

### Key Points:

- A systematic survey reveals 161 different confirmed or probable minerals on Mars
- Mars minerals form in at least 20 different ways
- The mineral diversity of Mars is an order of magnitude smaller than Earth's

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## On the Diversity and Formation Modes of Martian Minerals

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**Abstract** A systematic survey of 161 known and postulated minerals originating on Mars points to 20 different mineral-forming processes (paragenetic modes), which are a subset of formation modes observed on Earth. The earliest martian minerals, as on Earth, were primary phases from mafic igneous rocks and their ultramafic cumulates. Subsequent primary igneous minerals were associated with products of limited fractional crystallization, including alkaline and quartz-normative lithologies. Significant mineral diversification occurred via precipitation of primary phases from aqueous and atmospheric fluids, including authigenesis, hydrothermal and cryogenic precipitation, and evaporites, including freeze drying during eras of low atmospheric pressures. In particular, hydrothermal mineral formation associated with both volcanic fluids and sustained hydrothermal activity in impact fracture zones may have triggered significant mineral diversification, though as yet undocumented. At least 65 such primary minerals have been identified by flown missions to Mars and from martian meteorites. A host of secondary martian minerals were produced by near-surface processes related to water/rock interactions, including hydration/dehydration, oxidation/reduction, serpentinization, metasomatism, and a variety of diagenetic alterations. Additional mineral diversity resulted from metamorphic events, including thermal and shock metamorphism, lightning, and bolide impacts. However, several dominant sources of mineral diversity on Earth, including (a) extensive fluid/rock interactions and element concentration associated with plate tectonics; (b) high-pressure regional metamorphism associated with plate tectonics; and (c) biologically mediated mineralization—are not known to be in play on Mars. Consequently, we estimate the total mineral diversity of Mars to be an order of magnitude smaller than on Earth.

**Plain Language Summary** A half-century of investigations of the martian surface by orbiters, landers, and rovers, amplified by studies of martian meteorites, reveal more than 160 confirmed or likely minerals. These diverse phases represent a range of at least 20 mineral-forming processes, including the production of dozens of primary igneous, sedimentary, and near-surface metamorphic rocks, as well as numerous secondary weathering and alteration minerals. In many respects, the more than 4.5-billion-year mineral evolution of Mars mirrors that of Earth and other terrestrial planets and moons. In each case, the earliest stages of igneous activity are followed by a sequence of primary and secondary mineral formation mechanisms. A key finding is that the mineralogy of Mars is significantly less diverse than that of Earth. Several dominant sources of mineral diversity on Earth, including (a) extensive fluid/rock interactions and element concentration associated with plate tectonics; (b) high-pressure regional metamorphism; and (c) biologically mediated mineralization—are not known to have occurred on Mars. Consequently, we estimate the total mineral diversity of Mars to be an order of magnitude smaller than on Earth.

### 1. Introduction

The minerals of Mars reveal a range of physical and chemical processes that have shaped and modified the red planet over the past 4.5 billion years (Chapman, 2007; Fairén, 2013; Mutch & Arvidson, 1977; Oehler et al., 2021). In many respects, the mineral evolution of Mars mirrors that of Earth and other terrestrial planets and moons (Hazen et al., 2008), with a congruent sequence of primary and secondary formation mechanisms. Yet the history of Mars—the only world to possess an active near-surface hydrosphere without plate tectonics—is

unique in our solar system, and its mineralogy reflects distinct aspects of martian basaltic crustal composition, as well as geochemical, petrologic, and tectonic changes.

A key to understanding these changes is identifying and systematizing the varied mineral-forming processes that have shaped Mars through geologic time. Therefore, we have surveyed the modes of formation (i.e., “paragenetic modes”) of 161 confirmed and inferred martian mineral species (Table 1), most of which are also well-documented terrestrial species approved by the International Mineralogical Association’s Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC; Burke, 2006; Cleland et al., 2021; Mills et al., 2009; Schertl et al., 2018).

A principal motivation for this effort is to compare and contrast the diversity and distribution of minerals on Mars to the much richer mineral inventory of Earth, while attempting to deduce the nature of mineralogical change on Mars through deep time. Following the work of Hazen and Morrison (2022), we define a mineral paragenetic mode as “a natural process by which a collection of atoms in solid and/or fluid form are reconfigured into one or more new solid forms.” This definition, which embraces a wide range of natural processes, led Hazen and Morrison to catalog 57 modes, including primary mineral formation from a gas or liquid; physical transformations of preexisting phases by sudden (lightning, impacts) or more gradual (regional metamorphism) events; diverse forms of water/rock interactions; and bio-mediated mineralization. Note that our definition encompasses a range of solids that are typically excluded from IMA-CNMNC protocols, including volcanic and impact glass, amorphous soil phases, and other non-crystalline solids that play critical roles in the evolution of martian mineralogy.

As emphasized by Hazen and Morrison (2022), the definition of paragenetic modes requires knowledge of three aspects of the mineral-forming process: (a) the *initial state* of the system, notably pressure-temperature-composition (*P-T-X*) conditions; (b) the *mechanism of transformation*, including the rates and spatial scales of change; and (c) the *resulting mineral phase(s)*. In this regard, every mineral species or amorphous phase is associated with one or more paragenetic modes, with some species (e.g., calcite, pyrite, magnetite, quartz) known to form in more than a dozen ways on Earth.

Several constraints and assumptions frame our study. First, we assume that the >300 mineral species identified in the full range of meteorites that have fallen to Earth (e.g., Rubin & Ma, 2021) also occur in meteorites that have fallen to the surface of Mars. Therefore, we do not separately list those minerals that comprise Parts I through V of the “Evolutionary System of Mineralogy”—i.e., the parts that catalog those diverse meteorite phases (Hazen, 2019; Hazen & Morrison, 2020, 2021; Hazen et al., 2021; Morrison & Hazen, 2020, 2021). In addition, with the exception of terrestrial alteration phases, we include in Table 1 all minerals thus far identified in the more than 200 known martian meteorites (Meyer & Righter, 2017; Rubin & Ma, 2021, their Table 9.2).

Several previous studies have summarized mineralogical information for Mars in the context of the current mission technologies. For example, Bandfield (2002) reviewed the surface mineralogy of Mars based on Thermal Emission Spectrometer data from the Mars Global Surveyor orbiter, while P. R. Christensen et al. (2004) employed the Mini-TES instrument on the *Opportunity* rover—work that discriminated a range of oxide, silicate, and sulfate minerals. Orbital surveys by CRISM and OMEGA near-infrared instruments have proven especially important in demonstrating global mineralogical trends, for example, the ubiquity of clay minerals (Amador et al., 2018; Bibring et al., 2006; Carter et al., 2013; Ehlmann et al., 2009; Mustard et al., 2008). Mössbauer spectrometers on the Mars Exploration Rovers *Spirit* and *Opportunity* aided in identifying at least 10 different Fe-bearing phases (Klingelhöfer et al., 2004, 2005; Morris et al., 2004, 2008, 2019). As data from new orbiter, lander, and rover missions are compiled and compared, new efforts to synthesize a more nuanced picture of Mars mineralogy on both regional and global scales are emerging (Carter et al., 2013; Lai et al., 2019; McSween et al., 2008; Ruff et al., 2008; Tice et al., 2022). These seminal Mars mission studies have been complemented by mineralogical and petrological studies of a variety of martian meteorites, which provided the first detailed information on the compositions and crystal structures of Mars minerals and continue to reveal new insights (Agee et al., 2013; Bridges & Warren, 2006; McSween, 1985, 2015; Papike et al., 2009; Treiman et al., 2000).

The arrival of the Mars Science Laboratory *Curiosity* rover at Gale Crater on 6 August 2012, ushered in a new era of Mars mineralogical research (Grotzinger et al., 2012). *Curiosity* carried 10 instruments in total, four of which, in combination, have revolutionized our view of Mars mineralogy: (a) ChemCam uses laser-induced breakdown spectroscopy (LIBS) to measure compositions at the sub-millimeter scale (Maurice et al., 2012); (b) the Alpha Particle X-ray Spectrometer (APXS) combines X-ray fluorescence and alpha particle-induced X-ray emission for

**Table 1**  
*Observed and Inferred Martian Minerals, With Selected References<sup>a</sup>*

Mineral <sup>b</sup>	Chemical formula	Source <sup>c</sup>	Mode <sup>d</sup>	References <sup>e</sup>
<b>Native Elements</b>				
Sulfur	S	IN	P	1
<b>Sulfides</b>				
Chalcopyrite	CuFeS <sub>2</sub>	MT	P	2, 3
Greigite	Fe <sub>3</sub> S <sub>4</sub>	MT	P, S	4
Marcasite	FeS <sub>2</sub>	MT	S	3, 5
Pentlandite	(Ni, Fe) <sub>9</sub> S <sub>8</sub>	MT	P	2, 3
Pyrite	FeS <sub>2</sub>	MT, CM	P, S	3, 6
Pyrrhotite	Fe <sub>7</sub> S <sub>8</sub>	MT	P	2, 3
Rasvumite	KFe <sub>2</sub> S <sub>3</sub>	MT	S	7
Troilite	FeS	MT	P, M	3
<b>Halides</b>				
Antarcticite	CaCl <sub>2</sub> ·6H <sub>2</sub> O	IN	P, S	8, 9
Bischofite	MgCl <sub>2</sub> ·6H <sub>2</sub> O	IN	P, S	10
Fluorite	CaF <sub>2</sub>	IN	P, S	11
Halite	NaCl	MT	P	12, 13
Hydrohalite	NaCl·2H <sub>2</sub> O	IN	P, S	14
<b>Oxychlorine Compounds</b>				
Na perchlorate <sup>f</sup>	NaClO <sub>4</sub>	IN	S	15
Mg, Ca perchlorate <sup>f</sup>	(Mg, Ca) (ClO <sub>4</sub> ) <sub>2</sub>	IN	S	16
<b>Sulfates</b>				
Alunite	KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	IN	S	17
Anhydrite	Ca(SO <sub>4</sub> )	CM	P, S	18
Baryte	BaSO <sub>4</sub>	IN	P, S	19
Bassanite	Ca(SO <sub>4</sub> )·0.5H <sub>2</sub> O	CM	S	18
Celestine	SrSO <sub>4</sub>	IN	P, S	19
Copiapite	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>4</sub> (SO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> ·20H <sub>2</sub> O	IN	S	20
Epsomite	Mg(SO <sub>4</sub> )·7H <sub>2</sub> O	IN	S	21
Gypsum	Ca(SO <sub>4</sub> )·2H <sub>2</sub> O	CM	P, S	18
Hexahydrite	Mg(SO <sub>4</sub> )·6H <sub>2</sub> O	IN	S	21
Jarosite	KFe <sup>3+</sup> <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	CM	S	3, 22, 23
Kainite	KMg(SO <sub>4</sub> )Cl·2.75H <sub>2</sub> O	IN	S	24
Kieserite	Mg(SO <sub>4</sub> )·H <sub>2</sub> O	CM	S	25
Meridianiite	Mg(SO <sub>4</sub> )·11H <sub>2</sub> O	IN	S	26
Mirabilite	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	IN	S	21
Rhomboclase	(H <sub>3</sub> O <sub>2</sub> )Fe <sup>3+</sup> (SO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	IN	S	27
Sanderite	Mg(SO <sub>4</sub> )·2H <sub>2</sub> O	IN	S	17
Soluble anhydrite <sup>f</sup>	Ca(SO <sub>4</sub> )	CM	P, S	18, 28
Starkeyite	Mg(SO <sub>4</sub> )·4H <sub>2</sub> O	CM	S	21
Szomolnokite	Fe <sup>2+</sup> (SO <sub>4</sub> )·H <sub>2</sub> O	IN	S	27
Thénardite	Na <sub>2</sub> SO <sub>4</sub>	IN	S	10
Unnamed Fe sulfate	Fe(OH)SO <sub>4</sub>	IN	S	29

**Table 1**  
Continued

Mineral <sup>b</sup>	Chemical formula	Source <sup>c</sup>	Mode <sup>d</sup>	References <sup>e</sup>
<b>Phosphates</b>				
Bobdownsite	$\text{Ca}_9\text{Mg}(\text{PO}_3\text{F})(\text{PO}_4)_6$	MT	P	30
Brushite	$\text{CaPO}_3(\text{OH})\cdot 2\text{H}_2\text{O}$	IN	S	31
Chlorapatite <sup>g</sup>	$\text{Ca}_5(\text{PO}_4)_3\text{Cl}$	MT	P	2, 3, 10
Ferromerrillite	$\text{Ca}_9\text{NaFe}^{2+}(\text{PO}_4)_7$	MT	P	32
Fluorapatite <sup>g</sup>	$\text{Ca}_5(\text{PO}_4)_3\text{F}$	CM	P	8
Hydroxylapatite <sup>g</sup>	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	MT	P	10
Keplerite	$\text{Ca}_9(\text{Ca}_{0.5}\square_{0.5})\text{Mg}(\text{PO}_4)_7$	MT	M	33
Merrillite	$\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$	MT	P	3, 34
Monazite <sup>f</sup>	$\text{REE}(\text{PO}_4)$	MT	P	3, 35
Strengite	$\text{Fe}^{3+}(\text{PO}_4)\cdot 2\text{H}_2\text{O}$	IN	S	36, 37
Tuite <sup>f</sup>	$\text{Ca}_3(\text{PO}_4)_2$	MT	M	3, 38
Variscite	$\text{AlPO}_4(\text{H}_2\text{O})_2$	IN	S	10
Vivianite	$\text{Fe}^{2+}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$	MT	S	37, 39
Whitlockite	$\text{Ca}_9\text{Mg}(\text{PO}_3\text{OH})(\text{PO}_4)_6$	MT	P	40
Xenotime <sup>f</sup>	$\text{REE}(\text{PO}_4)$	MT	P	3, 35
<b>Carbonates</b>				
Ankerite	$\text{CaFe}(\text{CO}_3)_2$	MT	P, S	3, 42
Aragonite	$\text{CaCO}_3$	MT	P	43
Calcite	$\text{CaCO}_3$	MT	P, S	3
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	CM	P, S	44, 45
Ikaite	$\text{CaCO}_3\cdot 6\text{H}_2\text{O}$	IN	S	46
Magnesite	$\text{Mg}(\text{CO}_3)$	MT	P, S	3, 47, 48
Siderite	$\text{FeCO}_3$	MT	P, S	49
<b>Oxides/Hydroxides</b>				
Akaganeite	$\text{Fe}^{3+}_8(\text{OH}, \text{O})_{16}\text{Cl}_{1.25}\cdot n\text{H}_2\text{O}$	CM	S	13, 50
Baddeleyite	$\text{ZrO}_2$	MT	P	2, 3, 5
Brucite	$\text{Mg}(\text{OH})_2$	IN	P, S	51
Carbon Dioxide <sup>f</sup>	$\text{CO}_2$	IN	P	52
Chenmingite <sup>h</sup>	$\text{FeCr}_2\text{O}_4$	MT	M	3, 53
Chromite <sup>i</sup>	$\text{Fe}^{2+}\text{Cr}_2\text{O}_4$	MT	P	3, 6
Feiite <sup>h</sup>	$\text{Fe}^{2+}_2(\text{Fe}^{2+}\text{Ti}^{4+})\text{O}_5$	MT	M	3, 54
Ferrihydrite	$\text{Fe}^{3+}_{10}\text{O}_{14}(\text{OH})_2$	MT	S	49
Goethite	$\text{Fe}^{3+}\text{O}(\text{OH})$	MT, CM	S	55
Hematite	$\text{Fe}_2\text{O}_3$	CM	P, S	13, 22
Hercynite <sup>i</sup>	$\text{Fe}^{2+}\text{Al}_2\text{O}_4$	MT	P	3
Ice	$\text{H}_2\text{O}$	IN	P	52
Ilmenite	$\text{FeTiO}_3$	MT, CM	P	3, 56
Liuite <sup>h</sup>	$\text{FeTiO}_3$	MT	M	3, 54
Maghemite	$(\text{Fe}^{3+}_{0.67}\square_{0.33})\text{Fe}^{3+}_2\text{O}_4$	MT	S	56
Magnetite <sup>i</sup>	$\text{Fe}_3\text{O}_4$	MT, CM	P	2, 3, 13
Periclase	$\text{MgO}$	IN	P, S	51
Rutile	$\text{TiO}_2$	MT	P	2, 3

**Table 1**  
Continued

Mineral <sup>b</sup>	Chemical formula	Source <sup>c</sup>	Mode <sup>d</sup>	References <sup>e</sup>
Spinel <sup>i</sup>	MgAl <sub>2</sub> O <sub>4</sub>	MT	P	57
Titanomagnetite <sup>f</sup>	(Fe, Ti) <sub>3</sub> O <sub>4</sub>	MT	P	3
Tschaunerite <sup>h</sup>	Fe <sup>2+</sup> (Fe <sup>2+</sup> Ti <sup>4+</sup> )O <sub>4</sub>	MT	M	3, 53, 58
Ulvöspinel <sup>h</sup>	Fe <sup>2+</sup> Ti <sub>2</sub> O <sub>4</sub>	MT	P	2, 3
Wangdaodeite <sup>h</sup>	FeTiO <sub>3</sub>	MT	M	59
Wüstite <sup>h</sup>	FeO	MT	P, M	3
Xieite <sup>h</sup>	FeCr <sub>2</sub> O <sub>4</sub>	MT	M	3, 60
<b>Silicates</b>				
<b>Orthosilicates</b>				
Ahrensite <sup>h</sup>	Fe <sub>2</sub> SiO <sub>4</sub>	MT	M	3, 61
Fayalite <sup>i</sup>	Fe <sup>2+</sup> <sub>2</sub> SiO <sub>4</sub>	MT	P	2, 3
Forsterite <sup>j</sup>	(Mg, Fe <sup>2+</sup> ) <sub>2</sub> SiO <sub>4</sub>	MT, CM	P	3, 13
Laihunite	(Fe <sup>3+</sup> , Fe <sup>2+</sup> , □) <sub>2</sub> (SiO <sub>4</sub> )	MT	S	7, 62
Olivine <sup>f,j</sup>	(Mg, Fe) <sub>2</sub> SiO <sub>4</sub>	MT, CM	P	2, 3, 13
Ringwoodite <sup>h</sup>	Mg <sub>2</sub> SiO <sub>4</sub>	MT	M	3, 63
Tranquillityite	Fe <sup>2+</sup> <sub>8</sub> Ti <sub>3</sub> Zr <sub>2</sub> Si <sub>3</sub> O <sub>24</sub>	MT	P	64
Wadsleyite <sup>h</sup>	Mg <sub>2</sub> SiO <sub>4</sub>	MT	M	3, 65
Zircon	ZrSiO <sub>4</sub>	MT	P, M	3, 66, 67
<b>Inosilicates</b>				
Akimotoite <sup>h</sup>	MgSiO <sub>3</sub>	MT	M	3, 68
Augite	(Ca, Mg, Fe)SiO <sub>3</sub>	MT, CM	P	13, 69
Bridgmanite <sup>h</sup>	MgSiO <sub>3</sub>	MT	M	3, 70
Diopside	CaMg(SiO <sub>3</sub> ) <sub>2</sub>	IN	P	71
Enstatite	MgSiO <sub>3</sub>	MT, CM	P	3, 69
Ferro-kaersutite <sup>f</sup>	NaCa <sub>2</sub> (Fe <sup>2+</sup> <sub>3</sub> AlTi <sup>4+</sup> )(Si <sub>6</sub> Al <sub>2</sub> )O <sub>22</sub> O <sub>2</sub>	MT	P	3
Ferrosilite	Fe <sup>2+</sup> SiO <sub>3</sub>	CM	P	13, 72
Hastingsite	NaCa <sub>2</sub> (Fe <sup>2+</sup> <sub>4</sub> Fe <sup>3+</sup> )(Si <sub>6</sub> Al <sub>2</sub> )O <sub>22</sub> (OH) <sub>2</sub>	MT	S	73
Hedenbergite	CaMg(SiO <sub>3</sub> ) <sub>2</sub>	MT	P	3, 74
Hemleyite <sup>h</sup>	Fe <sup>2+</sup> SiO <sub>3</sub>	MT	M	3, 75
Kaersutite	NaCa <sub>2</sub> (Mg <sub>3</sub> AlTi <sup>4+</sup> )(Si <sub>6</sub> Al <sub>2</sub> )O <sub>22</sub> O <sub>2</sub>	MT	P	3, 76, 77
Majorite <sup>h</sup>	MgSiO <sub>3</sub>	MT	M	3, 54, 65
Pigeonite	(Mg, Fe, Ca)SiO <sub>3</sub>	MT, CM	P	13, 69
Pyroxferroite	Fe <sup>2+</sup> SiO <sub>3</sub>	MT	P	2, 3
Tissinite <sup>h</sup>	(Ca, Na, □)AlSi <sub>2</sub> O <sub>6</sub>	MT	M	3, 78
Zagamiite <sup>h</sup>	CaAl <sub>2</sub> Si <sub>3,5</sub> O <sub>11</sub>	MT	M	3, 54, 79
<b>Phyllosilicates</b>				
Beidellite	(Na, Ca) <sub>0.3</sub> Al <sub>2</sub> ((Si, Al) <sub>4</sub> O <sub>10</sub> )(OH) <sub>2</sub> ·nH <sub>2</sub> O	IN	S	80
Biotite <sup>f</sup>	K(Fe <sup>2+</sup> , Mg) <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	MT	P, S	3
Chamosite <sup>k</sup>	(Fe <sup>2+</sup> , Mg, Al, Fe <sup>3+</sup> ) <sub>6</sub> (Si, Al) <sub>4</sub> O <sub>10</sub> (OH, O) <sub>8</sub>	IN	S	81
Chlorite <sup>f,k</sup>	(Mg, Fe <sup>2+</sup> , Al, Fe <sup>3+</sup> ) <sub>6</sub> (Si, Al) <sub>4</sub> O <sub>10</sub> (OH, O) <sub>8</sub>	IN	S	21, 82
Corrensite	(Ca, Na, K) <sub>1-x</sub> (Mg, Fe, Al) <sub>9</sub> (Si, Al) <sub>8</sub> O <sub>20</sub> (OH) <sub>10</sub> ·nH <sub>2</sub> O	IN	S	83
Ferripyrophyllite	Fe <sup>3+</sup> Si <sub>2</sub> O <sub>5</sub> (OH)	CM	S	84
Greenalite <sup>l</sup>	(Fe <sup>2+</sup> , Fe <sup>3+</sup> ) <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	CM	S	42

**Table 1**  
Continued

Mineral <sup>b</sup>	Chemical formula	Source <sup>c</sup>	Mode <sup>d</sup>	References <sup>e</sup>
Hisingerite <sup>l</sup>	Fe <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ·2H <sub>2</sub> O	IN	S	85
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	IN	S	21
Minnesotaite	Fe <sup>2+</sup> <sub>3</sub> Si <sub>4</sub> 10(OH) <sub>2</sub>	CM	S	42
Montmorillonite	(Na, Ca) <sub>0.3</sub> (Al, Mg) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ·nH <sub>2</sub> O	IN	S	86
Muscovite <sup>m</sup> /illite <sup>f</sup>	KAl <sub>2</sub> (Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>2</sub>	IN	P, S	48
Nontronite	Na <sub>0.3</sub> Fe <sup>3+</sup> <sub>2</sub> (Si, Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ·nH <sub>2</sub> O	IN	S	87
Odinite <sup>l</sup>	(Fe <sup>3+</sup> , Mg, Al, Fe <sup>2+</sup> ) <sub>2.5</sub> (Si, Al) <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	MT	S	49
Phlogopite	KMg <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	MT	P, S	3, 88
Prehnite	Ca <sub>2</sub> Al(Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>2</sub>	IN	S	48, 99
Saponite	(Ca, Na) <sub>0.3</sub> (Mg, Fe) <sub>3</sub> (Si, Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ·4H <sub>2</sub> O	MT	S	90
Serpentine <sup>f, l</sup>	Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	MT	S	91
Stilpnomelane	(K, Ca, Na)(Fe, Mg, Al) <sub>8</sub> (Si, Al) <sub>12</sub> (O, OH) <sub>36</sub> ·nH <sub>2</sub> O	MT	S	3
Talc	Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	IN	S	48
Vermiculite	Mg <sub>0.7</sub> (Mg, Fe, Al) <sub>6</sub> (Si, Al) <sub>8</sub> O <sub>20</sub> (OH) <sub>4</sub> ·8H <sub>2</sub> O	IN	S	91
<b>Silica Minerals</b>				
Coesite <sup>h</sup>	SiO <sub>2</sub>	MT	M	3, 54
Cristobalite	SiO <sub>2</sub>	CM	P	13
Opal	SiO <sub>2</sub> ·nH <sub>2</sub> O	CM	P, S	92
Opal-CT <sup>f</sup>	SiO <sub>2</sub> ·nH <sub>2</sub> O	CM	P, S	93
Quartz	SiO <sub>2</sub>	MT, CM	P	8
Seifertite <sup>h</sup>	SiO <sub>2</sub>	MT	M	3, 94
Stishovite <sup>h</sup>	SiO <sub>2</sub>	MT	M	3, 54
Tridymite	SiO <sub>2</sub>	CM	P	93, 95, 96
<b>Framework Silicates</b>				
Albite <sup>n, o</sup>	NaAlSi <sub>3</sub> O <sub>8</sub>	MT	P	97
Alkali feldspar <sup>f, o</sup>	(Na, K)AlSi <sub>3</sub> O <sub>8</sub>	MT, CM	P	3, 13, 98
Analcime <sup>p</sup>	Na(AlSi <sub>2</sub> O <sub>6</sub> )·H <sub>2</sub> O	IN	S	48
Anorthite <sup>n</sup>	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	MT	P	97
Chabazite <sup>p</sup>	Ca <sub>2</sub> [Al <sub>4</sub> Si <sub>8</sub> O <sub>24</sub> ]·13H <sub>2</sub> O	IN	S	99
Clinoptilolite <sup>p</sup>	Ca <sub>3</sub> (Si <sub>30</sub> Al <sub>6</sub> )O <sub>72</sub> ·20H <sub>2</sub> O	IN	S	99
Lingunite <sup>h</sup>	NaAlSi <sub>3</sub> O <sub>8</sub>	MT	M	3, 100
Liebermannite <sup>h</sup>	KAlSi <sub>3</sub> O <sub>8</sub>	MT	M	3, 101
Nepheline	Na <sub>3</sub> K(Al <sub>4</sub> Si <sub>4</sub> O <sub>16</sub> )	MT	P	69
Orthoclase <sup>o</sup>	KAlSi <sub>3</sub> O <sub>8</sub>	MT, CM	P	13, 98
Plagioclase <sup>f, n</sup>	(Na, Ca)(Al, Si) <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	CM	P	3, 13
Sanidine <sup>o</sup>	KAlSi <sub>3</sub> O <sub>8</sub>	CM	P	3, 13
Stöfflerite <sup>h</sup>	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	MT	M	3, 102
Zeolites <sup>f, p</sup>	Na-K-Ca aluminosilicates	IN	S	103
<b>X-ray Amorphous Phases</b>				
Allophane <sup>f</sup>	(Al <sub>2</sub> O <sub>3</sub> )(SiO <sub>2</sub> ) <sub>1.3-2</sub> ·2.5-3H <sub>2</sub> O	IN	S	21; 104
Amorphous silica <sup>f</sup>	>90 wt % SiO <sub>2</sub>	IN	P, S	105
Amorphous sulfate <sup>f</sup>	(Ca, Mg, Fe)(SO <sub>4</sub> )·nH <sub>2</sub> O	CM	P, S	13, 106, 107
Basaltic glass <sup>f</sup>	(Ca, Mg, Fe, Si, O)	MT	P	69



**Table 1**  
Continued

Mineral <sup>b</sup>	Chemical formula	Source <sup>c</sup>	Mode <sup>d</sup>	References <sup>e</sup>
Iddingsite <sup>f</sup>	(Mg-Fe-Si-O-H)	MT	S	3, 108, 109
Imogolite	Al <sub>2</sub> SiO <sub>3</sub> (OH) <sub>4</sub>	IN	S	110
Maskelynite <sup>f,h</sup>	(Ca, Na) (Al, Si) <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	MT	M	3, 6
Palagonite <sup>f</sup>	(Na-K-Fe-Al-Si-O-H)	IN	S	21
Pyroxene glass <sup>f,h</sup>	(Ca, Mg, Fe)SiO <sub>3</sub>	MT	M	3

<sup>a</sup>Previous lists of martian minerals include Ming et al. (2009), Meyer and Righter (2017), Rampe, Blake, et al. (2020), and Rubin and Ma (2021). <sup>b</sup>Mineral: Minerals in boldface have been confirmed, either by their occurrence in martian meteorites or by CheMin X-ray diffractometry. <sup>c</sup>Source: CM, CheMin; MT, Unaltered meteorite; IN, Inferred from lander, orbiter, or rover data, or from phase equilibrium data. Note that “inferred” is listed only when a definitive identification has not been reported. <sup>d</sup>Mode: P, primary mineral (i.e., direct crystallization/solidification from a fluid); S, secondary mineral (alteration of prior minerals by fluid/rock interactions); M, metamorphism (alteration of prior minerals by changes in physical environment). <sup>e</sup>References: 1 = Nekvasil et al. (2019); 2 = McSween (1985); 3 = Rubin and Ma (2021); 4 = <https://curator.jsc.nasa.gov/antmet/mmc/alh84001.pdf>; 5 = Floran et al. (1978); 6 = Mittlefehldt (1994); 7 = Ling and Wang (2015); 8 = Bishop et al. (2021); 9 = Squyres et al. (2004); 10 = B. C. Clark and Van Hart (1981); 11 = Forni et al. (2015); 12 = Catling (1999); 13 = Rampe, Blake, et al. (2020); 14 = Craig et al. (1974); 15 = Tice et al. (2022); 16 = Hecht et al. (2009); 17 = Berdesinski (1952); 18 = Vaniman et al. (2018); 19 = Burt et al. (2004); 20 = Farrand et al. (2014); 21 = Wang et al. (2009); 22 = Klingelhöfer et al. (2004); 23 = Farrand et al. (2009); 24 = Borisov et al. (2022); 25 = Gendrin et al. (2005); 26 = Peterson et al. (2007); 27 = Pitman et al. (2014); 28 = A. N. Christensen et al. (2008); 29 = Lichtenberg et al. (2010); 30 = Gnos et al. (2002); 31 = Ming et al. (2006); 32 = Britvin et al. (2016); 33 = Britvin et al. (2021); 34 = Usui et al. (2008); 35 = Y. Liu et al. (2016); 36 = Lane et al. (2008); 37 = Treiman et al. (pers. comm.); 38 = Xie et al. (2003); 39 = Valley et al. (1997); 40 = Boctor et al. (2003); 41 = Horgan et al. (2020); 42 = Thorpe et al. (2022); 43 = <https://curator.jsc.nasa.gov/antmet/mmc/nwa2737.pdf>; 44 = Harvey and McSween (1996); 45 = Tirsch et al. (2018); 46 = Bischoff et al. (1993); 47 = Bandfield et al. (2003); 48 = Ehlmann et al. (2009); 49 = Piercy et al. (2022); 50 = Kuebler (2013); 51 = Schrenk et al. (2013); 52 = Byrne and Ingersoll (2003); 53 = Ma et al. (2019); 54 = Tschauer (2019); 55 = Bridges and Grady (2000); 56 = Agee et al. (2013); 57 = McCubbin and Nekvasil (2008); 58 = Ma et al. (2021); 59 = Xie et al. (2020); 60 = Chen et al. (2008); 61 = Ma et al. (2016); 62 = Gyollai et al. (2016); 63 = Walton (2013); 64 = Bläss and Langenhorst (2011); 65 = Malavergne et al. (2010); 66 = Cox et al. (2022); 67 = Moser et al. (2013); 68 = Baziotis et al. (2013); 69 = McSween (2015); 70 = Tschauer et al. (2014); 71 = Zastrow and Glotch (2022); 72 = Wiens et al. (2022); 73 = Gesting and Filiberto (2016); 74 = <https://curator.jsc.nasa.gov/antmet/mmc/nwa480.pdf>; 75 = Bindi et al. (2017); 76 = Treiman (1985); 77 = <https://curator.jsc.nasa.gov/antmet/mmc/chassigny.pdf>; 78 = Ma et al. (2015); 79 = Ma et al. (2017); 80 = Bishop et al. (2013); 81 = Poulet et al. (2005); 82 = Mustard et al. (2008); 83 = Bristow and Milliken (2011); 84 = Bristow et al. (2018); 85 = Tutolo et al. (2019); 86 = B. C. Clark et al. (2007); 87 = Bishop et al. (2018); 88 = Brearley (2000); 89 = Ehlmann, Mustard, Clark, et al. (2011) and Ehlmann, Mustard, Murchie, et al. (2011); 90 = Hicks et al. (2014); 91 = Cuadros et al. (2022); 92 = Squyres et al. (2008); 93 = Morris et al. (2016b); 94 = El Goresy et al. (2008); 95 = Morris et al. (2016a); 96 = Yen et al. (2021); 97 = Milam et al. (2010); 98 = Meyer and Righter (2017); 99 = Mousis et al. (2016); 100 = Gillet et al. (2000); 101 = Ma et al. (2018); 102 = Tschauer et al. (2021); 103 = Ruff (2004); 104 = Rampe et al. (2012); 105 = Frydenvang et al. (2017); 106 = R. J. Smith et al. (2020); 107 = R. J. Smith et al. (2021); 108 = Treiman et al. (1993); 109 = Kuebler (2013); 110 = Bishop and Rampe (2016). <sup>f</sup>This mineral name is not approved by the International Mineralogical Association (IMA). <sup>g</sup>Chlorapatite, fluorapatite, and hydroxylapatite are often undifferentiated and reported as “apatite.” <sup>h</sup>High-pressure phase caused by impact processes. <sup>i</sup>“Spinel” is reported by several authors; however, this term likely refers to the oxide spinel group (e.g., chromite; hercynite; magnetite; ulvöspinel) and not the species spinel (MgAl<sub>2</sub>O<sub>4</sub>). The occurrence of magnesium aluminate spinel as a martian mineral is uncertain (McCubbin & Nekvasil, 2008). <sup>j</sup>“Olivine” refers to the solid solution between the IMA-approved species forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) and fayalite (Fe<sub>2</sub>SiO<sub>4</sub>). Martian olivine, both from meteorites and as analyzed by CheMin, are typically intermediate in composition. <sup>k</sup>“Chlorite” is a group name for secondary phyllosilicates, including the plausible martian species chamosite, clinocllore, and sudoite. Of these minerals, only chamosite has been reported. <sup>l</sup>“Serpentine” is a non-approved name for the serpentine group, which includes the martian meteorite species hisingerite and odinite (Piercy et al., 2022; Tutolo et al., 2019). Additional plausible martian serpentine group minerals, though not yet identified, include the antigorite, chrysotile, and lizardite polymorphs of [Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>], as well as Al, Fe<sup>2+</sup>, and/or Fe<sup>3+</sup>-bearing amesite, berthierine, cronstedtite, and greenalite—all phases that may have been reported generically as “serpentine.” <sup>m</sup>Muscovite is also reported as “illite,” which is an unapproved name for fine-grained secondary muscovite. <sup>n</sup>Albite and anorthite are the IMA-approved species names for the Na- and Ca-end-members of the plagioclase feldspar series, respectively. Most martian plagioclases are intermediate in composition, ranging from andesine (An<sub>30-50</sub>) to labradorite (An<sub>50-70</sub>), as summarized by Morrison et al. (2018a) and Rampe, Blake, et al. (2020). <sup>o</sup>Albite, orthoclase, sanidine, and other members of the alkali feldspar solid solution [(Na,K)AlSi<sub>3</sub>O<sub>8</sub>] are sometimes reported as “alkali feldspar” or “K feldspar.” <sup>p</sup>“Zeolite” is a group name for hydrous framework aluminosilicates that have been inferred to occur as secondary phases on Mars. In some instances, individual zeolite species, including analcime, chabazite, and clinoptilite, have been reported.

chemical analysis (Gellert et al., 2015); (c) the Sample Analysis at Mars (SAM) instrument suite is a pyrolysis gas chromatograph mass spectrometer (Pyr-GCMS) that can characterize volatiles in minerals as well as suites of organic molecules (Mahaffy et al., 2012); and (d), most significantly for mineral identification and characterization, the CheMin instrument is the first X-ray diffractometer on another world (Blake et al., 2012; Downs, 2015; Velbel, 2018). In concert, these instruments are presenting an unparalleled view of the mineralogy of Mars (Ehlmann & Edwards, 2014; Wiens et al., 2022). Of special note, post-landing advances in CheMin data analysis (Morrison et al., 2018a, 2018b) have resulted in the identification of more than two dozen minerals, with details on their structures and compositions (Bish et al., 2013; Blake et al., 2013, 2023; Bristow et al., 2018, 2021; Lafuente et al., 2021; Morris et al., 2016a, 2016b; Rampe et al., 2017, 2018; Rampe, Blake, et al., 2020; Rampe, Bristow, et al., 2020; Thorpe et al., 2022; Treiman et al., 2016; Tu et al., 2021; Vaniman et al., 2014, 2018).

Our understanding of martian mineralogy is also being enhanced by discoveries of the Mars 2020 *Perseverance* rover. Of special note are the Planetary Instrument for X-ray Lithochemistry (PIXL), which is a micro-focus X-ray fluorescence spectrometer (Allwood et al., 2020), and the SuperCam instrument suite, which combines LIBS with Raman, visible, and infrared spectroscopies (Wiens et al., 2021). These findings provide a solid foundation for this review of the paragenetic modes of martian minerals.

On the one hand, we assume that a significant number of martian minerals occur in highly localized and/or subsurface deposits that have yet to be discovered, sampled, and described. In particular, hydrothermal systems associated with large volcanic complexes or extensive impact fracture zones are likely to host mineralized deposits that are similar in some ways to those on Earth (Pirajno, 2009, 2020). Prior studies have cataloged more than 100 such phases in surveys of Earth's earliest Hadean mineralogy (Hazen, 2013; Morrison et al., 2023; Morrison, Runyon, & Hazen, 2018). Similarly, subsurface thermal (contact) metamorphism may generate scores of martian phases not yet observed (Grapes, 2006). In addition, such localized phenomena as minerals formed at volcanic fumaroles, at shear zones, and by lightning are not yet well represented in the confirmed inventory of Mars minerals.

On the other hand, three significant drivers of mineral diversification on Earth are not known to have occurred on Mars: (a) large-scale fluid/rock interactions associated with orogenesis, subduction, plate margin volcanism, and other aspects of global tectonics; (b) regional, high-pressure metamorphism; and (c) biologically mediated mineralization and biological alteration of pre-existing minerals. These three processes account for more than 80% of Earth's mineral diversity (Hazen and Morrison 2022)—an inventory that includes thousands of phases unlikely to occur on Mars. In particular, we assume that processes on Mars do not result in the significant concentration of dozens of minor elements that form more than 2,000 rare minerals in complex pegmatites (e.g., with Li, Be, B, U; Černý, 2005; London, 2008; Tkachev, 2011); apatitic and carbonatite rocks (Ta, Nd, Zr, Sr; Jones et al., 2013; Marks & Markl, 2017; Mikhailova et al., 2019); layered igneous intrusive complexes (platinum group elements; Naldrett et al., 1987; O'Driscoll & VanTongeren, 2017; Zientek, 2012); Phanerozoic fumarolic systems (Cu, V, As, Sb; Vergasova & Filatov, 2016); metamorphosed Ba-Mn-Pb-Zn deposits (Cairncross & Beukes, 2013; Frondel, 1990; Spry et al., 2008); and highly evolved hydrothermal systems associated with plate margin volcanism (Bi, Sb, Se, As; Guilbert & Park, 2007; Hazen & Morrison, 2022; Huston et al., 2010; Sangster, 1972).

Given these constraints, we identify 20 paragenetic modes as likely to have contributed to mineral diversity on Mars (Table 2). Most of these modes are closely aligned with one or more of the 57 mineral formation processes identified on Earth (Hazen & Morrison, 2022; their Table 1).

## 2. Systematic Survey of Paragenetic Modes

In this section, we describe 20 paragenetic modes of martian minerals, as summarized in Table 2. In most instances, the paragenetic modes for each IMA-CNMNC-approved mineral species observed or predicted on Mars are assumed to be similar to those on Earth—information determined by consulting primary references, as well as one or more of the following sources: (a) lists of IMA-approved mineral species (<https://rruff.info/ima>, accessed 5 March 2023; Lafuente et al., 2015); (b) tabulations of mineral species and their geological contexts (<https://mindat.org>, accessed 5 March 2023); (c) detailed descriptions of paragenesis for rock-forming minerals in Deer et al. (1982–2013), *Rock-Forming Minerals*, Second Edition, 11 volumes; and (d) descriptions of “Occurrence” in Anthony et al. (1990–2003), *Handbook of Mineralogy*, 6 volumes.

As in the analysis of terrestrial paragenetic modes, our martian classification of 20 mineral-forming environments is subjective in several respects. For example, minerals may form over a significant range of pressures, temperatures, and/or compositions, thus blurring distinctions among some formation processes. Consequently, in several instances, we have lumped two or more modes from our previous study into a single process. For example, we combine primary minerals from ultramafic and mafic igneous rocks, from intrusive and extrusive acidic igneous rocks, from submarine hydrothermal vents and subaerial hot springs, and from xenolith thermal alteration and contact metamorphism into single categories.



We recognize three broad groups of paragenetic modes:

1. “Primary” minerals are solids formed directly from a fluid, for example, by crystallization from an igneous magma, by precipitation from an aqueous fluid, or by vapor deposition. We list nine modes of primary mineralization in Table 2.
2. We define a “secondary” mineral, by contrast, as a solid that forms by chemical alteration of a preexisting solid phase, usually by interaction with an aqueous fluid. While divisions among such aqueous processes may be inexact, we identify six important secondary mineral-forming processes, including hydration/dehydration, oxidation/reduction, serpentinization, crustal leaching, diagenesis, and mantle metasomatism.
3. Metamorphism is the alteration of prior minerals by changes in their physical environment, including sudden events (lightning; bolide impacts) or more gradual processes (thermal metamorphism; photo-alteration; shearing at fault zones). Here, we recognize five modes of martian metamorphism.

**Table 2**  
*Paragenetic Modes of Martian Minerals*

Mode	Selected mineral examples	Selected references <sup>a</sup>
Primary Mineralization (i.e., direct crystallization/solidification from a fluid)		
Primary Igneous Minerals		
1. Mafic/ultramafic/alkaline rocks	forsterite; augite; plagioclase; nepheline; magnetite	1–6
2. Acidic (quartz normative) rocks	quartz; alkali feldspar	7–9
Primary Vapor-Deposition Minerals		
3. Volcanic fumaroles	sulfur; gypsum; silica	10–12
4. Atmospheric condensation	carbon dioxide; ice	13–14
Primary Aqueous-Deposition Minerals		
5. Hydrothermal vents, hot springs	pyrite; opal; amorphous silica	15–17
6. Hydrothermal veins/fractures	sulfides; carbonates; sulfates	18–19
7. Chemical precip./authigenesis	halite; carbonates; sulfates	22–29
8. Freezing	ice; ikaite	13, 30
9. Detrital concentration	ilmenite; zircon; forsterite	31–32
Secondary Mineralization (alteration of prior minerals by fluid/rock interactions)		
10. Hydration/dehydration	gypsum/bassanite/anhydrite	33–35
11. Oxidation/reduction	magnetite/hematite; clay minerals	36–38
12. Serpentinization	serpentine; brucite; magnetite	39–40
13. Leaching	kaolinite; montmorillonite; anatase	41–43
14. Diagenesis		26, 43–55
Clay minerals	chlorite; serpentine; smectite	37, 55–75
Sulfates	jarosite; gypsum; starkeyite	33–35, 76–92
Carbonates	siderite; magnesite	24, 29, 93, 94
Phosphates	merrillite; vivianite	28, 37, 95, 96
Fe/Mn oxides and hydroxides	hematite; ferrihydrite; magnetite	38, 97–104
Silicates	prehnite; opal	105–109
Zeolites	chabazite; clinoptilolite; analcime	110–115
Amorphous phases	amorphous sulfate; amorphous silica	116–117
15. Mantle metasomatism	K-feldspar; muscovite	118–120
Metamorphism (alteration of prior minerals by changes in physical environment)		
16. Thermal metamorphism	cristobalite; sanidine; larnite	121–122
17. Lightning mineralization	silicate glass; graphite; iron	123–126
18. Impact mineralization	maskelynite; ringwoodite	127–133

**Table 2**  
*Continued*

Mode	Selected mineral examples	Selected references <sup>a</sup>
19. Photo-alteration	siderite; Mn oxides	134–136
20. Shear-induced mineralization	quartz; albite; epidote	137–139

<sup>a</sup>Selected References: 1 = McSween (1985); 2 = Treiman et al. (2000); 3 = Bridges and Warren (2006); 4 = McCoy et al. (2011); 5 = McSween (2015); 6 = Edwards et al. (2017); 7 = Wray et al. (2013); 8 = Morris et al. (2016b); 9 = Bowden et al. (2022); 10 = McCollom et al. (2015); 11 = Cockell et al. (2019); 12 = Simpson et al. (2020); 13 = Phillips et al. (2011); 14 = Bierson et al. (2016); 15 = Michalski, Dobrea, et al. (2017); 16 = Ruff and Farmer (2016); 17 = Ruff et al. (2020); 18 = Ojha et al. (2021); 19 = Osinski et al. (2013); 20 = Catling (1999); 21 = Bridges and Grady (2000); 22 = Tosca and McLennan (2006); 23 = Leask and Ehlmann (2022); 24 = Morris et al. (2010); 25 = Tosca et al. (2018); 26 = Bristow et al. (2015); 27 = Mojzsis and Arrhenius (1998); 28 = Adcock et al. (2013); 29 = Horgan et al. (2020); 30 = I. B. Smith et al. (2022); 31 = Payré et al. (2020); 32 = Cox et al. (2022); 33 = Vaniman et al. (2018); 34 = Chipera and Vaniman (2007); 35 = Wang et al. (2011); 36 = King and McSween (2005); 37 = Rampe, Blake, et al. (2020); 38 = Berger et al. (2022); 39 = Amador et al. (2018); 40 = Tutolo and Tosca (2023); 41 = Hurowitz et al. (2006); 42 = Retallack (2014); 43 = Ye and Michalski (2021); 44 = Murchie et al. (2009); 45 = McGlynn et al., 2012; 46 = Carter et al. (2013); 47 = Arvidson et al. (2014); 48 = Bridges et al. (2015); 49 = Yen et al. (2017); 50 = Mangold et al. (2019); 51 = Achilles et al. (2020); 52 = J. C. Liu et al. (2021); 53 = Sheppard et al. (2021); 54 = Farley et al. (2022); 55 = Thorpe et al. (2022); 56 = Poulet et al. (2005); 57 = Bibring et al. (2006); 58 = Mustard et al. (2008); 59 = Ehlmann et al. (2009); 60 = Milliken et al., 2009; 61 = Tosca and Knoll (2009); 62 = Carter et al. (2010); 63 = Ehlmann et al. (2010); 64 = Milliken and Bish (2010); 65 = Ehlmann et al. (2011a); 66 = Meunier et al. (2012); 67 = Hazen et al. (2013); 68 = Ehlmann et al. (2013); 69 = Bristow et al. (2015); 70 = Sun and Milliken (2015); 71 = Bishop et al. (2018); 72 = Cuardos et al. (2022); 73 = Peretyazhko et al. (2016); 74 = Bishop et al. (2018); 75 = Bristow et al. (2018); 76 = Vaniman et al. (2004); 77 = Gendrin et al. (2005); 78 = Aubrey et al. (2006); 79 = Bishop et al. (2006); 80 = Wang et al. (2006); 81 = Morris et al. (2007); 82 = Wang et al. (2007); 83 = Bishop et al. (2009); 84 = Wang et al. (2009); 85 = Farrand et al. (2009); 86 = Wray et al. (2009); 87 = King and McLennan (2010); 88 = Rice et al. (2010); 89 = Farrand et al. (2014); 90 = M. L. Smith et al. (2014); 91 = Benison (2016); 92 = Dehouck et al. (2012); 93 = Bandfield et al. (2003); 94 = Ehlmann et al. (2008); 95 = Yen et al. (2014); 96 = Usui et al. (2008); 97 = Morris and Klingelhöfer (2008); 98 = Morris et al. (2008); 99 = Fraeman et al. (2013); 100 = Arvidson et al. (2016); 101 = Lanza et al. (2016); 102 = Nekvasil et al. (2019); 103 = Rampe et al. (2023); 104 = Mitra et al. (2022); 105 = Milliken et al. (2008); 106 = Giesting et al. (2015); 107 = Giesting and Filiberto (2016); 108 = Frydenvang et al. (2017); 109 = Rapin et al. (2018); 110 = Ming and Gooding (1988); 111 = Ruff (2004); 112 = Ehlmann et al. (2009); 113 = Carter et al. (2013); 114 = Mousis et al. (2016); 115 = Kodikara et al. (2023); 116 = R. J. Smith and Horgan (2021); 117 = R. J. Smith et al. (2020); 118 = Treiman (2003); 119 = Day et al. (2018); 120 = Michalski et al. (2021); 121 = Grapes (2006); 122 = McSween et al. (2015); 123 = Ruf et al. (2009); 124 = Wang et al. (2023); 125 = L. Wilson and Head (1994); 126 = Brož et al. (2021); 127 = Tomioka and Miyahara (2017); 128 = Tschauer (2019); 129 = El Goresy et al. (2004); 130 = Min et al. (2004); 131 = Fritz and Greshake (2009); 132 = Fairén et al. (2010); 133 = Michalski, Glotch, et al. (2017); 134 = Kim et al. (2013); 135 = Rivera Banuchii et al. (2022); 136 = Schuttlefield et al. (2011); 137 = Andrews-Hanna et al. (2008); 138 = Yin (2012); 139 = Klimczak et al. (2018).

In this study, we tabulate 161 martian mineral species based on at least one of four criteria: (a) minerals that have been confirmed by studies of martian meteorites; (b) minerals confirmed by X-ray diffraction analyses by the CheMin instrument on *Curiosity*; (c) phases inferred through spectroscopic and other measurements by Mars orbiters, landers, and rovers; or (d) phases implied by petrologic/geochemical constraints (Table 1). Not included in this list are ~300 minerals that are assumed to fall to the martian surface in the form of extra-martian meteorites.

## 2.1. Primary Mineralization

We recognize three broad categories of primary martian mineralization (Table 2). (a) Primary igneous minerals, including from mafic/ultramafic/alkaline lithologies and from quartz-normative rocks, crystallize from a silicate magma. (b) Vapor deposition occurs in at least two environments on Mars: volcanic fumaroles and through atmospheric precipitation of water and carbon dioxide ices. (c) Aqueous precipitation includes hydrothermal (>100°C) near-surface and subsurface mineralization, and the lower-temperature processes of chemical precipitation, including evaporation, and freezing. We also include the selection and concentration of detrital grains as a primary process.

### 2.1.1. Mafic/Ultramafic/Alkaline Igneous Lithologies

The oldest minerals (>4.5 Ga) formed on Mars must have been in mafic igneous rocks, including volcanic basalt and its intrusive equivalent gabbro, as well as cumulate ultramafic lithologies. Consequently, olivine, pyroxene, and feldspar group minerals have been important in crustal lithologies or as detrital grains throughout the history

of Mars (Bridges & Warren, 2006; Day et al., 2018; Edwards et al., 2017; Hauber et al., 2011; McSween, 2015; McSween, Wyatt et al., 2006; Milam et al., 2010; Mustard et al., 2005; Payré et al., 2020; Treiman et al., 2016).

Mars mineralogy was first studied in the context of the Shergotty-Nakhla-Chassigny (SNC) group of martian meteorites, whose origins were revealed by their distinctive noble gas compositions (Becker & Pepin, 1985; McCoy et al., 2011; McSween, 1985; Meyer & Righter, 2017; Rubin & Ma, 2021; Stolper & McSween, 1979; Treiman et al., 2000). These mafic and ultramafic rocks reveal much about Mars' primary igneous mineralogy. Shergottites, which represent approximately three of every four martian meteorites, include a range of mafic (basaltic) and ultramafic lithologies with varying amounts of augite, plagioclase, forsterite, and oxides (Treiman, 2003; Treiman & Filiberto, 2015). These meteorites originate from a variety of deep mantle sources, from depleted to enriched (Day et al., 2018).

Nakhlite and chassignite meteorites, by contrast, may arise from a low degree of partial melting of a hydrated, metasomatized, and depleted lithospheric (i.e., relatively shallow) mantle source, resulting in sub-alkaline to alkaline basalts, in rare instances tending to olivine-rich, nepheline-normative compositions (McSween, 2015; Udry & Day, 2018). Nakhrites, with at least 10 representative examples, derive from basaltic magmas and feature augite and forsterite as major minerals (Treiman, 2005). These meteorites also contain carbonates and hydrous minerals. Rare chassignite meteorites are olivine cumulate rocks (dunites) with >90% forsterite and intercumulus feldspar, pyroxene, and oxides. At least four lines of evidence support the hypothesis that chassignites are crustal level cumulates: (a) their cumulate textures; (b) the wide range of olivine compositions from  $\sim\text{Fo}_{50}$  to  $\text{Fo}_{80}$ ; (c) volatile-bearing phases similar to those of nakhrites (McCubbin et al., 2013); and (d) textures and compositions similar to those observed in the Seitah formation in Jezero crater (Y. Liu et al., 2022).

Additional insights into Mars mantle processes are provided by unique ungrouped meteorites. The noted meteorite Allan Hills 84001, which generated debates regarding possible signs of martian life (McKay et al., 1996), is an orthopyroxene cumulate rock with interstitial augite, maskelynite (shocked plagioclase glass), chromite, apatite, pyrite, and Mg-Ca-carbonate (Mittlefehldt, 1994). Additional variety is represented by NWA 8159 and NWA 7635, which are highly oxidized and shocked augite-rich basalts with plagioclase (maskelynite), orthopyroxene, olivine, and magnetite (Agee et al., 2014; Lapen et al., 2017).

Data from meteorites are reinforced by the observations of Mars rovers, primarily from abundant float exposures. Exploration of Gusev crater by the Mars Exploration Rover *Spirit* revealed a significant range of igneous lithologies, primarily relatively oxidized basalt to sub-alkaline trachybasalt (McSween, 2015; McSween et al., 2008; McSween, Ruff, et al., 2006; McSween, Wyatt, et al., 2006). Subsequent studies of float and clasts within conglomerate in Gale crater by *Curiosity* have documented a preponderance of basalt and trachybasalt (sub-alkaline) lithologies (Edwards et al., 2017; McSween, 2015), with a few reports of nepheline normative alkali basalt (McSween, 2015; Schmidt et al., 2014; Stolper et al., 2013), as well. These alkaline lithologies may derive from decompression melting of deep mantle sources with subsequent fractionation (McSween, Ruff, et al., 2006; Stolper et al., 2013), though an origin through impact melting has also been proposed (Payré et al., 2020; Sautter & Payré, 2021).

Added to these mafic lithologies are a number of possible plagioclase-rich anorthosite rocks, first identified by the Mars Reconnaissance Orbiter (MRO) in the southern highlands—evidence for highly evolved mantle melts (Carter & Poulet, 2013). Feldspar cumulate rocks with 65% plagioclase were subsequently described by Bowden et al. (2022) from float rocks named “Askival” and “Bindi” in Gale crater.

Another unusual igneous lithology is a Ti and P-rich (>5 wt. %  $\text{P}_2\text{O}_5$ ; possibly merrillite-bearing) alkaline pyroclastic rock from Gusev crater (Usui et al., 2008). Dubbed “Wishstone Class tephrites,” these rocks may represent a residual melt following anorthosite crystallization, or perhaps even derived from a carbonatitic melt.

### 2.1.2. Acidic (Quartz Normative) Rocks

While mafic and ultramafic rocks are the volumetrically dominant primary igneous lithologies on Mars, detrital quartz and alkali feldspar are common, if minor, phases in martian sediments, as documented by orbital spectroscopy (Bandfield et al., 2004; Wray et al., 2013). Subsequent studies by the CheMin X-ray diffraction instrument (Blake et al., 2023; Morrison et al., 2018a; Rampe et al., 2023; Rampe, Blake, et al., 2020) support the idea that quartz-normative lithologies may be widely distributed. Possible potassic phyllosilicates (Le Deit et al., 2016) and fluorite (Forni et al., 2015) also point to granitic lithologies, while the discovery of tridymite (Morris et al., 2016a, 2016b) may point to eruptive acidic rocks [though see Yen et al. (2021), who suggest a hydrothermal origin for tridymite].

Additional evidence is provided by martian meteorite Northwest Africa (NWA) 7034 and paired samples NWA 7475 and NWA 7533 (Hewins et al., 2017; Wittmann et al., 2015). Nicknamed “Black Beauty,” these meteorites are remarkable polymict basaltic breccias with at least 7 kinds of lithologic clasts, including one with a predominantly quartz/alkali feldspar mineralogy. NWA 7034 and its paired samples are unique in their extreme antiquity (4.4 Ga) compared to other known martian meteorites. Black Beauty is also unique in its water content, 10 times that of other martian meteorites (Agee et al., 2012, 2013; Cassata et al., 2018). Note that in addition to granitic minerals, principal minerals include plagioclase (andesine), pigeonite, and augite, with a fine-grained groundmass featuring oxides and iron sulfide. Accessory minerals in NWA 7034 include chlorapatite, chromite, goethite, ilmenite, magnetite, maghemite, alkali feldspar, and pyrite.

### 2.1.3. Volcanic Fumaroles

Vapor deposition of minerals from hot volcanic gases is a feature of many volcanic terrains (Grapes, 2006; Vergasova & Filatov, 2016). Earth boasts more than 450 documented fumarole minerals, though most of those are not relevant to Mars mineralogy, as they incorporate scarce elements and/or are oxidized phases associated with Earth's atmosphere following the Great Oxidation Event (Hazen & Morrison, 2022). Nevertheless, some fumarolic phases on Earth, including native sulfur, gypsum, pyrite, pyrrhotite, cristobalite and tridymite, and iron oxides likely also occur in association with martian volcanoes (McHenry et al., 2020; Nekvasil et al., 2019; Ruff et al., 2020; Schmidt et al., 2008; Yen et al., 2008).

Volcanic fumaroles may have played roles on Mars beyond their sources of mineralogical novelty. As loci of chemical disequilibria, fumaroles have been invoked in some models of a possible origin of life on Mars (Cockell et al., 2019; McCollom et al., 2015; Simpson et al., 2020).

Though of minor importance from a volumetric perspective, high-temperature vapor deposition has also been suggested in the case of magnetite whiskers found in the unique ALH84001 meteorite (Bradley et al., 1996). Indeed, a variety of refractory minerals might form as a consequence of impact-induced vaporization and subsequent crystallization.

### 2.1.4. Atmospheric Condensation

Direct condensation of solid phases from the atmosphere, though not explicitly considered by Hazen and Morrison (2022), is commonly observed as a formation mechanism for water ice on Earth (Z. Zhang et al., 2018). On Mars, both water ice and solid carbon dioxide form in this way (Bierson et al., 2016; Byrne & Ingersoll, 2003; Phillips et al., 2011; I. B. Smith et al., 2022). An intriguing possibility on Mars is the vapor deposition of sulfate, nitrate, perchlorate, and other salts, as observed in the Atacama Desert of Chile (M. L. Smith et al., 2014).

### 2.1.5. Hydrothermal Vents, Hot Springs, and Geysers

For much of its history, the martian surface could have featured abundant near-surface expressions of hydrothermal activity, including subaqueous (i.e., both marine and lacustrine) hydrothermal vents and subaerial hot springs and geysers (e.g., Ruff et al., 2020; Yen et al., 2008). These mineral-forming environments with  $T > 100^{\circ}\text{C}$  represent part of a continuum among high-temperature volcanic fumaroles, deeper subsurface hydrothermal systems, and low-temperature aqueous environments.

Submarine hydrothermal vents, including sulfide-rich (e.g., “black smokers”) and carbonate-rich (ultramafic-hosted) structures, are zones of significant mineralization on Earth's ocean floors (Haymon & Kastner, 1981; Hekinian et al., 1980; Palandri & Reed, 2004; Schwarzenbach & Steele-MacInnis, 2020). Analogous hydrothermal vents on the floors of martian lakes or oceans are likely to have played similar roles (Farmer, 1996; Michalski, Dobreá, et al., 2017). Hazen and Morrison (2020) cataloged more than 20 relatively common hydrothermal vent minerals on Earth—phases that might occur in similar environments on Mars.

Hot springs and geysers on Mars may have produced a range of geothermal minerals, most notably opal, which has been identified at several sites (Brož et al., 2017; Munoz-Saez et al., 2021; Ruff & Farmer, 2016; Ruff et al., 2011; Skok et al., 2010; Squyres et al., 2008), though opal and hydrated amorphous silica also form through diagenesis and as a residue of acid-sulfate leaching (Frydenvang et al., 2017; Milliken et al., 2008; Rapin et al., 2018). In addition, Yen et al. (2021) speculated that occurrences of tridymite detected by CheMin might be products of hydrothermal activity at Gale Crater. While other hot spring minerals have yet to be positively identified, evidence for the surface expression hydrothermal fluids enriched in halogens, Zn, Ge, and S points to the significant potential for mineralogical diversity (Schmidt et al., 2008; Yen et al., 2008). Terrestrial analogs host deposits of calcite ( $\text{CaCO}_3$ ), sulfates [notably gypsum, but also baryte ( $\text{BaSO}_4$ )], and a variety of hydrated phases.

### 2.1.6. Hydrothermal Veins/Fractures

Subsurface hydrothermal systems, in which primary minerals are precipitated in veins, fractures, or pore spaces from hot ( $>100^{\circ}\text{C}$ ), solute-saturated aqueous fluids (or possibly immiscible sulfide-rich magmatic fluids; Burns & Fisher, 1990), are potentially among the most mineralogically diverse environments on Mars (Abramov & Kring, 2005; Farmer, 1996), as they are on Earth (Barnes & Rose, 1998; Guilbert & Park, 2007; Heinrich & Henley, 1989; Pirajno, 2009; Steele-MacInnis & Manning, 2020). However, with the exceptions of a few surface manifestations, notably sulfate veins (Berger et al., 2017; Nachon et al., 2014; Schwenzer et al., 2016) and silica deposits at hot springs (Rapin et al., 2018; Ruff & Farmer, 2016; Squyres et al., 2008), and suites of suspected hydrothermal minerals in martian meteorites (Lorand et al., 2018), little direct evidence of subsurface martian hydrothermal mineralization has yet been documented.

The two major loci of subsurface hydrothermal fluids are associated with volcanic complexes and bolide impacts. Deep volcanic hydrothermal systems are revealed by their near-surface manifestations of hot springs, geysers, and submarine vents, as detailed above (Ruff et al., 2020; Yen et al., 2008). Alternatively, large bolide impacts are known to generate active mineralizing hydrothermal systems (Abramov & Kring, 2005; Carrozzo et al., 2017; Marzo et al., 2010; Osinski et al., 2013; Turner et al., 2016). While circumferential fracture zones are particularly subject to hydrothermal reworking and mineralization, as found in some terrestrial economic metal deposits (Pirajno, 2009), several different impact-associated hydrothermal zones of potential mineralization, including those caused by hot impact ejecta and impact melts, have been outlined by Osinski et al. (2013).

In addition to volcanic and impact settings, other proposals for the origins of hydrothermal systems on Mars have included significant heat generated by serpentinization (Lowell & Rona, 2002; though see Allen & Seyfried, 2004) and amagmatic geothermal (i.e., radiogenic) heating (Ojha et al., 2020, 2021). In the case of radiogenic heating, Ojha and colleagues point to local enrichments of thorium and potassium, for example, in the Eridania basin. However, their proposal that heat-producing isotopes such as  $^{40}\text{K}$ ,  $^{232}\text{Th}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$  may have concentrated on Mars during granite formation, with corresponding crustal concentration of incompatible elements, invokes a mechanism that is relevant to terrestrial environments, but that may not occur on Mars.

Terrestrial subsurface hydrothermal deposits reveal a mineralogical richness that reflects the power of hot aqueous fluids to select, concentrate, and transport elements. A distinctive, indeed defining, characteristic of primary hydrothermal minerals is that their compositions are very different from that of their host rocks. Hazen and Morrison (2022) record more than 850 species of sulfides, arsenides, antimonides, and a wide range of sulfosalts bearing relatively rare elements such as Ge, Sn, Bi, Se, and Te, most of which are unique to hydrothermal environments. However, we postulate that these uncommon elements may not have been sufficiently concentrated in martian hydrothermal fluids to generate that wide range of compounds. Accordingly, in Table 1 we list a more modest suite of sulfides, sulfates, phosphates, carbonates, and other likely hydrothermal minerals (Ehlmann & Edwards, 2014; Lorand et al., 2018; Pirajno & Van Kranendonk, 2005; Schwenzer et al., 2016; Yen et al., 2008). If much greater mineral diversity is present at undiscovered martian sites, then hydrothermal deposits may offer the best hope for economic metal resources on Mars (Baumgartner, 2017; Ciązela et al., 2022).

### 2.1.7. Chemical Precipitation (Evaporite and Authigenic Minerals)

Precipitation of primary minerals from near-surface environments at low-temperature ( $T < 100^{\circ}\text{C}$ , in contrast to hydrothermal systems) has played a major role in the evolving mineralogy of Mars (B. C. Clark & Van Hart, 1981). We lump the closely related processes of surface deposition in evaporites (e.g., surface salt deposits), subaqueous chemical precipitation (e.g., in a stranded basin), and authigenesis, which we define in a restricted sense as in situ mineral formation by direct subsurface precipitation in detrital sediments (e.g., as a carbonate cement). In each example, new minerals precipitate directly from a solute-saturated aqueous fluid.

In this regard, an important distinction between Mars and Earth is the widespread occurrence of relatively long-lived, carbonate-rich alkaline lakes on Mars, often associated with impact craters (Hurowitz et al., 2023). On Earth, by contrast, marine basins were long-lived, while lakes have been more ephemeral features. As a consequence, authigenic minerals, including Fe-Ca-Mg carbonates, clays, hydroxides, and possibly zeolites, on Mars typically reflect the chemistry of an alkaline closed basin.

Several missions to Mars, including orbiters, landers, and rovers, have provided direct evidence for the widespread distribution of authigenic chemical precipitates (Forni et al., 2015; Glotch et al., 2010; Kodikara et al., 2023;



Leask & Ehlmann, 2022; Osterloo et al., 2010; Rapin et al., 2019; Thomas et al., 2019). In particular, data from Mössbauer spectroscopy (for Fe-bearing phases) and X-ray diffraction verify the presence of hematite, magnetite, akaganeite, gypsum, anhydrite, jarosite, and possibly ferrihydrite, greenalite, and minnesotaite, as well as abundant X-ray amorphous material, all of which could represent primary precipitates (Bishop et al., 2018; Blake et al., 2013, 2023; Klingelhöfer et al., 2004; Morris et al., 2008, 2019; Rampe et al., 2017, 2018, 2023; Rampe, Blake, et al., 2020; Rampe, Bristow, et al., 2020; Thorpe et al., 2022; Treiman et al., 2016; Vaniman et al., 2014). The identification of minerals formed by evaporation/chemical precipitation in martian meteorites has provided additional important evidence for these near-surface processes on Mars, as well as subsequent diagenetic alteration (Bridges & Grady, 2000; Needham et al., 2011).

Several authors have recorded precipitation sequences that are dependent on both fluid and atmospheric compositions (Catling, 1999; Tosca & McLennan, 2006). On early Mars, when atmospheric CO<sub>2</sub> concentration may have exceeded 0.1 bar and acidic, anoxic waters were enriched in Fe, Ca, Mg, and alkalis, siderite (FeCO<sub>3</sub>) may have been the initial precipitate as it was on Earth (Ohmoto et al., 2004), followed by Ca and Mg carbonates, gypsum, halite, and alkali sulfates and carbonates (Catling, 1999). In environments with greater concentrations of H<sub>2</sub>S or SO<sub>2</sub>, evaporitic jarosite and Mg or Ca sulfates may dominate (Gendrin et al., 2005; Tosca & McLennan, 2006).

An intriguing aspect of surface evaporite (halite-dominant) deposits on Mars is their relatively constrained ages—with a maximum age in the mid-Hesperian Period (~3.6 Ga) and no observed deposits after ~2.3 Ga (J. Hill & Christensen, 2019; Hynke et al., 2015; Leask & Ehlmann, 2022; Milliken et al., 2009). These results suggest that numerous recurrent episodes of halite precipitation and dissolution preceded the drying of the planet by the Early Amazonian Period (Thomas et al., 2019).

Mg- or Ca-perchlorate salts have been detected via wet chemistry and thermal and evolved gas analysis in mid-latitude icy soils by the Mars Phoenix lander (Hecht et al., 2009). SAM evolved gas analyses also support the presence of perchlorate and/or chlorate in ancient sedimentary rocks and modern regolith in Gale crater (J. Clark et al., 2021; Glavin et al., 2013). A combination of X-ray fluorescence and Raman data collected by *Perseverance* shows that Na perchlorate is present in aqueously altered olivine cumulate (Tice et al., 2022).

Several authigenic martian minerals have been proposed, including the iron oxides magnetite (Bristow et al., 2015; Vaniman et al., 2014) and hematite (Szczerba et al., 2023), ferrihydrite (Treiman et al., 2016), carbonates (Chang et al., 1996; Horgan et al., 2020; Morris et al., 2010; Thorpe et al., 2022), sulfates (Farrand et al., 2009), and possibly phosphates (Adcock et al., 2013; Mojzsis & Arrhenius, 1998). Clay minerals may also form by authigenesis in martian sediments (Chevrier et al., 2007; Milliken et al., 2009; Murchie et al., 2009; Thorpe et al., 2022). Authigenic zeolites, including chabazite and clinoptilolite, are also plausible (Basu et al., 1998; Kodikara et al., 2023; Mousis et al., 2016; Ruff, 2004), though zeolites are also readily formed via the diagenesis of volcanic ash (Deer et al., 2004). Each of these examples of authigenesis has well-documented analogs on Earth (Baturin & Bezrukov, 1979; Bekker et al., 2010; Boggs, 2006; Button, 1982; Delaney, 1998; Falkowski et al., 2000; Klein, 2005).

Clay minerals are among the most abundant phases in martian rocks and sediments sampled at Gale crater, at times exceeding 30 wt. % of the crystalline fraction (Blake et al., 2023; Bristow et al., 2021; Rampe et al., 2023; Thorpe et al., 2022). Clay minerals likely represent both primary and secondary phases on Mars, as they do on Earth (Ehlmann, Mustard, Clark, et al., 2011; Tu et al., 2021; M. J. Wilson, 2013). Possible martian authigenic clay minerals include kaolinite and both dioctahedral and trioctahedral smectites such as montmorillonite and saponite (Bristow et al., 2018; Bristow & Milliken, 2011; M. J. Wilson, 1977, 2013), though diagenetic processes have also been invoked for all of these clay minerals (see below).

A fascinating yet unresolved aspect of mineral precipitation relates to the observation of manganese-rich nodules and fracture fillings in Gale and Endeavor craters (Arvidson et al., 2016; Berger et al., 2022; Lanza et al., 2016; Mitra et al., 2022)—deposits reminiscent of the primary precipitation of Mn oxides and hydroxides in terrestrial sediments (Freitas et al., 2013; Post, 1999).

A distinctive and enigmatic mineralogical feature of Mars is the ubiquitous presence of X-ray amorphous phase(s) in sedimentary rocks and modern soils. Results from *Curiosity* indicate that all targets analyzed by CheMin contain 15 to 70 wt. % X-ray amorphous materials—an amount far exceeding what is observed in typical terrestrial soils (Achilles et al., 2020; Dehouck et al., 2014; Rampe, Blake, et al., 2020; R. J. Smith et al., 2020, 2021, 2022). Though primary volcanic glass and transformation via impacts could account for a fraction of this amorphous component, additional Si/Al-rich (e.g., palagonite; allophane) and Fe-rich (e.g., ferrihydrite) components, with



significant sulfate, phosphate, and Na- and/or Cl-bearing phases, are likely the result of near-surface aqueous processes, both through precipitation and diagenesis (e.g., Ming et al., 2009; Morris et al., 2008).

### 2.1.8. Freezing

The hydrosphere of Mars hosts a number of examples of minerals formed by freezing of aqueous solutions, precipitating water ice and other solid phases (e.g., Vincendon et al., 2010). Bishop et al. (2021) propose the occurrence of antarcticite ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ) as one of several plausible cryosalts. We also postulate occurrences of hydrohalite ( $\text{NaCl} \cdot 2\text{H}_2\text{O}$ ), which occurs via freezing of halite-saturated brines (Craig et al., 1974), and ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ), which precipitates below 25°C in calcite-saturated water (Bischoff et al., 1993). Morris et al. (2015) report cryo-precipitation of crystalline and amorphous sulfate phases from aqueous sulfate solutions. An intriguing additional possibility is the freezing of water clathrates or other molecular solids under cryogenic conditions of the martian poles (Miller & Smyth, 1970), as observed on Saturn's moon Titan (Hazen, 2018; Maynard-Casely et al., 2018).

### 2.1.9. Detrital Concentration

Detrital minerals form from the breakdown of rock and subsequent fluvial and/or aeolian transport and concentration of durable phases (Baker, 1962; McGlynn et al., 2012). Martian soils contain a variety of such mechanically robust minerals, including ferromagnesian silicates, feldspars, and fluorapatite (Cox et al., 2022; Payré et al., 2020). An intriguing aspect of martian detrital minerals is that, despite millions of years of surface mixing and transport by wind and water, significant local differences in detrital mineral populations, often related to local lithologies, are observed to persist, as observed at Gale crater (e.g., Rampe, Blake, et al., 2020).

## 2.2. Secondary Mineralization Associated With Fluid/Rock Interactions

During periods early in its history, Mars was a warm and wet planet (Bishop et al., 2018; Squyres & Kasting, 1984; Tosca & Knoll, 2009)—conditions that fostered crustal mineralization. Secondary mineralization involves the alteration of preexisting minerals through fluid/rock interactions that alter the original mineral by changes in chemistry and/or structure. We identify five paragenetic modes that produce secondary phases by fluid/rock interactions in near-surface crustal environments. A wide range of fluid/rock interactions, primarily with aqueous solutions and atmospheric gases, leads to modifications of existing minerals and new mineral assemblages. In some instances, such as hydration, dissolution, and serpentinization, new minerals arise from the alteration of primary igneous phases that are in disequilibrium with the near-surface environment. In many other cases, secondary mineral formation processes result from combinations of changes in temperature, pressure, and a wide range of compositional variables, including pH,  $f\text{O}_2$ , and solute concentrations, as well as the activity of water, itself.

Numerous other types of fluid/rock interactions involve the alteration of the compositions and/or structures of preexisting minerals. *Solubility reactions* refer to the loss of some or all of the chemical components of a solid phase by interactions with local fluids. Examples include (a) dissolving, for example, when preexisting evaporite deposits are dissolved by fresh water; and (b) leaching, for example, when percolating acidic fluids selectively remove Fe and Mn from a sediment column to form a laterite or bauxite deposit and leave behind a residue of high-silica material plus insoluble phases, for example, zircon ( $\text{ZrSiO}_4$ ) and ilmenite ( $\text{FeTiO}_3$ ) that may concentrate in detrital deposits.

### 2.2.1. Hydration/Dehydration

Hydration and dehydration reactions, by which  $\text{H}_2\text{O}$  molecules or  $\text{OH}^-$  ions are added to or removed from a pre-existing solid phase, represent a relatively simple formation mode of secondary minerals. Numerous examples have likely occurred on Mars, as revealed by coexisting phases in differing hydration states. For example, the CheMin instrument on *Curiosity* has identified three calcium sulfate minerals: anhydrite ( $\text{CaSO}_4$ ), bassanite ( $\text{CaSO}_4 \cdot \sim 0.5\text{H}_2\text{O}$ ), and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )—phases that transform as environmental conditions vary, both on the martian surface and within the instrument (Vaniman et al., 2018).

Other likely hydration/dehydration reactions include halite ( $\text{NaCl}$ )  $\leftrightarrow$  hydrohalite ( $\text{NaCl} \cdot 2\text{H}_2\text{O}$ ) in brines (Craig et al., 1974); calcite ( $\text{CaCO}_3$ )  $\leftrightarrow$  ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) in calcite-saturated water (Bischoff et al., 1993); hema-

tite ( $\text{Fe}_2\text{O}_3$ )  $\leftrightarrow$  ferrihydrite [ $\text{Fe}^{3+}_{10}\text{O}_{14}(\text{OH})_2$ ] in diagenetically altered sediments (Szczerba et al., 2023); and periclase ( $\text{MgO}$ )  $\leftrightarrow$  brucite [ $\text{Mg}(\text{OH})_2$ ] in zones of serpentinization (see below; Schrenk et al., 2013).

Of special interest are hydration/dehydration reactions among at least 11 hydrated magnesium sulfates, ranging in water content from kieserite [ $\text{Mg}(\text{SO}_4)\cdot\text{H}_2\text{O}$ ] to meridianiite [ $\text{Mg}(\text{SO}_4)\cdot 11\text{H}_2\text{O}$ ] (Berdiesinski, 1952; Chipera & Vaniman, 2007; Peterson et al., 2007; Wang et al., 2006, 2009, 2011; <https://rruff.info/ima>; accessed 10 March 2023), as well as their  $\text{Fe}^{2+}$ -bearing analogs (e.g., Pitman et al., 2014). These phases are useful in understanding the near-surface evolution of Mars because of their sensitivity to formational environments (Vaniman et al., 2004). While kieserite and starkeyite [ $\text{Mg}(\text{SO}_4)\cdot 4\text{H}_2\text{O}$ ] are the only crystalline magnesium sulfates to be identified with confidence by CheMin, other members of the series that might be relevant to martian conditions include sanderite [ $\text{Mg}(\text{SO}_4)\cdot 2\text{H}_2\text{O}$ ], pentahydrate [ $\text{Mg}(\text{SO}_4)\cdot 5\text{H}_2\text{O}$ ], hexahydrate [ $\text{Mg}(\text{SO}_4)\cdot 6\text{H}_2\text{O}$ ], epsomite [ $\text{Mg}(\text{SO}_4)\cdot 7\text{H}_2\text{O}$ ], and meridianiite [ $\text{Mg}(\text{SO}_4)\cdot 11\text{H}_2\text{O}$ ]. An intriguing scenario relevant to Mars is the possibility of daily cycles of hydration/dehydration coupled to increases and decreases of humidity (e.g., Vaniman et al., 2018)—processes that likely result in variable water contents in clay minerals, zeolites, and other phases.

It is important to note that many of the phases mentioned above originate as primary minerals (e.g., Vaniman et al., 2004), for example, anhydrite in hydrothermal veins, halite as an evaporite, and Fe-Mg carbonates and sulfates as precipitates from saline lakes. However, once formed, subsequent hydration/dehydration reactions represent secondary processes.

The tendency of some Mars minerals to dehydrate or effloresce under changes in atmospheric conditions is likely to affect martian samples returned to Earth. Consequently, samples will need to be maintained in a dry environment.

### 2.2.2. Oxidation/Reduction

Chemical reactions by which oxygen is added or removed, while an accompanying ion changes oxidation state, are important in understanding the redox evolution of the near-surface martian environment. Note that in this restricted context oxidation reactions involving multiple chemical changes, such as the oxidation of iron sulfides to iron oxides, are included under diagenetic processes. The oxides and hydroxides of two metal elements, Fe and Mn (Bowles et al., 2011), are frequently invoked in discussions of near-surface redox reactions on Mars (Berger et al., 2022; King & McSween, 2005; Mitra et al., 2022).

Of note is the observed regional transition in Gale crater from more reduced, magnetite-bearing strata in lower beds of drill sites from Yellowknife Bay to the Buckskin drill site at Marias Pass (Morrison et al., 2018a; Rampe, Blake, et al., 2020), to hematite-dominant beds at and above Vera Rubin ridge at drill sites Oudam and above (Rampe et al., 2023; Rampe, Blake, et al., 2020; Rampe, Bristow, et al., 2020).

Also of special importance is the possible oxidation of  $\text{Fe}^{2+}$ -bearing clay minerals. Global surveys reveal that smectites are largely  $\text{Fe}^{3+}$ -bearing, such as nontronite (Michalski et al., 2015). However, the reducing atmosphere of early Mars should have favored the formation of  $\text{Fe}^{2+}$ -bearing smectites, such as ferrosaponite (Hazen et al., 2013). The oxidation of  $\text{Fe}^{2+}$ -bearing clay minerals, especially at the surface, would explain this discrepancy, while masking details of the martian redox history (e.g., Chemtob et al., 2015). Though not as yet documented on Mars, anions may also participate in oxidation/reduction reactions. Intriguing possibilities include aqueous sulfide/sulfite/sulfate or phosphide/phosphite/phosphate reactions in the extremely reducing environments of iron meteorites (e.g., Pasek, 2017) or lightning (Bindi et al., 2023).

### 2.2.3. Serpentinization

Serpentinization, though but one of many planetary processes that forms minerals through water/rock interactions, is possibly the most ubiquitous near-surface chemical reaction on wet terrestrial planets (e.g., Holm et al., 2015; Lowell & Rona, 2002; Schrenk et al., 2013), including Mars (Ehlmann et al., 2010; Quesnel et al., 2009; Tutolo & Tosca, 2023). Serpentinization is the hydrothermal alteration at moderate temperature (typically  $T < 250^\circ\text{C}$ , but at times to  $> 300^\circ\text{C}$ ) of mafic/ultramafic lithologies by which anhydrous ferromagnesian minerals (olivine; pyroxene) are converted into hydrous phases, including serpentine, brucite, and magnetite. The associated oxidation of  $\text{Fe}^{2+}$  minerals to  $\text{Fe}^{3+}$ -bearing magnetite and  $\text{Fe}^{3+}$ -bearing serpentine may result in a significant release of hydrogen—a reductant that has been invoked in models of prebiotic chemistry (Holm et al., 2015; Menez et al., 2018; Schrenk et al., 2013). Consequently, we list serpentinization as a distinct paragenetic mode on Mars.

At least five of the secondary minerals listed in Table 1 are typical of serpentinization alteration zones (Amador et al., 2018; Blais & Auvray, 1990; Lowell & Rona, 2002; Palandri & Reed, 2004; Schrenk et al., 2013).

#### 2.2.4. Leaching

Leaching, the chemical alteration or chemical weathering of minerals by selective dissolution of elements, has long played a significant role in pedogenesis—the evolution of martian soils (Dreibus et al., 2008; Hurowitz et al., 2006; Retallack, 2014; Thorpe et al., 2021, 2022; Ye & Michalski, 2021). Of special importance to near-surface processes on Mars, leaching generates fluids rich in elements that can then migrate and participate in authigenic and diagenetic mineralization over a wide range of temperatures (Bullock & Moore, 2004).

Basalt, ash, and other volcanic deposits are particularly subject to hydration and selective leaching when exposed to acidic precipitation. Of note, a variety of X-ray amorphous materials that may have formed by basalt or ash alteration have been detected via orbital infrared spectroscopy. These phases include opaline silica, allophane, and imogolite (Bishop & Rampe, 2016; Horgan & Bell, 2012; Milliken et al., 2008; Rampe et al., 2012; Sun & Milliken, 2018), which are common low-temperature alteration products of basalt and volcanic ash.

Fe and Mn leaching is evident by localized layered deposits of Fe and Mn minerals, juxtaposed with layers depleted in those elements but relatively enriched in Al and Si (Berger et al., 2022; McKeown et al., 2009; Morris et al., 2008). Leaching also results in the loss and transport of a host of incompatible minor elements, including K, U, Th, and light rare earth elements, which are selectively dissolved from martian basalt and consequently concentrated in the crust (Taylor et al., 2006).

Carbonate dissolution represents another important consequence of crustal leaching—a phenomenon well developed in limestone cave environments on Earth (C. Hill & Forti, 1997), and a possibility on Mars, as well. Whether or not Mars boasts carbonate caverns, carbonate leaching at a smaller scale has been documented. Piercy et al. (2022) describe the dissolution of siderite ( $\text{FeCO}_3$ ) in the Lafayette nakhlite meteorite, with the subsequent formation of the iron-rich clays odinite and saponite.

Leaching results in two important mineralogical consequences. Most obviously, a number of minerals formed as a direct consequence of leaching, including several clay minerals and Al-rich hydrous minerals from martian laterite-type deposits (e.g., Helgren & Butzer, 1977; I. G. Hill et al., 2000). For example, Bishop et al. (2008) and Le Deit et al. (2012) describe the occurrence of kaolinite-bearing layers likely formed by leaching above smectite-bearing materials at Valles Marineris. In addition, solute-rich aqueous fluids participate in subsequent diagenetic alteration (see below) and precipitation of residue phases.

#### 2.2.5. Diagenesis

We define diagenesis to encompass a complex, intertwined suite of near-surface, relatively low-temperature ( $T < 100^\circ\text{C}$ ) water/rock interactions that chemically and physically transform crustal rocks and soils. Ubiquitous aqueous alteration of the martian crust has spanned billions of years of sequential, often cyclical processes that are modified by hydrothermal systems (including serpentinization), disrupted by bolide impacts, and significantly influenced by the effects of other primary and secondary chemical processes, including evaporation, precipitation, hydration/dehydration, oxidation/reduction, and leaching (Achilles et al., 2020; Arvidson et al., 2014; Bridges et al., 2015; Bristow et al., 2021; Carter et al., 2013; Farley et al., 2022; J. C. Liu et al., 2021; Mangold et al., 2019; McGlynn et al., 2012; Ming et al., 2009; Murchie et al., 2009; Sheppard et al., 2021; Thorpe et al., 2022; Ye & Michalski, 2021; Yen et al., 2017). Indeed, “diagenesis” is a grab bag of chemical processes that may often represent a continuum with these other modes of mineral formation. Therefore, rather than attempt to catalog numerous diagenetic chemical reactions, we consider the major groups of minerals that are thought to be formed and/or modified by diagenesis. In this regard, an important contrast between diagenesis on Earth and Mars is that martian sediments tend to be relatively “juvenile”—i.e., diagenetically undeveloped compared to sediments on Earth owing to relatively brief interludes of martian aqueous alteration (Tosca & Knoll, 2009). In Table 1, we record at least 50 martian minerals that plausibly form by diagenesis. This modest suite of mineral species contrasts with the almost 2,000 oxidized/weathered species that appeared on Earth following the Great Oxidation Event (Hazen & Morrison, 2022; Lyons et al., 2014).

**Clay minerals:** Clay minerals, which form through a variety of primary and secondary processes, are the most abundant, ubiquitous, and revealing diagenetic minerals in the martian crust (Bibring et al., 2006; Bristow et al., 2015, 2018; Carter et al., 2010; Ehlmann et al., 2009, 2010, 2013; Ehlmann, Mustard, Clark, et al., 2011;

Ehlmann, Mustard, Murchie, et al., 2011; Hazen et al., 2013; Meunier et al., 2012; Milliken & Bish, 2010; Milliken et al., 2009; Mustard et al., 2008; Poulet et al., 2005; Rampe, Blake, et al., 2020; Sun & Milliken, 2015; Tosca & Knoll, 2009; Tu et al., 2021). Included in this inventory are members of several clay mineral groups (Table 1; M. J. Wilson, 2013).

Diagenetic clays on Mars appear to fall into two distinct groups. The earliest diagenetic clays on Mars likely formed by the aqueous alteration of basalt and other mafic lithologies to trioctahedral (Mg-Fe<sup>2+</sup>-dominant) ferromagnesian clay minerals such as saponite and corrensite (a mixed-layer chlorite/smectite; Bristow & Milliken, 2011; Bristow et al., 2015; Hazen et al., 2013; Peretyazhko et al., 2016; Vaniman et al., 2014)—alteration processes that may continue to this day in deep hydrothermal zones.

Subsequent near-surface transformations of those phases via chemical weathering (leaching and oxidation) produced a complementary suite of dioctahedral (Al-Fe<sup>3+</sup>-dominant) clays such as kaolinite, montmorillonite, nontronite, and possibly vermiculite—phases that may reflect the chemical weathering in a changing martian climate (Bibring et al., 2006; Bishop et al., 2018; Bristow et al., 2018; Cuadros et al., 2022; Dehouck et al., 2023; Hazen et al., 2013).

**Sulfates:** Sulfate minerals provide important clues to diagenetic processes (Chang et al., 1996). Active sulfur cycling on Mars, involving atmospheric gases, S-rich acidic waters, magmatic and hydrothermal sulfides, and varied oxidized and hydrated sulfate phases, is a key feature of martian diagenesis (Chipera & Vaniman, 2007; King & McLennan, 2010; M. L. Smith et al., 2014; Wang et al., 2011). Sulfates of magnesium, calcium, iron, and alkalis are widespread minerals in martian soils and represent key indicators of diagenetic environments on Mars (Aubrey et al., 2006; Bishop et al., 2006; Farrand et al., 2009; Gendrin et al., 2005; Morris et al., 2007; Rampe et al., 2023; Vaniman et al., 2004; Wang et al., 2006, 2009, 2011; Wray et al., 2009). Almost 20 sulfate species have been identified or inferred on Mars (Table 1; Benison, 2016; Bishop et al., 2009; Farrand et al., 2009, 2014; Klingelhöfer et al., 2004; Morris & Klingelhöfer, 2008; Rice et al., 2010; Vaniman et al., 2018; Wang et al., 2007).

Sulfate diagenesis may occur in a variety of ways, including by reaction of carbonates with S-rich fluids (Catling, 1999), reactions of primary vapor-deposited minerals on cooling (Nekvasil et al., 2019), sulfide weathering (Dehouck et al., 2012), alteration of basalt by SO<sub>2</sub>-bearing fluids (McCollom et al., 2013), and evaporation accompanied by alteration of sediments by acidic solutions (Schwenzer et al., 2016; Wray et al., 2009).

Note that two likely martian sulfate minerals, baryte (BaSO<sub>4</sub>) and celestine (SrSO<sub>4</sub>), should be readily detected by thermal IR spectroscopy (Burt et al., 2004), yet have not yet been reported. We include these inferred phases in Table 1 as possibly forming via both primary and secondary processes.

**Carbonates:** The Mg-Ca-Fe carbonate minerals, including the IMA-approved species ankerite, calcite, dolomite, magnesite, and siderite, in some instances reported as the unapproved phases breunnerite or Mg-calcite, display a remarkably wide range of igneous, metamorphic, and sedimentary parageneses (Chang et al., 1996; Hazen & Morrison, 2022; Thorpe et al., 2022). These and other carbonates have long been recognized as important primary and secondary phases on Mars (Bandfield et al., 2003; Ehlmann et al., 2008; Horgan et al., 2020; Morris et al., 2010). Carbonate minerals participate in active diagenetic cycling as phases form and transform under changing environmental conditions. For example, local concentrations of S-rich gases SO<sub>2</sub> or H<sub>2</sub>S would have resulted in Ca-Mg-Fe sulfates forming at the expense of Ca-Fe-Mg carbonates (Catling, 1999), whereas carbonate dissolution may enhance the formation of clay minerals such as hisingerite or odinite (Fe<sup>3+</sup>-dominant serpentines) and saponite (Fernández-Remolar et al., 2011; Piercy et al., 2022; Tutolo et al., 2019). On the other hand, sulfide weathering may lead to enhanced formation of carbonates (Dehouck et al., 2012).

Though carbonate minerals are relatively common on Mars, a major difference in rock-forming minerals on Mars versus Earth is the extensive formation of biologically mediated carbonates on the latter.

**Phosphates:** Phosphate minerals occur commonly as both primary and secondary phases on Mars (Adcock & Hausrath, 2015; Hausrath et al., 2013; Tu et al., 2014), with phosphate-rich sediment horizons documented at Endeavor, Gusev, and Gale craters (Yen et al., 2014). Plausible martian phosphorus-bearing phases have been shown to dissolve and precipitate under changing physical and chemical conditions (e.g., Delaney, 1998), thus suggesting the potential for an active near-surface P cycle on Mars (Adcock et al., 2013). The only phosphate mineral confidently identified by CheMin thus far is fluorapatite, presumably a detrital phase from igneous rocks (Rampe et al., 2023; Rampe, Blake, et al., 2020). However, local soil enrichments of P<sub>2</sub>O<sub>5</sub>, at times

exceeding 5 wt. % and correlating with Ca abundance suggest the presence of one or more diagenetic phosphates, perhaps merrillite (Usui et al., 2008) or whitlockite (Boctor et al., 2003). Note that inferences of brushite [ $\text{CaPO}_3(\text{OH})\cdot 2\text{H}_2\text{O}$ ] in Gusev crater based on APXS data by Ming et al. (2006) remain speculative. In addition, compositional data from the *Perseverance* rover in Jezero crater indicate the presence of merrillite in altered olivine cumulate on the crater floor (Y. Liu et al., 2022; Tice et al., 2022).

**Fe/Mn oxides and hydroxides:** Oxides and hydroxide minerals of the redox-sensitive elements Fe and Mn are important indicators of martian paleoenvironments (Bowles et al., 2011). The iron oxide/hydroxide minerals hematite, magnetite, possible maghemite, goethite, and akageneite have been recorded from Mars (Fraeman et al., 2013; Morris & Klingelhöfer, 2008; Morris et al., 2008; Nekvasil et al., 2019; Rampe et al., 2023). In addition, one or more Fe-bearing X-ray amorphous phases, including ferrihydrite, hisingerite, and superparamagnetic (small particle) hematite and goethite in unknown proportions, have been generically described as nanophase ferric oxide (npOx; Morris & Klingelhöfer, 2008; Morris et al., 2008).

Though no specific Mn minerals have been definitively identified, manganese phases have been inferred from locally enhanced concentrations (Arvidson et al., 2016; Berger et al., 2022; Lanza et al., 2016; Mitra et al., 2022).

**Silicates:** Though incompletely documented, a number of hydrous silicates in addition to clay minerals, including opal and/or X-ray amorphous hydrated silica (Frydenvang et al., 2017; Milliken et al., 2008; Rapin et al., 2018); amphiboles (Deer et al., 1997; Giesting & Filiberto, 2016; Giesting et al., 2015), epidote (Deer et al., 1986), and zeolites (see below), may form through diagenetic processes.

**Zeolites:** Zeolite group minerals are low-temperature aluminosilicates that commonly form as secondary phases in varied environments on Earth (Basu et al., 1998; Deer et al., 2004; Mumpton, 1977). Zeolite minerals, which readily form through the alteration of basaltic glass by aqueous fluids, have long been proposed as likely phases in diagenetically altered martian sediments, as well as in the vesicles of cooling basalt (Kodikara et al., 2023; Ming & Gooding, 1988; Mousis et al., 2016). Though not yet positively identified on Mars using X-ray diffraction, evidence for the widespread distribution of zeolites, identified as chabazite and clinoptilolite, was provided by Mars Global Surveyor spectral data (Ruff, 2004), as well as subsequent observations of these phases and possibly analcime (Carter et al., 2013; Ehlmann et al., 2009; Mousis et al., 2016).

**Amorphous Phases:** Among the distinctive mineralogical characteristics of Mars is the widespread and voluminous presence of amorphous phases, including X-ray amorphous nano-crystalline materials, on the martian surface. Detected both in situ and via orbital IR spectroscopy, amorphous phases have been observed to account for significantly more than 50 vol. % of many sedimentary rock samples analyzed by CheMin (Rampe, Blake, et al., 2020; R. J. Smith & Horgan, 2021; R. J. Smith et al., 2020, 2021, 2022; Wang et al., 2007). Of special note is the high sulfate content of the amorphous material at many localities (R. J. Smith et al., 2022). The parageneses of amorphous phases are uncertain, though a combination of primary precipitation from cold aqueous solutions and diagenetic alteration, for example, of volcanic glass, is plausible.

### 2.2.6. Mantle Metasomatism

As seen above, a range of secondary mineralization processes fall under the general heading of aqueous alteration. In its most general meaning, “metasomatism” is a term for the subsurface hydrothermal alteration of prior lithologies through mass transfer in an open system (Harlov & Austrheim, 2013). This definition includes a wide range of diagenetic processes, including hydration/dehydration, dissolution/precipitation, and ion exchange reactions—all of which we have subsumed under other headings listed above. We adopt a more restrictive definition of “mantle metasomatism,” which refers to higher temperature and pressure interactions between igneous rocks and aqueous fluids in the martian mantle—processes that can selectively concentrate incompatible elements and dramatically alter the compositions of resulting magmas (Day et al., 2018; Michalski et al., 2021; Treiman, 2003).

Additional complexity arises through auto-metasomatism—the self-alteration of an igneous body by interaction with its own hot fluids during cooling. Terrestrial examples that might be relevant to martian lithologies include myrmekitization (the metasomatic alteration of K-feldspar to quartz plus Na-rich plagioclase; Castle & Lindsley, 1993); rodingitization (auto-metasomatism of ultramafic rocks; Salvioli-Mariani et al., 2020); and saussuritization (the *in-situ* alteration of calcic plagioclase to epidote/zoisite, chlorite, and other phases; Deer et al., 1986). An intriguing example on Mars is the occurrence of potassic-chloro-hastingsite, an amphibole from



nakhlite MIL 03346 that Giesting & Filiberto (2016) suggested formed by auto-metasomatism from a K-Fe-Cl-rich magmatic fluid.

Cannon et al. (2017) propose that additional mineralization, notably formation of clay minerals, might have arisen from interactions of deep crustal lithologies with dense steam or supercritical fluids outgassed during magma ocean cooling.

### 2.3. Metamorphism

We define metamorphism as the alteration of prior minerals by changes in their physical environment. Some ambiguity arises owing to the continuum of conditions from lower-pressure hydrothermal environments, serpentinization, and diagenesis to higher-pressure metamorphic environments. Here, we distinguish diagenesis and other forms of relatively low-temperature ( $T < \sim 200^\circ\text{C}$ ) alteration processes from metamorphism. On Earth, a wide range of metamorphic rocks and their distinctive suites of minerals play a major role in crustal geology, primarily owing to tectonic processes that lead to burial, alteration, uplift, and erosion (Carswell, 1990; Carswell & Compagnoni, 2003; Philpotts & Ague, 2009). Accordingly, Hazen and Morrison (2022) tabulated more than 1,200 metamorphic mineral species on Earth.

Metamorphism on Mars is different from that on Earth (McSween et al., 2015). High-pressure metamorphic assemblages—for example, as represented by transformations of basalt to eclogite—may exist in the deep martian interior (Papike et al., 2013). However, Mars lacks two attributes that are key to Earth's varied metamorphic environments, as well as the near-surface occurrences of diverse high-pressure metamorphic minerals: (a) martian sedimentary sections, which are generally less than 1 km thick (Watters et al., 2017), though perhaps exceeding 5 km in deep crater environments (Grotzinger & Milliken, 2012; Grotzinger et al., 2015), are insufficiently thick to initiate burial metamorphism; and (b) Mars lacks tectonic cycles of deep burial and uplift that would create and expose wide expanses of regionally metamorphosed martian rocks. In this regard, key diagnostic low-grade metamorphic phases, such as laumontite or pumpellyite, have not yet been found on Mars (McSween et al., 2015), though the detection of prehnite by Ehlmann et al. (2009) from MRO data suggests relatively high-temperature alteration ( $>200^\circ\text{C}$ ). Consequently, unless large martian impacts have locally exhumed deep lithologies (e.g., Ehlmann, Mustard, Clark, et al., 2011), the higher-pressure metamorphic petrology of Mars will likely remain a matter of speculation. On the other hand, a variety of near-surface metamorphic processes do occur on Mars. Here we describe five of those paragenetic modes.

#### 2.3.1. Thermal Metamorphism

High-temperature, low-pressure metamorphism is a ubiquitous characteristic of both intrusive and extrusive crustal igneous rocks. Though as yet poorly documented on Mars, significant mineralogical variety must be present both in the form of thermally altered xenoliths derived from mantle and crustal lithologies, and contact metamorphism of country rocks (Grapes, 2006). Thermally metamorphosed zones are likely to be highly localized and volumetrically minor. However, given the widespread distribution of primary igneous rocks, both across Mars' surface and through much of its 4.5-billion-year history, it is likely that most of the primary and secondary phases outlined above will have been at some point subjected to metamorphism at high temperatures (300–900°C) and relatively low pressures ( $<0.2$  GPa), corresponding to albite-epidote hornfels, hornblende hornfels, pyroxene hornfels, and sanidinite facies (Philpotts & Ague, 2009).

Note that an added uncertainty related to thermal metamorphism is the possible introduction of hot fluids rich in ions of C, P, S, B, halogens and other solutes—metasomatizing elements that generate significant mineralogical novelty in contact zones on Earth (Button, 1982; Falkowski et al., 2000; Frondel, 1990; Klein, 2005).

#### 2.3.2. Lightning Mineralization

Martian lightning is likely to have been a significant localized mineral-forming agent, especially during periods of explosive volcanism. Under most circumstances, the present atmosphere of Mars is too tenuous to support lightning. However, electrostatic emissions that affect chemical changes, for example, in the chlorine cycle, have been observed to be associated with recent martian dust storm activity (Ruf et al., 2009; Wang et al., 2023). However, severe lightning storms may have been associated with episodes of explosive volcanism, which are thought to have generated extensive, dynamic eruptive ash clouds (Brož & Hauber, 2012, 2013; Brož et al., 2021;



Halevy & Head, 2014; L. Wilson & Head, 1994). Similarly, turbulent dust clouds initiated by bolide impacts would have been accompanied by frequent lightning.

On Earth, lightning strikes on soils and rocks have been shown to generate more than a dozen high-temperature reduced phases, including silicon metal, graphite, iron, moissanite, and schreibersite (Bindi et al., 2023; Essene & Fisher, 1986; Grapes, 2006; Hess et al., 2021; Pasek et al., 2012). Pasek and Block (2009) suggested that lightning-induced reduction of phosphate minerals might have provided a source of biologically useful P compounds prior to life's origins—an idea amplified by Hess et al. (2021) and Bindi et al. (2023).

### 2.3.3. Impact Mineralization

Bolide impacts on Mars produced a range of more than 20 high-pressure shock-induced phases, as they have on other terrestrial bodies (Tomioka & Miyahara, 2017; Tschauner, 2019), and as preserved in shocked martian meteorites (El Goresy et al., 2004; Fritz & Greshake, 2009; Min et al., 2004; Rubin & Ma, 2021). In Table 1, we list 24 martian impact species, including high-pressure forms of phosphate (tuite), oxides (liuite; xieite), SiO<sub>2</sub> (coesite; stishovite), feldspar (maskelynite; stöfflerite), and Mg-Fe silicates (wadsleyite; ringwoodite)—a small fraction of what may ultimately be found in martian impact sites. Note that many of these phases have been identified in the highly shocked Shergotty, Tissint, and Zagami martian meteorites (Baziotis et al., 2013; Britvin et al., 2021; Langenhorst & Poirier, 2000; Malavergne et al., 2010; Rubin & Ma, 2021; A. Zhang et al., 2006).

An intriguing finding is that many clay minerals in martian sediments are relatively unaffected by the thermal shock of impacts. Only in the most altered zones, at  $P > 40$  GPa and  $T > 600^\circ\text{C}$ , do clay minerals display partial dehydroxylation and oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> (Fairén et al., 2010; Michalski, Glotch, et al., 2017). Amphiboles, by contrast, may display significant shock dehydroxylation (Giesting et al., 2015).

Note that large bolide impacts have had profound geological and mineralogical consequence beyond the near-instantaneous production of a few high-pressure phases. A potentially more significant mineralizing process associated with impacts is the generation of long-lived hydrothermal systems (see #7 above; Abramov & Kring, 2005; Osinski et al., 2013). In addition, Deng et al. (2010) suggest that partitioning of redox-sensitive elements in impact-produced melts led to significant, early oxidation of the martian crust—changes that, in turn, may have dramatically altered the composition of the early martian atmosphere.

Finally, it is worth noting that we may soon gain additional insights on impact mineralization as the *Perseverance* rover exits Jezero crater and traverses what is thought to be the highly shocked terranes associated with the Isidis impact basin. One tantalizing possibility is that associated mega-breccias may contain uplifted mantle and Noachian basement—lithologies that may be included in the sample return stage of the Mars 2020 mission.

### 2.3.4. Photo-Alteration

The surface of Mars has been exposed to ionizing ultraviolet radiation for much of its history. Therefore, the near-surface environment was susceptible to UV photo-oxidation—a potentially widespread but yet incompletely studied mineral-altering phenomenon (Heard & Dauphas, 2017). Only a few minerals are known from laboratory studies to form by photo-oxidation processes. Kim et al. (2013) demonstrated the photo-oxidation of siderite to iron oxides, while Rivera Banuchii et al. (2022) described the oxidation of Fe<sup>2+</sup>-bearing smectite to Fe<sup>3+</sup>-bearing nontronite. Manganese oxides are also susceptible to UV alteration, both the photo-oxidation of Mn<sup>2+</sup> and the photo-reductive dissolution of Mn<sup>4+/3+</sup> oxides (Anbar & Holland, 1992; Lu et al., 2021).

Interactions between mineral surfaces and UV radiation may have played additional roles in the chemistry of Mars' near-surface environment. For example, Schuttlefield et al. (2011) documented the photo-oxidation of chloride to perchlorate by oxide minerals—a process relevant to the chlorine cycle on Mars. Ponczek and George (2018) also demonstrate that atmospheric mineral dust, when exposed to UV radiation, can promote heterogeneous surface reactions—possible pathways to organic chemistry.

### 2.3.5. Shear-Induced Mineralization

Minerals generated by recrystallization under shear strain represent a distinct paragenetic mode that is most commonly associated with mylonite zones at polished fault surfaces (Passchier & Trouw, 2005; Trouw et al., 2009). Reviews of Mars' tectonics (Golombek & Phillips, 2010; Scott & Dohm, 1990) reveal that faulting is not uncommon (Andrews-Hanna et al., 2008). For example, Yin (2012) reported large-scale strike-slip faulting in the Valles Marineris fault zone, though such dynamics do not necessarily represent incipient plate tectonics

on Mars (Pruis & Tanaka, 1995; Sleep, 1994). In addition, Klimczak et al. (2018) presented evidence for large martian thrust faults, which could also produce shear zone minerals.

### 3. Implications

#### 3.1. Comparisons of Mars and Earth Mineralogy

In what ways do the minerals of Mars differ from those of Earth? On the one hand, we recognize only four Mars minerals—frozen carbon dioxide, perchlorates of Na and Mg-Ca, and an iron sulfate  $[\text{Fe}(\text{OH})\text{SO}_4]$ —that are not known to form under Earth's warmer environment. All other documented martian minerals (Table 1) have also been included in terrestrial mineral inventories.

On the other hand, thousands of Earth's minerals are unlikely to have formed on Mars. Hazen and Morrison (2022) recognized several factors that have contributed to Earth's remarkable mineral diversity, now numbering close to 6,000 approved species (<https://ruff.info/ima>; accessed 04 March 2023). First and foremost is Earth's dynamic, tectonically driven hydrosphere, which operates on vast scales of cycling among the atmosphere, oceans, crust, and mantle. More than 80% of the Earth's minerals have arisen as a consequence of varied water-rock interactions, with 56% incorporating both hydrogen and oxygen. While Mars has had an active hydrosphere, it did not experience plate tectonics. Therefore, its hydrosphere is not as extensive as Earth's in depth (i.e., via subduction and associated volcanism), nor in the diversity of lithologies that have been subjected to water/rock interactions.

Related to these processes are the profound effects of the selection and concentration by water/rock interactions of more than 40 rare elements that collectively represent only 0.01% of crustal atoms in Earth, yet are essential to more than 40% of Earth's mineral diversity—a finding that echoes the observation that most terrestrial minerals are volumetrically trivial and rare (Gavryliv et al., 2022; Hazen & Ausubel, 2016; Hazen et al., 2015; Hystad et al., 2015). Most of these rare-element minerals are not expected on Mars. Furthermore, in spite of fictional imaginings of a robust future martian mining industry, many of Earth's ore-forming processes (Guilbert & Park, 2007) are unlikely to occur on Mars, potentially limiting mining opportunities on the red planet.

Water-dependent life also plays a significant role in Earth's mineral diversity, mediating the formation of almost half of all known mineral species, while providing the only known formation pathways for more than 34% of species, many of which are the consequence of atmospheric oxygenation. Such uniquely biogenic minerals are also unlikely phases on Mars.

Furthermore, Earth boasts more than 1,200 metamorphic minerals, most of which are unique to high-pressure and temperature metamorphic environments and thus are unlikely to occur on Mars (Hazen & Morrison, 2022).

Our analysis of martian mineral diversity is limited by the sites explored by landers and the detection limits of orbital and in situ mineralogical instruments. All NASA-led martian rovers have been sent to locations with geomorphological and/or mineralogical evidence for liquid water on the surface to evaluate the history of liquid water on Mars and identify habitable environments (e.g., Grotzinger et al., 2014). Exploration of these subaqueous deposits may be limiting the types of minerals we observe, and future in situ exploration of deep crustal exposures or volcanic edifices, for example, would elucidate different mineral assemblages than recorded thus far (e.g., Ehlmann et al., 2009).

The detection limit of the CheMin instrument is  $\sim 1$  wt. % (Blake et al., 2012), so many trace minerals in Gale crater may evade identification. Orbital IR spectrometers have spatial resolutions on the order of 10–100s of square meters, which can affect mineral identification and inferred formation mechanisms (e.g., Viviano & Moersch, 2013), and mineral detection limits using the most advanced identification algorithms are about 1–5 vol. % (e.g., Wu et al., 2021). Orbital detections of minerals can also be substantially hampered by coatings of dust on the surface. Indeed, CheMin revealed a variety of minerals in locations in Gale crater that did not have distinct mineralogical signatures from orbit (e.g., Fraeman et al., 2020). Results from CheMin emphasize the importance of in situ mineralogical measurements for our understanding of mineral evolution on Mars—work that should be a significant focus of future research.

The diversity of known martian minerals is expected to increase substantially with the delivery to Earth of rock cores and unconsolidated sediments currently being collected by *Perseverance* (Simon et al., 2023). Detailed mineralogical analyses of these samples using techniques that cannot be miniaturized for space flight will not only facilitate mineral identification but also allow for interpretation of paragenetic mode based on petrological relationships.

### 3.2. Minerals yet to Be Discovered and Described From Mars

The 161 martian minerals identified thus far with relative confidence (Table 1) are undoubtedly a modest fraction of the total martian mineral diversity. Specific examples of these plausible “missing” martian phases are listed by Morrison et al. (2023), who reviewed Earth's earliest Hadean mineralogy. Their list of 262 plausible phases (in addition to ~300 minerals hosted by those meteorites not derived from Mars) constitutes a reasonable proxy for Mars, as well.

Collectively, the 161 confirmed or inferred martian minerals in Table 1 incorporate only 22 essential elements. Note that Cu and Ni are known only from sulfides in martian meteorites, while Ba and Sr are inferred from the sulfate minerals, baryte and celestine. Mn minerals are present but are not yet represented by a confirmed mineral species (Lanza et al., 2016, 2021; Zeng et al., 2021). We discount reports based on spectral data (Rice et al., 2010) of the boron-bearing mineral datolite, a phase difficult to justify from a paragenetic perspective. By contrast, Earth's minerals incorporate 72 different essential elements. It remains to be seen if relatively common minerals of less common elements occur on Mars. Minerals containing lithium (spodumene; Li-bearing micas), beryllium (beryl; phenakite), boron (tourmaline; borates), arsenic (arsenopyrite; realgar), molybdenum (molybdenite; powellite), uranium (uraninite; coffinite), and many other scarce elements, though as yet undetected on Mars, may well form in localized martian zones of unusual concentrations. However, we think it unlikely that the majority of the more than 2,500 rare-element minerals on Earth will be found on Mars because the selective dissolution and subsequent concentration of most of these scarce elements on Earth appear to have required at least 1.5 billion years of vigorous crust and mantle fluid/rock interactions (e.g., Hazen et al., 2023).

While we have only sparse data from martian meteorites and surface sites, and localized pockets of extreme mineralogical diversity cannot be ruled out, orbital surveys of the surface of Mars suggest a relative paucity of exotic chemical or mineralogical sites. Consequently, we speculate that the frequency distribution of minerals on Mars may differ fundamentally from that of Earth, with a significantly smaller fraction of exotic chemical concentrations and associated rare phases. The search for such sites of significant chemical differentiation remains an enticing prospect for future exploration. Nevertheless, we conclude that Earth's mineralogical diversity is an order of magnitude greater than that of Mars.

### 3.3. Mars Mineral Evolution

This survey of 20 paragenetic modes of minerals on Mars suggests that the diversity and distribution of martian minerals has changed through time—a topic that will be the focus of a forthcoming contribution. The first primary minerals on Mars were in mafic rocks, likely formed through decompression and/or impact melting to produce basaltic magma. More diverse alkaline and quartz-normative igneous lithologies must have occurred later, in part through partial melting of metasomatized mantle rocks. Primary processes of vapor and aqueous mineral deposition also followed the first phases of igneous mineral crystallization.

Secondary and metamorphic minerals, by definition, must alter prior generations of rocks and minerals, thus suggesting an evolutionary sequence. In some instances, such as lightning, thermal metamorphism, and near-surface hydrothermal activity, these processes were likely more intense early in martian history than over the past 2 billion years. By contrast, atmospheric condensation, freezing, and low-temperature diagenesis are likely to have been more active later in the evolution of Mars. Such considerations raise intriguing questions that will drive future investigations. For example, does Mars' mineralogy display a progressive rise in complexity, as seen on Earth (Grew et al., 2016; Krivovichev, 2012; Krivovichev et al., 2018)? Might mineral diversification have been enhanced during, or even confined to, certain periods of martian history?

Comparative studies of mineralogy on Mars and Earth also highlight questions regarding what mineral-forming environments occur on the Moon, Venus, Mercury, and other terrestrial worlds. Enumerating paragenetic modes and placing each mineral species into one or more of those categories offers an opportunity to evaluate extraterrestrial mineralogy with a new perspective. If the Moon, Venus, or Mercury had a hydrological cycle, what mineralogical manifestations might we expect? And do extraterrestrial bodies display paragenetic processes not seen on Earth, such as cryo-volcanism on Titan (Hazen, 2018; Maynard-Casely et al., 2018)? Such studies in comparative planetology hold the promise of elucidating features of planetary evolution, especially in the context of the co-evolution of minerals and life.

## Data Availability Statement

All data employed in this study come from publications, as listed in the citations in the following Reference section. There are no additional new data resources, models, or data analysis associated with this contribution.

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