Table 1. Gamma-Ray Photopeaks of Interest for This Work, Along With Their Sources and Relevant Spectral Backgrounds

Element	Gamma-Ray Energy (keV)	Source	Backgrounds[a]
Potassium	1461	Radioactive decay	S_R
Silicon	1779	$^{28}Si(n, n'\gamma)\ ^{28}Si$	S_B, S_N
Oxygen	6129	$^{16}O(n, n'\gamma)^{16}O$	S_B, S_N
Thorium	2615	Radioactive decay	S_R

[a] S_R, S_B, and S_N denote spacecraft backgrounds originating from radioactive elements on the spacecraft, GCR-induced gamma-ray production within the spacecraft, and planetary-neutron-induced gamma-ray production within the spacecraft, respectively (see Appendix C for the details).

characterizing the behavior of the K/Th abundance ratio over the surface.

2. Gamma-Ray Spectroscopy

2.1. Sources of Gamma Rays

[4] Gamma-ray emission from a planetary surface arises from both the natural decay of radioactive elements (e.g., K, Th, and U) and the excitation of stable elements (e.g., Si and O) by surface-incident galactic cosmic rays (GCRs) [e.g., *Reedy*, 1978]. The GCR flux consists primarily of protons, but there are small contributions from alpha particles (6–7%) [*McKinney et al.*, 2006] and heavy ions (~1%). GCRs with energies greater than 100 MeV per nucleon interact with atomic nuclei in the surface to produce "fast" (>1 MeV) neutrons through nuclear spallation. These fast neutrons undergo inelastic scattering with nuclei within several hundred g/cm^2 of the surface, exciting them into unstable states that subsequently decay back to stability via the emission of gamma rays at energies that are characteristic of the source element. Fast neutrons also downscatter to thermal energies (<1 eV), where they can be captured by stable elements to produce new isotopes with an additional neutron. The newly created isotopes are typically populated in excited nuclear states that also decay to stable states via gamma-ray emission at characteristic energies. The identification of these gamma rays from orbit allows for the remote characterization of the elemental composition of a planetary surface [e.g., *Prettyman et al.*, 2006; *Boynton et al.*, 2007]. Due to the large mean free paths of neutrons and gamma rays within a planetary surface, gamma-ray spectroscopy is sensitive to elemental composition to depths of tens of centimeters. This depth sensitivity contrasts with other remote sensing techniques, such as X-ray spectroscopy, which is sensitive to composition within 100 μm of the surface.

2.2. MESSENGER Gamma-Ray Spectrometer

[5] The MESSENGER GRS is comprised of two sensitive volumes, a high-purity Ge crystal (HPGe) and a borated plastic scintillator. The scintillator surrounds the HPGe on all sides except the front of the instrument and acts as an anti-coincidence shield by vetoing charged particle and neutron-induced signals originating from GCRs and spallation neutrons generated within the spacecraft. The resulting anti-coincidence spectra have a substantially reduced background continuum and therefore provide a higher signal-to-noise ratio for the gamma-ray peaks of interest. The unshielded front view of the HPGe defines the instrument boresight direction, which is aligned with the instrument deck of the spacecraft and generally faces the planet during periods when the spacecraft is at low altitudes (see Appendix A). Further details on the design and capabilities of the GRS have been given by *Goldsten et al.* [2007].

[6] The GRS is sensitive to incident gamma rays with energies between 0.06 and 9 MeV, a range that includes discrete-energy gamma rays resulting from radioactive decay as well as neutron inelastic scattering and neutron capture reactions. Gamma rays that deposit their full energy in the HPGe produce photopeaks in the GRS spectra. The number of events in these photopeaks, when combined with knowledge of the detector efficiency and measurement geometry, is a direct measure of the gamma-ray flux at the detector. These measurements are compared with models of the surface gamma-ray flux as propagated to the spacecraft altitude in order to determine the abundances of the corresponding elements on the surface. This process is complicated by the highly eccentric orbit of the MESSENGER spacecraft about Mercury (Appendix B). An additional complication arises from the contamination of many of the photopeaks of interest by spacecraft-originating gamma rays. In order to determine the fraction of the measured count rates that originate from the surface, the background contributions for each photopeak must be identified and removed. Table 1 lists the gamma-ray photopeaks used in this study, along with the relevant sources of background (Appendix C).

[7] The gamma-ray flux (φ_γ) measured by the GRS is altitude dependent, varying as

$$\varphi_\gamma = 1 - \sqrt{1 - \frac{R_M{}^2}{(R_M + h)^2}} \quad (1)$$

where h is the altitude of the spacecraft above the surface of Mercury in km and R_M is the radius of Mercury (2440 km). This altitude dependence facilitates the definition of two data-collection regimes of interest: low and high altitudes. Low altitudes are defined to be less than 2000 km, a value that was chosen to maximize the signal-to-noise ratio for the detection of planet-originating gamma rays. The reduced signal-to-noise ratio for data acquired at altitudes greater than 2000 km, coupled with the nature of the MESSENGER orbit about Mercury, limits elemental mapping to northern latitudes [*Peplowski et al.*, 2011a]. High altitudes are defined to be greater than 14,000 km, a value chosen such that the maximum contribution of planet-originating gamma rays to the high-altitude signal is an order of magnitude lower than in the low-altitude spectrum, making the high-altitude spectrum ideal for characterizing non-planetary background signals in the detector.

3. Data Processing

3.1. Data Selection

[8] The analysis in this paper utilized GRS anti-coincidence (AC) spectra collected from orbital observations of Mercury from 24 March 2011 to 28 September 2011. AC spectra were chosen for their optimal signal-to-background ratio for gamma-ray photopeaks. Sub-optimal data were removed from the data set prior to analysis. This includes measurements acquired during orbits with reduced signal-to-noise ratios (e.g., spacecraft-incident solar energetic particle