

## RESEARCH ARTICLE

10.1002/2015JE004960

## Special Section:

The Mars Science Laboratory Rover Mission (Curiosity) at The Kimberley, Gale Crater, Mars

## Key Points:

- Summary of DAN active measurements of the Smooth Hummocky unit in the Kimberley
- DAN demonstrates stratigraphic variation in the WEH and chlorine equivalent at different geological members of the Kimberley formation
- The analysis of DAN data has shown that WEH and Cl-equivalent concentrations from DAN are consistent with APXS and SAM measurements

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## Citation:

Litvak, M. L., et al. (2016), Hydrogen and chlorine abundances in the Kimberley formation of Gale crater measured by the DAN instrument on board the Mars Science Laboratory Curiosity rover, *J. Geophys. Res. Planets*, 121, 836–845, doi:10.1002/2015JE004960.

Received 17 OCT 2015

Accepted 20 APR 2016

Accepted article online 23 APR 2016

Published online 14 MAY 2016

## Hydrogen and chlorine abundances in the Kimberley formation of Gale crater measured by the DAN instrument on board the Mars Science Laboratory Curiosity rover

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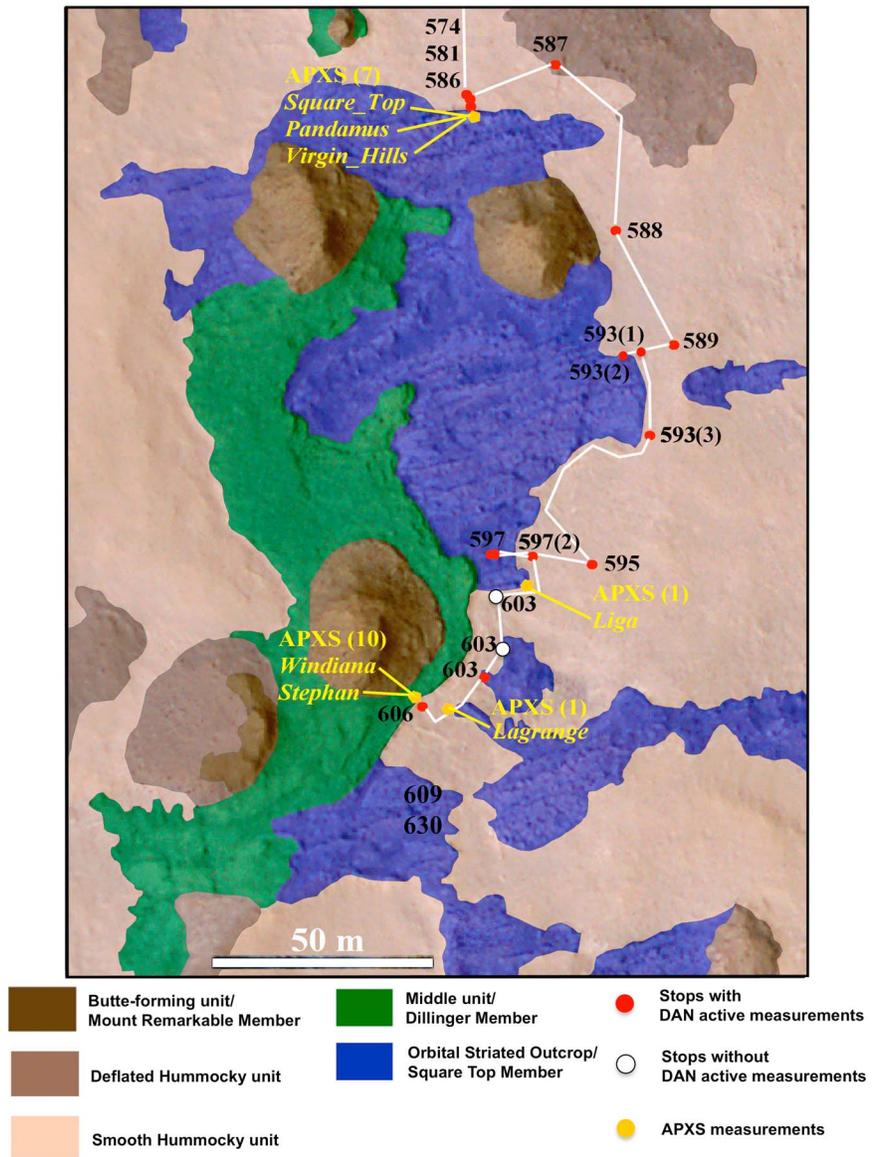
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**Abstract** The Dynamic Albedo of Neutron (DAN) instrument on board the Mars Science Laboratory Curiosity rover acquired a series of measurements as part of an observational campaign of the Kimberley area in Gale crater. These observations were planned to assess the variability of bulk hydrogen and neutron-absorbing elements, characterized as chlorine-equivalent concentration, in the geologic members of the Kimberley formation and in surface materials exposed throughout the area. During the traverse of the Kimberley area, Curiosity drove primarily over the “Smooth Hummocky” unit, a unit composed primarily of sand and loose rocks, with occasional stops at bedrock of the Kimberley formation. During the Kimberley campaign, DAN detected ranges of water equivalent hydrogen (WEH) and chlorine-equivalent concentrations of 1.5–2.5 wt % and 0.6–2 wt %, respectively. Results show that as the traverse progressed, DAN observed an overall decrease in both WEH and chlorine-equivalent concentration measured over the sand and loose rocks of the Smooth Hummocky unit. DAN measurements of WEH and chlorine-equivalent concentrations in the well-exposed sedimentary bedrock of the Kimberley formation show fluctuations with stratigraphic position. The Kimberley campaign also provided an opportunity to compare measurements from DAN with those from the Sample Analysis at Mars (SAM) and the Alpha-Particle X-ray Spectrometer (APXS) instruments. DAN measurements obtained near the Windjana drill location show a WEH concentration of ~1.5 wt %, consistent with the concentration of low-temperature absorbed water measured by SAM for the Windjana drill sample. A comparison between DAN chlorine-equivalent concentrations measured throughout the Kimberley area and APXS observations of corresponding local surface targets and drill fines shows general agreement between the two instruments.

### 1. Introduction

During the first 2 years of surface operations in Gale crater, the Mars Science Laboratory (MSL) Curiosity rover completed several observational campaigns along its path from the Bradbury landing site to the mission's main strategic target at Aeolis Mons (informally named Mount Sharp). By sol 650 Curiosity had driven about 6.5 km and performed observational campaigns at waypoints informally named Darwin, Cooperstown, and Kimberley [Grotzinger et al., 2015; Treiman et al., 2016; Stack et al., 2016]. The latter contained a particularly well exposed outcrop of sedimentary strata, informally designated the Kimberly formation, identified during orbital geologic mapping using Mars Reconnaissance Orbiter (MRO) High Resolution Imaging Science Experiment (HiRISE) images (Figure 1). Like previous Curiosity observational campaigns, complementary multi-instrument measurements were executed at the Kimberley waypoint campaign to better understand the geologic history and potential habitability of this interval of the Gale crater rock record.

The Dynamic Albedo of Neutron (DAN) instrument is an active neutron spectrometer on the Curiosity rover used to provide monitoring of shallow subsurface hydrogen and neutron-absorbing elements as an indicator of physically adsorbed water, water bound in hydrated minerals, and elements such as chlorine [Litvak et al., 2008, 2014; Mitrofanov et al., 2012, 2014]. DAN was used during the Kimberley campaign to acquire multiple



**Figure 1.** An orbital geologic map of the Kimberley outcrop showing the Curiosity rover traverse (white line), locations where DAN active observations were acquired (red dots) and targets where APXS observations of elemental composition were performed (yellow dots). In the key, both the “orbital” unit names and the “ground-based” geologic members are given. North is up.

measurements representing surface materials traversed by the rover, bedrock measurements of different geologic members of the Kimberley formation, and the Windjana drill location (Figure 1).

In this paper, we use previous experience gained during surface operations to characterize changes in bulk water and chlorine-equivalent distributions derived from DAN as a function of stratigraphic position for different geological members of the Kimberley formation and to understand spatial variations in the water and chlorine content of surface materials traversed by the rover during the Kimberly campaign. We also compare DAN measurements with observations from the Alpha-Particle X-ray Spectrometer (APXS) and Sample Analysis at Mars (SAM) instruments [Campbell *et al.*, 2012; Mahaffy *et al.*, 2012; Gellert *et al.*, 2014; Gellert and Clark, 2015] to analyze the diversity of local surface (with APXS/SAM) and subsurface (with DAN) chlorine- and water-equivalent distributions at Kimberley.

## 2. Geologic Context of the Kimberley Waypoint Campaign

The Kimberley outcrop was chosen for detailed investigation by the Curiosity rover team because of its well-exposed stratigraphy observed first in orbital images from the High Resolution Imaging Science Experiment

(HiRISE) camera on board the Mars Reconnaissance Orbiter (MRO) [Grotzinger *et al.*, 2015; Stack *et al.*, 2016]. The main goal of the Kimberley observational campaign was to study the geologic units present at this location, utilizing multiinstrument observations to determine the depositional processes, paleoflow directions, relative stratigraphy, and potential habitability of the Kimberley strata.

Surface observations from the Curiosity rover revealed sedimentary facies at the Kimberley including conglomerates, cross-bedded medium to very coarse grained sandstones, and fine-grained, cross-laminated sandstones, all of which are overlain by massive butte-forming rocks of unknown grain size [Rice *et al.*, 2014]. The most distinct unit at Kimberley, identified during HiRISE mapping as the Orbital Striated Outcrop (OSO) [Grotzinger *et al.*, 2015], is characterized from orbit by NE-SW trending sets of lineations that span several tens of meters in length [Grotzinger *et al.*, 2015]. Rover image mosaics of the OSO correspond to exposures of southward dipping, decimeter-thick sandstone beds of medium to very coarse sandstone informally named the Square Top member of the Kimberley formation. This member was selected as one of the primary science targets for Curiosity's ground-based observations during the Kimberley campaign.

As the rover traversed the Smooth Hummocky unit, which corresponds primarily to deposits of sand, loose rocks, and the occasional conglomerate outcrop [Stack *et al.*, 2016], from north to south around the eastern edge of the Kimberley outcrop (Figure 1), it made several approaches onto the Square Top member to perform multiinstrumental remote and contact science observations, as well as a deviation to conglomerate outcrops of the Point Coulomb member and coarse pebble sandstones of the Liga member (Figure 1). The Kimberley campaign culminated at the southeast end of the Kimberley outcrop at the base of a butte informally named Mount Remarkable (Figure 1). Here examination of the Dillinger member of the Kimberley formation, which corresponds with the "Middle unit" identified in orbital images, involved contact science observations, drilling operations at the Windjana drill hole, and sample analysis with SAM and CheMin instruments [Treiman *et al.*, 2016]. The Dillinger member was chosen for drill sampling due to a set of parameters favorable for the potential preservation of organic molecules, including an estimated young surface exposure age and very fine grain size, and engineering considerations including minimal damage for the wheels and optimal conditions for the following south exit traverse from the Kimberley. Joint analyses of the science observations gathered by Curiosity at Kimberley waypoint have shown complex stratigraphic relationships suggesting that past fluvial-deltaic processes transported sediments from the northern rim of Gale crater [Grotzinger *et al.*, 2015].

As part of the Kimberley science campaign, 16 DAN active measurements were acquired at the Square Top, Point Coulomb, Liga, and Dillinger members of the Kimberley formation and over surface materials of the Smooth Hummocky unit. (Table 1 and Figures 1 and 2). DAN active measurements were acquired at the end of each drive of the Kimberley campaign and were specially requested at middrive stops when Curiosity crossed an important geologic contact prior to the completion of a drive. Although engineering constraints at the Windjana drill site were such that it was not possible to center the DAN footprint over the drill hole, DAN was able to obtain one measurement where the DAN footprint covered at least a part (about 30–35% of DAN footprint) of the Dillinger member, near the drill hole.

### 3. Instrument and Methods

#### 3.1. The DAN Instrument

DAN is located at the back of the rover near the Multi-Mission Radioisotope Thermoelectric Generator (MMRTG) and consists of two separate subsystems integrated onto both sides of the rover: a pulsed neutron generator (DAN/PNG) and a detector element (DAN/DE). The DAN/DE consists of two neutron detectors ( $^3\text{He}$  proportional counters) that detect thermal and epithermal neutrons from the Martian subsurface. The DAN/PNG produces very short (2  $\mu\text{s}$ ) pulses of high-energy neutrons (14.1 MeV) [Litvak *et al.*, 2008; Mitrofanov *et al.*, 2012].

In DAN active mode, high-energy neutrons emitted by DAN/PNG interact with soil nuclei and lose their energy through inelastic scattering reactions. During this process some of the moderated epithermal and thermal neutrons leak back out of the subsurface and are detected by DAN/DE, which measures their arrival time after the moment of each neutron pulse. The shape and amplitude of the resulting time profile (unofficially known as a "neutron die-away curve") strongly depends on the local depth profile and distribution of hydrogen from absorbed water, hydrated minerals or even water ice, and neutron-absorbing elements such

**Table 1.** The Comparison Between DAN and APXS Estimations of Chlorine Concentrations Versus Geological Units Identified in the Kimberley

DAN Observations (sols)	Geological Unit	APXS Analog Target	APXS, Cl (%)	APXS, Fe (%)	DAN Chlorine-Equivalent (%)	DAN Corrected Cl <sup>a</sup> (%)
574, 581, 586, 588, 606, 609, 630 (end of drive)	Smooth Hummocky (sand and loose rocks)	Lagrange	0.76 ± 0.02	15.9 ± 0.2	1.0 ± 0.1	0.9 ± 0.1
630 (middrive)	Middle Unit-Dillinger member (very fine to fine sandstone)	Windjana Drill Fines; Windjana (post-DRT)	0.79 ± 0.05	20.3 ± 0.1	0.6 ± 0.1	0.4 ± 0.1
593 (middrive 2)	OSO-Square Top member outcrop (coarse sandstone)	Square Top, Pandanus Yard, Virgin Hills	1.0 ± 0.1	17.5 ± 0.2	2.0 ± 0.2	1.7 ± 0.2
597 (middrive), 597 (end of drive), 603	OSO-Liga member (coarse sandstone/pebble conglomerate)	Liga	1.86 ± 0.02	12.9 ± 0.2	1.2 ± 0.1	1.2 ± 0.1
587, 589, 593 (middrive 1), 593 (end of drive), 595	Deflated Hummocky unit-Point Coulomb member (conglomerate/ pebble sandstone)	Jum Jum RP (sol 550) <sup>b</sup>	1.4 ± 0.1	12.1 ± 0.2	1.8 ± 0.2	1.8 ± 0.2

<sup>a</sup>The DAN Cl corrected values are derived from the DAN chlorine-equivalent values corrected for the Fe concentrations measured by APXS at the analog targets (see column # 5).

<sup>b</sup>There is no analog of APXS observations made at Kimberley at Deflated Hummocky Unit. Based on the analysis of surface properties we selected for that purpose, Jum Jum RP target was measured by APXS on sol 550.

as chlorine in the near subsurface. DAN samples a cylindrical volume of the subsurface defined at the surface by the footprint of the instrument, which has a radius of about 1.5 m, down to a depth of ~60 cm. DAN's ability to measure several cubic meters of the shallow subsurface makes it the ideal instrument to test how representative Curiosity's surface measurements of water and Cl obtained by SAM analysis of drill samples (taken from a depth ~6 cm) and APXS measurements at a very shallow depth (~50 μm) are at greater depths below the surface.

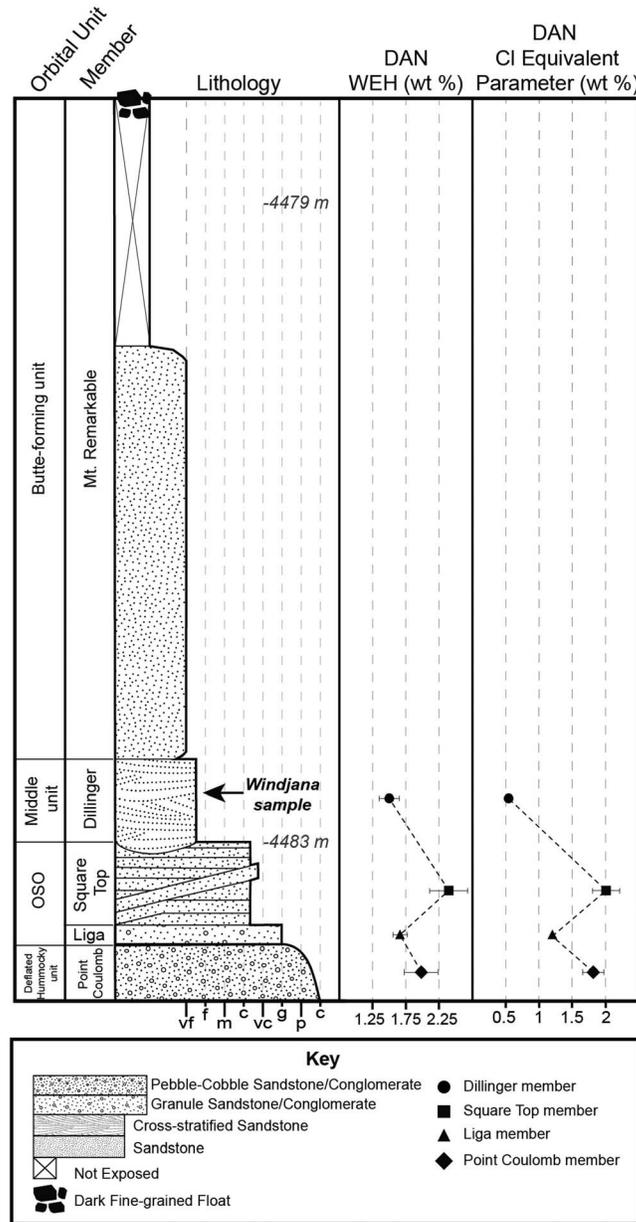
### 3.2. Overview of DAN Data Reduction Procedures

Numerical modeling of the epithermal and thermal neutron die-away curves measured during DAN active measurements can be used to convert experimental data into estimates of subsurface water and chlorine. The modeling procedure uses a two-layer model that tests the hypothesis that DAN die-away curves can be produced by a given distribution of hydrogen/water and neutron-absorbing elements in the Martian subsurface. (see Litvak *et al.* [2014], Mitrofanov *et al.* [2014], and Sanin *et al.* [2015] for a detailed explanation). If the thickness of the top layer is larger or comparable with the depth to which DAN is sensitive, 40–60 cm, then DAN observes it as homogeneous layer. A particular active measurement is compared to a set of numerical models with different regolith parameters [Mitrofanov *et al.*, 2014; Litvak *et al.*, 2014, Sanin *et al.*, 2015], and a best fit correspondence is performed between experimental data and the models using the Pearson  $\chi^2$  statistical criterion.

The presence of elements such as Cl, Fe, Ti, Mn, and Gd in Martian regolith or rock can influence observed thermal neutron count rates and the timing of die-away curves [Hardgrove *et al.*, 2011; Litvak *et al.*, 2014; Mitrofanov *et al.*, 2014]. Mitrofanov *et al.* [2014] showed that the content of chlorine should be selected as a variable parameter in DAN modeling using fixed abundances of other neutron-absorbing elements at the average level measured by APXS. This model parameter was introduced as a chlorine-equivalent parameter to account for all absorbers of thermal neutrons in DAN measurements [Mitrofanov *et al.*, 2014; Litvak *et al.*, 2014, Sanin *et al.*, 2015, Tate *et al.*, 2015]. In the analysis presented here, we compare the chlorine-equivalent parameter with Cl concentrations measured by APXS. APXS also measured the elemental abundance of Fe in regolith and bedrock targets [Gellert *et al.*, 2014; Gellert and Clark, 2015]. After Cl, Fe is the second most important neutron absorber that can influence DAN die-away curves [Hardgrove *et al.*, 2011; Mitrofanov *et al.*, 2014], and Mitrofanov *et al.* [2014] showed that large variations of Fe could modify chlorine-equivalent concentrations from the true concentration of chlorine by 5–10% (relative). In the DAN-APXS comparison presented here, we selected APXS observations measured at the same locations as DAN measurements when possible or compared measurements of similar geologic members and surface materials encountered at the Kimberley waypoint. We used APXS Fe concentrations to correct DAN estimations of the chlorine-equivalent parameter to the true concentration of Cl and compared it with APXS Cl measurements.

### 3.3. Geologic Classification of DAN Measurements

DAN measurements were classified according to geologic unit mapped in orbital HiRISE images and according to geologic members identified on the surface using images from Curiosity's rear engineering camera (Hazcam)



**Figure 2.** A composite stratigraphic column for the Kimberley formation modified from *Stack et al.* [2016] showing the correlation between Kimberley formation members, orbital units, and lithology. The relative thicknesses of the different members are approximately to scale, with elevations annotated within the lithology column. Average values of WEH and the CI-equivalent parameter for each member measured by DAN are plotted against the stratigraphic column.

parameter, and APXS-corrected CI concentration are averaged for all measurements within the category and are reported in Table 1. These measured values are also plotted against the stratigraphic column (see also *Stack et al.* [2016]) presented in Figure 2 in order to evaluate the change in these values as a function of stratigraphic position within the Kimberley formation examined by the rover.

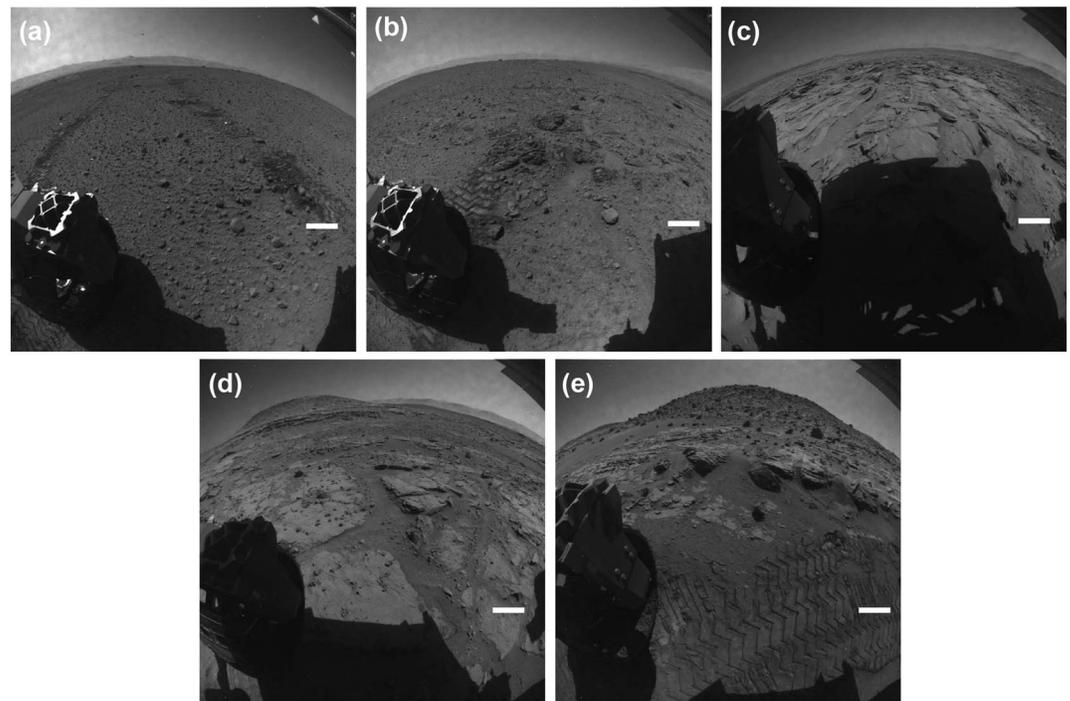
#### 4. Results From the Kimberley Observational Campaign

Raw experimental data acquired from DAN measurements during the Kimberley campaign show significant variability in the bulk water and chlorine distributions. In addition, WEH measured at the Kimberley area in

that were acquired during each DAN active observation (Table 1 and Figure 3). Hazcam images are representative of the rear half of DAN footprint, which is centered on the back two wheels of Curiosity. Therefore, the rear Hazcams only capture about half of the material that each DAN observation is sensitive to.

DAN observations of sand and loose rock of the Smooth Hummocky unit were distinguished from those measured over bedrock of the Kimberley formation. Observations of Smooth Hummocky unit (first row in Table 1) are best compared to the Lagrange APXS soil target. To determine whether the composition of this unit changed spatially throughout the rover's traverse of the Kimberley waypoint, the time series of water concentration in top and bottom layers modeled by DAN and the same time series for chlorine-equivalent values are presented in Figure 4. Both the Square Top member and the Liga members were mapped from orbital images as part of the Orbital Striated Outcrop. Since it is sometimes difficult to distinguish the coarse pebble sandstones of the Liga member from the very coarse sandstones of the Square Top member in the rear Hazcams, we have grouped DAN observations in the vicinity of the Liga target together (sol 597 and sol 603 DAN observations) and categorized these measurements as OSO-Liga member; the DAN observation from Sol 593, which was clearly measured Square Top, is referred to as OSO-Square Top member.

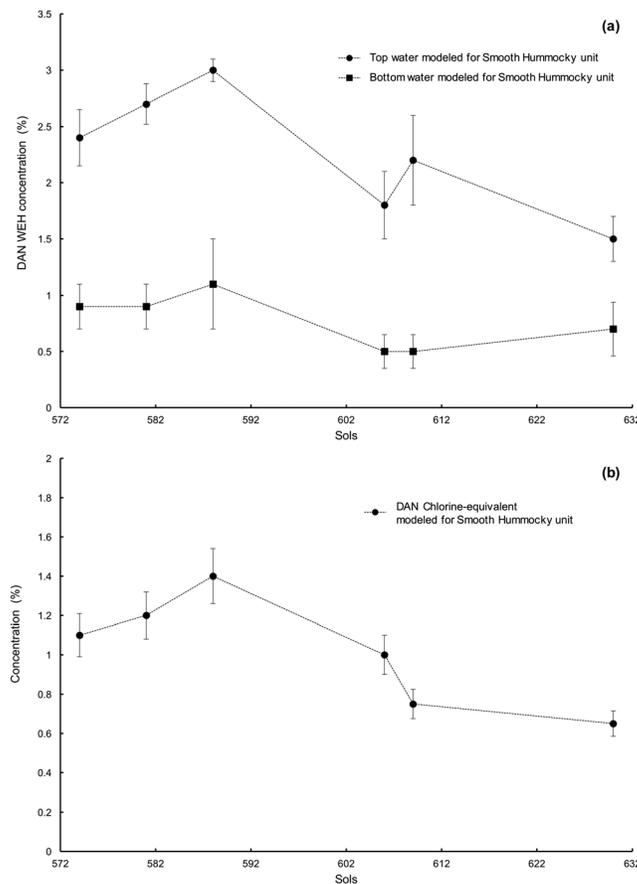
For each category, the water equivalent hydrogen (WEH), chlorine-equivalent



**Figure 3.** Example geologic units sampled by the DAN instrument at Kimberley viewed in radiometrically corrected images from Curiosity's left Rear Hazard Avoidance Camera (Hazcam). Scale bar in each image represents 10 cm at the distance at which it is placed. (a) Sand and loose rocks of the Smooth Hummocky unit, sol 581 end-of-drive location. (b) Conglomerate of the Point Coulomb member of the Kimberley formation, sol 593 first middrive stop. (c) Coarse sandstone of the OSO-Square Top member, sol 593, second middrive stop. (d) Coarse sandstone and pebble sandstone of the OSO-Liga member, sol 597 second middrive stop. (e) Partial view of the very fine sandstone of the Dillinger member in the vicinity of the Windjana drill hole, sol 630 middrive stop.

average is lower than values observed along the whole Curiosity traverse [see *Mitrofanov et al.*, 2014, 2016] and those observed during the DAN observational campaign in Yellowknife Bay area [*Litvak et al.*, 2014]. An average of DAN measurements of the Smooth Hummocky unit (sand and loose rocks) results in a bulk WEH concentration equal to  $1.6 \pm 0.2$  wt %. It is heterogeneously distributed with depth:  $2.1 \pm 0.2$  wt % WEH in the top layer with the thickness equal to  $14 \pm 2$  cm and  $0.5 \pm 0.1$  wt % WEH modeled for the bottom layer. The average chlorine-equivalent parameter for DAN measurements of the Smooth Hummocky unit is  $1.0 \pm 0.1$  wt %. For comparison, an APXS observation on the Lagrange target shows 0.8 wt % Cl and 16 wt % Fe. Correcting the chlorine-equivalent parameter measured by DAN with the Fe concentration measured by APXS (in comparison to the value of 12 wt % of Fe used in the DAN numerical model) leads to a DAN estimation of  $0.9 \pm 0.1$  wt % for the true bulk concentration of chlorine in this unit, which is very close to local and uppermost surface estimations from APXS. DAN measurements of the Smooth Hummocky unit plotted as a function of sol number (Figure 4) shows that both WEH and Cl decreased slightly as Curiosity drove from north to south along the edge of the main Kimberley outcrop (Figure 1). The Cl and WEH of the loose sand and soils of the Smooth Hummocky unit are lower than the Cl and WEH measured for the bedrock of the Kimberley formation (excluding the Dillinger member).

The average WEH distribution detected in the conglomerates of the Point Coulomb member, the basal member of the Kimberley formation (mapped as Deflated Hummocky unit in orbital images) is  $2.0 \pm 0.3$ % and the chlorine-equivalent parameter is  $1.8 \pm 0.2$ %. Unfortunately, APXS did not measure conglomerates at the Kimberley outcrop, although the Jum Jum conglomerate target in nearby Moonlight Valley is proposed as a suitable analog. According to APXS, Jum Jum contains 1.4 wt % chlorine and 12.1 wt % iron. The concentration of iron measured by APXS for Jum Jum is equivalent to the assumption of iron composition in the DAN elementary model of the subsurface, so correction of the DAN chlorine-equivalent value was not needed. For the Point Coulomb member conglomerates, DAN and APXS measured comparable chlorine composition.



**Figure 4.** (a) DAN estimations of water distribution in the subsurface while rover was crossing Smooth Hummocky unit (boundary with Kimberley formation). (b) DAN estimations of chlorine-equivalent concentration in the subsurface while rover was crossing Smooth Hummocky unit (boundary with Kimberley formation).

member,  $2.0 \pm 0.2\%$ , is also relatively high compared to measurements elsewhere in the Kimberley formation and surrounding area. APXS analog measurements for the OSO-Square Top member include Square Top, Pandanus Yard, and the Virgin Hills targets. APXS detected 0.9–1.1 wt % chlorine and 15.9–18.1 wt % Fe for these OSO-Square Top targets. The concentration of iron in the OSO-Square Top targets measured by APXS is significantly higher than those used in the DAN elemental composition model. Correcting the DAN chlorine-equivalent parameter using the true bulk chlorine concentration leads to a DAN Cl value of  $1.8 \pm 0.2$  wt %, which is still significantly higher than local surface measurements provided by APXS.

DAN observations of the Dillinger member in the vicinity of the Windjana drill show that WEH distribution is best modeled with bulk water  $1.5 \pm 0.2$  wt % and a chlorine-equivalent parameter of  $0.6 \pm 0.1$  wt %. DAN measurements are compared with SAM estimations of low-temperature absorbed  $H_2O$  extracted from the Windjana drilled sample and APXS measurements of the elemental composition of drill fines. SAM revealed that absorbed water in a small sample taken from the very top layer of the outcrop surface (drilling depth is about 6 cm) is equal to  $1.8 \pm 0.4$  wt % [Mahaffy *et al.*, 2012]. This measurement corresponds well with DAN estimations evaluated across the DAN footprint radius of 1.5 m within measurement uncertainties. In both cases the amount of water estimated is less than 2 wt %. The APXS analysis of drill fines found chlorine and Fe concentrations of  $\sim 0.8$  wt % and  $\sim 20$  wt %, respectively. Applying the correction for APXS Fe concentration using these values to the DAN chlorine-equivalent values results in a true range in the concentration of chlorine of 0.4 wt %, which is less than but comparable with the APXS measurement.

Figure 2 and Table 1 show fluctuations in the WEH measured by DAN as a function of stratigraphic position. WEH measured within the Kimberley formation ranges from 1.5 TO 2.4 wt %. The coarse sandstone outcrops (OSO/Square Top member) and some measurements acquired near the conglomerates of the Point Coulomb

DAN measured the OSO-Liga member during a middrive observation on sol 597. The water distribution in this area is well described by a homogeneous model with  $1.7 \pm 0.1$  wt % of WEH. The chlorine-equivalent parameter for the OSO-Liga member was measured to be 1.2 wt %. The APXS Liga target, which detected 1.9 wt % chlorine and 13 wt % Fe, is used as the analog for these DAN measurements. The Fe value measured by APXS for Liga is very similar to the Fe value used in the DAN model, suggesting that in this case, correction of the chlorine-equivalent parameter measured by DAN is not necessary. It means that for the OSO-Liga member, DAN measures 1.2 wt % bulk chlorine compared to 1.9 wt % chlorine measured by APXS on the surface.

On sol 593, DAN rover acquired the first measurements of the OSO-Square Top member. The measurements reveal a nearly homogeneous distribution of WEH with an average concentration of  $2.4 \pm 0.3$  wt %. The OSO-Square Top measurement is one of the highest observations of water content made during the entire Kimberley campaign (Table 1 and Figure 2). The concentration of chlorine in the Square Top

member show elevated concentrations of bulk water. Average WEH decreases from the conglomerates of the Point Coulomb member into the coarse pebble sandstone of the OSO-Liga member. WEH then increases from the OSO-Liga member into the OSO-Square Top member, but decreases significantly from the OSO-Square Top member to the Dillinger member. The lowest values of WEH detected by DAN at Kimberley are in the fine sandstones of the Dillinger member.

DAN also measures a decrease in CI from the basal conglomerates of the Point Coulomb member into the coarse sandstones and pebble conglomerates of the OSO-Liga member (Figure 2). CI then increases from the OSO-Liga member into the OSO-Square Top member before decreasing significantly from the OSO-Square Top member to the Dillinger member.

In summary, the DAN measurements demonstrate spatial and stratigraphic variation in the distribution of WEH and chlorine-equivalent concentrations at different geological members of the Kimberley formation and between bedrock and surface materials sampled by the rover. The comparison of DAN measurements with those from SAM and APXS demonstrate that the derived WEH and CI-equivalent parameters from DAN are consistent with geochemical measurements from other instruments and show similar correlations with stratigraphy.

## 5. Discussion

DAN profiles of deconvolved WEH distribution (Figure 4a) show that the subsurface of the Smooth Hummocky unit around Kimberley is best described by a two-layer model with  $2.1 \pm 0.2$  wt % water in a top layer (with thickness of  $14 \pm 2$  cm) and  $0.5 \pm 0.1$  wt % water in the bottom layer. It is accepted with confidence level about 30% (this probability demonstrates correspondence between model and experimental data, see *Sanin et al.* [2015]) while simplest homogeneous model of subsurface could be rejected because its confidence level is about 1% only. This suggests that DAN measurements of the Smooth Hummocky unit are best modeled by an “inverse” two-layer distribution, with a higher concentration of water in the relatively thin top layer. This deviates from a natural geological assumption that a wetter layer should be located at shallow depth and a drier layer on the top, although the quantity of water measured by DAN in the top layer of the Smooth Hummocky unit is consistent with SAM measurements of  $\sim 2$  wt % low-temperature absorbed  $H_2O$  extracted from scoop at Rocknest (best analog of Smooth Hummocky where SAM measurements were performed).

Although the majority of DAN measurements obtained along the Curiosity traverse are most consistent with either a homogenous single-layer (containing  $\sim 2.1$  wt % WEH) or a two-layer model containing a dry upper soil layer (2.1 wt % WEH,  $\sim 25$  cm thick) and a wetter layer below (5.5 wt % WEH), an inverse water distribution similar to that observed in the Smooth Hummocky unit at Kimberley has been periodically observed before [*Mitrofanov et al.*, 2014, 2016]. Even still, it is difficult to explain the origin of the inverse two-layer model fit for the Smooth Hummocky unit at Kimberley, given the comparatively short traverse and uncertainties about the true thickness of the sand and rock mantle that appears to comprise the upper part of the Smooth Hummocky unit, and about what bedrock units may occur beneath the surface mantle. One possibility is that the “wetter” upper layer observed by DAN at Kimberley can be explained by the distribution of hydrated minerals in the near subsurface. The loose rocks that comprise the Smooth Hummocky unit may have been transported to Kimberley from other parts of Gale crater or even from outside of the crater and could contain an increased proportion of hydrous minerals relative to the in-place bedrock or other transported materials encountered throughout the majority of Curiosity’s traverse. The presence of intermittent conglomerate outcrops exposed in the Smooth Hummocky and Deflated Hummocky units may also contribute to the hydrous upper layer observed by DAN in the Smooth Hummocky unit at Kimberley. The presence of slighter elevated water content in the uppermost Smooth Hummocky layer could be also explained by increased adsorbed water in the soil [*Mitrofanov et al.*, 2014]. Comparison between DAN model results with local variations in thermal inertia and water vapor derived from the REMS data may provide additional insight into the origin of DAN measurements, but this analysis was considered outside the scope of this present effort.

DAN measurements also show an overall decrease in WEH and CI in the Smooth Hummocky unit as the rover traversed from north to south around the main Kimberley outcrop (Figure 4). The fact that this overall decrease correlates with Curiosity’s transition from the Point Coulomb, OSO-Square Top, and OSO-Liga members (relatively higher WEH and CI) to the Dillinger member (lower WEH and CI) suggests that DAN may be detecting this change in bedrock underlying the surface materials of the Smooth Hummocky unit. Continued analysis of DAN

observations along the Curiosity rover traverse in the context of the local geology and transported surface materials may make correlations between DAN model results and geological units more robust.

Previous studies have shown that DAN measurements are also sensitive to the presence of neutron-absorbing elements (foremost chlorine and iron [Hardgrove *et al.*, 2011; Mitrofanov *et al.*, 2014]). DAN can evaluate the chlorine-equivalent concentration, for which the variability in subsurface neutron absorption capability is attributed to chlorine while concentrations of other neutron absorption elements (like Fe) are fixed at their average level. DAN measurements at Kimberly show that the variability of chlorine-equivalent concentration is significant and varies between 0.6 and 2.0 wt % depending on the geologic unit measured (Figure 2) and as WEH estimations correlated with the stratigraphy of Kimberly formation. The variations in Cl and WEH observed by DAN in the members of the Kimberly formation are consistent with variations observed by DAN in similar surface materials observed previously in Gale [Mitrofanov *et al.*, 2014; Litvak *et al.*, 2014].

The DAN results at Kimberly are consistent with measurements made by Curiosity's APXS instrument. The concentrations of major neutron-absorbing elements detected by APXS ranged in 0.7–3.0 wt % for Cl and 17–27 wt % for FeO. In our analysis, DAN and APXS measurements of chlorine were compared using additional correction of DAN chlorine-equivalent values for different Fe concentration measured by APXS. A comparison of these results is presented in Table 1. In most cases surface measurements of chlorine provided by APXS show relative good correlation with bulk abundances (in several metric tons of material under the rover) derived from the DAN data.

It is important to note that the average bulk water and chlorine contents measured in the Kimberly formation are significantly different compared to estimates obtained from global orbital mapping of the Gale region from neutron and gamma spectrometers on board the Mars Odyssey mission [Boynton *et al.*, 2002, 2006; Feldman *et al.*, 2002, 2011; Maurice *et al.*, 2011; Mitrofanov *et al.*, 2002]. The orbital observations acquired above the Gale region corresponds to 5–7% of WEH and ~0.6% in chlorine. This difference, in principle, could be explained by the difference in footprint size between orbital- and ground-based instruments. For Odyssey horizontal resolution covers the area with radius of about 300 km, which is significantly larger than the size of the Gale crater. The DAN instrument, with its ability to sample the subsurface at a scale intermediate between large-scale orbital observations and small-scale observations made by the rover's other geochemistry instruments, fills a crucial gap in our understanding of subsurface hydration and elemental geochemistry. Therefore, we conclude that the results of a comparative analysis of DAN, APXS, and SAM data for similar stratigraphic units presented in this study show the benefits of complimentary measurements and illustrate how cross-calibrated measurements from multiple rover instruments can be used to study the heterogeneity of the Martian subsurface.

#### Acknowledgments

The numerical simulations of water distribution performed in this work are supported by grant 14-22-00249 from the Russian Science Foundation. U.S. DAN team members, coauthors of this paper, are supported by contracts from NASA/JPL. Part of the research was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. Instrument data used here are publically available through the NASA Planetary Data System ([https://pds.jpl.nasa.gov/tools/subscription\\_service/SS-Release.shtml](https://pds.jpl.nasa.gov/tools/subscription_service/SS-Release.shtml), see, for details, Mars Science Laboratory Data Releases with APXS and DAN data). The DAN team is thankful to the highly professional MSL project team members who have maximized opportunities for DAN measurements on Mars. The DAN team very much appreciates the work of colleagues from the N.L. Dukhov Institute for Automatics for the development of the reliable pulse neutron generator for this experiment. Finally, the team thanks the Curiosity science team, which provided essential comments and advice to the DAN team during numerous discussions.

## 6. Conclusion

1. An average of DAN measurements of the Smooth Hummocky unit (sand and loose rocks) results in a WEH concentration equal to  $1.6 \pm 0.2$  wt % with the average WEH in the top layer modeled at  $2.1 \pm 0.2$  wt % WEH, the thickness of the top layer equal to  $14 \pm 1$  cm, and  $0.5 \pm 0.1$  wt % WEH modeled for the bottom layer. The average chlorine-equivalent parameter for DAN measurements of the Smooth Hummocky unit is  $1.0 \pm 0.1$  wt %.
2. DAN measurements of the Smooth Hummocky unit plotted as a function of sol number (Figure 4) shows that both WEH and Cl decreased as Curiosity drove from north to south along the edge of the main Kimberly outcrop. This decrease may represent a change in the composition of the bedrock underlying the Smooth Hummocky unit.
3. DAN measurements demonstrate stratigraphic variation in the distribution of WEH and chlorine-equivalent concentrations at different geological members of the Kimberly formation. WEH measured within the Kimberly formation ranges from 1.5 to 2.4 wt %, while Cl measured within the Kimberly formation ranges from 0.4 to 1.8 wt %.
4. The comparison of DAN measurements with those from SAM and APXS demonstrates that the derived WEH and Cl-equivalent parameters from DAN are consistent with geochemical measurements from these other geochemical instruments on board Curiosity.

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