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## RESEARCH LETTER

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### Key Points:

- Results support hypothesis that indigenous fluids incorporated into Tissint fissures on Mars and resulting chemical signatures preserved
- Differences between soluble chemistry of Tissint and strewn field soil suggest that terrestrial contamination from recovery site is unlikely
- Analyses provide a glimpse into the chemical composition of a potentially habitable brine on early Mars

### Supporting Information:

- Supporting Information S1

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## Indigenous Organic-Oxidized Fluid Interactions in the Tissint Mars Meteorite

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**Abstract** The observed fall and rapid recovery of the Tissint Mars meteorite has provided minimally contaminated samples of the Martian surface. We report analyses of Tissint for organic compounds by pyrolysis-gas chromatography-mass spectrometry and for soluble salts by ion chromatography. Pyrolysis-gas chromatography-mass spectrometry analysis shows the presence of organic compounds similar to those in the Mars EETA79001 and Nakhla meteorites. The organic profile is dominated by aromatic hydrocarbons, including oxygen and nitrogen-containing aromatics, and sulfur-containing species including thiophenes. The soluble salts in Tissint are dominated by sulfate and various oxidation states of chlorine, including perchlorate. The organic compounds and salts in the soils from the Tissint recovery strewn field differ significantly from those found in Tissint suggesting minimal terrestrial contamination. Our results support the hypothesis that the soluble inorganic components of Tissint are most likely a result of indigenous fluid inclusion, thus providing a glimpse into the composition of early Martian fluids.

**Plain Language Summary** Meteorites that come from Mars usually become contaminated after landing on Earth. One Mars meteorite, named Tissint, was seen falling in the dry Moroccan desert, and many of its pieces were collected within months. We analyzed the meteorite and the local soil for organic compounds and soluble salts. We found differences between the Tissint meteorite and the local soil that suggest that Tissint is uncontaminated. The analyses also showed that the soluble salts in Tissint most likely came from Martian fluids that were similar to terrestrial seawater.

### 1. Introduction

Although landed and orbital missions have observed evidence of past aqueous alteration of much of the Martian surface (Bandfield et al., 2011; Ehlmann et al., 2009; Ming et al., 2008), little is known about the chemistry of indigenous Martian fluids. Analyses of Martian meteorites are used to understand the history of geological processes, the presence of trapped volatiles, and the historical persistence of water on Mars (Chen Sutter et al., 2015; Wentworth et al., 2005a; Karlsson et al., 1992; Gooding et al., 1988). Thus, soluble inorganic salts trapped in these meteorites can contribute to our understanding of the aqueous history of Mars, but few analyses have been reported (Grady et al., 1995; Kounaves et al., 2014; Wright et al., 1999). The Nakhla and ALH 84001 Mars meteorites have been found to contain water soluble sulfate ( $\text{SO}_4^{2-}$ ) and chloride ( $\text{Cl}^-$ ), suggesting that they may have been in contact with a briny water on Mars (Bridges & Schwenzer, 2012; Hicks et al., 2014; Sawyer et al., 2000). Similarly, a sample of sawdust obtained from a cross section of the Mars meteorite EETA79001 was found to contain a variety of soluble salts, including perchlorate ( $\text{ClO}_4^-$ ), chlorate ( $\text{ClO}_3^-$ ), nitrate ( $\text{NO}_3^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ), indicating highly oxidizing conditions (Kounaves et al., 2014). Although isotopic analysis of the sawdust and surrounding terrestrial material indicated no contamination, prolonged terrestrial residence time of EETA79001 within the Antarctic ice complicated assessments of any indigenous alteration.

Organic matter is also expected on the surface of Mars due to meteoritic input (Flynn, 1996; Flynn et al., 2004) but has so far proven difficult to detect in situ (Freissinet et al., 2015; Leshin et al., 2013; Ming et al., 2014) with only a limited range of putative indigenous organics being detected (Eigenbrode et al., 2018; Freissinet et al., 2015). This is due to not only the limits of landed scientific payloads but also the confounding effects of oxidizing minerals, especially perchlorate salts, initially discovered by the Phoenix

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Wet Chemistry Lab (WCL) and whose presence in the regolith can prevent their analysis and/or contribute to their alteration or destruction (Glavin et al., 2013; Hecht et al., 2009; Kounaves et al., 2010; Sutter et al., 2015). Until a successful Mars sample return mission, Martian meteorites represent a unique opportunity for laboratory-based organic and geochemical study of Mars' surface. Unfortunately, most Mars meteorites have been collected long after falling to Earth and have thus experienced variable degrees of weathering and exposure to organic contaminants, confounding attempts to discriminate between relative contributions of contamination (Bada et al., 1998).

Tissint is the most pristine Mars meteorite collected to date, having been observed to fall on 18 July 2011 near the Oued Drâa Valley in Morocco, with fragments collected over the following months in this remote and arid desert area. Initial mineralogical and geochemical studies of Tissint have indicated that it is a depleted shergottite, containing entrained Martian atmosphere and possible surface components within impact glass veins (Aoudjehane et al., 2012). The inclusion of organic carbon and elemental enrichments within the melts have generated uncertainty as to whether they are the result of inclusion of a Mars surface component, sub-surface weathering from fluid interactions, or contamination from the Moroccan soils (Aoudjehane et al., 2012; Brennecka et al., 2014; Lin et al., 2014; Barrat et al., 2014; Chen Sutter et al., 2015; Peters et al., 2015). Here we present analyses of the organic compounds and soluble inorganic salts extracted from a crushed homogenized internal fragment of Tissint and compare them to a statistical sampling of the strewn field soils, thus adding the important context of the terrestrial environment from which it was collected. By analyzing these soils, we are able to identify and quantify potential terrestrial contamination and thus constrain the provenance of the soluble inorganic salts and organic compounds in Tissint as Martian. Furthermore, our direct measurements of  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$ , and  $\text{SCN}^-$  confirm the hypothesis of Steele et al. (2018) that indigenous Martian fluids were incorporated into fissures in the Tissint meteorite's host rock on the surface of Mars.

## 2. Materials and Methods

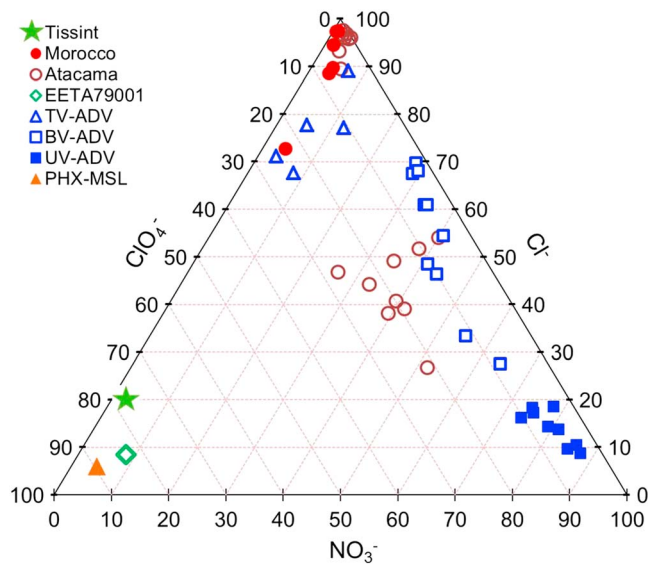
### 2.1. Description of Tissint Fragment and Strewn Field Samples

The  $4.0 \pm 0.1$ -g Tissint fragment used (Figure S1 in the supporting information) was obtained from the Natural History Museum (London) and was originally part of a larger 25-g piece (BM.2012.M3) collected within the meteorite strewn field site centered at  $29^\circ 28.917' \text{N}$ ,  $7^\circ 36.674' \text{W}$ , sometime between October and December 2011. One side of the fragment (~25%) was coated with a thin layer of fusion crust. The petrology of Tissint has been previously described (Aoudjehane et al., 2012; Gattacceca et al., 2013; Walton et al., 2014). It is classified as a Martian basaltic shergottite with olivine macrocrysts set in a fine-grained matrix of pyroxene and feldspathic glass with a highly fractured matrix penetrated by dark shock veins and patches filled with black glassy material enclosing bubbles. The petrology of Tissint is similar to that of other picritic shergottites and especially lithologies A and C of EETA79001 (Aoudjehane et al., 2012).

Details of the strewn field soil sampling and analyses are described elsewhere (Oberlin et al., 2018). In summary, 12 sampling sites were centered within a 6-km radius of the center of the strewn field, spanning a morphologically stable plateau and a valley floor with evidence of ephemeral fluvial alteration. Two shallow pits were dug at each site; one underneath a location in which the soil was protected by a well-developed rocky desert pavement and another from a location within 20 m that appeared to have interacted with water or wind more recently, as indicated by fluvial channels or localized patches of light soil. At each site, the top layer of large desert pavement rocks was cleared and samples were taken from 0- to 5- and 15 to 20-cm depth. Samples were stored in sterile Whirl-Pak bags. The procedure was repeated throughout the strewn field to obtain representative coverage. Soil samples were returned to the laboratory and split into three fractions: coarse ( $>2$  mm), sand (2 mm to  $75 \mu\text{m}$ ), and fine ( $<75 \mu\text{m}$ ).

### 2.2. Soluble Inorganic Analysis

The sample of Tissint analyzed consisted of a 1.0-g fragment cleaved as far as possible from the fusion crust and ground to a powder in an agate mortar and pestle. The powder was leached in 18.2-M $\Omega$  water at a ratio of 1:10 for 1 hr with gentle rocking. The leachate was removed and filtered through a 0.2- $\mu\text{m}$  syringe filter prior to analysis by ion chromatography (IC) with conductivity detection (conditions in Table S1). A second 1.0-g fragment closer to the fusion crust was cut, ground, and leached in the same manner and sent for



**Figure 1.** A ternary  $\text{NO}_3\text{-ClO}_4\text{-Cl}$  normalized ratio plot for direct measurements of the Martian regolith by Phoenix and Curiosity (orange triangle), leaching analysis of Tissint (green star) and EETA79001 (green diamond), and various Mars analog environments surface measurements including the Antarctic Dry Valleys (blue triangles and squares), the Atacama Desert (brown circles), and the Tissint strewn field (filled red circles).

meter (GC-MS). The GC inlet was held at 270 °C and operated in split mode (10:1) with a column flow rate of 1.1 ml/min. Separation was performed on a DB-5MS Ultra Inert column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). The GC oven was held for 2 min at 40 °C and then ramped at a rate of 5 °C/min to 310 °C where it was held for 10 min. Mass spectra were acquired over a range of  $m/z$  45–550. Identification of peaks in the resulting chromatographs was carried out using the Agilent MSD Chemstation® software package and peak identification was by comparison to the NIST database and published literature.

### 3. Results

#### 3.1. IC

The soluble anions leached from Tissint were dominated by  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , while cations were dominated by  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . Several other oxidation states of chlorine were present with  $\text{ClO}_3^-$  the most abundant (4.2 ppm) followed by  $\text{ClO}_2^-$  (0.6 ppm) and  $\text{ClO}_4^-$  (70 ppb). In addition, bromide ( $\text{Br}^-$ ), nitrate ( $\text{NO}_3^-$ ), and phosphate ( $\text{PO}_4^{3-}$ ) were detected at trace levels (see Table S2 for all ions measured). The second portion from closer to the fusion crust did not reveal  $\text{ClO}_4^-$  above the limit of detection (2.5 ppb in the leach) when analyzed via IC. However, analysis by ion chromatography-mass spectrometry with a detection limit of 0.05 ppb confirmed the presence of 2 ppb  $\text{ClO}_4^-$  in the solid sample of the second portion. During analysis with the ultralow hydrophobicity AS16 column, an unidentified peak was observed at approximately 10.4-min retention time; this peak was not observed during the interference and recovery experiments performed with the EETA79001 powder. Subsequent testing of all ions identified in the Tissint leachate, as well as for thiosulfate, iodide, and thiocyanate, which are known to be retained by the AS16 column, revealed that thiocyanate ( $\text{SCN}^-$ ) elutes under the method conditions at  $\sim$ 10.5 min, suggesting it as a likely source of the unidentified peak. An independent calibration of  $\text{SCN}^-$  was performed from 1 to 1,000 ppb, and the peak area correlated with a concentration of  $\sim$ 150 ppb.

Detailed analysis of the soluble inorganic component of strewn field samples is presented elsewhere (Oberlin et al., 2018). In summary, analysis of the strewn field samples indicated no surface  $\text{ClO}_4^-$  concentrations above a 25-ppb limit of detection. Of the 36 samples taken from 20-cm depth, 17 showed evidence of  $\text{ClO}_4^-$  above the limit of detection with only eight samples containing concentrations at or above those observed in the Tissint meteorite sample. The surface strewn field data for  $\text{NO}_3\text{-ClO}_4\text{-Cl}$  shown in Figure 1, along with data from Mars (Tissint, EETA79001, Phoenix WCL), Curiosity Sample Analysis on

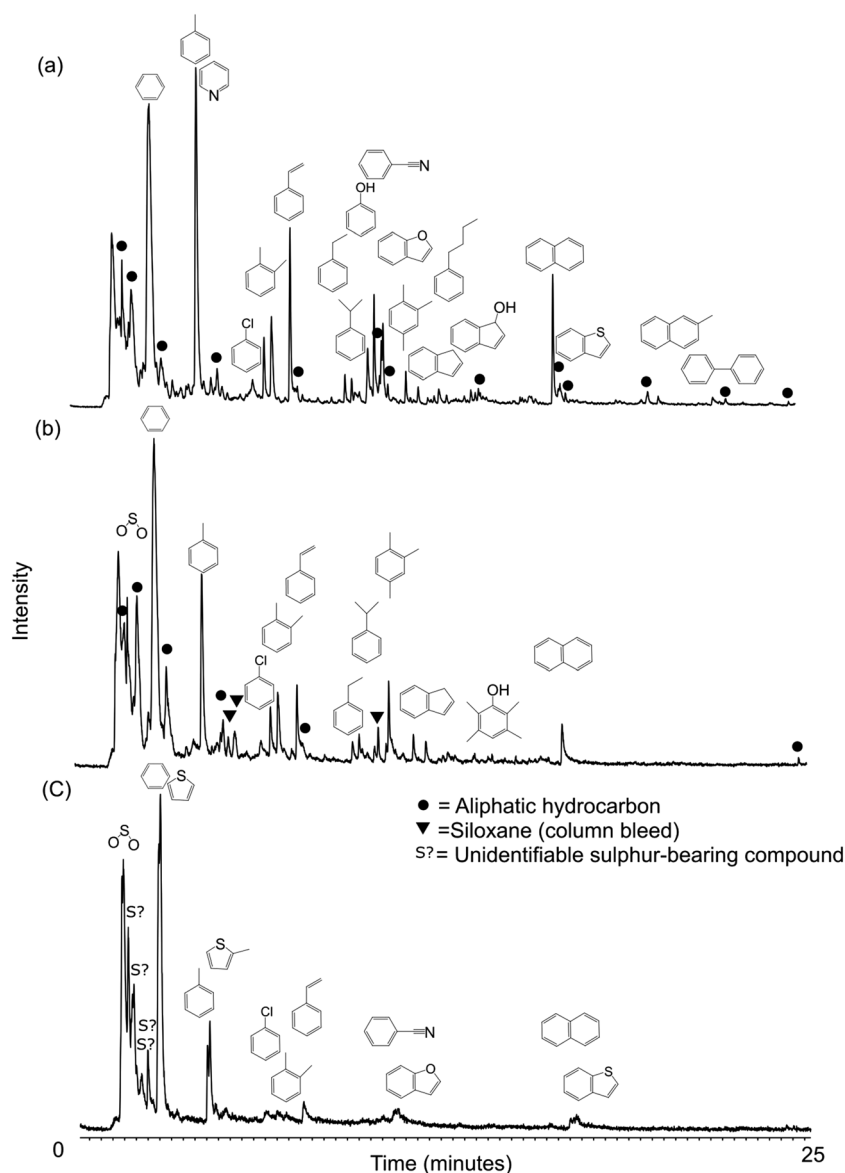
analysis by ion chromatography-mass spectrometry to Exova Inc (Santa Fe Springs, CA). Approximately 2 ml of the leachate from this second fragment was analyzed by IC for  $\text{ClO}_4^-$ . Matrix interference and recovery experiments for the Dionex AS16 column were performed on previously leached portions of EETA79001 powder remaining from previous Mars meteorite work (Kounaves et al., 2014). Concentration of the original spiking solution fell within the error of the recovered concentrations (Figure S2).

A 1.0-g portion of each strewn field sample of sand and fine fraction was leached at a 1:10 soil:water ratio and analyzed for  $\text{ClO}_4^-$  under the same chromatographic conditions as the Tissint meteorite sample. The samples were then diluted to a conductivity of 50  $\mu\text{S/cm}$  and analyzed for inorganic anions and cations.

#### 2.3. Organic Analysis

Powders of individual Moroccan strewn field soil and meteorite samples were loaded into quartz pyrolysis tubes, held in place with quartz wool, and placed inside the platinum coil of a 2500 Pyroprobe via a 1500 Valve Interface (both Chemical Data Systems Analytical) held at 280 °C under helium and heated at a rate of 20 °C/ms to the target temperature of 650 °C where it was held for 15 s.

Separation and identification of products were achieved using an Agilent Technologies 6890 gas chromatograph coupled to a 5973 mass spectro-

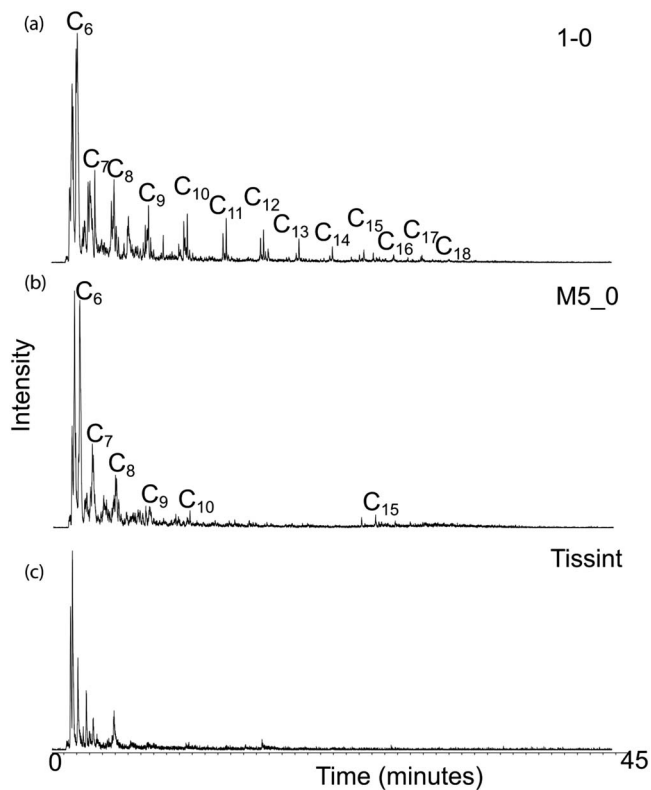


**Figure 2.** Pyrolysis-gas chromatography-mass spectrometry chromatograms of representative samples of (a) wetter strewn field surface soils (1\_0), (b) dryer surface soils (M5\_0), and (c) Tissint meteorite.

Mars (SAM)), and other terrestrial Mars analog environments, highlight the distinct ratios of soluble salts seen in Martian samples.

### 3.2. Pyrolysis-GC-MS

All Moroccan soil samples analyzed produced similar chromatograms with low organic compound responses indicating a low abundance of pyrolyzable organic matter. Similar molecules were identified in all samples (Figures 2a, 2b, 3a, and 3b) but in varying abundance, with alkenes/alkanes and aromatic hydrocarbons dominating. The chlorinated aromatic hydrocarbon chlorobenzene was present in small amounts in numerous samples, and nitrogen-containing pyridine and sulfur-containing benzo[b]thiophene were occasionally present in samples retrieved from sites with indication of fluvial activity. In general, there was a greater abundance and variety of organic compounds in the wetter locality samples than the drier locality ones. Contamination from collection and storage of materials is a possibility, but the exclusive appearance of alkene/alkane doublets in the sample with greatest habitability (i.e., wetter) implies a terrestrial biological origin for these compounds.



**Figure 3.** Pyrolysis-gas chromatography-mass spectrometry partially reconstructed chromatograms  $m/z$  55 and  $m/z$  57 showing aliphatic hydrocarbon composition of representative samples of (a) wetter locality surface soils (1-0), (b) dryer locality surface soils (M5\_0), and (c) Tissint meteorite. Alkene, alkane pairs are labeled with the carbon number of their chain length.

The Tissint meteorite (Figures 2c and 3c) also had a low abundance of organics, with the major pyrolysis products being the aromatic and alkyl-substituted aromatic hydrocarbons benzene, toluene, xylene, styrene, and naphthalene. The oxygen-containing aromatic benzofuran was present as was the nitrogen-containing benzonitrile. Chlorobenzene was also present. Sulfur-bearing compounds were significant with a range of thiophenes, sulfur dioxide, and a few unidentifiable but potentially sulfur bearing compounds eluting in the 1.30- to 2.30-min period. The large peak at the beginning of each trace, with a 45.1 base peak in the mass spectra, represents the coelution of low molecular weight volatile species.

#### 4. Discussion

Geochemical analyses of the Tissint meteorite reported by several groups on separate meteorite portions have shown varying results. Some have reported a light rare earth element enrichment, high sulfur concentrations, and abundant volatiles within impact melt veins compared to the whole rock (Aoudjehane et al., 2012; Brennecka et al., 2014; Gattacceca et al., 2013; Lin et al., 2014; Walton et al., 2014). However, analysis of several other impact melt pockets within Tissint failed to show these features (Barrat et al., 2014; Peters et al., 2015), and still other analyses reported variable abundances within a single sample and even within a single impact vein (Chen et al., 2015; Walton et al., 2014).

Several hypotheses have been proposed to explain this heterogeneity in Tissint: (1) regolith-derived components introduced in the absence of fluids (Gattacceca et al., 2013), (2) terrestrial contamination from the interaction of desert sand and dew during Tissint's brief residence in the hot desert environment (Barrat et al., 2014), and (3) fluid inclusions resulting in oxidation and precipitation of soluble material (Aoudjehane et al., 2012; Chen et al., 2015; Lin et al., 2014; Steele et al., 2018).

##### 4.1. Source of Organic Compounds in the Tissint

The compounds observed in Tissint are similar to compounds observed in other Mars meteorites. Although using a slightly different method and solvent to extract the samples to remove low molecular weight terrestrial contamination before pyrolysis, Sephton et al. (2002) also found the major pyrolysis products of EETA79001 and Nakhla to be predominately aromatic and alkyl-substituted aromatic hydrocarbons (benzene,  $C_1$ - $C_2$  alkylbenzenes and naphthalene) along with oxygen-containing (phenol) and nitrogen-containing (benzonitrile) aromatics.

Although they did not observe the sulfur and chlorine-bearing compounds we observed, chlorobenzene is one of the few indigenous organic molecules that has been detected on Mars by the SAM GC-MS onboard Curiosity (Freissinet et al., 2015). Thiophenes were also detected in samples of mudstone from Gale crater (Eigenbrode et al., 2018) and are routinely identified in extraterrestrial samples (Bandurski & Nagy, 1976; Komiya et al., 1993; Simmonds et al., 1969).

The organic compounds detected in the Moroccan soil samples are all typical breakdown products of biopolymers: benzofuran is a typical carbohydrate decomposition product (e.g., from cellulose; Pastorova et al., 1994), nitrogen-bearing compounds are indicative of amino acids or proteins (Tsuge & Matsubara, 1985), and the detection of midchain length alkene/alkane dominated aliphatic doublets up to  $C_{18}$  is indicative of pyrolysis of an aliphatic biopolymer (Boon et al., 1994; Oudemans et al., 2007). These compounds all indicate an extant or recent biological source (presumably algal) for the soil organic component in the wetter localities. The reduced abundance and variety of organic compounds in the drier soils, especially the disappearance of the unsaturated and longer chain (less stable) aliphatics, indicates a degraded, extinct, or "fossil" biological source. This is to be expected due to the more recently habitable conditions indicated by the evidence of current or recent water at the wetter localities.

**Table 1**  
Soluble Inorganics

Ion	Concentration (mmol/g)		Phoenix/ Tissint ratio
	Tissint	Phoenix	
Chloride	$5.4 \times 10^{-3}$	$1.1 \times 10^{-2}$	2
Bromide	$1.2 \times 10^{-4}$	$<1 \times 10^{-4}$	<1
Sulfate	$4.9 \times 10^{-3}$	$1.3 \times 10^{-1}$	27
Nitrate	$3.7 \times 10^{-2}$	$2.5 \times 10^{-2a}$	1
Perchlorate	$7.2 \times 10^{-6}$	$5.8 \times 10^{-2}$	8,115
Sodium	$1.8 \times 10^{-2}$	$3.3 \times 10^{-2}$	2
Potassium	$5.7 \times 10^{-4}$	$7.6 \times 10^{-3}$	13
Magnesium	$7.7 \times 10^{-3}$	$7.4 \times 10^{-2}$	10
Calcium	$2.3 \times 10^{-4}$	$1.3 \times 10^{-2}$	57

Note. Comparison of the soluble components of Tissint to the soluble portion of the Martian regolith analyzed by the Phoenix WCL.

<sup>a</sup>See Note 1 in supporting information.

Few compounds found within Tissint are unique to the sample, but the lack of identifiable aliphatics, which are abundant in the soil samples, precludes the terrestrial biological source we suggest for the organics in the soil samples. The dominance of sulfur-bearing compounds such as thiophenes, along with simple aromatics in the meteorite, suggests that these are indigenous compounds—or have, at least, come from a source other than the local Moroccan soil. The organic composition of Tissint is found to be very similar to that of EETA79001 and Nakhla, which were collected from the Antarctic ice and Egyptian farmland, respectively. The similarity of the detected compounds, despite the widely different fall site environments and subsequent terrestrial interactions, supports the suggestion that the detected organic matter comes from a common abiotic Martian source (Sephton et al., 2002).

The nondetection of aliphatic hydrocarbons distinguish Tissint and other Martian meteorites from carbonaceous chondrites. Both Murchison (a well-studied carbonaceous chondrite) and interplanetary dust particles

have been shown to contain aliphatic hydrocarbons, while aromatics (or olefins) have been detected in the Murchison but not interplanetary dust particles (Flynn et al., 2004). Pyrolysis GC-MS of selected carbonaceous chondrite meteorites, carried out by the same method as used for the Tissint sample, showed aliphatic hydrocarbons at detectable levels (Figure S3). The absence of aliphatic hydrocarbons in Tissint is, therefore, not an artifact of the analytical technique. The aliphatic hydrocarbons detected in the carbonaceous chondrites have been identified as terrestrial contaminants using compound-specific carbon isotope analysis (Sephton et al., 2001), and these contaminated meteorite samples contrast with the contaminant-free Tissint. This is in agreement with studies (Steele et al., 2012; Steele et al., 2016) which suggest a Martian fluid source for the organic carbon in Tissint.

Noting the spatial relationships between macromolecular carbon (MMC) and spinel group minerals, sulfides, chlorides, and oxychlorine species, Steele et al. (2018) proposed that the organic carbon present in Tissint is a result of electrochemical synthesis of indigenous organic carbon on Mars. In this scenario, aqueous CO<sub>2</sub> in a Cl-rich near-surface brine (favored over a deeper hydrothermal fluid as  $\delta D$  of the MMC indicates fluid equilibration with the Martian atmosphere) is reduced through galvanic processes operating at the nanometer-scale due to charge differentiation between Ti-rich and Fe-rich spinel group minerals. This electrochemical reduction of CO<sub>2</sub> occurs alongside the evolution of hydrogen ions on the surface of the Ti-rich minerals, which act as cathodes, to produce simple reduced organic carbon species from CO precursors. Secondary reactions, including those catalyzed by Fe, Ti, and Mn oxides, lead to the aromatization of these low carbon number compounds to form the more complex aromatic-dominated MMC detected in Tissint and in situ on the Martian surface (Eigenbrode et al., 2018). Electrochemical reduction of nitrides, or aqueous N<sub>2</sub>, and sulfides could have provided the precursors to form the benzonitrile and range of thiophenes detected in the current study.

#### 4.2. Source of Inorganic Compounds in the Tissint Meteorite

The concentration of soluble inorganic salts present in this sample of the Tissint meteorite seems unlikely to have arisen simply through the introduction of a small portion of Martian regolith. It has been previously suggested that the introduction of regolith-derived sulfur could be responsible for the low metal pyrrhotite phase observed without any contribution from hydrothermal fluid alterations (Gattacceca et al., 2013). A quick comparison between the soluble NO<sub>3</sub>-ClO<sub>4</sub>-Cl portion of Tissint to previously measured Martian samples (Phoenix WCL, Curiosity SAM and EETA79001) clearly indicates a clustering (Figure 1); however, the concentrations of soluble salts measured within the Tissint meteorite compared with the regolith near the Phoenix lander (Kounaves Kounaves et al., 2010) do not support Martian regolith as their primary origin. Specifically, ClO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are more enriched in the Martian regolith compared to Cl<sup>-</sup> within this fragment of the Tissint meteorite (Table 1). A more detailed explanation of how the Phoenix nitrate concentration was obtained can be found in the supporting information (Kounaves et al., 2010; Stern et al., 2015).

The inorganic salts identified in this study are not likely to be the result of terrestrial contamination. With such a short terrestrial residence time, the most likely source of contamination of the Tissint meteorite

would be through deposition of desert surface dust, absorption of ambient humidity, and subsequent leaching of that material into fissures and cracks within the meteorite. The detection of a lower concentration of  $\text{ClO}_4^-$  closer to the fusion crust when compared to that from further away does not support terrestrial contamination as a source of the  $\text{ClO}_4^-$ . This is supported by previously reported isotopic analyses of volatiles within the meteorite that do not indicate contamination of the Tissint meteorite by terrestrial water (Chen et al., 2015). Furthermore, our analysis of the soluble chemistry of the strewn field indicates that the highly soluble  $\text{ClO}_4^-$ , derived from the terrestrial atmosphere and preserved in desert environments (Catling et al., 2010), is not present in significant enough quantities to leach into the Tissint until ~20 cm below the surface (Oberlin et al., 2018). Figure 1 demonstrates that the bulk soluble ion ratios in the southern Moroccan soil surface are distinct from those measured in Tissint, in a manner that would be challenging to explain via terrestrial contamination.

The EETA79001 and Tissint meteorites share similar ejection ages and lithologies, and it has been suggested that they were ejected during the same impact event (Aoudjehane et al., 2012). Both the similarities and differences between these two meteorites may provide insights into the types of processes that occurred on Mars up until this ejection event. Previous analysis of the soluble salts in EETA79001 revealed high levels of  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  relative to Tissint but was depleted in  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{ClO}_3^-$  (Kounaves et al., 2014; Stroble et al., 2013). Similarly, analyses of the soluble salts of EETA79001 did not show evidence of  $\text{Br}^-$  or  $\text{SCN}^-$ . These differences suggest that the entrained soluble chemistry of Tissint is the result of different surface processes than those preserved in the atmospherically altered regolith of EETA79001. Hydrothermal assemblages have been previously reported in the Martian nakhlite meteorites (e.g., Nakhlhla, Lafayette, NWA 817), ALH 84001, and brecciated meteorites (e.g., NWA 7475, NWA 7034, and NWA 7533; Hicks et al., 2014; Bridges & Schwenzer, 2012; McKay et al. 1996). These meteorites have been mineralogically characterized (clay and soluble salts) and found to contain halite, gypsum, and anhydrite, thus linking the mineralogy and interstitial fluid to their soluble chemistry.

While this work does not set temporal bounds or provide direct evidence for the source or persistence of an indigenous Martian terrestrial-like seawater brine, previous work (Chen et al., 2015) used secondary ion mass spectrometry to elucidate the origin and temporally constrain sources of water within Tissint. Their work suggests that limited and transient water activity that interacted with the Martian atmosphere <600 Myr is preserved in volatile-rich elements within Tissint. Our results support the hypothesis that an indigenous briny Martian fluid was incorporated into fissures in the Tissint host rock on the surface of Mars and the resulting chemical signatures preserved. Furthermore, our measurements of the soluble inorganic ions include direct measurements of  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$ , and  $\text{SCN}^-$ , species predicted to be generated via electrochemical oxidation in the Cl-rich near-surface brine by the hypothesis of Steele et al. (2018).

## 5. Conclusions

The dissimilarities between the soluble and organic geochemistry of the Tissint meteorite and that of the soil in its strewn field effectively rule out contamination from the terrestrial environment from which it was recovered. Furthermore, the similarities with other analyzed Martian meteorites in both organic and soluble ion content suggest a common Martian origin for these components. While inclusion of regolith within the Tissint during ejection cannot be ruled out, disproportionate enrichment between soluble salts in Tissint compared with the soluble portion of the Martian regolith as determined by the Phoenix WCL and EETA79001 analyses makes this an unlikely scenario. The most plausible origin for the soluble salts observed within Tissint is due to the inclusion of indigenous Martian fluids, providing potential insights into their chemistry on Mars. The presence of high concentrations of  $\text{SO}_4^{2-}$  associated with trace levels of  $\text{Br}^-$  and several oxidation states of chlorine suggests an oxidizing fluid with similarities to terrestrial seawater. Furthermore, our study detected the presence of soluble salts of the primary biologically relevant elements (CNOPS) in the form of  $\text{SCN}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , and  $\text{NO}_3^-$ . These salts, along with an organic carbon feedstock in the form of indigenous organic molecules, and evidence of <600-Myr-old water-rock interaction, could point toward a temporary habitable brine during the late Amazonian on Mars.

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