

INCIPIENT SPACE WEATHERING ON 162173 RYUGU RECORDED BY CRYSTALLOGRAPHIC CHANGES OF PYRRHOTITE.

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Introduction: Hayabusa2 has successfully explored the C-type Near-Earth Object (NEO) 162173 Ryugu and collected regolith samples at two sites [1]. The material returned to Earth contains up to mm-sized regolith particles and confirms Ryugu's hydrated nature and petrological similarity to CI chondritic meteorites [2]. It is the first ever opportunity to study space weathering of a carbonaceous and water-bearing body of the Solar System – an opportunity that has tremendous implications for future remote studies of NEOs for scientific exploration and in-situ space resource utilization (ISRU). The latter mainly concerns carbon and hydrogen that could contribute to human lunar and cis-lunar activities [3]. We have studied pyrrhotite (Fe_{1-x}S), which is abundant in Ryugu's rocks and a potentially good indicator of early space weathering due to its highly variable and composition-sensitive crystallographic superstructure [4].

Sample and Methods: We have examined the surfaces of pyrrhotite-bearing grains of Hayabusa2 fines sample A0104 using a field-emission scanning electron microscope (FESEM; JSM-7001F at Kyoto Univ.) and extracted an electron-transparent section of a large pyrrhotite crystal partially exposed on a grain's surface using a focused ion beam system (FIB; Helios NanoLab G3 CX at Kyoto Univ.). The section (A0104-00700101) was studied using transmission electron microscopy and selected area electron diffraction (TEM-SAED; Tecnai G2 FEG at Univ. of Jena).

Results: Where the crystal is partially embedded in phyllosilicates it shows well-formed faces displaying the forms {001}, {010} and {011}. Where the crystal stands out of the matrix, the surfaces appear irregular and pitted – however, the phyllosilicates (mainly serpentine) show no discernable effects of space weathering. The 8.6 x 4.3 μm section of the euhedral pyrrhotite shows a strong variability of its superstructures. The buried and internal parts of the crystal display superstructures with N values ranging between 4.0 (4C-pyrrhotite, x ≈ 0.125) and 5.3 with values near or slightly below 5.0 ('5C-pyrrhotite', x ≈ 0.100) being frequent in the interior of the crystal. Within 500 nm from the exposed surface higher N values can be observed, which range between 5.3 to 5.9 (close to '6C-pyrrhotite', x ≈ 0.083), indicating elevated Fe/S ratios. Some diffraction patterns obtained near the surface do not show clear superstructure reflections of pyrrhotite, suggesting that these regions may be troilite (stoichiometric FeS). The variability of superstructures indicates chemical heterogeneity and disequilibrium of the Fe/S ratio near the exposed surface with respect to the bulk crystal. Within the bulk of the crystal the association of 4C-pyrrhotite and NC-pyrrhotite with N near or slightly below 5.0 is similar to terrestrial intermediate pyrrhotites [4]. 4C-pyrrhotite appears to be typical of CI chondrites [5] and has also been detected in other Hayabusa2 samples (allocated to Univ. of Jena).

Discussion: The surface pitting of the pyrrhotite crystal appears to be an effect of space weathering due to the loss of sulfur. The systematic variations of the Fe/S ratio indicated by the changing N value of the pyrrhotite superstructures support this hypothesis. The N value and the corresponding Fe/S ratios are largest where the crystal stands out the most from the phyllosilicate matrix. No evidence for metallic iron on the exposed surface was detected despite intensive search. Our explanation is that – unlike troilite, where metallic iron forms through sulfur loss [6] – the initially Fe-deficient pyrrhotite will increase its Fe/S ratio due to the inward diffusion of excess Fe from the sulfur-depleted surface before the nucleation of metallic Fe commences. As the bulk of the crystal appears to be intermediate between 4C- and 5C-pyrrhotite (Fe/S ≈ 0.875 to 0.9) the superficial formation of 6C-pyrrhotite (Fe/S ≈ 0.92) or troilite (Fe/S ≈ 1) requires only a small amount of Fe to be moved over short distances of less than 500 nm. Even at Ryugu's surface temperatures this seems viable based on Fe self-diffusion in magnetically ordered Fe_{1-x}S [7].

Conclusion: Pyrrhotite appears to be highly and more sensitive to space weathering than phyllosilicates and may serve as a benchmark for assessing the time required for spectral cloaking of hydrous minerals by space exposure.

References: [1] Watanabe S. et al. (2019) *Science* 364, 268-272. [2] Yada T. et al. (2021) *Nat. Astron.*, 1-7. [3] Jedicke et al. (2018) *Planet. Space Sci.* 159, 28-42 [4] Harries et al. (2011) *Am. Mineral.* 96, 716-731. [5] Berger et al. (2016) *MAPS* 51, 1813-1829 [6] Matsumoto T. et al. (2020) *Nat. Commun.* 11, 1-8. [7] Herbert et al. (2015) *Phys. Chem. Chem. Phys.* 17, 11036-11041.