

first order source of uncertainty in interpreting these sedimentary rocks. Apart from field experiments carried out by *Opportunity*, which clearly indicate that spherules are composed of hematite  $\pm$  basaltic debris  $\pm$  minor sulfates (see below), no mineralogical identification or inference can be related unambiguously to any textural feature.

Chemical components are dominated by some combination of Mg-, Fe- and Ca-sulfates. The only sulfate mineral unambiguously identified by Mössbauer spectroscopy is jarosite (either mixed Na- and K-jarosite and/or hydronium jarosite), and makes up about 10% of the rocks. Occurrence of jarosite is particularly important because it is stable only under low pH conditions of about five or less [17,25]. On Earth, jarosite typically forms during acid-sulfate alteration of volcanic rocks or during pyrite alteration in acid mine drainage settings (e.g., [29,30]). However, on Mars where near surface water chemistry is likely to be dominated by basalt alteration, jarosite is also a plausible evaporite mineral under low pH conditions [15,17]. Mini-TES spectra of outcrops identified an absorption edge at  $1250\text{ cm}^{-1}$ , consistent with the presence of sulfates. Spectral deconvolution, using a library consisting of various Ca-, Mg-, Na- and Fe-sulfates, indicates a best fit for a mixture of Ca- and Mg-sulfates [28].

Chlorine is not so high (0.3–1.3%) as to demand separate chloride phases and may simply substitute in dominantly sulfate or mixed sulfate-chloride minerals. On the other hand, Br/Cl ratios are highly variable [25,26] suggesting that late-forming evaporitic minerals, such as chlorides or bromides, may have formed in this geochemical system. Clark et al. [25] carefully evaluated the chemical mass balance and suggested that Mg- and Ca-chlorides are likely candidates.

Hematite constitutes about 6% of these rocks on average. Much of it is contained in spherules, but as much as one-half of the hematite may be dispersed throughout the outcrop (the exact amount depending on how much hematite is contained in spherules, a value that is not well constrained; see Section 5.2 below). The chemical composition remaining after removal of plausible chemical components suggests a basaltic composition, likely one that has been significantly altered. The various components that are identified or inferred can be illustrated on two ternary diagrams plotting mole fraction  $\text{SO}_3\text{-MgO-FeO}_T$  (Fig. 2a) and  $\text{Al}_2\text{O}_3(\times 5)\text{-SO}_3\text{-SiO}_2$  (Fig. 2b). In Fig. 2a, the abraded outcrop analyses cluster near the center of the diagram, consistent with a mixture of both basaltic debris and a variety of chemical constituents. In Fig. 2b, outcrop rocks form a clear linear trend that

intersects the  $\text{Al}_2\text{O}_3\text{-SiO}_2$  join in the vicinity of typical martian basalts with relatively high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. The trend extrapolates to about 0.20–0.30 on the  $\text{SO}_3\text{-SiO}_2$  join, consistent with about 5–8% secondary silica. On abraded outcrop surfaces, the amount of  $\text{SiO}_2$  does not drop off with increasing  $\text{SO}_3$  content at the same rate as other elements that are likely concentrated in the siliciclastic component (e.g., Al, Ti, K) also suggesting excess silica. Model-dependent geochemical mass balance calculations result in as much as 25% secondary silica [25].

Although these rocks have a fairly complex diagenetic history (see below) it is likely that most of the detrital sand grains are evaporite-cemented basaltic mud (see below) derived from penecontemporaneous playa lakes [2; also see below], suggesting that transported intrabasinal chemical (i.e., allochemical) components make up a significant fraction of the rocks ( $\sim 25 \pm 10\%$ ). Accordingly, these rocks are best described as impure allochemical sandstones [31].

#### 4. Constraints on provenance

Provenance of these sedimentary rocks can be considered on three levels: origin of detrital grains, origin of the siliciclastic components, and source of chemical constituents.

##### 4.1. Provenance of grains

Detailed examination of sedimentary textures indicates that these rocks are fine to medium-grained sandstones. Where well defined, the grains are mostly moderately well rounded fine to coarse sand sized, typically in the range of 0.1–1 mm. Grains smaller than about 0.08–0.10 mm cannot be resolved with the MI and so any mode of very fine sand or silt cannot be discerned. In any case, relatively uniform grain size distributions in individual MI images, and especially within individual laminae, suggest that these are well-sorted sandstones with individual laminae being very well sorted. Abraded outcrop surfaces reveal no textural evidence suggesting that grains are simply volcanic rock or relatively unaltered siliciclastic mineral fragments. For example, there are no systematic variations in albedo from grain to grain or from grain surfaces to grain interiors. Mössbauer results indicate that  $\text{Fe}^{3+}/\text{Fe}_T$  ratios are in the range of 0.85–0.90 for abraded outcrop surfaces suggesting that the bulk of Fe-bearing siliciclastic components making up grains is composed largely of altered material. Evidence for any primary igneous minerals in Mössbauer spectra of