STABILITY FIELD OF FERRIC-FERROUS GARNET SKIAGITE (Fe₃Fe₂Si₃O₁₂)

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Introduction. The composition of deep seated garnets generally can be expressed by using four main end-members: pyrope, almandine, grossular, and knorringite. There is recent evidence, however, that some mantle derived garnets contain up to 12% ferric iron (Luth et al., 1990). The incorporation of Fe³⁺ in Al- and Cr-bearing garnets has important petrologic implications. The stability of garnet peridotites and eclogites should be depended not only on P-T conditions, but on oxygen fugacity as well. Garnet could be an important Fe³⁺-bearing phase in the upper mantle area of spinel unstability. Moreover, the presence of Fe³⁺ in garnet seems to affect the geothermobarometric estimates, based upon Mg-Fe exchange equilibria.

Mössbauer spectroscopy of garnets indicates that Fe^{3+} usually resides on the octahedral sites (Amthauer et al., 1976; Woodland, O'Neill,1993). Therefore the $Fe_3Fe_2Si_3O_{12}$ (skiagite) can be assumed in natural multicomponent garnets along with other garnet endmembers. This component is exceptionally interesting because it contains both Fe^{2+} and Fe^{3+} cations and so it would be expected to be indicator of the fO₂ environment. According to available data pure $Fe_3Fe_2Si_3O_{12}$ has been synthesized only at pressure no less than 93-100 kbar. Run products, apart from garnet, included a quantity of other phases, such as spinel and SiO_2 (Karpinskaya et al., 1982; Woodland, O'Neill, 1993). Schreyer and Baller(1980) synthesized manganese-iron garnets contained 9-18% of the skiagite molecule at 30-35 kbar. They estimated lower pressure limit for pure $Fe_3Fe_2Si_3O_{12}$ at 60 kbar by using Novak and Gibbs(1971) diagram for the cation radii of the garnets. Considering that many of the known garnet end-members agree satisfactorily with this diagram the main purpose of this work was to verify the discrepancy arisen between the theoretically predicted and experimental results.

Experimental methods. Experiments were concluded in a multianvil split sphere apparatus in pressure range 50-65 kbar. The pressure cell was ZrO_2 -doped CaO cube heated by a graphite resistance heater. Temperature was monitored by $PtRh_{30}$ - $PtRh_6$ thermocouples located in the immediate vicinity of sample. The pressure at room temperature was calibrated in each run using the transition Bi or PbSe and PbTe. Pressure calibration at high temperature was performed using olivine - γ -spinel (Yagi et al., 1987) transition. The pressure uncertainty is estimated to be \pm 2 kbar over a range investigated. The starting material was prepared as a mixture of metallic Fe, Fe₂O₃, and SiO₂ high pure reagents taken in the appropriate proportion to provide the skiagite composition. These components were mixed and ground under acetone in tungsten carbide mortar. After drying at 70°C in vacuum the starting material was sealed in Au capsule by electrical weld. The duration of the experiments was 24 to 50 hours. The run products were analyzed by interferometric and polarizing microscopes, X-ray diffraction, and electron microprobe. The powder diffractograms were obtained from X-ray diffractometer scans over the range 16-80° 20 using Ni-filtered CuK α radiation and Si (a=5.43088A°) as an internal standard. Unit cell parameters were calculated by the least square technique applied to values of 20 angles measured. The elements were measured in energy-dispersive mode, using CAMECA microprobe (CAMEBAX Microbeam) at the Geological Institute of Mainz University, Germany. Calculation of garnet and spinel composition assumed the ideal stoichiometry of 8 and 24 cations per formula unit, respectively.

Results and discussion. The conditions and results of experiments are shown in fig.1. Most of the runs were conducted in direction of synthesis. Two runs were performed with skiagite seeds (5-10%) added to the starting material. These runs did not give the disagreement with other experiments. The spinelss, coesite and ferrosilite were present in all run products whereas the garnet appeared at pressure 60 kbar and higher. The optical features of skiagite are the same as described by Woodland and O'Neill (1993). namely, the dark redbrown euhedral grains. The guantity of skiagite varies in run products from several percents to more than 90% in run at 65 kbar and 950°C. It was from this run product that microprobe analysis and unit cell parameter of garnet were obtained. The unit cell pa-



Fig. 1. The probable area (shaded) of the lower pressure boundary of skiagite. Filled points -skiagite is present; Open - skiagite is absent; squares - runs with seeded skiagite.

rameter of skiagite $a_0=11.7286(3)A^{\circ}$ determined from the measurement of 15 peak positions is close to that $(a_0=11.7278(6)A^{\circ})$ reported by Woodland and O'Neill (1993). The results of microprobe analysis converted from total FeO value to FeO and Fe₂O₃ are presented in table 1. The garnet is very homogenous and corresponds to the skiagite composition. The spinel shows some varies in γ -fayalite component content. The phase relations at high pressure in the system Fe-Si-O are out of the questions of this short paper and seem to invite further investigations, although it can be done some preliminary conclusions. Spinel phase can form the wide hematite - γ -fayalite solid solution at studied P-T conditions. The Fe²⁺/Fe³⁺ ratio of spinel₃₅ (i.e., content of γ -fayalite component) controlling by medium conditions may have influence on possibility of Fe₃Fe₂Si₃O₁₂ garnet formation. According to performed experiments the most probably area of the lower pressure

Table 1. Microprobe analyses of garnet and spinel from run at 65kbar, 950°C (total FeO are converted to FeO and Fe2O3)

		garnet				spinel		
SiO2	32.47	32.36	32.32	16.69	16.94	16.35	16.47	15.35
Fe2O3	28.66	28:89	28.81	29.12	28.77	29.58	30.43	32.29
FeO	38.33	38.70	38.65	53.02	53.47	52.42	53.10	51.25
total	99.96	99.95	99.78	98.83	99.18	98.35	100.00	98.89
Si	3.003	2.994	2.995	4.829	4.880	4.759	4.719	4.465
Fe ³⁺	1.994	2.011	2.009	6.341	6.237	6.480	6.560	7.068
Fe ²⁺	3.003	2.995	2.996	12.830	12.883	12.762	12.722	12.468
	8.000	8.000	8.000	24.000	24.001	24.001	24.001	24.001
γ-Fa	-		-	60.4	61.0	59.5	59.0	55.8

boundary of skiagite is shown on the fig.1. This garnet can exist at pressure about 60 kbar as it was predicted by Schreyer and Baller (1980). This experimental result disagreed with other known ones suggests that the stability of $Fe_3Fe_2Si_3O_{12}$ garnet is determined not only by P and T but substantially by oxygen fugacity as well. The possibility of fO_2 variations in different cell assemblages must not be ruled out and buffering technique should be used in further investigations of ferric-ferrous contained phases.

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