Introduction: The Martian crust is an important geochemical reservoir. It is the only portion of the planet surveyed by broad-scale remote sensing observations (beginning with the Mariner program through the Mars Reconnaissance Orbiter) or by in situ lander experiments (from the Viking missions through the Mars Exploration Rovers). Mars experienced a unique mechanism for crustal emplacement, resurfacing, and recycling [1] — different from the continuous plate tectonic regime of Earth or the episodic, widespread basalt flooding of Venus.

Further, it is well-established that crusts of the inner planets and rocky satellites become substantially enriched in a suite of geochemically important elements during early differentiation and further evolution [2, 3]. Therefore, all planetary crusts have an enhanced chemical significance disproportional to their small relative volume with respect to the parent planet. The Martian crust is especially significant in this respect since, compared to other inner planets, the Martian crust is volumetrically larger compared to Mars as a whole (>4%) and may be the primary repository for many trace elements, including the geochemically important heat producing elements (K, Th, and U). The Martian crust therefore serves as an important constraint on the chemical composition of the entire planet.

The great number of complete and mature datasets now available from several successful, relatively recent, Mars missions allows us to revisit issues of Martian bulk crustal composition and evolution. Here we review our recent work detailing surface chemical homogeneity; variations in chemistry across different Martian age provinces [4]; variations in global chemistry as compared to global mineralogy and dust abundance [5]; and consider an approach for estimating the chemical composition of the upper Martian crust.

Overview of Relevant Mars Mission Data Sources: Although limited to a narrower suite of elements than surface in situ observations (H, Fe, Si, Cl, K, Th, Al, and Ca), the GRS can reliably analyze most of the planet from orbit (high abundances of surface or sub-surface polar ice limit resolution at higher latitudes) [6]. Penetration depths are mostly dependant on the density of the underlying matrix and the elements measured, but are on the order of tens of centimeters. This deeper penetration depth allows the GRS to be less sensitive to thin coatings of air-fall dust that can partially obscure most other remote sensing methods (e.g., TES, THEMIS, and OMEGA) [7-9]. However, the Odyssey GRS has an inherently low resolving capacity with a spatially large footprint and thus cannot be used effectively for fine-scale regional analysis. Additionally, element abundance maps are subject to considerable smoothing and auto-correlation effects due to element correction factors, the large footprint and necessary data processing [6, 10]. This too, limits GRS analysis to areally-large regional or global studies. For cross-instrument data analysis (e.g., comparing GRS elemental abundances to TES mineralogies or USGS relative apparent surface ages), higher-resolution global datasets (e.g., TES mineralogical maps) must be smoothed to GRS’s lower-resolution.

The Mars Exploration Rovers, Spirit and Opportunity, have each traveled several kilometers across the surface studying diverse geological terrains [11, 12]. The Alpha-Particle X-ray Spectrometer (APXS) is the primary instrument for determining elemental compositions [13, 14]. In conjunction with the Rock Abrasion Tool (RAT) (which can brush away dust coatings or grind away alteration rinds), chemical analyses have been performed on undisturbed rock surfaces,ushed rock surfaces, rock interiors, trenched subsurfaces, as well as disturbed and undisturbed soils. For a given target, the APXS provides reliable analysis for all the major elements and several trace elements (notably: Zn, Cr, Br, and Ni). However, even with MER’s enhanced mobility, landed missions have only explored a miniscule fraction of the planet’s surface in any detail.

Martian Surface Chemical Homogeneity: It has been suggested that the Martian surface has been chemically homogenized over time and that the chemical composition of averaged soil analyses would therefore reflect the bulk chemical composition of the Martian surface [15] — much in the same way terrestrial sedimentary chemistry can be used as a proxy for the bulk terrestrial crust [2]. There are several lines of evidence supporting this. Most importantly, despite wide geographic separation, soils chemistries from landing site analyses (MER, Pathfinder, and Viking) are remarkably similar with most variation attributed to the addition of some local component [13, 14, 16, 17]. While the number of successful landings is few, and there is some landing site selection biases that favor specific scientific goals and mission safety, this chemical similarity strongly implies that the unconsolidated component of the Martian surface has been reasonably well-homogenized (see Figure 1 for comparisons of MER and GRS data for the Spirit and Opportunity landing sites). GRS elemental abundance maps agree
well with surface analyses and, with some notable exceptions [6, 18, 19], global GRS elemental abundance maps reveal less broad-scale chemical variation compared to the terrestrial or lunar surfaces.

There are several reasons why we expect some degree of surface chemical homogeneity. Although not definitively disproven, there is no apparent evidence of present or past plate tectonic processes on Mars [1]. Mars has a basaltic crust and although there is some evidence of subtle chemical variation between different crustal age provinces [4], the planet does not appear to have experienced the complex crustal recycling, fractionation, and evolution seen on the tectonically-active Earth. The Martian surface has been extensively physically homogenized through impact gardening – especially during past periods of heavier bombardment [20]. Also, globally distributed air-fall dust, transported planet-wide by periodic storms, contributes to surface chemical homogeneity [21].

Chemistry of Martian Age Provinces and Implications for Igneous vs. Secondary Processes: The various Martian crustal age provinces are the only geologic records available that preserve evidence of the secular chemical variations produced by the planet’s development and evolution [4]. In Hahn et al., [4], using Martian geologic maps produced by the USGS [22-24], a 1°x1° per pixel grid was produced identifying the Amazonian, Hesperian and Noachian age units. This grid was further smoothed to 5°x5° per pixel for comparison to GRS elemental abundances. Summing the GRS spectra for each primary age province provided a mean chemical composition for each age unit (for H, Fe, Si, Cl, K, and Th; there is insufficient spatial resolution available for Al and Ca). Because chemical diversity across the Martian surface is often muted (as measured by the GRS instrument), differences between calculated means are generally subtle. Z-statistic tests were used to determine if differences in the calculated means across age categories were statistically significant. It was found that average GRS-determined K and Th abundances generally decrease by 9% and 7%, respectively, between the Hesperian and Amazonian. Also, GRS-determined Fe and Cl averages increase by 12% and 19% respectively with younger apparent relative surface age (Figure 2). While H abundance was found to vary with surface age, the relationship is more likely latitude dependant as well as governed by long-term obliquity changes, not processes of crustal growth and evolution. No statistically reliable apparent surface age relation was found for Si (the least varying element measured by GRS) [4].

K and Th are highly incompatible elements that do not significantly fractionate from one another through purely igneous processes. K, Th and the K/Th ratio do vary across the surface of Mars [18, 25]. However,
GRS observations show that these variations are muted when compared to K and Th variations measured on Earth or in lunar samples. The K/Th ratio varies subtly; primarily a response to varying Th and broadly independent of K abundance which has less variance globally. Generally, K and Th are preferentially sequestered into crustal materials during planetary differentiation and mantle melting; resulting in an enriched crust and depleted upper mantle [26]. Consequently, planetary crusts derived from older, primitive mantle sources will have chemical compositions highly enriched in incompatible elements, while younger crustal material will typically be depleted in incompatible elements relative to older crusts, but still enriched with respect to the bulk planet. This expected secular variation in K and Th is supported by GRS observations. K and Th can and do fractionate from one another through certain aqueous alteration processes, but the most likely result of broad scale aqueous alteration would be the gradual depletion of K and Th in the older terrains. For these reasons, K and Th variation is likely caused by variations in primary igneous composition and, while regional exceptions exist [18, 25], planet-wide, weathering is likely a second order cause of K and Th variation.

The increasing Fe concentrations with decreasing surface age may be caused by either primary igneous processes or broad-scale secondary alteration. The processes affecting the weathering and mobility of Fe on the Martian surface are very different from those normally seen in terrestrial environments [27, 28]. With lower pH and increased solubility, Fe could have been preferentially leached out of the southern highlands and been deposited onto the northern lowlands through long-term, aqueous transport. However, this is not supported by the K and Th data. A relatively modest compositional change in a parent magma could explain the Fe abundance different between the Noachian and Hesperian surfaces [29]. Therefore, it is more likely iron, too, varies due to igneous compositional changes [4].

Cl displays the most variation across the Martian surface [19]. The strong correlation between Cl and H implies that Cl is involved in the Martian hydrologic cycle. Also, in situ soil measurements by lander and rover missions generally show correlations between Cl and S concentrations, again supporting a hydrologic control [30].

GRS Elemental Concentrations vs. TES Mineralogies and Dust Abundances: In the same manner used for comparing the chemistry of the age provinces, we analyzed GRS-derived global elemental abundances with respect to several TES-derived mineralogies and surface dust abundances [5]. Although several spectroscopic instruments capable of detecting specific mineralogies have been or are currently in operation around Mars, data supplied by the Thermal Emission Spectrometer (TES) instrument provide the global coverage and a lower resolution more easily compared to GRS data [7, 8, 18].

We ran pixel-by-pixel comparisons between GRS Fe, Si, H, Cl, K, and Th abundances and selected TES mineralogies (see Figure 3 for examples). We smoothed publicly available 1°×1° mineralogical maps from the TES Science Team website to a 5°×5° pixel resolution to allow comparison with the GRS data. Using a method similar to that employed by Hahn et al., [4], each TES mineralogical or dust abundance dataset was divided into three categories representing High, Medium, and Low areal abundances (e.g., High, Medium, and Low Plagioclase). These three categories were determined for a particular mineralogy such that each category contains enough pixels (>100 pixels) to allow good statistics. We limited ourselves to only the TES datasets designated: Surface Dust, High-Calcium Pyroxene, Sheet Silicates/High-Si Glass, and Plagioclase. These four TES datasets are the only global-scale maps available that provide a large number of pixels registering near or above the TES detection threshold.
limit at smoothed 5°×5° resolution and, therefore, are the only TES datasets likely to provide statistically robust comparisons with GRS.

While variations are subtle and some comparisons do not show a statistically reliable correlation, a number of chemical trends are evident using this method. GRS means generally agree with the chemical trends one would expect for a particular mineralogy (Figure 3 – top). For example, Fe concentrations decrease with an increasing areal abundance of plagioclase and high-Si glass/silicate and Si concentrations increase as these Si-rich phases become more areally dominant. Since the penetration depths of these two instruments are very different (a few tens of centimeters for GRS compared to a few hundred microns for TES) [6, 7], this agreement with expected results provides a degree of cross-instrument reliability.

TES can determine the areal abundance of surface dust. Comparisons of varying dust content with GRS data show dusty regions significantly enriched in the volatile elements Cl and H (Figure 3 – bottom). Other variations are muted, but generally the variation between low and medium dust regions is more significant than the variation between medium and high dust regions. This may suggest a saturation effect on GRS chemistry for regions where dust is dominant. Work is ongoing regarding this feature in an attempt to better constrain the chemistry of Martian surface dust.

The Chemical Composition of the Martian Upper Crust: Previous estimates of Martian crust and mantle chemistry have been largely dependent on analyses of the SNC meteorites. However, although ejected from the Martian surface, it is unclear to what degree they are representative of the Martian bulk crust [31]. Their generally young ages imply source regions that are not areally extensive and do not make up a majority of the crust. We cannot determine their geographic origin with any confidence, as they were removed by impact from unknown Martian provinces. Consequently, additional chemical datasets must be analyzed for a robust determination of the Martian bulk crust.

Several landed missions have returned geographically disparate measurements of surface chemistry. However, the two Viking missions consisted of stationary landers and the Sojourner rover used by the Pathfinder mission had limited mobility and operating lifetime. Spirit and Opportunity provided many more detailed chemical and mineralogical analyses of soils and rocks from geographically diverse locales on opposite sides of the planet.

Weathering, sedimentary transport, and deposition naturally sample a wide array of source rocks with the resultant chemistry being an efficient mixture of source terrains. Given the similarity of soil chemistry measurements gathered at all lander sites and the apparent chemical homogeneity of the Martian crust, it is likely that these soil chemistry averages closely represent the bulk chemistry of the Martian upper crust from which there were derived.

With carefully screened MER APXS data, we are developing an estimate of major and trace element crustal chemistry based upon these soil averages. GRS global chemical averages for certain elements are used to corroborate compositions calculated from the soil data and in some cases GRS global averages for a particular element are assumed to represent the bulk upper crust. Where applicable, SNC chemistry and canonical cosmochemical relationships will also be incorporated into the bulk determination.