Crichton, 2014). Some of these non-conventional iron oxides are quenchable at ambient condition with appropriate oxygen fugacity (Guignard and Crichton, 2014; Lavina et al., 2011). Besides pure iron oxides, their variants have been identified by substituting Fe^{2+} with Mg^{2+} (Ballaran et al., 2015; Uenver-Thiele et al., 2017a; Uenver-Thiele et al., 2017b). These non-conventional oxides could be incorporated into the "oxide scale" to constrain the P-T-fO_2 history of petrological assemblages, once their phase diagrams and stability fields are established.

In the study by Uenver-Thiele et al. (2017a), the phase relations of magnesium-iron oxide spinels were explored at high pressure and high temperature conditions. Two starting materials, $MgFe_2O_4$ and $Mg_{0.5}Fe^{2+}_{0.5}Fe^{3+}_2O_4$, were compressed with multi-anvil presses to 23 GPa and

1500 °C. The oxygen fugacity was carefully controlled in the experiments. The run products were quenched to ambient conditions before further analysis with electron microprobe, backscattered electron image and X-ray powder diffraction.

Uenver-Thiele et al. first investigated the $MgFe_2O_4$ system. They found that MgO + Fe_2O_3 were the stable assemblage at 1200 °C. At 20 GPa and 1400-1500 °C, the coexistence of $Mg_2Fe_2O_5$ + Fe_2O_3 and hp-$MgFe_2O_4$ phases were observed, and a new phase with the stoichiometry of $Mg_3Fe_4O_9$ were found at 20 GPa, 1300 °C and 23 GPa, 1500 °C, coexisting with Fe_2O_3 and hp-$MgFe_2O_4$. Uenver-Thiele et al. suggested that MgO, Fe_2O_3, $Mg_2Fe_2O_5$ and $Mg_3Fe_4O_9$ could coexist at ~19 GPa and 1200-1250 °C.

As for the $Mg_{0.5}Fe^{2+}_{0.5}Fe^{3+}_2O_4$ system, periclase was no longer observed in the investigated P-T range. The $Mg_{0.5}Fe^{2+}_{0.5}Fe^{3+}_2O_4$ spinel brokedown to $MgFe^{2+}Fe^{3+}_2O_5$ + Fe_2O_3 at 11 GPa and 1000-1600 °C, and the phase boundary was indistinguishable from the Fe_3O_4 endmember (Woodland et al., 2012). When the pressure went higher than 16 GPa, a single phase of hp-$Mg_{0.5}Fe^{2+}_{0.5}Fe^{3+}_2O_4$ became stable. At 15 GPa and 1600 °C, Uenver-Thiele et al. identified a new phase of $Mg_{1.37}Fe^{2+}_{1.63}Fe^{3+}_4O_9$, another solid solution in the (Mg, Fe^{2+})$_3Fe^{3+}_4O_9$ series. X-ray powder diffraction suggested that the (Mg, Fe^{2+})$_3Fe^{3+}_4O_9$ had the same C*2/m* structure as Fe_7O_9 (Sinmyo et al., 2016).

One interesting application of this study is to constrain the precipitation condition of magnetite inclusions in diamonds. Uenver-Thiele et al. propose an empirical way to determine the precipitation pressure of the quenched magnetite inclusions in diamonds: since the phase

diagrams presented in this study suggest that the hp-(Mg, Fe^{2+})$Fe^{3+}{}_2O_4$ phase cannot directly transform into the spinel structure, if the precipitated magnetite inclusion has an euhedral morphology, it is likely to come from the partial oxidation of ferropericlase; otherwise, if the magnetite inclusion demonstrates a twinned texture, some kind of precursor phases such as the (Mg, Fe^{2+})$_2Fe^{3+}{}_2O_5$ and/or (Mg, Fe^{2+})$_3Fe^{3+}{}_4O_9$ phases might be involved in the precipitation process. To sum up, this study has extended our understanding about the high pressure-temperature phase diagrams of magnesium-iron oxides, and provides more detailed constraints on the petrological history of natural diamonds that contain magnesium-iron oxide inclusions.

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