Stratigraphy of hydrated sulfates in the sedimentary deposits of Aram Chaos, Mars

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1 Sedimentary deposits within the 280 km wide crater containing Aram Chaos (~3°N, 339°E) have been differentially eroded by wind to expose a stratigraphic column 900–1000 m thick that unconformably overlies the chaos bedrock. A detailed stratigraphic and mineralogical description of the deposits is presented based on data from the Mars Reconnaissance Orbiter Compact Reconnaissance Imaging Spectrometer for Mars, Context Imager, and High Resolution Imaging Science Experiment. Two sedimentary units overlie the basement chaos material representing the original plains fill in Aram Crater: the first and oldest is composed of (1) a 50–75 m thick dark-toned basal unit containing ferric hydroxysulfate intercalated with monohydrated-sulfate-bearing materials, (2) a 75–100 m thick light-toned unit with monohydrated sulfates, and (3) a 175–350 m thick light-toned resistant capping unit with nanophase ferric oxides and monohydrated sulfates. After a period of wind erosion, these deposits were partially and unconformably covered by the second sedimentary unit, a 75–100 m thick, discontinuous dark-toned unit containing crystalline hematite and polyhydrated sulfate material. These sedimentary deposits were formed by evaporite deposition during at least two distinct rising groundwater episodes fed by regional-scale recharge. Later groundwater event(s) formed the polyhydrated materials, indicating that environmental conditions changed to a higher water-to-rock ratio. Wind has continued to shape the landscape after the last wetting event to produce the features and exposures observed.


1. Introduction

[2] The discovery from orbit of layered sedimentary hydrated sulfate deposits in analyses of Mars Express Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité (OMEGA) data [Gendrin et al., 2005; Arvidson et al., 2006], subsequently confirmed and extended in analyses of Mars Reconnaissance Orbiter (MRO) Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) data [Murchie et al., 2009; Roach et al., 2009], has revolutionized our understanding of the evolution of Mars. The measurements obtained by the Mars Exploration Rover Opportunity during its exploration of the top of a thick sequence of sulfate-rich deposits in Meridiani Planum provide a detailed view of the depositional environment of these types of deposits. Specifically, results point to an acidic-sulfate-dominated lacustrine system alternating with more arid conditions in which aeolian deposits accumulated [Squyres et al., 2004; Grotzinger et al., 2005; Tosca and McLennan, 2006]. With continued groundwater rise on a regional level the deposits were cemented and preserved [Arvidson et al., 2006; Andrews-Hanna et al., 2007].

[3] In this paper we build on previous studies of Aram Chaos [Gendrin et al., 2005; Glotch and Christensen, 2005; Massé et al., 2008b; Dobrea et al., 2008] by contributing (1) detailed mapping of the layered deposits using a combination of MRO Context Imager (CTX) with 5 m/pixel data [Malin et al., 2007], High Resolution Imaging Science Experiment (HiRISE) data with 0.31 m/pixel observations [McEwen et al., 2007], Mars Orbiter Laser Altimeter (MOLA) data at ~465 m/pixel [Smith et al., 2001], and Mars

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The extent of the layered sedimentary deposits in Aram Chaos is illustrated in these CTX-based mosaics. (a) Locations of OMEGA and morphologically identified extents of monohydrated and polyhydrated sulfates. CRISM targeted observations are indicated with white outlines; locations of Figures 6a, 6b, and 10 are indicated with yellow boxes. (b) Same area as Figure 2a but with CRISM-based mineral detections. Key is as follows: 1.9 and 2.4 μm absorptions indicative of polyhydrated sulfates (red), 1.9 μm absorption indicating enhanced hydration but without a corresponding 2.4 μm absorption indicating hydrated sulfate (light red), 2.1 and 2.4 μm absorptions indicative of monohydrated sulfates (blue), 2.23 μm absorption indicative of ferric hydroxysulfates (green). The cross section in Figure 3 is indicated by the white line (A to A').
Figure 2. (continued)
inferences of the various layered units superimposed on the basement chaos materials.

CRISM is a hyperspectral imager that can acquire up to 544 spectral channels between 0.39 to 3.9 µm with two detectors: a short-wavelength detector that functions between 0.39 and 1.04 µm (S detector) and a long-wavelength detector that functions from 1.0 to 3.9 µm (L detector) [Murchie et al., 2007]. CRISM has two operational modes: a hyperspectral targeted mode (FRT, HRL, and HRS) and a multispectral nadir-looking mode (MSP). The multispectral mode is designed to provide mineralogical information for as much of the surface as possible, whereas the hyperspectral mode is designed to probe the mineralogy of relatively small areas in great detail. In the hyperspectral mode, gimbaling allows the instrument to be pointed at specific locations to the left or right of the spacecraft track while acquiring data at full spectral (544 bands, 0.39–3.9 µm) resolution and either full or half spatial resolution (~18 or ~40 m/pixel, respectively) [Murchie et al., 2007]. Multiple images are taken on the incoming and outgoing spacecraft track to sample different path lengths through the atmosphere, but in this paper only the center observation is used. Targeted observations cover ~1300 km² of the sedimentary deposit in Aram Chaos.

CRISM data presented in this paper were converted to I/F by dividing radiance on sensor by the solar radiance. Atmospheric gas band absorptions were removed by normalizing to a gas transmission spectrum. This spectrum, from data acquired over Olympus Mons where the surface spectra are dominated by dust signatures, is obtained by dividing I/F values at the base of Olympus Mons by values at the summit. The variation in atmospheric path length from the base to the top of the volcano provides a transmission at the summit. The variation in atmospheric path length from data acquired over Olympus Mons where the surface spectra are dominated by dust signatures, is obtained by dividing I/F values at the base of Olympus Mons by values or combinations of spectral features that some minerals have in the visible/near-infrared wavelengths, and are a first-order tool for identifying locations to explore in greater detail with the full wavelength range of the data set. For example, most hydrated sulfates have a spectral feature at 2.4 µm [Cloutis et al., 2006], and, therefore, a mathematical expression which takes into account the overall slope of the spectrum in that wavelength region and the actual absorption at 2.4 µm can be used to identify the possible signature of sulfates in a spectrum [Pelkey et al., 2007]. Multiple parameters can be used together to identify monohydrated sulfates (absorptions at both 2.1 and 2.4 µm) or polyhydrated sulfates (absorptions at 1.4, 1.9, and 2.4 µm). Initial detections of hydrated minerals within the layered deposits were made over Aram Chaos using the spectral parameters or combinations of spectral parameters indicated in Table 1. A new parameter algorithm was developed after examination of both I/F and ratioed data showed the pres-
ence in some locations of a sharp and relatively deep band at 2.238 μm. The parameter to map the depth of this band was defined as follows:

\[
BD_{2230} = 1 - \frac{R_{2.2318}}{0.468 \times \frac{R_{2.2120} + R_{2.1988}}{2} + 0.532 \times \frac{R_{2.2583} + R_{2.2517}}{2}}
\]

where \(R(\lambda)\) is the reflectivity at wavelength \(\lambda\). This band depth parameter (BD2230) is now incorporated into the spectral summary parameters in CAT versions 6.5 and higher.

Detections of specific minerals were confirmed by examining the wavelength range between 0.4 and 2.6 μm of the atmospherically and photometrically corrected hyperspectral data over each detection and comparing the spectra to laboratory-based mineral spectra resampled to CRISM band passes in the visible NIR wavelength range. As already noted, Figure 4 presents I/F spectra for end-members retrieved from CRISM data, along with the spectrally “neutral” spectrum used to generate ratio presentations. Also shown in Figure 4 are ratioed data for the L detector spectral range and laboratory spectra of likely analogs. The end-
member spectra were extracted from the CRISM spectra by inspection of band parameter maps and detailed examination of a large number of I/F and ratioed spectra where parameter maps indicated a relatively high abundance of a given mineral species.

The imaging and spectral data sets were used in tandem to generate maps that show the locations of mineral identifications with CRISM data (Table 2), mineral identifications with OMEGA and TES data from previous work, and geologic units that contain the specific mineral signatures (Figures 2a and 2b). Grided global topography data from MOLA (1 m vertical resolution) [Smith et al., 2003] and digital elevation maps generated from stereo HRSC data (20–100 m vertical resolution) [Ansari et al., 2008] were used in conjunction with the other data sets to define embayment and superposition relationships among the various units and to define the map units and stratigraphic relationships shown in Figures 2b and 3.

3.2. Laboratory Measurements

To support spectral identification of sulfate-bearing minerals, visible and near-infrared (VNIR), Mössbauer (MB), and powder X-ray diffraction (XRD) measurements were acquired for synthetic melanterite (FeSO₄·7H₂O; Fisher Scientific) heated in air at 80°C, 110°C, 130°C, 150°C, 200°C, and 240°C for 2, 3, 18, 21, 18 h, respectively. An Analogue Spectral Devices FieldSpec RS³ spectrometer with a Muglight option was used to obtain VNIR spectra at room temperature. Transmission Mössbauer spectra were obtained at room temperature with a Ranger Scientific spectrometer (Model MS-1200) using a ⁵⁷Co(Rh) source and analyzed using the methods outlined by Morris et al. [2000]. The values of the doublet Mössbauer parameters isomer shift (δ = (ν1 + ν2)/2) and quadrupole splitting (∆E_Q = ν1 - ν2) were calculated from the center positions (ν̄₁ and ν̄₂ with ν̄₂ > ν̄₁) of the two peaks. The value of δ is reported relative to the center position of the spectrum of metallic iron foil at room temperature. A Scintag XDS 2000 X-ray diffractometer using CuKα radiation and a step size of 0.02°/θ was employed to obtain X-ray diffraction powder patterns (~293 K). On the basis of XRD patterns, the powders obtained by thermal decomposition of synthetic melanterite at 80°C and 240°C are synthetic szomolnokite (FeSO₄·H₂O) and ferric hydroxysulfate (Fe(OH)SO₄), respectively. VNIR and MB spectra of the synthetic melanterite, szomolnokite, and ferric hydroxysulfate are shown in Figure 5. As will be shown in section 4, melanterite is an example of a polyhydrated phase that matches CRISM-based spectra and szomolnokite is a possible match for the monohydrated phase in Aram Chaos. Fe(OH)SO₄ can be identified as a specific phase based on detailed comparison of CRISM-based and our laboratory data, as shown in Figure 4.

4. Stratigraphy and Mineralogy of Sedimentary Deposits

Two major stratigraphic units unconformably overlying the basaltic basement chaos terrain were mapped in detail as part of our work (Figures 2b and 3). The chaos terrain beneath and surrounding the sedimentary deposits was described elsewhere in detail and will not be covered in this paper [Glotch and Christensen, 2005; Oosthoek et al., 2007; Massé et al., 2008b; Noe Dobrea et al., 2008]. CRISM spectra for the chaos surfaces are consistent with the presence of nanophase ferric oxides variably mixed with basaltic materials. Descriptions for the two overlying sedimentary units incorporate both the results of this study and previous work in this area and are described in this section from oldest to youngest. The areal extents of the units in CRISM and OMEGA/OTES data are given in Table 3. As already noted, a schematic cross section showing the current topographic relationships of the sedimentary units and basement chaos materials is shown in Figure 3.

4.1. Ferric Hydroxysulfate, Monohydrated Sulfate, and Nanophase Ferric Oxide Unit

The first of the two sedimentary units has three distinctly different stratigraphic horizons. From oldest to youngest these are monohydrated sulfates with ferric hydroxysulfate, monohydrated sulfates, and monohydrated sulfates with nanophase ferric oxides. The changing mineralogy represents a facies change and likely temporal evolution in the environments of deposition and/or alteration.

<table>
<thead>
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<th>Table 1. Summary Parameter Mineral Indicators</th>
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<tr>
<td>Material</td>
</tr>
<tr>
<td>Monohydrated sulfate</td>
</tr>
<tr>
<td>Polyhydrated mineral</td>
</tr>
<tr>
<td>Polyhydrated sulfate</td>
</tr>
<tr>
<td>Ferric hydroxysulfate</td>
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<table>
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<th>Table 2. CRISM Targeted Observations Used in This Paper</th>
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<tr>
<td>FRT0000C815</td>
</tr>
<tr>
<td>FRT0000D26B</td>
</tr>
</tbody>
</table>

*Observations are listed in chronologic order.
*Date format is year_day.
4.1.1. Ferric Hydroxysulfate, Monohydrated Sulfates

[14] The sedimentary section sitting directly and unconformably on the chaos bedrock surface is spectrally dominated by monohydrated-sulfate-bearing materials, but together with ferric hydroxysulfate-bearing materials exposed in a number of areas (Figures 2b, 3, and 4). Examination of these exposures with HRSC DEM data shows that these deposits in total are 50 to 75 m thick. The Fe(OH)SO₄-bearing material occurs in small exposures that are intercalated with dehydrated ferricopiapite reported by Milliken et al. [2008] and interpreted to be an Al–OH bearing mineral by Milliken et al. [2008a]. As noted previously in this paper, synthetic melanterite (FeSO₄·7H₂O) was heated in laboratory air at ~240°C for 21 h, resulting in production of H₂O and H₂ by-products, Fe³⁺ from oxidation of Fe²⁺, and formation of Fe(OH)SO₄. VNIR laboratory spectrum of the synthetic Fe(OH)SO₄ is shown compared to the ratioed CRISM spectrum of this material in Figure 4. Figure 5 shows the synthetic melanterite, szomolnokite, and ferric hydroxysulfate VNIR spectra along with Mössbauer spectra confirming the transition from Fe²⁺ to synthetic melanterite to Fe³⁺ as the sample was heated and converted to ferric hydroxysulfate. The VNIR spectra also show the shift of the ~1.9 μm absorption due to H₂O in the melanterite to ~2.1 μm in the szomolnokite. The spectra of the ferric hydroxysulfate in Aram Chaos are similar to the spectra of dehydrated ferricopiapite reported by Milliken et al. [2008] and Bishop et al. [2009], although their data show neither an absorption at 1.82 μm nor the distinctive spectral structure shortward of 2.24 μm. The Aram Chaos ferric hydroxysulfate is also distinct from the ferric-bearing sulfates found at Gusev crater and Meridiani Planum on the basis of Mössbauer data (Figure 5 and Morris et al. [2006a, 2006b, 2008]).

4.1.2. Monohydrated Sulfates

[15] Above approximately 75 m above the contact with the underlying chaos bedrock, the sedimentary deposit transitions without any major unconformities to a mono-

Table 3. Unit Characteristics

<table>
<thead>
<tr>
<th>Compositional Information</th>
<th>Extent of Coverage With CRISM Data</th>
<th>Extent of Coverage With OMEGA Data</th>
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<tr>
<td>polyhydrated sulfate⁵; crystalline hematite⁶; enhanced hydration; ferric oxides nanophase ferric oxides; monohydrated sulfate⁴; monohydrated sulfate⁴; ferric hydroxysulfate; monohydrated sulfate⁶</td>
<td>170 km²</td>
<td>~2770 km²</td>
</tr>
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| ⁵Also detected with OMEGA data. ⁶Detected with TES data [Christensen et al., 2001; Glotch and Christensen, 2005].
hydrated–sulfate-dominated material (Figures 2b, 3, and 4). This material, similar to the monohydrated sulfate signatures lower in the section, is characterized by spectral absorptions at ∼2.1 and 2.4 μm and is dominated by flat, layered terrains with occasional scalloped textures due to wind erosion. This material is laterally extensive throughout the sedimentary deposit, covering approximately 1200 km². Although the spectral absorptions correspond most strongly with exposures of light-toned, scalloped material (Figure 7) the distinctive signatures are also apparent in flat-lying places of medium albedo (Figure 8). Based on examination of CTX data, these areas are most likely outcrops of the light-toned monohydrated sulfate-bearing material covered with a thin aeolian cover of basaltic sands [Glotch and Christensen, 2005]. The widespread but sporadic occurrence of this unit throughout the sedimentary deposit suggests it may be more common than indicated, but exposed by erosion only in certain places and obscured by basaltic sands in other locations. The total thickness of this monohydrated sulfate unit ranges from 75 to 100 m.

Gendrin et al. [2005] identified this material as the magnesium monohydrated sulfate kieserite (Mg(SO₄)·H₂O) based on the lack of an Fe absorption between 0.6 and 1.0 μm. However, an absorption at ∼1.0 μm in the nonratioed spectrum (Figure 4) suggests a possible iron-bearing sulfate such as szomolnokite, an interpretation that we prefer. The ferric hydroxysulfate that is spectrally a match to the material we see in Aram Chaos was formed by dehydration and oxidation of szomolnokite, lending credence to the presence of szomolnokite in the region.

### 4.1.3. Monohydrated Sulfates and Nanophase Ferric Oxides

The monohydrated sulfate signature transitions to a cliff-forming section that attains a thickness of between 175 and 350 m and forms a capping plateau ∼4600 km² in area, partially covered with basaltic sands. The exposed walls of this unit are light toned and indurated, with erosional scars down the sides where material has undergone gravity-induced erosion, exposing blocks of the chaos bedrock.
induced slumping and sliding (Figure 9). Chaos bedrock can be seen as “kipukas” standing above and surrounded by these deposits in the southwest corner of Aram Chaos (Figure 2), and in certain places this material has been deeply eroded to reveal the basement chaos terrain [Glotch and Christensen, 2005]. The spectral signature of the light-toned cliffs is dominated by nanophase ferric oxides [Morris et al., 2006a, 2006b; Massé et al., 2008b], but minor absorptions at 2.1 and 2.4 μm indicate that the material also contains monohydrated sulfates [Massé et al., 2008b].

[19] HiRISE images covering this unit (Figure 9) show that the exposed walls of this deposit are finely layered, with thicknesses similar to those inferred from the middle or monohydrated sulfate portion of the deposit. In fact, in CRISM observation FRT7FA4 up to twelve distinct layers are exposed within the monohydrated sulfate (middle) unit, forming a stair step pattern with some of the layers traceable to beneath the cliff-forming deposits.

4.2. Polyhydrated Sulfates, Hydrated Materials, and Hematite Deposits

[20] This second sedimentary unit is 75–100 m thick and is characterized by an absorption at 1.9 μm indicating the presence of one or more polyhydrated minerals and a plateau-like morphology. Compared to the monohydrated sulfates, the polyhydrated materials are darker and smoother and appear more indurated and resistant to weathering than the monohydrated deposits. Previous work in Aram Chaos with OMEGA data has shown that one of the hydrated minerals is most likely a polyhydrated sulfate based on an additional absorption at 2.4 μm [Gendrin et al., 2005; Noe Dobrea et al., 2008]. Examination of the locations where the 1.9 μm band depth is present in CRISM data over the plateau (Figure 10) shows that polyhydrated minerals are present, but that their locations are not ubiquitous throughout the region as mapped by OMEGA (Figure 2a).

[21] This unit also coincides spatially with the detection of crystalline hematite, identified from Thermal Emission Spectrometer data [Christensen et al., 2001; Glotch and Christensen, 2005; Noe Dobrea et al., 2008]. Using OMEGA data Massé et al. [2008b] showed that goethite, ferrihydrite, or schwertmannite may also be present in this unit along with hematite. These ferric oxides are not expected to be stable under present-day Martian conditions.

Figure 8. CTX mosaic over an area with strong 2.1 and 2.4 μm absorptions indicative of monohydrated sulfate. Blue shaded areas indicate the presence of monohydrated sulfate; green shaded areas indicate the presence of the ferric hydroxysulfate. Although most of the material that exhibits strong monohydrated sulfate signatures has a high albedo (Figure 7), the area enclosed by the dashed line does not, although some brighter material can be seen at the right edge. We interpret this to be an exposure of the monohydrated sulfate-bearing material in Figure 7 that is minimally covered with wind-blown sands.

Figure 9. HiRISE image PSP_003406. The spectral signature of the walls is dominated by nanophase ferric oxides but also has faint absorptions at 2.1 and 2.4 μm indicating the presence of monohydrated sulfates. Locations of strong 2.1 and 2.4 absorptions (indicating the material is dominated by monohydrated sulfates) are shown here just below the cliff. The layered nature of both the monohydrated sulfate plus npOx material and the monohydrated sulfate material is visible in the blowup on the right. The outcrop of ferric hydroxysulfate in this area is not covered in this HiRISE observation.
Massé et al. [2008b] suggest that their continued existence can be explained by very slow transformation kinetics. The strongest ferric oxide and enhanced hydration detections occur on the slightly raised plateau in the northeast part of the deposit (Figures 2a and 2b), although hematite is detected in lower concentrations at slightly lower elevations due to erosion and transport onto lower-lying regions [Glotch and Christensen, 2005].

In contrast to previous work, the analysis of high-resolution MRO data shows that this unit is unconformably superimposed on the monohydrated sulfate-bearing sedimentary section described in section 4.1. We see no evidence for polyhydrated signatures in these older deposits and we see no morphologic evidence that the polyhydrated deposits are beneath or included in the older deposits. For example, CRISM observations that cover parts of the older cliff-forming deposits (FRTC14E, FRTBE2D, and FRT7FA4) do not show spectral indications of polyhydrated sulfates in the wall exposures (Figure 9). In addition, examination of the cliff walls in CTX and HiRISE images show no indications of a low-albedo layer which might indicate the presence of polyhydrated/hematite/iron oxide material (Figure 11). Thus, even though this material is topographically below the cliff-forming unit (monohydrated sulfates and nanophase ferric oxides), we conclude the monohydrated sulfate-bearing unit was already emplaced and differentially eroded by the time the polyhydrated deposits formed. This inference is also consistent with mapping the spatial distribution of these materials using OMEGA data, morphology, and albedo [Gendrin et al., 2005; Noe Dobrea et al., 2008]. We infer that the polyhydrated deposits formed in local topographic lows after formation and differential erosion of the older, monohydrated sulfate-bearing sedimentary unit.

5. Summary and Implications

Our work shows that the sedimentary deposits in Aram Chaos first formed with intercalated ferric hydroxysulfate (Fe(OH)SO_4) and monohydrated sulfates (likely, szomolnokite) at the base of the section, followed by monohydrated sulfates, followed by a mix of monohydrated sulfates and nanophase ferric oxides. The data show that these deposits were then differentially eroded by wind, after which polyhydrated materials (e.g., polyhydrated sulfates) with hematite and other ferric oxides were deposited in low-lying areas during a second depositional event. Work by Wang and Freemenn [2009] shows that relative humidity is a critical factor in determining hydration/dehydration states of forming Mg sulfates. In conjunction with their work, our work indicates a possible change in environmental humidity between depositional events in Aram Chaos, beginning with the formation of ferric hydroxysulfate and monohydrated sulfate under relatively dry conditions and ending with the formation of polyhydrated materials under relatively wet conditions.

We favor a formation mechanism involving groundwater recharge/evaporation and multiple wetting events to explain the stratigraphic section observed in the sedimentary deposits in Aram Chaos. Regional-scale groundwater distribution modeling by Andrews-Hanna et al. [2007] predicts Aram Chaos to have one of the thickest evaporite deposits in the region. A regional-scale groundwater system would link the deposits in Aram Chaos to those in Meridiani Planum to...
the east and Valles Marineris to the west, so evaporite deposits in these regions should show similarities to the deposits in Aram Chaos. Analysis of sulfate deposits in Meridiani [Wiseman et al., 2010] shows that monohydrated and polyhydrated sulfate species in the northern valley are likely separated from the main Meridiani sequence by erosion, indicating a pause between depositional events in this area too. The sequence of polyhydrated sulfates overlying monohydrated sulfates is mimicked to the west in Candor Chasma, where Murchie et al. [2009] found that polyhydrated materials in Candor Chasma are younger than the monohydrated sulfates and occupy topographic lows. Both the sequence of polyhydrated materials overlying intercalated ferric hydroxysulfate and monohydrated sulfates and the unconformable contact between them signifying a period of erosion between depositional events in multiple locations throughout this region indicate that a plausible formation method is a series of groundwater upwelling events fed by groundwater recharge, as modeled by Andrews-Hanna et al. [2007].

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