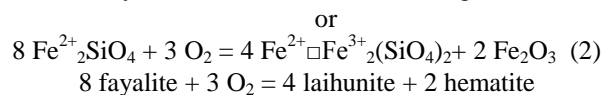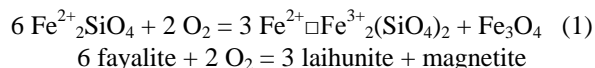**FAYALITE OXIDATION PROCESSES: EXPERIMENTAL EVIDENCE FOR THE STABILITY OF PURE FERRIC FAYALITE?**
A.M. Martin[1], K. Righter[1], L.P. Keller[1], E. Médard[2], B. Devouard[2] and Z. Rahman[1], [1]Johnson Space Center (2101 NASA Parkway, Mailcode KT, Houston TX 77058 USA; email: audrey.m.martin@nasa.gov / aud.martin23@gmail.com), [2]Laboratoire Magmas et Volcans (5 rue Kessler, 63000 Clermont-Ferrand, France).

Introduction: Olivine is one of the most important minerals in Earth and planetary sciences. Fayalite $Fe_2^{2+}SiO_4$, the ferrous end-member of olivine, is present in some terrestrial rocks and primitive meteorites (CV3 chondrites [1,2]). A ferric fayalite (or ferrifayalite), $Fe^{2+}\square Fe_2^{3+}(SiO_4)_2$ laihunite, has been reported in Earth samples (magnetite ore, metamorphic and volcanic rocks… [3,4]) and in Martian meteorites (nakhlites [5]). Laihunite was also synthesized at 1 atmosphere between 400 and 700°C [6]. This mineral is believed to form by oxidation reactions such as:

$$6\ Fe^{2+}_2SiO_4 + 2\ O_2 = 3\ Fe^{2+}\square Fe^{3+}_2(SiO_4)_2 + Fe_3O_4 \quad (1)$$
$$6\ \text{fayalite} + 2\ O_2 = 3\ \text{laihunite} + \text{magnetite}$$
$$\text{or}$$
$$8\ Fe^{2+}_2SiO_4 + 3\ O_2 = 4\ Fe^{2+}\square Fe^{3+}_2(SiO_4)_2 + 2\ Fe_2O_3 \quad (2)$$
$$8\ \text{fayalite} + 3\ O_2 = 4\ \text{laihunite} + 2\ \text{hematite}$$

It is characterized by superstructures along the c axis which accomodate the XFe^{3+} ($=Fe^{3+}/(Fe^{3+}+Fe^{2+})$) ~0.66 in the mineral structure [6,7]. Until now, fayalite was believed to have no pure Fe^{3+} end-member. Here, we show evidence for the stability of a pure ferrifayalite end-member and for potential minerals with XFe^{3+} between 2/3 and 1.

Experimental and analytical methods: A synthetic fayalite sample was mixed with other components in order to get a basalt+anhydrite+calcite (BCA) composition (see [8] for details on this study). The sample was analyzed after low temperature non-equilibrated experiments in order to get information about the destabilization processes of fayalite.

Experimental. The starting BCA mixture was introduced in Au capsules which were welded at the two extremities in order to limit exchange with the surrounding assembly. A piston-cylinder was used to impose a pressure of 1 GPa and temperatures of 700°C, 800°C and 900°C for 1 h. Oxidation conditions during the experiments are estimated to be at or above FMQ.

Analytical. Samples were mounted in epoxy resin, ground and polished. Phase relations were determined by scanning electron microscopy and phases were analyzed using an electron microprobe (EPMA, 1μm beam). Some fayalite grains were then selected for transmission electron microscope (TEM) analyses on sections prepared using focused ion beam (FIB) techniques.

Results: After the experimental runs, fayalite grains are still present but are clearly oxidized. Spinel structure iron oxides (magnetite or maghemite) have also formed.

Micro-analyses. The oxidized fayalite contains micrometer-sized regions that have a Fe/Si ratio below that of fayalite and contain less than 0.05wt% MgO and less than 0.1wt% MnO. Microprobe analyses of these regions fall into two compositional groups. Group 1 has a mean Fe/Si ratio around 1.6, corresponding to laihunite, while Group 2 has a mean Fe/Si ratio around 1.3. This latter composition, which does not correspond to any known mineral, is on the oxidation trend defined by fayalite and laihunite (Fig. 1).
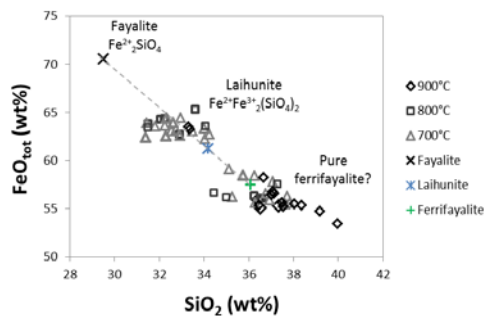

Figure 1 *Composition of laihunite and potential pure ferrifayalite observed in the samples compared with theoretical compositions.*

Nano-analyses. TEM imaging and analyses of the oxidized fayalite regions show that they are heterogeneous: "pure ferrifayalite" regions (group 2 compositions) are made of a nano-scale assemblage of SiO_2 and fayalite or laihunite (Fig. 2), while laihunite regions (group 1) contain nano-grains of magnetite and SiO_2.
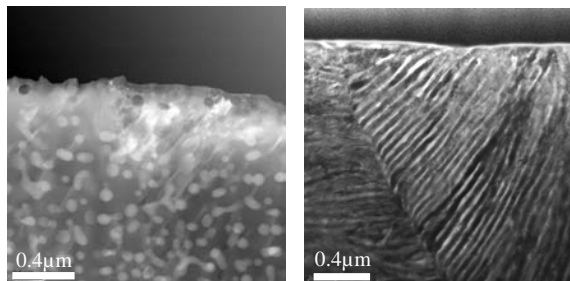

Figure 2 *(a) "inclusions" of amorphous SiO_2 in a crystalline fayalite matrix in the "pure ferrifayalite" zone at 800°C (b) lamellas of SiO_2 (light) and laihunite (dark) in the "pure ferrifayalite" zone at 900°C. A potential grain boundary between two "pure ferrifayalite" grains can be seen on the left.*

Crystal structure. Structural characterization of fayalite and laihunite was made using a Selected Area Electron Diffraction Patterns (SAED) in the TEM (Fig. 3). The structure of the "pure ferrifayalite" could not be determined, as it is systematically exsolved into SiO_2 and fayalite or laihunite (Fig. 2).
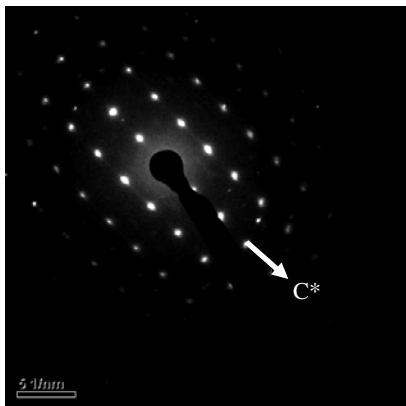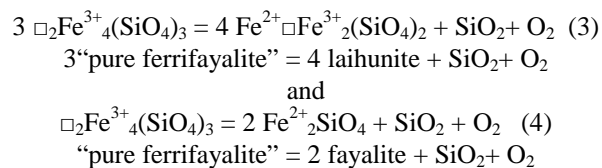

Figure 3 *Diffraction pattern of the dark lamella in the "pure ferrifayalite" zone at 900°C. d-spacing and the strong streaking appearing along c* (arrow) are consistent with laihunite.*

Iron oxidation state. The Fe^{3+} content was determined using Electron Energy Loss Spectroscopy. Our analyses confirm the presence of Fe^{3+} in phase infered to be laihunite and its absence in fayalite.

Discussion: Our experiments resulted in the oxydation of the fayalite starting product. But while EPMA analyses at the micrometer scale suggest oxydation products close to laihunite and pure ferrifayalite composition, TEM nano-analyses revealed more complex assemblages. We suggest that the assemblages formed in a two-stage process:

Oxidation of fayalite. This oxidation was probably produced by reaction with calcite and anhydrite. Laihunite and iron oxide formed by an oxidation reaction such as (1). From EPMA micro-analyses, fayalite oxidation also lead to stoichiometric ferrifayalite. The fact that EPMA analyses plot close to the composition expected for these end-members is strong evidence, since such compositions could not be produced by mixtures of the starting fayalite or/and the produced laihunite with Fe-oxydes, or with silica (Fig. 1). Our experiments therefore suggest a possible solid solution between fayalite and its Fe^{3+} equivalent, with cation ordering on the M-sites creating at least one intermediate member, laihunite. The stability conditions and structure of the pure ferric fayalite remain, however, to be determined.

Exsolution-reduction. We suggest that the nanometric "inclusions" and "lamellar" textures observed in the "pure ferrifayalite" regions result from exsolution processes. Following our observations in the 900 and 800°C samples, the "pure ferrifayalite" regions (group 2) were reduced following, respectively, the reactions:

$$3 \; \square_2 Fe^{3+}_4(SiO_4)_3 = 4 \; Fe^{2+}\square Fe^{3+}_2(SiO_4)_2 + SiO_2 + O_2 \quad (3)$$
$$3\text{"pure ferrifayalite"} = 4 \text{ laihunite} + SiO_2 + O_2$$
$$\text{and}$$
$$\square_2 Fe^{3+}_4(SiO_4)_3 = 2 \; Fe^{2+}_2 SiO_4 + SiO_2 + O_2 \quad (4)$$
$$\text{"pure ferrifayalite"} = 2 \text{ fayalite} + SiO_2 + O_2$$

The laihunite regions (group 1) were destabilized following the reaction:

$$Fe^{2+}\square Fe^{3+}_2(SiO_4)_2 = Fe_3O_4 + 2 \; SiO_2 \quad (5)$$
$$\text{laihunite} = \text{magnetite} + 2 \; SiO_2$$
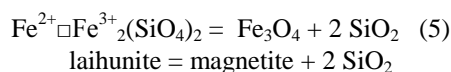
The causes of these breakdown reactions are not known. They could be due to the quenching of temperature at the end of the experiments, or to equilibration processes during the experiments. These destabilisations might explain why highly oxidized fayalite ($XFe^{3+}>2/3$) has never been observed in nature so far.

References: [1] Hua and Buseck (1995) *GCA, 59,* 563-578. [2] Jogo K. et al. (2009) *EPSL, 287,* 320-328. [3] Kitamura M. et al. (1984) *Am. Min., 69,* 154-160. [4] Dyar M. D. et al. (1998) *Am. Min., 83,* 1361-1365. [5] Noguchi T. et al. (2009) *JGR, 114,* E10004. [6] Kondoh S. et al. (1985) *Am. Min., 70,* 737-746. [7] Shen B. et al. (1986) *Am. Min., 71,* 1455-1460. [8] Martin A.M. et al. (2010) *AGU Fall Meeting.*