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Saltonseaite, $K_3NaMn^{2+}Cl_6$, the Mn analogue of rinneite from the Salton Sea, California

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ABSTRACT

Saltonseaite, $K_3NaMn^{2+}Cl_6$, is a new mineral from the Salton Sea, Imperial County, California, U.S.A., which formed as the result of the evaporation of geothermal (hydrothermal) brines enriched in K, Na, Mn, and Cl. It occurs as lozenge-shaped and bladed crystals to about 10 cm that are composites of parallel-grown {012} rhombohedra. It is associated with large, well-formed crystals of sylvite and halite. Crystals are transparent and colorless, but appear light orange due to inclusions of akaganéite. The streak is white and the luster is vitreous to oily, the latter being due to deliquescence. The Mohs hardness is about 2½, the tenacity is brittle, the fracture is irregular, and crystals exhibit one very good cleavage on {110}. The mineral has an astringent taste and is markedly hygroscopic. The measured and calculated densities are 2.26(1) and 2.297 g/cm^3, respectively. Saltonseaite is soluble in water at room temperature and crystallizes from solution above 52 °C. Optically, saltonseaite is uniaxial positive, with $\omega = 1.577(1)$ and $\varepsilon = 1.578(1)$ (white light) and is non-pleochroic. Energy-dispersive spectroscopic analyses (average of 5) provided: K 28.79, Na 5.35, Mn 13.48, Fe 0.24, Cl 52.19, total 100.05 wt%. The empirical formula (based on 6 Cl atoms) is: $K_{3.00}Na_{0.95}Mn^{2+}_{1.00}Fe^{2+}_{0.02}Cl_6$. Saltonseaite is trigonal, $R\overline{3}c$, with cell parameters $a = 12.0966(5)$, $c = 13.9555(10)$ Å, $V = 1768.48(16)$ Å^3, and $Z = 6$. The nine strongest lines in the X-ray powder diffraction pattern are [d_{obs} in Å(I)(hkl)]: 5.83(61)(012); 3.498(25)(300); 2.851(68)(131); 2.689(32)(312); 2.625(62)(214); 2.542(100)(223); 1.983(32)(324); 1.749(20)(600), and 1.384(22)(multiple). The structure of saltonseaite ($R_1 = 1.08\%$ for 558 $F_o > 4\sigma F$) contains face-sharing chains of alternating $Mn^{2+}Cl_6$ octahedra and $NaCl_6$ polyhedra along **c**. The chains are joined via bonds to eight-coordinated K atoms. Saltonseaite is isostructural with rinneite, $K_3NaFe^{2+}Cl_6$, and very similar in structure with chlormanganokalite, $K_4Mn^{2+}Cl_6$. Existing chemical analyses for saltonseaite and rinneite fail to confirm a solid-solution series between them; experimental studies are needed.

Keywords: Saltonseaite, new mineral, crystal structure, rinneite, chlormanganokalite, evaporite, geothermal brine, Salton Sea, California

INTRODUCTION

In May of 1981, California mineral collector/dealer John Seibel collected the world's finest sylvite crystals from along the southern shoreline of the Salton Sea (Imperial County, California). According to a report at that time (Wilson 1982), the material came from a water-filled pocket about 18 inches (46 cm) beneath the surface crust. The pocket was about 1½ × 20 feet (½ × 6 m) in extent and produced about 4000 lbs. (8800 kg) of specimens. John Seibel (personal communication) confirmed those details and provided the approximate location, an evaporite area along the SE shoreline of the Salton Sea near where the New River empties into the Salton Sea (33°07′N 115°41′W). Seibel noted that the site was immediately above a then-active natural hot spring and that, although the area had been diked to inhibit the encroachment of the lake water, the mineralization was clearly of natural origin (this was not a geothermal well).

The sylvite crystals from the pocket were colorless to yellow octahedra and cubo-octahedra with lustrous faces, some crystals reaching 8 cm across. Associated with the sylvite were orange-tinted halite cubes up to 10 cm across and bladed masses up to 15 cm across of what was, at the time, tentatively identified by one of the authors (A.R.K.) as rinneite, $K_3NaFeCl_6$, based solely on powder X-ray diffraction. Numerous specimens of the supposed rinneite were sold and presumably still reside in collections around the world.

Recently, one of the authors (A.V.K.) reawakened interest in the bladed mineral from this find, suggesting that, based upon its composition, it might represent a new mineral species. Powder X-ray diffraction and semi-quantitative chemical analysis by energy-dispersive spectroscopy of material on a small specimen confirmed it to be an analog of rinneite in which Mn^{2+} replaces Fe^{2+}. Subsequently, crystals on a much larger specimen from the 1981 discovery in the collection of the Natural History Museum of Los Angeles County were also found to be the new mineral. Material from this specimen was used for the characterization of the new mineral.

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The new species is named saltonseaite in recognition of its discovery just off the southern shoreline of the Salton Sea, Imperial County, California. The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2011-104). The holotype specimen is in the collections of the Natural History Museum of Los Angeles County under catalog number 23604. Fragments of the holotype have also been deposited in the collections of Museum Victoria (Melbourne, Australia) under catalog number M51615. Saltonseaite is the Mn analog of rinneite, $K_3NaFeCl_6$. According to group nomenclature (Mills et al. 2009), saltonseaite, and rinneite belong to the rinneite group.

OCCURRENCE AND PARAGENESIS

On the holotype specimen, saltonseaite is associated with sylvite and halite, which occur as well-formed crystals, as granular aggregates of small rounded crystals, and as inclusions in the saltonseaite. Some saltonseaite is partially replaced by sylvite and halite, as evidenced by small equant crystals of these minerals intergrown along the edges of some saltonseaite crystals. Akaganéite commonly occurs as inclusions in the saltonseaite, imparting an orange color.

Saltonseaite is an evaporite mineral formed from solutions enriched in K, Na, Mn, and Cl. The solutions evidently emanated from a natural hot spring, related to the Salton Sea geothermal field. Robinson et al. (1976) describe the field as follows:

> The Salton Sea geothermal field lies in the Salton Trough, the landward extension of the Gulf of California, an area of active crustal spreading. The Salton Buttes volcanoes lie within the Salton Sea geothermal field where temperatures measured in wells drilled for geothermal brines range up to 360 °C at depths of 1500 to 2500 m (Helgeson 1968). The wells produce a hot brine containing up to 160 000 ppm of dissolved solids, chiefly Cl, Na, K, Ca, and Fe (White 1968). Under the influence of this hot saline brine, the sediments of the Salton Trough are being transformed into metamorphic rocks of the greenschist facies (Muffler and White 1969).

McKibben et al. (1987) provide a review of research on the geochemistry and distribution of the brines in the Salton Sea geothermal system (SSGS). They note that “Deep geothermal fluids produced from SSGS wells are mainly Na-Ca-K-Fe-Mn-Cl brines.” They further provide the following overview of the genesis of the fluids:

> Metallogenesis in the Salton Sea geothermal system is caused by the unique coincidence of several geologic and tectonic factors: trans-axial entry of a major river into an active continental rift-zone, deposition of metal-bearing deltaic sediments to form a closed-basin sedimentary environment, saline basin waters built up by episodic lake-filling and evaporite formation, and injection of heat and elements by rift-related magmatic intrusions at depth. These processes lead to leaching of metals and salt from the deltaic-lacustrine host sediments and the formation of hot hypersaline brines, which rise diapirically to mix with shallow oxidized waters and deposit hydrothermal ore minerals.

It is worth noting that the formation of saltonseaite from a brine related to a magmatic system provides an interesting parallel to one of the occurrences of rinneite and to the only occurrence of chlormanganokalite, $K_4Mn^{2+}Cl_6$, in sublimates on Mt. Vesuvius, Italy.

FIGURE 1. Holotype specimen of saltonseaite, 22 cm tall. (Color online.)

FIGURE 2. Composite blades of saltonseaite (colored orange by inclusions of akaganéite) associated with halite crystals on the holotype specimen; FOV 5 cm across. (Color online.)

PHYSICAL AND OPTICAL PROPERTIES

Saltonseaite occurs as lozenge-shaped and bladed crystals (Figs. 1 and 2) to about 10 cm that are composites of parallel-grown {012} rhombohedra (Fig. 3). Crystals are colorless, but typically appear light orange due to inclusions of akaganéite. The streak is white. Crystals are transparent with vitreous to oily luster, the latter being due to deliquescence. Saltonseaite does not fluoresce in long- or short-wave ultraviolet light. The Mohs hardness is about 2½, the tenacity is brittle, the fracture is irregular, and crystals exhibit one very good cleavage on {110}. The mineral has an astringent taste and is markedly hygroscopic. The density measured using a Berman balance is 2.26(1) g/cm^3, but this is likely to be low because of inclusions of sylvite and halite. The calculated density based on the empirical formula, and the unit cell refined from the single-crystal data is 2.297 g/cm^3. Saltonseaite readily dissolves in water at room temperature. Upon heating an aqueous solution in which saltonseaite has been dissolved, the phase begins to crystallize above 52 °C. Optically, saltonseaite is uniaxial positive, with ω = 1.577(1) and ε = 1.578(1), measured in white light. The mineral is non-pleochroic.

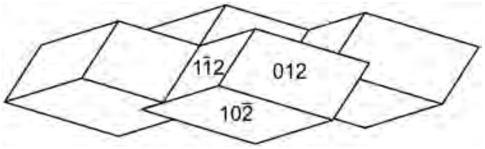

FIGURE 3. Crystal drawing demonstrating how the large lozenge-shaped and bladed crystals of saltonseaite are composites of parallel-grown rhombohedra (clinographic projection in standard orientation).

TABLE 1. Analytical results (in wt%) for saltonseaite

	1	2	3	4	5	Average	S.D.
K	28.82	29.10	29.02	28.70	28.33	28.79	0.27
Na	5.23	5.14	5.35	5.20	5.85	5.35	0.26
Mn	13.79	13.67	13.28	13.41	13.25	13.48	0.21
Fe	0.04	0.07	0.42	0.20	0.45	0.24	0.17
Cl	52.02	52.01	52.14	52.40	52.37	52.19	0.17
Total	99.90	99.99	100.21	99.91	100.25	100.05	

CHEMICAL COMPOSITION

Early attempts to prepare samples and conduct electron microprobe analyses in two different laboratories provided very poor results because of the very hygroscopic nature of the mineral. Energy-dispersive spectroscopic analysis was found to be less affected by adsorbed surface water. To further mitigate sample deterioration, after mounting crystals in epoxy resin, polishing was conducted using a ligroin (petroleum ether).

Chemical analyses (5 points on two crystals) were carried out on crystals from the holotype specimen using a Stereoscan S360 Cambridge electron microscope with an Oxford Instruments INCA analyzer energy-dispersive X-ray spectrometer, equipped with a Link Pentafet SATW detector. The working conditions were: 15 kV accelerating voltage, 1.5 nA beam current, 2.0 μm beam dimension, and 100 s live-time. The standards used were MAD-10 feldspar (for K), albite (for Na), Mn metal (for Mn), Fe metal (for Fe), and KCl (for Cl). Other elements were looked for, but were found to be below detection limits. The INCA software processed the data based upon Cl by stoichiometry and provided the analyses reported in Table 1. The empirical formula (based on 6 Cl atoms) is $K_{3.00}Na_{0.95}Mn^{2+}_{1.00}Fe^{2+}_{0.02}Cl_6$. The simplified formula is $K_3NaMn^{2+}Cl_6$, which requires K 28.75, Na 5.64, Mn 13.47, Cl 52.14, total 100.00 wt%.

TABLE 2. Powder X-ray diffraction data for saltonseaite*

I_{obs}	d_{obs}	d_{calc}	I_{calc}	*h k l*
14	6.084(7)	6.0483	27	1 1 0
61	5.831(5)	5.8074	45	0 1 2
4	4.187(7)	4.1890	3	2 0 2
3	3.814(5)	3.8092	5	2 1 1
18	3.693(3)	3.6874	11	1 1 3
25	3.4980(12)	3.4920	23	3 0 0
10	3.325(2)	3.3101	9	1 0 4
5	3.040(4)	3.0242	6	2 2 0
13	2.9107(9)	2.9037	19	0 2 4
68	2.8509(4)	2.8445	60	1 3 1
32	2.6886(9)	2.6823	30	3 1 2
62	2.6250(8)	2.6177	56	2 1 4
100	2.5424(4)	2.5355	100	2 2 3
6	2.3700(14)	2.3685	5	3 2 1
16	2.3344(11)	2.3259	10	0 0 6
16	2.2873(7)	2.2860	8	4 1 0
		2.2813	8	1 2 5
		2.2723	3	2 3 2
11	2.2379(10)	2.2327	9	1 3 4
7	2.1774(9)	2.1709	6	1 1 6
4	2.099(4)	2.0945	3	4 0 4
		2.0517	2	1 4 3
5	2.0153(19)	2.0161	5	3 3 0
		2.0128	2	3 1 5
32	1.9829(5)	1.9792	30	3 2 4
		1.9358	3	3 0 6
4	1.907(7)	1.9046	3	4 2 2
7	1.8691(7)	1.8647	8	5 1 1
12	1.8470(8)	1.8437	10	2 2 6
3	1.8219(6)	1.8212	1	2 3 5
		1.8167	4	1 5 2
9	1.7811(18)	1.7962	2	0 5 4
		1.7807	3	2 1 7
20	1.7486(3)	1.7460	20	6 0 0
6	1.7246(5)	1.7219	1	2 4 4
		1.7207	7	0 1 8
12	1.6786(5)	1.6775	7	5 2 0
		1.6721	4	3 4 2
14	1.6479(7)	1.6551	2	2 0 8
		1.6439	11	1 3 7
		1.6304	3	1 4 6
9	1.5899(6)	1.5964	1	1 2 8
		1.5872	7	1 6 1
		1.5780	2	2 5 3
4	1.5623(5)	1.5601	4	1 5 5
		1.5573	2	6 1 2
5	1.5368(8)	1.5344	5	3 2 7
3	1.5065(8)	1.5020	2	1 1 9
3	1.4662(7)	1.4633	6	5 3 2
5	1.4402(15)	1.4449	1	6 2 1
		1.4380	3	4 4 3
8	1.4105(13)	1.4223	1	2 6 2
		1.4118	3	2 3 8
		1.4048	2	2 4 7
		1.3963	2	0 6 6
22	1.3841(7)	1.3865	6	6 1 5
		1.3833	3	1 0 10
		1.3798	2	2 2 9
		1.3754	12	3 5 4
7	1.3428(6)	1.3411	2	6 2 4
		1.3406	5	5 0 8
4	1.3194(15)	1.3189	1	5 3 5
		1.3172	2	4 5 2

* Only calculated lines with intensities greater than 2 are listed unless they correspond to observed lines.

The Gladstone-Dale compatibility index 1 – (K_P/K_C) as defined by Mandarino (1981) provides a measure of the consistency among the average index of refraction, calculated density, and chemical composition. For saltonseaite, the compatibility index is 0.028 based on the ideal formula, within the range of excellent compatibility.

X-RAY CRYSTALLOGRAPHY AND STRUCTURE REFINEMENT

Both powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatized Mo*K*α radiation. For the powder-diffraction study, a Gandolfi-like motion on the φ and ω axes was used to randomize the sample and observed *d*-spacings and intensities were derived by profile fitting using JADE 9.3 software. The powder data are presented in Table 2. Unit-cell parameters refined from the powder data using whole pattern fitting are: $a = 12.103(4)$, $c = 13.979(5)$ Å, and $V = 1773.3(1.0)$ Å^3.

The Rigaku CrystalClear software package was used for processing the structure data, including the application of an empirical multi-scan absorption correction using ABSCOR (Higashi 2001). The initial atomic positions were based upon those in the structure determination of rinneite (Figgis et al. 2000). SHELXL-97 software (Sheldrick 2008) was used, with neutral atom scattering factors, for the refinement of the structure. The details of the data collection and the final structure refinement are provided in Table 3. The final fractional coordinates and atom displacement parameters are provided in Table 4. Selected interatomic distances are listed in Table 5 and bond valences in Table 6. (CIF and table of structure factors and observations are available[1].)

DESCRIPTION OF THE STRUCTURE

The structure of saltonseaite (Fig. 4) contains face-sharing chains of alternating $Mn^{2+}Cl_6$ octahedra and $NaCl_6$ polyhedra along **c**. The chains are joined via bonds to eight-coordinated K

TABLE 3. Data collection and structure refinement details for saltonseaite

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation/power	Mo*K*α (λ = 0.71075 Å)
Temperature	298(2) K
Structural formula	$K_3NaMnCl_6$
Space group	$R\bar{3}c$
Unit-cell dimensions	$a = 12.0966(5)$ Å $c = 13.9555(10)$ Å
V	1768.48(16) Å^3
Z	6
Density (for above formula)	2.300 g/cm^3
Absorption coefficient	3.513 mm^{-1}
F(000)	1170
Crystal size	230 × 160 × 150 μm
θ range	4.87 to 30.48°
Index ranges	$-17 \leq h \leq 17, -17 \leq k \leq 17, -19 \leq l \leq 19$
Reflections collected/unique	7087/585 [$R_{int} = 0.0197$]
Reflections with $F_o > 4\sigma F$	558
Completeness to θ = 30.48°	97.2%
Max. and min. transmission	0.6208 and 0.4988
Refinement method	Full-matrix least-squares on F^2
Parameters refined	19
GoF	1.115
Final *R* indices [$F_o > 4\sigma F$]	$R_1 = 0.0108$, w$R_2 = 0.0245$
R indices (all data)	$R_1 = 0.0117$, w$R_2 = 0.0247$
Largest diff. peak/hole	+0.19/–0.21 *e* A^{-3}

Notes: $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$. GoF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where *a* is 0.0110, *b* is 0.7260, and *P* is $[2F_c^2 + \text{Max}(F_o^2,0)]/3$.

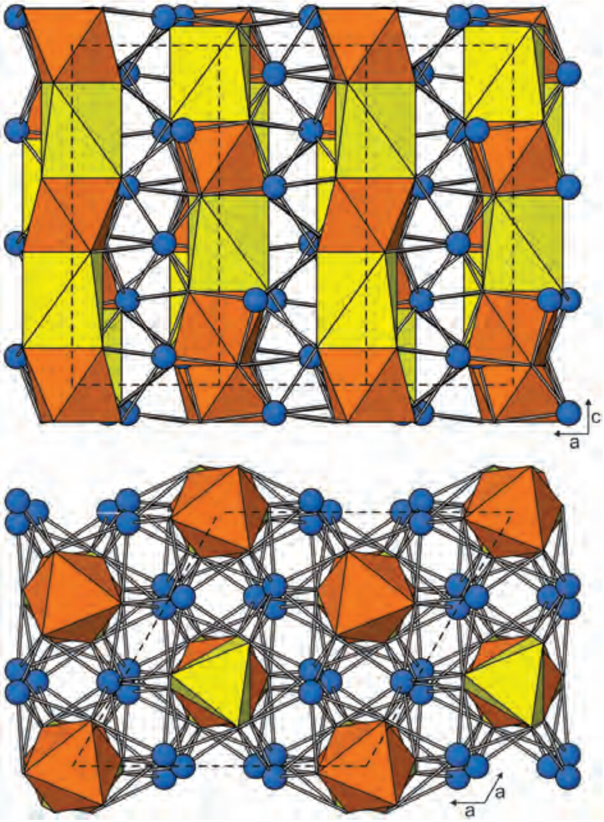

FIGURE 4. Crystal structure of saltonseaite. $MnCl_6$ octahedra are dark gray (orange online); $NaCl_6$ polyhedra are light gray (yellow online); K atoms shown as dark gray spheres (blue online).

TABLE 5. Selected bond distances (Å) in saltonseaite

K-Cl (×2)	3.2021(2)	Na-Cl (×6)	2.8441(2)
K-Cl (×2)	3.2093(3)		
K-Cl (×2)	3.2713(2)	Mn-Cl (×6)	2.55311(19)
K-Cl (×2)	3.3555(3)		
<K-Cl>	3.2596		

TABLE 4. Fractional coordinates and equivalent atomic displacement parameters (Å^2) for saltonseaite

	x/a	*y/b*	*z/c*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K	0.29052(2)	0.3333	0.0833	0.02685(7)	0.02627(9)	0.02558(12)	0.02846(12)	–0.00548(8)	–0.00274(4)	0.01279(6)
Na	0.0000	0.0000	0.2500	0.02882(17)	0.0344(3)	0.0344(3)	0.0178(3)	0.000	0.000	0.01718(13)
Mn	0.0000	0.0000	0.0000	0.01644(6)	0.01713(8)	0.01713(8)	0.01504(11)	0.000	0.000	0.00857(4)
Cl	0.181550(17)	0.027130(18)	0.108876(12)	0.02324(6)	0.02080(9)	0.02933(10)	0.02162(9)	–0.00062(6)	–0.00331(6)	0.01406(7)

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[1] Deposit item AM-13-005, Table and CIF. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 6. Bond-valence summations for saltonseaite

	K	Na	Mn	Σ
Cl	0.158 ×2↓ 0.155 ×2↓ 0.131 ×2↓ 0.104 ×2↓	0.153 ×6↓	0.321 ×6↓	1.022
Σ	1.096	0.918	1.926	

Notes: Multiplicity is indicated by ×↓; K-Cl and Mn^{2+}-Cl bond strengths from Brown and Altermatt (1985); Na-Cl bond strength from Brese and O'Keeffe (1991).

atoms. The $MnCl_6$ octahedron has close to ideal geometry, with all Mn-Cl bond distances equal and all octahedral angles between 88.2 and 91.8°. The $NaCl_6$ polyhedron also has six equivalent cation-anion bond distances; however, to accommodate the longer Na-Cl bonds and the opposing faces shared with $MnCl_6$ octahedra, the $NaCl_6$ polyhedron is severely elongated. The $NaCl_6$ coordination polyhedron can be considered an elongated octahedron, but it is probably better described as a twisted trigonal prism. The shape of the KCl_8 coordination polyhedron is not easily described, but the K-Cl bonds fall within a fairly narrow range, 3.202 to 3.355 Å. The Cl is coordinated to one Mn, one Na, and four K atoms in an approximately octahedral arrangement.

Saltonseaite is isostructural with rinneite, $K_3NaFe^{2+}Cl_6$ (Beattie and Moore 1982; Figgis et al. 2000), and very similar in structure with chlormanganokalite, $K_4Mn^{2+}Cl_6$ (Bellanca 1947a 1947b). The structure of chlormanganokalite was originally described using the trigonal rhombohedral cell with parameters a = 8.468 Å and $\alpha = 89.53°$, which corresponds to the non-primitive hexagonal cell with cell parameters a = 11.926 and c = 14.787 Å. The much longer c cell dimension for chlormanganokalite compared to saltonseaite and rinneite is particularly significant as it reflects a KCl_6 polyhedron in the face-sharing chain that is much more severely elongated than the $NaCl_6$ polyhedron in the chains in saltonseaite and rinneite. As a consequence, the K atoms linking the chains in chlormanganokalite are six-coordinated, rather than eight-coordinated, as they are in saltonseaite and rinneite.

The Mn-Cl bond length of 2.55311(19) Å in saltonseaite is significantly longer than, but comparable to, the Fe-Cl bond length of 2.5124(5) Å in rinneite (Figgis et al. 2000). This raises the question of whether a complete, or even a limited, solid-solution series exists between saltonseaite and rinneite. Existing evidence is limited to the published chemical analyses for rinneite from evaporite deposits (Eskdale, North Yorkshire, England; Wolkramshausen, Thuringia, Germany; and Hildesheim, Lower Saxony, Germany), which at most show only a trace of Mn (0.18 wt% for Esdale; Stewart 1951), and our analyses for saltonseaite, which show only a trace of Fe (0.24 wt%). The fact that rinneite analyses exhibit little or no Mn could simply be due to the low abundance of Mn in the solutions that formed the evaporite deposits in which the rinneite occurs. Interestingly, rinneite has also been reported from a single 1922 discovery in a fumarole at Mt. Vesuvius (Zambonini and Restaino 1924); however, the authors note that they found only a trace of Mn and do not report any in their analytical results. The very low Fe content of saltonseaite may be more telling, because Fe is known to be enriched in fluids in the Salton Sea geothermal system (Robinson et al. 1976; McKibben et al. 1987). The presence of akaganéite, $Fe^{3+}O(OH)$, as inclusions in saltonseaite, further confirms the presence of Fe in the solution from which saltonseaite crystallized; however, the lack of greater incorporation of Fe into the saltonseaite structure could be attributable to crystallization under moderately oxidizing conditions in which most Fe was present as Fe^{3+}, but Mn was present as Mn^{2+}. Experimental studies are clearly needed to determine the extent of the solid-solution series between saltonseaite and rinneite.

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