

**COMPARISONS OF TIR AND LA-ICP-MS DERIVED BULK CHEMISTRIES FOR NATURAL SURFACES OF IGNEOUS ROCKS.**

M. B. Wyatt<sup>1</sup>, U. N. Horodyskyj<sup>1</sup>, K. A. Kelley<sup>2</sup>, and K. M. Neal<sup>1</sup>,  
<sup>1</sup>Department of Geological Sciences, Brown University, Providence, RI 02912, <sup>2</sup>Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882.

**Introduction:** Recent thermal emission spectroscopy laboratory studies reveal that secondary alteration products on rock surfaces can cause non-linear mixing between spectral end-members and thus affect the modeled abundances of primary minerals [1]. This is significant because small amounts of weathering products on the martian surface may result in modeled primary mineral abundances that differ from the actual composition, leading to a possible misclassification of igneous lithologies.

In this study, we examine the accuracy of bulk chemical oxide abundances derived from thermal infrared laboratory measurements of chemically weathered natural surfaces and fresh cut surfaces of Antarctic Ferrar Dolerite. We analyze the bulk chemistries of natural and cut surfaces using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and compare chemistries to values derived from thermal emission data. The goal of this study is to determine if thermal emission derived chemistries of natural surfaces are accurate and can be used as indicators of chemical alteration processes.

**Antarctic Ferrar Dolerite:** The Ferrar Group consists of lavas (Kirkpatrick Basalt), sills (Ferrar Dolerite), a large mafic intrusion (Dufek Gabbro), and minor pyroclastics. The formation of the Ferrar Dolerite is tied to a mantle upwelling associated with the break-up of Gondwanaland in the early to mid-Jurassic approximately 177 Ma [e.g. 2]. Ferrar sills intruded Devonian-Triassic sedimentary sequences (Beacon Supergroup) and Ordovician granites (Granite Harbour Intrusives).

Most of the exposed Ferrar shows surface weathering that appears as a distinct reddish-brown alteration coating. The natural surface is an iron-stained, silica-rich material (minor amounts of Al, Mg, and S) with poorly crystalline mineral-phases that varies from several to hundreds of microns thick [e.g. 3]. Textural features exhibited on the Ferrar include variable amounts of ventifaction, desert varnish development, and cavernous weathering.

Fresh-cut surfaces of Ferrar dolerite are a gray-green color and typically contain both ortho- and clinopyroxene, plagioclase and alkali feldspars, and Fe and Ti oxides. Dolerite sills show variable compositions and can be more evolved than lavas, having higher SiO<sub>2</sub> (52-58 wt. %) and FeO (9-11 wt. %) and lower MgO (3-6 wt. %) [4].

**Laboratory Thermal Emission Spectroscopy:**

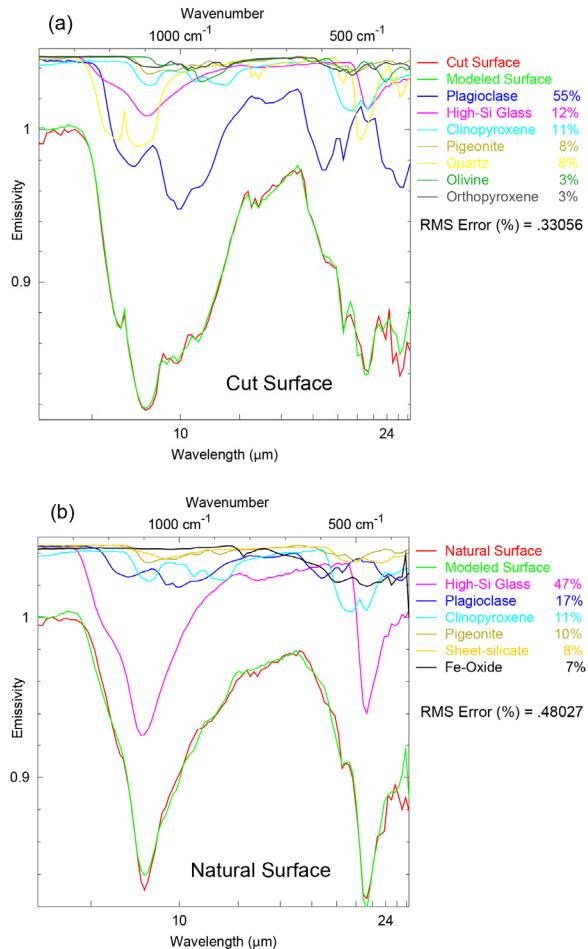
Thermal emission data for this study were collected at Arizona State University over a wavelength range of 2000 - 200 cm<sup>-1</sup> at a spectral sampling of 2 cm<sup>-1</sup>. The Ferrar Dolerite sample was broken so that a fresh surface was analyzed, ensuring an accurate representation of bulk mineralogy. The natural surface was measured without any sample preparation, ensuring an accurate representation of primary and secondary surface mineral-phases. The radiances of large portions of the sample surface were measured to reduce the likelihood of observing nonrepresentative areas in a heterogeneous sample.

*Linear Deconvolution Results.* Spectral deconvolutions of laboratory thermal emission spectra of the (a) cut and (b) natural surfaces of a Ferrar Dolerite from Depot Nunatak are shown in Figure 1. The individual minerals that fit to the spectra have been summed into mineral groups. The mineral abundances shown are best-fit values from the linear least squares deconvolution model; the endmember spectra are shown scaled by these abundances to show how each contributes to the measured spectrum. Derived abundances have accuracies of +/- 5 to 10 %.

The cut-surface of the Ferrar Dolerite is dominated by primary igneous minerals. Plagioclase is the most abundant mineral (55 vol. %) followed by total pyroxene (22 vol. %) and high-silica phases (20 vol. %). The high-silica glass and quartz are interpreted as primary phases found within the groundmass of the rock. Olivine is not commonly identified in Ferrar Dolerite and is modeled below the detectability limit.

The natural-surface of the Ferrar Dolerite is dominated by secondary alteration mineral-phases. High-Si glass is the most abundant phase (47 vol. %) followed by total pyroxene (21 vol. %) and plagioclase (17 vol. %). The high-silica glass is interpreted as a secondary alteration product, consistent with previous studies [e.g. 3]. Sheet-silicate (8 vol. %) and oxide (7 vol. %) minerals are modeled near the detectability limit. Compared with the cut surface, plagioclase abundances in the natural surface decreased by almost 40 vol.% and high-silica glass abundances increased almost 30 vol.%.

*TIR Chemistry.* Bulk chemical compositions can be calculated from deconvolved modal mineralogies (vol. %) by combining the compositions of spectral



**Figure 1:** Spectral deconvolutions of laboratory thermal emission spectra of the (a) cut and (b) natural surfaces of a Ferrar Dolerite from Depot Nunatak

endmembers (wt. % oxides) in proportion to their relative modeled abundances [5-6]. Table 1 shows TIR bulk chemistries for the cut- and natural-surface of the Ferrar Dolerite reflect modeled mineralogies.

The cut-surface is higher in total  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  reflecting higher modeled plagioclase and mafic mineral abundances. The natural-surface is higher in total

**Table 1**

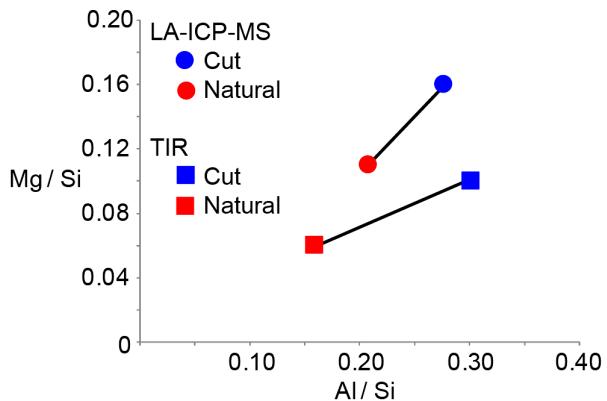
	Cut	Natural	+/-
$\text{SiO}_2$	59.1	64.3	1.4
$\text{Na}_2\text{O}$	2.9	2.1	0.4
$\text{K}_2\text{O}$	0.7	1.8	0.4
$\text{CaO}$	8.8	5.1	0.7
$\text{MgO}$	5.7	3.0	2.6
$\text{FeO}$	6.7	15.4	2.6
$\text{Al}_2\text{O}_3$	15.6	8.9	1.5
$\text{Al/Si}$	0.29	0.16	
$\text{Mg/Si}$	0.12	0.06	

$\text{SiO}_2$  and  $\text{FeO}$ , reflecting higher modeled high-silica glass and Fe-oxide mineral-phase abundances. The increase in  $\text{SiO}_2$  and  $\text{FeO}$  is consistent with reddish-brown alteration coating compositions described in previous studies [e.g. 3].

Below, we compare TIR  $\text{Al/Si}$  and  $\text{Mg/Si}$  derived trends with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) measured values to determine the accuracy of TIR derived chemistries of natural surfaces.

**LA-ICP-MS:** Preliminary LA-ICP-MS analyses were performed at the University of Rhode Island. The lab is equipped with a New Wave UP 213 nm Nd-Yag LA Microprobe and Thermo X-Series II Quadrupole ICP-MS to provide both bulk and in situ trace element data (e.g. Si, K, Th) over the spatial scales (microns to centimeters) needed for this study. LA-ICP-MS analyses with a 10  $\mu\text{m}$  spot size were performed on cut and natural surfaces over a grid size of approximately 1.2 mm to ensure a representative sampling of primary and secondary mineral-phases.

**Results:** Both TIR and LA-ICP-MS show decreasing  $\text{Al/Si}$  and  $\text{Mg/Si}$  from the cut to natural surface (Figure 2). There is a difference in the overall magnitude of the variations, but the trends are the same. These preliminary results provide confidence for interpreting TIR derived chemistries of chemically altered natural surfaces. Further work is ongoing to characterize additional samples and chemical trends in the Ferrar Group.



**Figure 2:** TIR and LA-ICP-MS  $\text{Al/Si}$  and  $\text{Mg/Si}$  trends for Ferrar Dolerite

**References:** [1] Rampe et al. (2007) LPSC XXXVIII, Abstract # 2227. [2] Encarnacion et al. (1996) GSA Abstracts w/ Programs 28, 162. [3] Giorgiotti and Baroni (2007) Eur. J. Mineral. 19, 381-389. [4] Hergt et al. (1989) Contrib. Min. Petr. 102, 298-305. [5] Hamilton and Christensen (2000) JGR, 105, 9717-9733. [6] Wyatt et al. (2001) JGR, 106, 14711.