

Redox States of Shergottite Martian meteorites as Inferred from Iron Micro-XANES Analysis of Maskelynite and Plagioclase

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1 Introduction

Shergottite is the largest group of Martian meteorites that crystallized at 160-550 Ma near the Martian surface as shallow intrusions or thick lava flows [e.g., 1]. Recent petrological and isotopic studies have revealed that shergottites show obvious correlations between oxidation state and geochemical characteristics, and such correlation must have important information about their mantle sources and are directly relevant to Martian evolution [e.g., 2]. The difference in such geochemical characteristics can divide them into three subgroups: depleted, enriched and intermediate shergottites [e.g., 3]. Enriched shergottites show high La/Yb, low Sm/Nd, and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Enriched shergottites crystallized under the oxidized environment at the oxygen fugacity ($f\text{O}_2$) of $\log f\text{O}_2 = \text{QFM}-1.0$ by Fe-Ti oxide oxybarometer [e.g., 2].

From such studies, there are two models regarding the two geochemical source reservoirs for the shergottites. One model proposes assimilation of oxidized crust by mantle-derived, reduced magmas [2, 4]. In this model, the assimilated enriched reservoir occurs as domains in the crust, which must be traversed by ascending mantle magmas. Herd et al. [2] proposed that the assimilated material may be the product of early and extensive hydrothermal alteration of the Martian crust, or it may be amphibole- or phlogopite-bearing basaltic rock within the crust. The other model proposes mixing of two distinct mantle reservoirs during melting as stated above [3, 5-6]. In this model both geochemical reservoirs reside in the mantle and were formed as a result of either crystallization of a magma ocean to produce geochemically-depleted and enriched domains [5], or fluid-induced metasomatism that produced mantle heterogeneity [6].

However, redox states of many shergottites have not been estimated. Typically, iron titanium oxide oxybarometer and/or orthopyroxene-olivine-spinel oxybarometer are used to estimate redox states of shergottites. However, sometimes these minerals are not in equilibrium because most shergottites are rapidly cooled lava, and therefore, this method cannot be used to estimate redox states of all shergottites.

Therefore, we focused on iron valence of plagioclase and maskelynite (shocked plagioclase glass) which can be a good indicator of redox condition, because all shergottites contain plagioclase and/or maskelynite. In this study, we estimated $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of plagioclase and maskelynite in 14 shergottites by using the synchrotron micro-XANES (X-ray Absorption Near Edge

Structure) analysis to discuss the redox states and the origin of shergottites.

2 Samples

We analyzed thin sections of two geochemically-depleted (Dar al Gani 476 and Dhofar 019), four geochemically-intermediate (EETA 79001 lithology A., ALH 77005, LEW 88516 and NWA5029) and eight geochemically-enriched (NWA 856, Dhofar 378, Zagami, Shergotty, RBT 04262, NWA 4468, NWA 1068 and LAR 06319) shergottites.

3 Experiment

$\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of minerals can be estimated from the energy shift of a pre-edge peak in XANES spectra obtained using the synchrotron X-ray fluorescence because the pre-edge peak is independent of influence of self-absorption effects [7]. Pre-edge peak is always observed on the low-energy side of K-absorption edges (main-edge) of first-row transition elements. The region below the absorption edge typically contains a pre-edge peak due to electronic transition from $1s$ to $3d$. This pre-edge position shifts to higher energy with increasing the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of the minerals. Bajt et al. [7] observed a linear relationship between pre-edge peak position and the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in silicate and oxide minerals by using the shift of pre-edge position.

We performed XANES experiment at the BL-4A, PF. The transmitted and fluorescent X-rays were measured by an ionization chamber and a Si (Li) detector, respectively. The angle between the incident beam and the detector was fixed at 90° . Kirkpatrick-Baez geometry mirrors were used to focus the beam to about a $5 \times 5 \mu\text{m}$ square on the specimen. Spectra were recorded from 7087 to 7183 eV using a 0.11 eV step for the pre-edge and main-edge regions. The energy was calibrated by defining the first derivative peak of Fe foil to be 7111 eV and standard kaersutites ($\text{NaCa}_2(\text{Mg}, \text{Fe}^{2+})_4\text{TiSi}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$) were measured at regular intervals to determine the energy reproducibility [8].

4 Results and Discussion

From all samples, sharp pre edge spectra of Fe XANES analysis were obtained. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of maskelynite and plagioclase in depleted, intermediate, and enriched shergottites are about 0.24-0.49 (0.42-0.49 in Dar al Gani 476 and 0.24-0.28 in Dhofar 019), 0.13-0.66 (0.13-0.29 in ALH77005, 0.47-0.60 in EETA 79001 lithology A., 0.65-0.66 in LEW 88516 and 0.32-0.41 in NWA 5029,) and 0.41- 0.74 (0.55-0.69 Dhofar 378, 0.54-

0.56 in LAR 06319, 0.44-0.59 in NWA 856, 0.58-0.62 in NWA 1068, 0.65-0.71 in NWA 4468, 0.52-0.58 in Zagami, 0.74-0.75 in RBT 04262, and 0.41-54 in Shergotty), respectively. (Table1). Thus, the $Fe^{3+}/\Sigma Fe$ ratio of all shergottites that we analyzed shows a wide range from about 0.13 to 0.75.

DaG 476 crystallized under depleted environment ($\log fO_2=QFM-2.5$), EETA 79001 lithology A crystallized under intermediate redox state ($\log fO_2=QFM-1.7$) and two enriched shergottites (Zagami and Shergotty) crystallized under similar oxidized environment ($\log fO_2=QFM-1.0$) [2]. The $Fe^{3+}/\Sigma Fe$ ratios of enriched shergottites are clearly higher than those of the depleted shergottites. Therefore, we conclude that all eight enriched shergottites (Dhofar 378, LAR 06319, NWA 856, NWA 1068, NWA 4468, Zagami, RBT 04262 and Shergotty) may have crystallized under oxidized environment with similar fO_2 ($fO_2=QFM-1.0$) although Fe-Ti oxide oxybarometer has not been performed on Dhofar 378, NWA 856, NWA 4468 and RBT 04262 some samples.

The ϵNd of enriched shergottites shows negative value, on the other hand, the ϵNd of depleted shergottites shows positive value [e.g., 3]. It showed that the $Fe^{3+}/\Sigma Fe$ ratio of shergottites is consistent with geochemical characteristic ϵNd . Furthermore, the similar young crystallization ages of enriched shergottites ~ 190 Ma [1] suggest that all of enriched shergottites may have been formed by related magmatic events because these shergottites are similar in many ways.

In the case of depleted shergottites, Dhofar 019 which has not been performed by Fe-Ti oxide oxybarometer has the $Fe^{3+}/\Sigma Fe$ ratios lower than the Dag 476. Thus, we also conclude that Dhofar 019 depleted shergottite may have crystallized under oxidized environment with even lower fO_2 than Dag476 ($fO_2=QFM-2.5$). Because these two depleted shergottites have the similar values of ϵNd [e.g., 3] (crystallization ages are slightly different), these two meteorites (Dhofar 019 and Dag 476) have the same origin.

The $Fe^{3+}/\Sigma Fe$ ratios of intermediate shergottites have very wide range (0.13-0.66) covering both depleted and enriched shergottites (Table1). The ϵNd value of intermediate shergottites is intermediate between those of depleted and enriched shergottites [3]. In contrast, the crystallization age of intermediate shergottites is similar to those of enriched shergottites [1]. It is indicated that intermediate and enriched shergottites crystallized at almost the same age, but they were of different origin. If enriched shergottites were produced from the mantle-derived reduced magmas that were affected by early and extensive hydrothermal alteration of the Martian crust [2], intermediate shergottites sources were also affected, because intermediate and enriched shergottites have similar crystallization ages [1]. It can be explained that the model proposes mixing of two distinct mantle reservoirs during melting as stated above [3, 5-6]. Based on these considerations, we conclude that the wide ranges of $Fe^{3+}/\Sigma Fe$ ratios obtained from intermediate shergottites

show the evidence for mixing of two distinct mantle reservoirs during melting.

Recently, LAR06139 was reported to show the redox change during crystallization [9]. Because plagioclase crystallizes in a wide temperature range, Fe-XANES analysis of shergottite maskelynite with core-rim zoning allows tracking the possible redox change during plagioclase crystallization, which we plan to work on to further compare different shergottite samples.

Table 1 The $Fe^{3+}/\Sigma Fe$ ratios of all analyzed shergottites.

Sample	Group	The $Fe^{3+}/\Sigma Fe$ ratio (%)
DAG476	Depleted	42-49
Dhofar019	Depleted	24-28
ALH77005	Intermediate	13-29
EETA79001 lithology A.	Intermediate	47-60
LEW88516	Intermediate	65-66
NWA5029	Intermediate	32-41
Dhofar378	Enriched	55-69
LAR06319	Enriched	54-56
NWA856	Enriched	44-59
NWA1068	Enriched	58-62
NWA4468	Enriched	65-71
Zagami	Enriched	52-58
RBT04262	Enriched	74-75
Shergotty	Enriched	41-54

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