MÖSSBAUER SPECTROSCOPY ON THE MARTIAN SURFACE: CONSTRAINTS ON INTERPRETATION OF MER DATA.

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Introduction: Mössbauer spectrometers will be used on martian landers and rovers to identify and quantify relative amounts of Fe-bearing minerals, as well as to determine their Fe^{3+}/Fe^{2+} ratios, allowing more realistic modeling of martian mineralogy and evolution. However, derivation of mineral modes, Fe^{3+}/Fe^{2+} ratios, and phase identification via Mössbauer spectroscopy (MS) does have limitations. We discuss here the exciting potential of MS for remote planetary exploration, as well as constraints on interpretation of remote Mössbauer data.

Summary of the capabilities of the technique: The Mössbauer technique is sensitive only to the Fe atoms in the materials being studied. A Mössbauer spectrometer *cannot* determine the amount of total Fe in a material; it *only determines relative amounts* of Fe atoms in various types of sites and valence states.

Two types of spectra can arise from each Fe atom in a distinctive site or valence state: a doublet for sites experiencing electric monopole and electric quadrupole interactions (paramagnetism), and a sextet when the electric monopole and magnetic dipole interactions combine (magnetically ordered). In both cases, the doublet/sextet can be defined by its isomer shift (arising from the difference in s-electron density between the source and the absorber). When the magnetic moment is zero, a doublet is formed, and the difference in energies of the two peaks is its quadrupole splitting (arising from the electric field gradient at the nucleus). If the magnetic moment is non-zero, the sextet is further characterized by a hyperfine field. The isomer shift, quadrupole splitting, and hyperfine field are characteristic of various coordination environments and valence states for various materials; these parameters are tabulated in [1].

Mineral Identification from Mössbauer Data: From the above, it is apparent that Fe atoms in a distictive site geometry and valence state will have distinctive parameters that might be used to identify phases. However, the number of mineral species is large and the range of hyperfine parameters is small, so in many cases they do not uniquely identify a phase. This is particularly true for Fe^{3+}-rich phases, because the range of Mössbauer parameters known for Fe^{3+} in any coordination is small. For Fe^{2+}, there is a better chance of identifying phases based upon their Mössbauer parameters, although there are MANY mineral species known to have Fe^{2+} in octahedral coordination. Unless unusual site distortion is present, minerals with Fe atoms in the same type of site will have roughly the same spectra. Only serendipitous combinations of minerals will allow resolution of doublets arising from distinct species [2].

Consider, for example, a rock containing a mixture of feldspar, clinopyroxene and orthopyroxene. Both Fe-bearing phases have essentially the same structure, so the doublets will overly each other; the Mössbauer spectrum of the mixture will not allow the relative contributions of each type of pyroxene to be determined (and, of course, the feldspar is invisible to the Mössbauer spectrometer). As a different example, the whole rock Mössbauer spectrum of the martian meteorite Nahkla is shown in Figure 1. Its spectrum is the superposition of two phases containing ~97% octahedral Fe^{2+}. The distortion of the coordination polyhedra surrounding the Fe^{2+} atoms in each of these minerals is different, so the Mössbauer doublets have distinctly different parameters, and the relative Fe^{2+} contributions of olivine and pyroxene can be discerned. However, it is impossible to determine from this spectrum which of the two phases hosts the 3% Fe^{3+}.
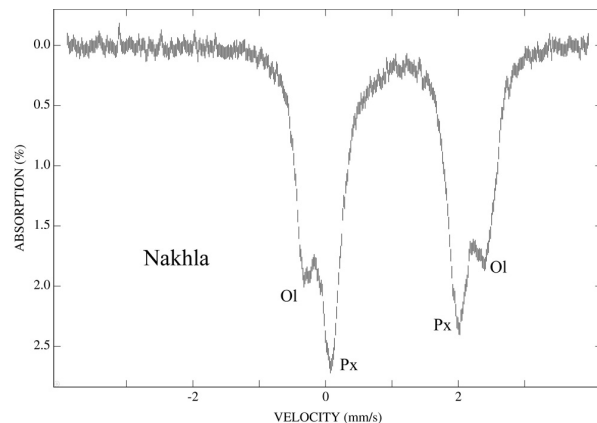
Figure 1. Mössbauer spectrum of SNC Nahkla.

Lack of Low Temperature Data: It is well known that Mössbauer parameters change as a function of temperature. The amount of change is not predictable, and must be experimentally determined. At this writing, the temperature dependence of Mössbauer parameters for common rock-forming minerals and glasses is known *only for a few minerals*, but is strong! In recognition of the lack of variable temperature lab-based data, these authors are currently running mineral

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separates of likely martian-analog mineral species over the range 12-300 K; graphs of spectra and raw data are being posted on a web site for use by the scientific community. We hope to acquire suites of spectra on up to 90 different mineral species by January of 2004 when MERs will land.

Complications from Acquiring Data at Variable Temperatures on the Martian Surface: Planned spectral acquisition times on the martian surface will be roughly 12 hours per spectrum; depending on the landing site chosen, this could result in temperature changes of perhaps 70-80 K *during acquisition*. This temperature change is being modeled in our laboratory using a progammable temperature controller. The resultant Mössbauer spectra are difficult to interpret. They do not resemble the average of end member temperature spectra because the shifts with temperature are non-linear. The resultant peaks are asymetrical and considerably broader, which will make overlapping peaks far more difficult to extract and interpret.

Unquantified Recoil-Free Fraction Effects: Under ideal laboratory conditions, doublet or sextet areas can be extracted from spectral models, and each can then be assigned to represent Fe in a specific valence state and/or site. However, these peak areas do NOT directly correspond to the abundances of Fe in the minerals that give rise to them. The correction factor (which can be as high as roughly 30%) for making this calculation is the recoil-free fraction, or *f*, and it is known for only a handful of mineral species. It is also highly composition dependent. We are in the process of determining values of *f* for various likely martian minerals, but the need to acquire >16 spectra at various temperatures for each mineral makes this process slow.

Unknown Particle Size: For iron oxides, dramatic differences in the appearance of Mössbauer spectra can result between bulk samples and their microcrystalline counterparts. These changes arise because long-range regularities that are present in bulk structures may be reduced, in nanometer scale particles, to such an extent that cooperative phenomena are seriously inhibited [3]. Magnetic ordering disappears from room temperature spectra due to such superparamagentism in goethites with grain sizes <15 nm and hematites <8 nm [4]. Furthermore, recoil-free fractions of Fe in such small particle sizes are also drastically changed [e.g. 5]. Such effects of small particle sizes can be remediated by acquisition of extremely low T Mössbauer spectra (usually <4.2 K)[6], but such a remedy is of course impractical for remote instruments. As a result, phase identification based upon spectra acquired on the martian surface will be complicated if small particles, or a range of particle sizes, are present -- and that will, of course, be unknown.

Lack of Uniqueness in Determining Mineral Modes from Mössbauer Spectra: One of the stated goals of the MER Mössbauer instrument is to quantify the relative amounts of Fe-bearing minerals on Mars, but this goal will not be easily attained. Given that the Mössbauer effect reports only the percentage of Fe atoms present in difference sites, it might seem that it should be easy to infer mineral modes from Mössbauer data simply by comparing peak areas (corrected, of course, for *f*). However, this is only true if the molar volume and total Fe contents of the phases are the same. For example, consider again Figure 1. Nahkla has a mode that is 80% cpx and 10% olivine, but these data combined with the chemical compositions (and resultant calculated formulas and known molar volumes) suggest a Mössbauer spectrum with doublet areas of 75% cpx and 25% olivine. This difference occurs because the olivine is more Fe-rich than the co-existing pyroxene, and it has a different molar volume.

However, doublet areas in the Mössbauer spectrum of a mixture of minerals *cannot be used to estimate modal mineralogy* unless their chemical compositions are known. In cases where the bulk rock is completely a mixture of, say, hematite and magnetite (i.e., phases where the chemical compositions are relatively constant), modal estimates can be made based on Mössbauer spectra of mixtures. Such rock types are rare. Unfortunately, in cases where the bulk rock contains silicates with variable Fe contents (i.e., nearly any silicate!) and/or silicates or oxides mixed with Fe-poor phases like feldspar, *it is impossible to deduce modes from Mössbauer doublet areas*. Interpretation of MER data for which compositions will not be known will be (regrettably) complicated by this simple constraint.

Conclusions: There is great excitement in the Mössbauer community over the involvement of MS in remote planetary exploration. However, a large amount of new data will need to be generated to allow proper interpretation of the remotely-acquired data, and many experimental parameters will not be able to be constrained in such circumstances. As a result, careful consideration of the above-mentioned constraints on interpretation of remote Mössbauer data is urged in order to ensure successful interpretations.

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