

THE OXIDATION STATE OF ALTERED RIMS ON ILMENITE FROM LUNAR SOILS. Lindsay P. Keller¹, Roy Christoffersen², and David S. McKay². ¹MVA, Inc., 5500 Oakbrook Parkway, Suite 200, Norcross, GA 30093. ²Code SN, NASA Johnson Space Center, Houston, TX 77058.

Ilmenite grains in lunar soils are commonly surrounded by complex rim sequences that result from their exposure to the lunar "weathering" environment [1,2]. These rims consist of an outer, thin amorphous rind of vapor-deposited silicate material, and a relatively thick, inner layer that is depleted in Fe relative to stoichiometric ilmenite. TEM studies have shown that the inner rim is not amorphous [1,2], but consists of a microcrystalline assemblage of ilmenite containing platy precipitates of rutile and probable Fe metal grains (the R and M grains of [1]). In this study, electron energy-loss spectroscopy (EELS) was used to demonstrate that the altered rims on soil ilmenites contain significant trivalent titanium. Our data indicate that the disordered rims are chemically "reduced" and that oxygen has been lost from the rims. These results have implications regarding the processes responsible for the formation of disordered rims on ilmenite as well as their potential effects on the optical properties of lunar soils.

Aliquots of a <20 μm sieve fractions of 10084 and individual ilmenite grains from the same soil were embedded in low viscosity epoxy, and TEM specimens were prepared by ultramicrotomy. The thin sections were analyzed using a JEOL 2010 (200kV) transmission electron microscope equipped with a LaB₆ filament, a thin-window energy-dispersive x-ray detector, and a GATAN 666 parallel EEL spectrometer. EELS spectra were collected in TEM image-mode at 15KX magnification with a collection semi-angle of ~ 100 milliradians at a dispersion of 0.1 eV/channel. The FWHM of the raw (unprocessed) zero-loss peak was ~ 0.7 eV. The relative energy of features in the spectra for the Ti L_{2,3} edges were calibrated relative to the C π^* peak maximum, which was set to 286 eV [3]. For the Ti L_{2,3} spectra, the characteristic edge structure results from the promotion of inner shell (2p) electrons to valence and conduction bands (3d states). The EELS data provide information on the local solid state environment, including oxidation states. Differences in oxidation state are manifested by "chemical" shifts in energy of the edge onset and by changes in the near-edge structure.

EELS spectra of the Ti L_{2,3} edge have been obtained from over 10 (<20 μm in dia.) individual ilmenite grains from the Apollo 11 soil 10084, and all spectra show significant differences between the altered rims and the core ilmenite (a typical example is shown in Fig.1). For comparison, EELS data from synthetic Ti-oxides with well-constrained Ti³⁺/Ti⁴⁺ ratios are also included in Figure 1. The spectra from the altered rims exhibit a chemical shift of ~ 0.5 eV towards lower energy relative to the position of the Ti L_{2,3} edge in the core of the ilmenite grains. In addition, the splitting of the L₃ and L₂ peaks is reduced in spectra from the disordered rims as compared to the core ilmenite. Both the chemical shift and the change in the near-edge structure are consistent with a Ti³⁺/Ti⁴⁺ ratio of ~ 0.25 in the disordered rims.

The EELS data given here and the EDX measurements reported earlier [1], show that the development of rims was at least partly a chemical process in which the outer margin of the original ilmenite underwent a decrease in Fe/Ti ratio and moved to a more reduced cation-to-oxygen stoichiometry. The analytical and microstructural evidence is consistent with both chemical changes having penetrated to approximately the same depth as the microstructural widths of the rims, which vary from 40-100 nm. Although our working model holds that the inner layer of the ilmenite rims developed because of solar ion bombardment, the penetration depth of these chemical changes is a challenge to explain. Because the thermal history of

the grains limits the depth of chemical transport that can be attained by classical diffusion, possible deep-acting chemical effects of solar ion bombardment need to be considered. Several such deep chemical effects have been postulated for ion-irradiated ceramics and metals [4], almost all of which accomplish deep-level chemical changes using various radiation-enhanced chemical transport mechanisms to promote mixing between the target interior and a preferentially-sputtered surface layer

We are also investigating the effects of mixed Ti oxidation states on the optical properties of lunar soils. Intervalence charge transfer between Ti^{3+} and Ti^{4+} results in strong absorption of the visible wavelengths [5] and reflectance spectra from reduced Ti-oxides (e.g. Ti_4O_7) have low albedos (~5% reflectance at 550 nm) [6]. The presence of mixed Ti oxidation states is potentially a significant darkening agent in mare soils.

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References. [1] Christoffersen, R. *et al.*, (1994) LPSC XXV, 259. [2] Bernatowicz, T. J. *et al.*, LPSC XXV, 105. [3] Egerton, R. F. and Whelan, M. J. (1974) *J. Electron. Spectr. Rel. Phenom.*, 3, 232. [4] Betz, B. and Wehner, G. K. (1983) *Sputtering by Particle Bombardment II*, Chapter 2 pp. 11-84, Springer-Verlag. [5] Burns, R. G. (1993) *Mineralogical Applications of Crystal Field Theory*, Cambridge Univ. Press, 551pp. [6] Bradley, J. P. *et al.*, 1994, LPSC XXV, 159.

Figure 1. Electron energy-loss spectra for the Ti L_{2,3} edge for a typical ilmenite core/rim pair, along with data for Ti^{3+} bearing oxides. The spectra are shifted vertically for clarity.

