Breakdown of hydrous ringwoodite to pyroxene and Fe$_{3+}$-bearing-wadsleyite at high P and T and oxidizing conditions

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The stability relations in the systems M$_2$SiO$_4$ (M = Mg, Fe, Ni, Co) have been the subject of numerous studies because of their significance for the mantle transition zone. In the Mg$_2$SiO$_4$ system three polymorphs exist: at ambient conditions olivine, at pressure $> 13$ GPa (1000 °C) wadsleyite and at P $> 18$ GPa (1000 °C) ringwoodite. This is quite different to the Fe$_2$SiO$_4$ system where no intervening wadsleyite phase has been observed but fayalite directly transforms to Fe$_{3+}$-ringwoodite at 5.3 GPa (100 °C). Experiments in the system Fe$_2$SiO$_4$ – Fe$_3$O$_4$ by Woodland and Angel (1998) at 5.6 GPa (1100 °C) revealed that Fe$_{3+}$-wadsleyite can only be stabilised if significant amounts of Fe$_{3+}$ are incorporated. To get deeper insight into the phase relation in the endmember system Fe$_2$SiO$_4$ as well as in the system Fe$_1$Mg$_1$SiO$_4$ we investigated the phase relations as a function of P, T and f$_{O_2}$. The experiments were performed in a multi-anvil apparatus at 7- 14 GPa at 1100 °C. Oxygen fugacities were varied using the solid oxygen buffer systems Fe/FeO, QFM and Ni/NiO. The run products were analysed with electron microprobe, Raman spectroscopy, X-ray powder diffraction and transmission electron microscopy. The X-ray data were analysed using the GSAS software. At f$_{O_2}$ corresponding to Ni/NiO Fe-ringwoodite transforms to Fe$_{3+}$-pyroxene at 5.3 GPa (1000 °C). Experiments in the system Fe$_2$SiO$_4$ – Fe$_3$O$_4$ by Woodland and Angel (1998) at 5.6 GPa (1100 °C) revealed that Fe$_{3+}$-wadsleyite can only be stabilised if significant amounts of Fe$_{3+}$ are incorporated. To get deeper insight into the phase relation in the endmember system Fe$_2$SiO$_4$ as well as in the system Fe$_1$Mg$_1$SiO$_4$ we investigated the phase relations as a function of P, T and f$_{O_2}$. The experiments were performed in a multi-anvil apparatus at 7- 14 GPa at 1100 °C. Oxygen fugacities were varied using the solid oxygen buffer systems Fe/FeO, QFM and Ni/NiO. The run products were analysed with electron microprobe, Raman spectroscopy, X-ray powder diffraction and transmission electron microscopy. The X-ray data were analysed using the GSAS software. At f$_{O_2}$ corresponding to Ni/NiO Fe-ringwoodite transforms to ferrosilite and Fe$_{3+}$-wadsleyite according to the reaction: 9 Fe$_2$SiO$_4$ + O$_2$ = 6 FeSiO$_3$ + 5 Fe$_{2.42}$Si$_{0.58}$O$_4$. Refinement of site occupancies in combinations to stoichiometric Fe$_{3+}$ calculations show that 32 % of the total Fe is incorporated as Fe$_{3+}$ according to Fe$^{2+}$Fe$^{3+}$3Fe$^{3+}$6Si$_{0.62}$Fe$_{0.39}$O$_4$. Similar phase relations are observed in the system Fe$_1$Mg$_1$SiO$_4$.

Reference

Miocene oceanography of the Mediterranean area deduced from C-, O-, Sr-, and Nd-isotopes

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A detailed study of the isotopic composition of fossils and whole samples from a composite Oligo-Miocene pelagic sequence of the Umbria-Marche region in Italy has been made with the goal to constrain oceanographic and climatic conditions of the Mediterranean Sea during this period. Stable C and O isotope compositions of benthic and planktic foraminifera mimic global changes, supporting that these fossils have been well preserved and that the regional climate of this area was controlled by global climate changes.

Neodymium and strontium isotope compositions of bulk carbonateous fossils were measured and compared to those of the detrital silicate fraction of the embedding sediment. The compositions of the fossils are expected to closely relate to the former seawater composition, while the sediment would represent the hinterland. The relation between the two signals helps to evaluate oceanic circulation in the region. To broaden the spatial distribution and trace connections between different water masses, marine deposits from northern Italy and Slovenia were also investigated.

Results to date indicate a strong local influence on the $\varepsilon_{Nd}$ value and possibly a weaker influence on the Sr isotope composition of the Mediterranean seawater during the Chattian-Aquitanian. During the Burdigalian-Serravallian a mixed seawater composition between the Atlantic and Indian Ocean water masses was registered with a stronger Indian Ocean influence in the Umbria-Marche region, while analyzes from the west (Moransengo) might reflect a strengthening Atlantic effect. The $^{87}$Sr/$^{86}$Sr is still lower than that of the Miocene open ocean, probably due to erosion and influence of Sr derived from Mesozoic carbonates. The dataset also shows short-term deviations in the $\varepsilon_{Nd}$ values of the fossils coinciding with major sea-level decreases.

During the Late Serravallian-Tortonian normal open ocean Sr values were recorded, while the $\varepsilon_{Nd}$ values vary considerably. A low $\varepsilon_{Nd}$ value at 12-11 Ma could indicate inflow of water from the Atlantic Ocean, which stopped at 10 Ma due to major regression and allowed for the development of a locally controlled water mass with $\varepsilon_{Nd}$ of $-8.5$. Thereafter, the $\varepsilon_{Nd}$ again approaches compositions typical for the Atlantic Ocean.