論文内容の要旨

論文題目：Mineralogical and experimental study of shergottite martian meteorites:
Implication for crystallization under low oxygen fugacity condition

(シャーゴッタイト火星隕石の鉱物学的・実験的研究：低酸素分圧下での鉱物結晶化過程)

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Martian meteorites are only samples that we can handle directly, and can give us the information about the martian interior. Recently, geochemical study on martian meteorites reported that shergottite, which is the largest group of martian meteorites having wide mineralogical variations, could be classified into two groups ("reduced" shergottite group and "oxidized" shergottite group). The source melt of these groups seems to be formed from the magma ocean at 4.5 Ga and has never been mixed with each other. Reduced shergottites have no evidence for assimilation with the martian crustal material although oxidized shergottites have it. Therefore, reduced shergottite group could retain the information about the early-stage of the martian formation and evolution. In order to verify this issue, I investigated the crystallization histories, relationships, and the possibility of environmental change of reduced shergottites.

In this study, three martian meteorites of five reduced shergottites were studied. Y 980459 (Y98) is an olivine-phyric shergottite that consists of olivine megacryst with the groundmass composed of olivine, pyroxene and glassy mesostasis, and no plagioclase. The core compositions of olivine (Fo_{86}) and pyroxene ($En_{81}Fs_{17}Wo_2$) are the most mafic compositions among martian meteorites found so far. The equilibrium calculation and crystallization experiment with the bulk composition of Y98 indicated that Y98 crystallized from the source melt having the bulk composition of Y98 in a closed system. This mafic reduced shergottite crystallized at cooling rate of 1 ^{o}C/hr according to the Mg-Fe diffusion calculation considering fractional crystallization on olivine megacryst of Y98.

Dar al Gani 476 (DaG) is also an olivine-phyric shergottite that consists of olivine megacryst with the groundmass composed of pyroxene and maskelynite. Although the core compositions of olivine (Fo_{76}) and pyroxene ($En_{78}Fs_{19}Wo_{3}$) are more Fe-rich than those of Y98, the bulk composition and REE pattern of DaG are nearly identical to those of Y98. These facts and other mineralogical features indicate that both meteorites could be derived from the same melt. In order to investigate the DaG crystallization history from the Y98 melt, MELTS calculation was performed with the bulk composition of Y98. According to the calculation result, both olivine and pyroxene having the same compositions as those of core composition of DaG were equilibrium with the melt at 1250 °C. This result indicated that DaG crystallized at slow cooling rate, which could equilibrate olivine and pyroxene by elemental diffusion. Mg-Fe diffusion calculation on DaG olivine megacryst gave ~ 0.035 °C/hr cooling rate for the DaG crystallization.

QUE 94201 (QUE) is a basaltic shergottite that consists of coarse-grained pyroxene and maskelynite. QUE is one of the most Fe-rich martian meteorites, but the REE pattern is similar to that of Y98. The MELTS calculation was performed to verify the relation between these meteorites, and the result suggested that the similar composition to the bulk composition of QUE could be produced as the residual melt from Y98 melt at 1160 °C. The temperature of 1160 °C was the estimated liquidus temperature of the QUE bulk composition from crystallization experiments. Crystallization experiments also revealed that the major mineral phases such as pyroxene and plagioclase crystallized from the source melt whose composition was similar to the bulk composition of QUE. It is difficult to calculate the cooling rate by diffusion calculation because QUE has no olivine unlike Y98 and DaG. The results from the cooling experiments at various cooling rates gave the upper limit of cooling rate (0.5 °C/hr) for the QUE crystallization.

The results about three reduced shergottites reveal that these reduced shergottites were derived from the same melt having the bulk composition of Y98, and that the differences of cooling rates could produce the mineralogical differences among these meteorites. Because Y98 is the most mafic martian meteorite, its bulk composition might be the same as or similar to that of source melt of reduced shergottite group.

Oxygen fugacity is one of the important factors to control the martian interior conditions. If reduced shergottites have never suffered the secondary events that could change the redox condition, they have the possibility to retain the information about the early martian evolution. In order to verify the influence of the oxygen fugacity on mineral crystallization, isothermal experiments with the QUE bulk composition under various oxygen fugacities were performed. The results from these experiments showed that the liquidus phase changed from oxidized condition (olivine) to reduced condition (pyroxene) from the same melt. One of the plausible reasons for this change is the valence change of iron. Synchrotron XANES analysis was performed on the glass that was formed under various oxygen fugacities to verify this hypothesis, and the shift of pre-edge peaks to higher energy with increasing $Fe^{3+}/\Sigma Fe$ ratio was observed.

Although the oxygen fugacity has large influence on the meteorite formation, the estimated oxygen fugacities have large gaps (1-2.5 log units) between two methods. One method is using the composition of Fe-Ti oxides and the other is using the Eu partitioning into augite. One of the appropriate reasons for these gaps is that the oxygen fugacity changed during crystallization between the early-stage (pyroxene crystallization) and late-stage (Fe-Ti oxide crystallization). There should be large-scale assimilation of crustal materials or hydrous rocks if such change of oxygen fugacity occurred. I verified whether such environmental change really occurred or not by analyzing pyrrhotite. Determining crystal structure of pyrrhotite is useful because it has several superstructures depending upon oxygen fugacity and other environmental functions (*e.g.*, temperature, pressure, hydrous alternation). However, there had been few studies on pyrrhotites in martian meteorites mainly because of their small abundances and sizes. Electron microprobe and EBSD analyses were performed to determine structures of pyrrhotites in reduced shergottites. According to these analyses, all pyrrhotites in reduced shergottites are 1C type, which is stable at high temperature under low pressure, suggesting that these meteorites seem to have experienced no environmental change such as hydrous alternation during and after the meteorite formation.

This study revealed that reduced shergottites could be derived from the melt of Y98, and Y98 seems to retain the information of primitive reservoir of reduced shergottites that were formed from the martian magma ocean. Therefore, I compared the bulk composition of Y98 with the partial melt composition of the martian mantle. Partial melt compositions of the martian mantle were obtained from the partial melting experiment with the estimated martian mantle composition (DW) by Bertka and Holloway (1994). The partial melt composition that was formed at 1500 °C is similar to the bulk composition of Y98. This similarity indicated that the source melt of reduced shergottites could be formed in the magma ocean that was produced by partial melting of the martian mantle, and thus shows direct relationship with the martian mantle. Therefore, the melt of Y98 seems to be the first sample that has direct relationship with the martian mantle, and the model of the evolution from martian mantle to differentiated rocks was first established by this study.