

Article

Anomalous High Cretaceous Paleobrine Temperatures: Hothouse, Hydrothermal or Solar Heating?

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Abstract: Elevated surface paleobrine temperatures (average 85.6 °C) are reported here from Cretaceous marine halites in the Maha Sarakham Formation, Khorat Plateau, Thailand. Fluid inclusions in primary subaqueous “chevron” and “cumulate” halites associated with potash salts contain daughter crystals of sylvite (KCl) and carnallite (MgCl₂·KCl·6H₂O). Petrographic textures demonstrate that these fluid inclusions were trapped from the warm brines in which the halite crystallized. Later cooling produced supersaturated conditions leading to the precipitation of sylvite and carnallite daughter crystals within fluid inclusions. Dissolution temperatures of daughter crystals in fluid inclusions from the same halite bed vary over a large range (57.9 °C to 117.2 °C), suggesting that halite grew at different temperatures within and at the bottom of the water column. Consistency of daughter crystal dissolution temperatures within fluid inclusion bands and the absence of vapor bubbles at room temperature demonstrate that fluid inclusions have not stretched or leaked. Daughter crystal dissolution temperatures are reproducible to within 0.1 °C to 10.2 °C (average of 1.8 °C), and thus faithfully document paleobrine conditions. Microcrystalline hematite incorporated within halite crystals also indicate high paleobrine temperatures. We conclude that halite crystallized from warm brines rich in K-Mg-Na-Cl; sylvite and carnallite daughter crystals were nucleated during cooling of the warm brines sometime after deposition. Hothouse, hydrothermal, and solar-heating hypotheses are compared to explain the anomalously high surface paleobrine temperatures. Solar radiation stored in shallow density stratified brines is the most plausible explanation for the observed paleobrine temperatures and the progressively higher temperatures downward through the paleobrine column. The solar-heating hypothesis may also explain high paleobrine temperatures documented from fluid inclusions in other ancient halites.

Keywords: Maha Sarakham Formation; Khorat Plateau; fluid inclusions in halite; daughter crystals; Cretaceous hothouse; solar heating; hydrothermal activity

1. Introduction

Primary fluid inclusions in halite are brine-filled vacuoles trapped during crystal growth [1]. These aqueous inclusions record the temperature and the chemical composition of the ambient brines from which the halite precipitated. Great efforts have been made to use fluid inclusions in ancient halite to reconstruct quantitative paleobrine temperatures [2–7] and seawater chemistry [8–11]. Single phase aqueous inclusions formed at temperatures >~50 °C may undergo phase separation into liquid + vapor, liquid + daughter crystal, or liquid + vapor + daughter crystal as they cool to room temperature [1,12,13]. Two-phase liquid + vapor inclusions can be heated in the laboratory

to produce one homogeneous fluid at the “homogenization temperature” (Th); this technique has been used extensively to study crystal growth temperatures, particularly for the mineral quartz in ore deposits [14,15]. Liquid + vapor homogenization temperatures in fluid inclusions in halite, however, are problematic [3] because the required constant fluid inclusion volume and mass may be changed during heating and cooling by halite dissolution/precipitation on fluid inclusion walls, permanent deformation “stretching” during heating, collapse of fluid inclusion walls due to tensile stress during cooling, or leakage of fluid into or out of inclusions [3,16]. In contrast, dissolution of daughter crystals is controlled by mineral solubility and the chemical composition of a brine at a given pressure and temperature, not fluid inclusion volume. Thus, daughter crystal dissolution temperatures are more reliable for obtaining ambient temperatures of halite precipitation than liquid-vapor homogenization techniques [17]. Daughter crystals of sylvite and carnallite are common in fluid inclusions in halite associated with potash salts. Sylvite and carnallite solubilities are strongly temperature-dependent, so these minerals readily precipitate as daughter crystals in brine inclusions upon cooling.

Sylvite and carnallite daughter crystals in fluid inclusions in halite dissolve at high temperatures compared to most surface waters on Earth. Roedder [17] documented dissolution temperatures of carnallite daughter crystals of 56–57 °C in primary “chevron” halite and 98–120 °C in recrystallized halite from the Pennsylvanian Paradox Basin, Utah (Table 1). He attributed the highest temperatures to secondary entrapment of saline fluids during deep burial recrystallization. Lowenstein and Spencer [13] measured dissolution temperatures of sylvite and carnallite daughter crystals in chevron halites from the Oligocene Rhine Graben, France, the Permian Salado Formation, New Mexico, and the Devonian Prairie Formation, Saskatchewan, Canada. Daughter crystals in halite from these deposits dissolved at 20–83 °C, 28–150 °C, and 5–80 °C, respectively (Table 1). Lowenstein and Spencer [13] speculated that solar heating or leakage of fluid inclusions may account for the high paleobrine temperatures. Cendón et al. [18] reported dissolution temperatures of 50–110 °C from sylvite daughter crystals in Eocene chevron halite from the Subiza mine, Spain. They interpreted these sylvite crystals as “accidentals” trapped during halite precipitation, not true daughter crystals. Other studies confirm the high paleobrine temperatures from dissolution of sylvite and carnallite daughter crystals in fluid inclusions in ancient marine halites ranging in age from Neoproterozoic to Permian [19–22] (Table 1).

Table 1. Range of dissolution temperatures of sylvite and carnallite daughter crystals in fluid inclusions in halite, Neoproterozoic to Eocene in age.

Location	Age	Crystal	T (°C)	Daughter crystal	Reference
Rhine Graben, France	Oligocene	chevron	20–83	sylvite	[13]
Subiza mine, Spain	Late Eocene	chevron	50–110	sylvite	[18]
Khorat Plateau, Thailand	Late Cretaceous	chevron	45.7–119.5	Sylvite + carnallite	This study
Zechstein Basin, Poland	Late Permian	chevron	50–62	sylvite	[22]
Carlsbad, New Mexico, USA	Permian	chevron	28–150	sylvite	[13]
Paradox Basin, USA	Early Pennsylvanian	chevron recrystallized	56–57 98–120	carnallite	[17]
Moncton Subbasin, Canada	Early Carboniferous	chevron	50–60	sylvite	[19]
Saskatchewan, Canada	Devonian	chevron	5–80	Sylvite + carnallite	[13]
East Siberian, Russia	Early Cambrian	chevron diagenetic	60–86 70–116	Sylvite + carnallite	[20]
Salt Range, Pakistan	Neoproterozoic	recrystallized	55–100	sylvite	[21]
Amadeus Basin, Australia			60–62		

The unusually high dissolution temperatures of sylvite and carnallite daughter crystals reported from many evaporites have never been fully explained. Do they represent true temperatures of surface

brines? Here we report dissolution temperatures of sylvite and carnallite in fluid inclusions in the primary halite from the Cretaceous Maha Sarakham Formation, Khorat Plateau, Thailand and discuss mechanisms that could produce high surface paleobrine temperatures: hothouse climate, hydrothermal heating or solar heating? We conclude that daughter crystal dissolution faithfully records elevated surface paleobrine temperatures, and we speculate that solar radiation stored in salinity-stratified brines may be responsible.

2. Sampling and Methods

2.1. Khorat Plateau and Sampling

The Khorat Plateau is situated in Thailand and Laos on the Indo-China Block (Figure 1). The plateau is divided by the Phu Phan anticlinorium into the Sakon Nakhon Basin to the north and the Khorat Basin to the south [23,24]. The Sakon Nakhon and Khorat Basins formed due to extension following collision between the Shan Thai and Indo-China Blocks in the early middle Triassic [25]. The extension created half-grabens that filled with nonmarine deposits, the Khorat Group, with up to 5 km of Late Triassic to late Early Cretaceous fluvial and lacustrine redbeds [26]. Evaporites of the Cretaceous Maha Sarakham Formation unconformably overlie the Khorat Group and have been dated to 112–93 Ma using palynomorphs [27,28].

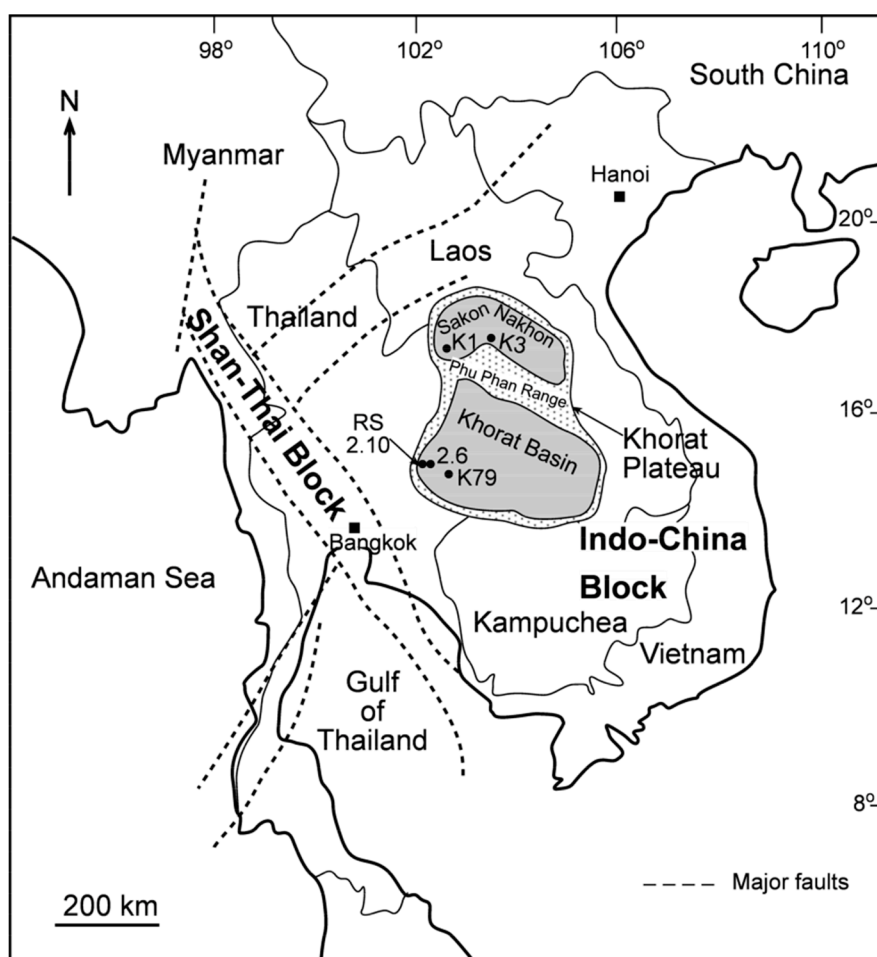


Figure 1. Geological map of Southeast Asia showing the Khorat Plateau, the Khorat Basin (cores RS2.10, RS2.6, and K79) and the Sakon Nakhon Basin (cores K1 and K3), major faults, and tectonic blocks (modified from El Tabakh et al. [24]).

The Maha Sarakham Formation contains three depositional cycles, the Lower, Middle, and Upper Members, each consisting of evaporites overlain by siliciclastic redbeds [23,24,29]. The Lower Member is laterally continuous and composed of anhydrite overlain by halite and laminated anhydrite, potash (carnallite, sylvite, and tachyhydrite [$\text{CaCl}_2 \cdot \text{MgCl}_2 \cdot 12\text{H}_2\text{O}$]), borate minerals, and clay (Figure 2) [23,24,29]. The Middle and Upper Members also contain evaporite-siliciclastic redbed cycles but post-depositional dissolution has, in places, removed the evaporites or reduced them to thin anhydrite [30]. The marine versus non-marine origin of the Maha Sarakham Formation has been debated because the mineral sequence (halite–carnallite–sylvite–tachyhydrite) cannot precipitate from modern seawater. Evaporites were initially interpreted as marine in origin [23] but later as non-marine because subaerial features such as desiccation cracks, caliche, and anhydrite nodules were identified in the associated clastic redbeds [29]. More recently, correlation of anhydrites [23], sulfur isotope measurements of anhydrites [24], and fluid-inclusion analysis in primary chevron halites [31] show that the evaporites of the Maha Sarakham Formation are indeed marine in origin and formed when seawater flooded the Khorat Plateau. Siliciclastic redbeds represent continental deposits between marine incursions.

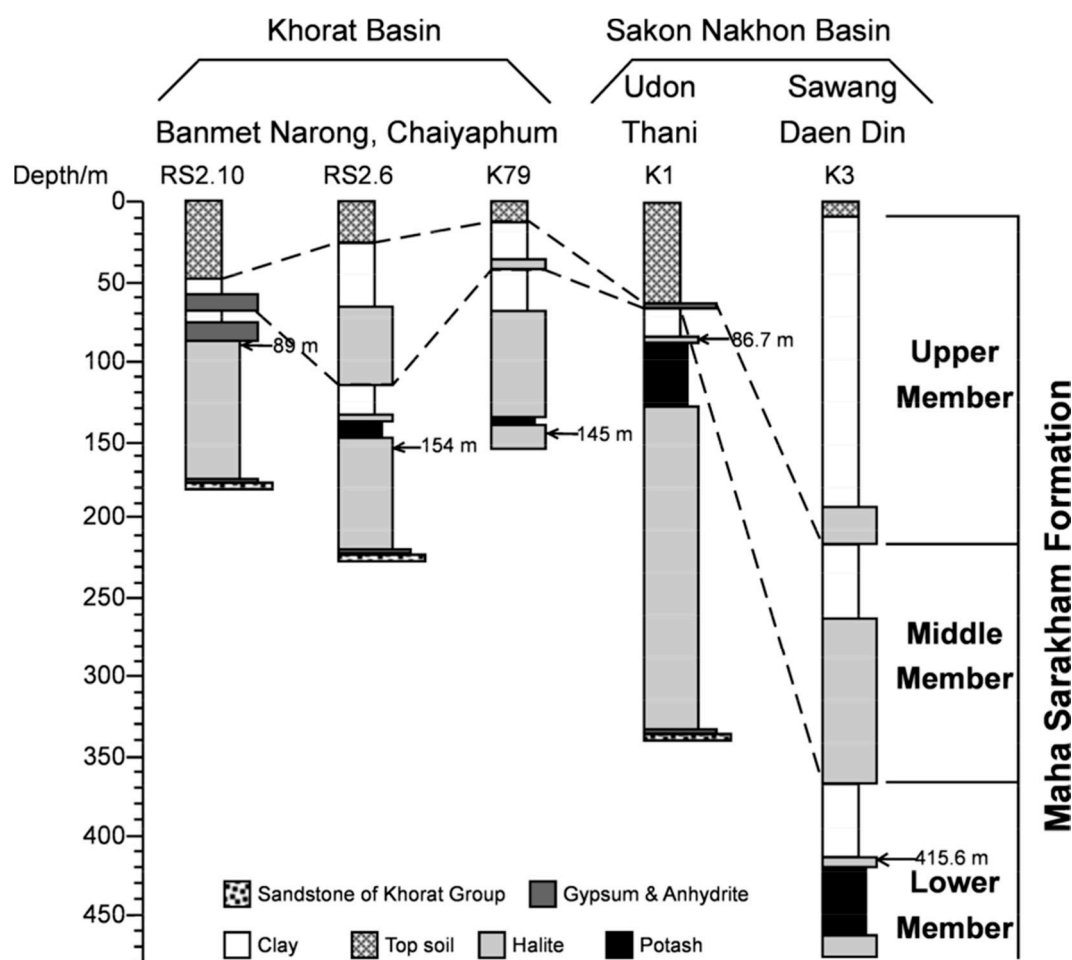


Figure 2. Stratigraphy of the Cretaceous Maha Sarakham Formation in cores RS2.10, RS2.6, K79, K1, and K3. Core K3 contains the complete sequence (Lower, Middle, and Upper Members). Each Member contains evaporites overlain by siliciclastic redbeds. The Middle and Upper Members are missing or incomplete in the other cores, most likely due to post-depositional dissolution [30].

Dissolution temperatures of sylvite and carnallite daughter crystals in fluid inclusions in halite were studied from five boreholes. Cores K1 (349.4 m in length) and K3 (477.6 m in length) are located

in the Sakon Nakhon Basin, and cores RS2.10 (178.6 m in length), RS2.6 (222.5 m in length), and K79 (152.4 m in length) are from the Khorat Basin (Figures 1 and 2). Cores K1, RS2.10, and RS2.6 were drilled through the Maha Sarakham Formation and reached the basal anhydrite and sandstone of the Khorat Group (Figure 2). Potash units are composed of halite, carnallite, sylvite, and tachyhydrite. They occur in the Lower Member of the Maha Sarakham Formation in all the cores except core RS2.10 (Figure 2). Halite samples were selected from five stratigraphic intervals adjacent to the potash unit or from the topmost section of the Lower Member (89 m in core RS2.10, 154 m in core RS2.6, 145 m in core K79, 86.7 m in core K1, and 415.6 m in core K3) where sylvite and carnallite daughter crystals were most likely to occur in fluid inclusions (Figure 2).

2.2. Methods

2.2.1. Microscopy

An important first step is petrographic analysis to distinguish primary halite formed in a surface brine body from diagenetic halite that formed later from groundwater brines. Primary halite is characterized by (1) cumulate crystals that precipitated at the air-brine interface or in the water column and (2) bottom-growth halite with or without fluid inclusion banding, the former called chevron halite and the latter clear bottom-growth halite [32–36]. Cumulate and chevron halite commonly contain well-defined fluid inclusion banding parallel to crystal growth faces. Clear bottom-growth halite consists of vertically-oriented, elongated crystals, with sparse fluid inclusions and no chevron bands, suggesting slow growth of halite at the bottom of a perennial hypersaline lake. Fluid inclusions in clear bottom-growth halite occur as oriented assemblages aligned parallel to crystal growth faces, not dense enough to form chevron banding. This type of halite has been found in ancient halite from Death Valley, California [34] and the Qaidam Basin, China [35], and from the modern Dead Sea [36]. Clear bottom-growth halite is distinct from recrystallized halite. Fluid inclusions in recrystallized halite are commonly large (hundreds of microns), isolated, and irregularly shaped, and the host halites do not retain primary depositional textures and fabrics. Samples of primary halite were selected for further study because they can be used to determine the temperatures of the surface brines from which they crystallized.

Five thin sections ($7.5 \times 5 \text{ cm}^2$) were prepared and examined using a Leica Wild M3Z stereomicroscope and a Zeiss compound microscope with an oil-immersion objective (PLAN APO $100\times/1.4 \text{ OIL}$) (Leica, Wetzlar, Germany) to document halite textures and interpret paleoenvironments.

Red halite layers from two thin sections were further analyzed by scanning electron microscopy (SEM) on a Zeiss Supra 55VP field-emission scanning electron microscope (SEM) (Carl Zeiss, Jena, Germany). Halite chips from the red layers were dissolved in deionized water and filtered to retrieve minute insoluble red crystals of hematite. These crystals were then mounted on 25 mm aluminum stubs with double-sided carbon tape, carbon coated, and analyzed under vacuum at 5–10 kV in the SEM with secondary electrons (SE) to observe the morphology of the hematite.

2.2.2. X-ray Powder Diffraction (XRD)

X-ray powder diffraction, used to determine the mineralogy of halite samples, was undertaken with a Philips Xpert PW3040-MPD diffractometer operated (Philips, Eindhoven, The Netherlands) at 40 kV and 20 mA, using Cu-K α radiation. Powders ran in a continuous scan from 5.00° to 70.00° 2θ with step sizes of 0.030° at 0.80 s per step. Bulk powder samples were obtained from thin-section chips using a 1 mm diameter Dremel drill bit. In addition, insoluble residues of halite samples, dissolved in water, were collected and analyzed by X-ray diffraction (XRD).

2.2.3. Microthermometry

Following petrographic observation of the Khorat halites, chevron and cumulate halites were selected for microthermometric analysis because they contain abundant fluid inclusions with daughter

crystals. Three to four cleavage fragments from each halite sample, 1 mm to 2 mm thick, were prepared. Most fluid inclusions in these fragments contained cubic, isotropic sylvite or hexagonal, birefringent carnallite daughter crystals at room temperature. In some fluid inclusions, cooling to as low as $-40\text{ }^{\circ}\text{C}$ was necessary to nucleate the daughter crystals.

Halite cleavage fragments were mounted on microscope cover glasses and inserted into a TMS 94 Linkam heating/freezing stage equipped with a Leitz Ortholux petrographic microscope. Fluid inclusions with daughter crystals were heated at a rate of $2\text{ }^{\circ}\text{C}$ per minute below $30\text{ }^{\circ}\text{C}$ and then slowed to $0.2\text{ }^{\circ}\text{C}$ per minute. As the fluid inclusions were heated, daughter crystals decreased in size and became rounded. Eventually, the daughter crystals disappeared due to dissolution. When the final dissolution temperature was approached, the cycling method was used to accurately record the dissolution temperature [1]. This method involves rapid cooling of the halite sample when daughter crystals near complete dissolution. Upon cooling, the daughter crystal in the fluid inclusion, if still present, enlarge, indicating complete dissolution did not occur. On the other hand, if total dissolution of the daughter crystal occurred, rapid cooling would not cause immediate growth of the daughter crystal because considerable super cooling is required to nucleate daughter crystals. This procedure was followed until all daughter crystals in fluid inclusions dissolved. Dissolution temperatures of daughter crystals from ~20 inclusions in one cleavage fragment were recorded. Dissolution temperatures were recorded for daughter crystals $>10\text{ }\mu\text{m}$, because dissolution behavior could be readily observed. In total, 17 halite cleavage fragments (12 cumulate halite and 5 chevron halite crystals) from five cores were analyzed. It is important to note that although liquid + vapor homogenization temperatures in fluid inclusions in the Khorat halites were not tested, future studies focused on comparison between homogenization temperatures of liquid + vapor fluid inclusions and dissolution temperatures of daughter crystals would enhance understanding of ancient brine temperatures.

Reproducibility of dissolution temperatures of daughter crystals was studied. After dissolution of daughter crystals, halite cleavage fragments were chilled to $-40\text{ }^{\circ}\text{C}$ at $30\text{ }^{\circ}\text{C}$ per minute and maintained at that temperature for 10 min to allow daughter crystals to nucleate. Under the same heating procedure described above, dissolution temperatures of renucleated daughter crystals in fluid inclusions were measured a second time.

3. Results

3.1. Microscopy

3.1.1. Khorat Halite and Fluid Inclusion Microscopy

Three types of primary halite were identified from thin sections of the Maha Sarakham Formation: (1) chevron halite, (2) clear bottom-growth halite, and (3) cumulate halite.

Chevron halite is cloudy in appearance due to numerous fluid inclusions in discreet submillimeter-scale fluid inclusion-rich bands that alternate with inclusion-poor bands (Figure 3a,b). Fluid inclusions in chevron halite are typically negative cubes, commonly less than $30\text{ }\mu\text{m}$, and oriented in bands parallel to crystal growth faces. Studies of modern evaporite deposition show that chevron halite forms by rapid crystallization (days to weeks) at the sediment-brine interface [33]. The second common type of primary halite, clear bottom-growth halite, differs from chevron halite because it lacks dense fluid-inclusion banding. Crystals several millimeters to 1 cm in size generally exhibit vertically elongated growth fabrics (Figure 3d). Primary fluid inclusions in clear bottom-growth halite are isolated, negative cubes. The small number of fluid inclusions in clear bottom-growth halite indicate slow crystallization (months to years) at the brine bottom [33,34]. Cumulate halite consists of densely packed accumulations of millimeter-scale, well-sorted cubes and rectangular and square-shaped plates (Figure 3e). Dense fluid inclusions occur in some cumulate halite (Figure 3f). Cumulate halite precipitates at the brine surface or in the water column and then sinks to the brine bottom to form well-sorted accumulations [33–36].

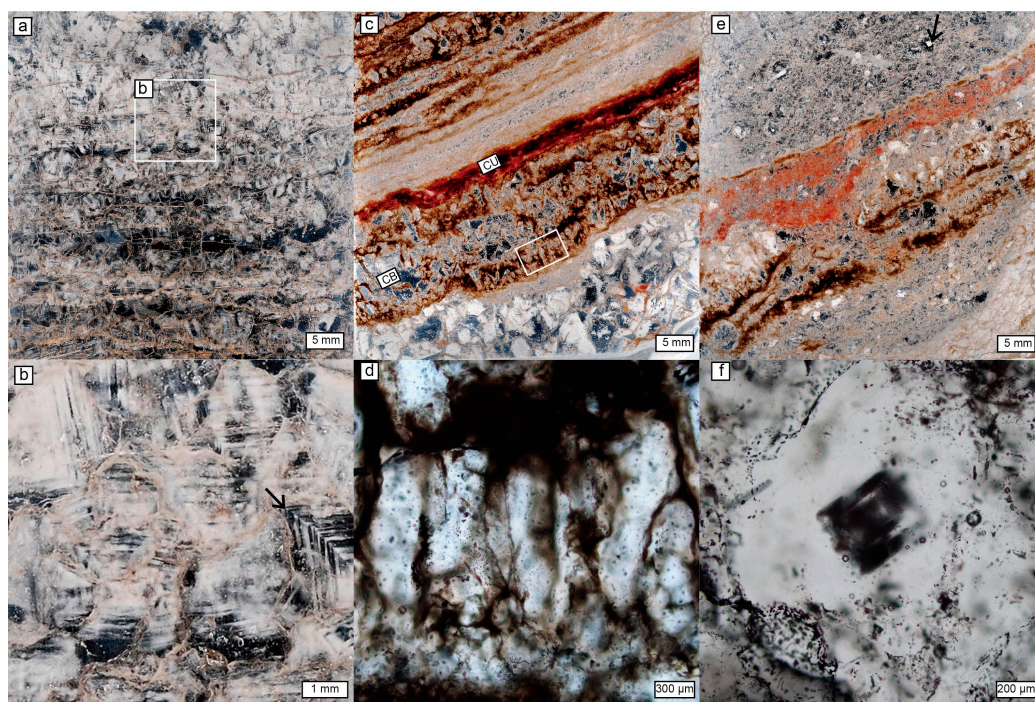


Figure 3. Thin section photomicrographs of halite from the Maha Sarakham Formation. (a) Vertically elongated halite crystals with dense clouds (white) of primary fluid inclusions. Core K79, 145 m; (b) enlarged area of Figure 3a. Vertically elongated chevron halite with alternations of fluid inclusion-rich (white) and fluid inclusion-poor (dark) bands (arrow); (c) chevron halite (white) at bottom, overlain by clear bottom-growth halite (CB) and cumulate halite (CU) stained red by microcrystalline hematite. Core RS2.6, 154 m; (d) enlarged rectangular area of Figure 3c. Clear bottom-growth halite crystals exhibit vertically elongated growth fabrics; (e) cumulate halite with scattered crystals dense with fluid inclusions (white patches-black arrow). Red layer in the middle contains cumulate halite and sylvite crystals. Core RS2.10, 89 m; (f) photomicrograph of cumulate halite crystal (indicated by black arrow in Figure 3e) with dense cloudy fluid inclusions (dark center).

Most halites from core K1, 86.7 m, are composed of chevrons and submillimeter-size cumulates. Two cumulate layers are colored red by tiny hematite crystals incorporated within halite crystals. Halite crystals from core K79, 145 m, are chevrons with well-developed vertical competitive growth fabrics (Figure 3a,b). Bedded halite in core RS2.6, 154 m, contains chevrons, cumulates, clear bottom-growth halite, and mud laminae (Figure 3c,d). Halite from core K3, 415.6 m, and core RS2.10, 89 m, consists of equant cumulate crystals with mosaic textures, some with platy and cubic shapes defined by cloudy fluid inclusions (Figure 3e,f). Petrographic textures and structures described above demonstrate that halite from the Maha Sarakham Formation precipitated from a perennial brine body. Earlier work on the chemical composition of fluid inclusions in halite established a marine seawater origin for these salts [31].

3.1.2. Daughter Crystal Microscopy

At room temperature, most primary fluid inclusions in chevron and cumulate halite examined from the Maha Sarakham Formation contained a single daughter crystal of sylvite or carnallite. Sylvite was identified by its cubic shape, isotropic character, and highly temperature dependent solubility (Figure 4a,b). The second daughter mineral, carnallite, exhibits hexagonal habit (Figure 4c), strong birefringence (Figure 4d), low relief, and temperature-dependent solubility. Daughter crystals of sylvite and carnallite can both occur in one halite crystal (Figure 4b).

Daughter crystals in fluid inclusions are interpreted to have formed via cooling of originally single-phase brines trapped in halite crystals. They are not accidentally-trapped crystals because (1) they occur in all fluid inclusions; (2) fluid inclusions from a given assemblage show similar solid-to-fluid ratios (Figure 4a); (3) their dissolution temperatures fall within a relatively narrow range; and (4) following dissolution, daughter crystals are readily renucleated in fluid inclusions during cooling. Accidentally-trapped crystals, in contrast, are highly variable in abundance within fluid inclusions and do not undergo consistent phase changes during heating and cooling [17].

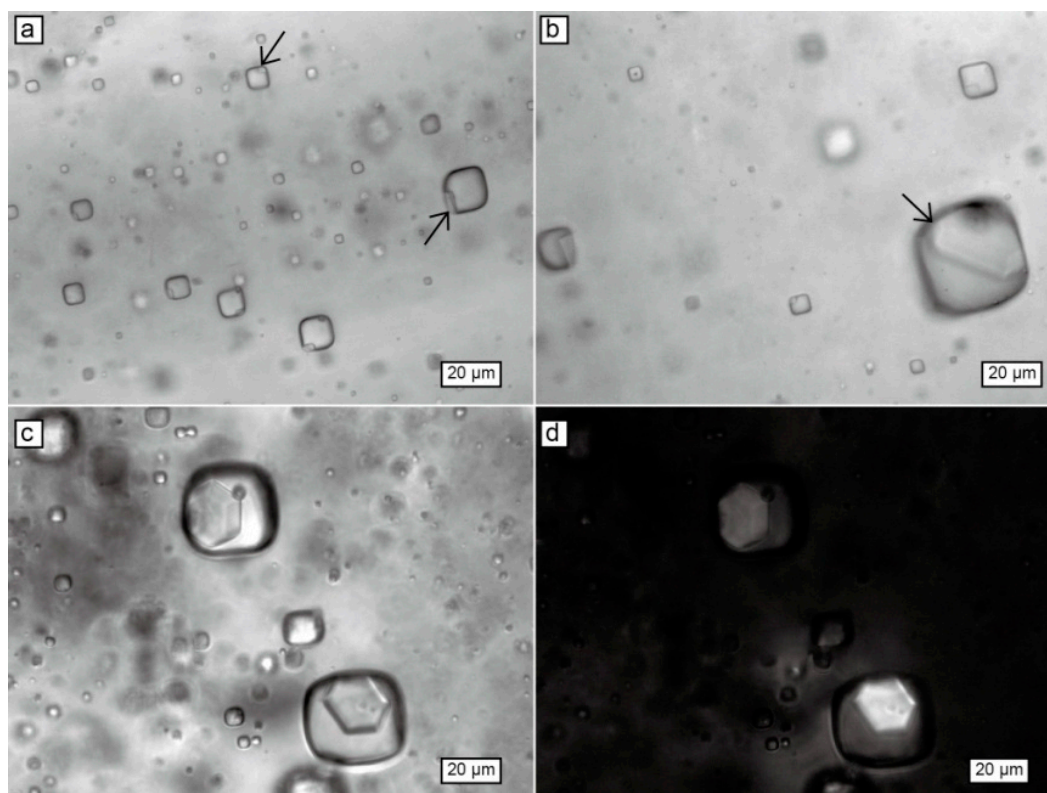


Figure 4. Photomicrographs of daughter crystals in fluid inclusions, Maha Sarakham Formation halite. (a) Sylvite daughter crystals (arrows) in fluid inclusion bands. Note the identical solid-liquid ratios in the fluid inclusions. Core K79, 145 m; (b) occurrence of sylvite and carnallite (arrow) daughter crystals in adjacent fluid inclusions. Core K79, 145 m; (c,d) carnallite daughter crystals (hexagonal, low relief, and birefringent under cross-polarized light) in fluid inclusions from Core RS 2.10, 89 m.

3.2. Dissolution Temperature Data

Daughter crystals from the Maha Sarakham Formation halites had relatively high dissolution temperatures, similar to those reported from previous studies (Table 2). Dissolution temperatures of daughter crystals measured in 277 primary fluid inclusions from 17 individual halite fragments range from 45.7 °C to 119.5 °C with an average of 85.6 °C (Figure 5). Dissolution temperatures measured from one chevron halite crystal at 145 m, core K79, for example, show a narrow range of 83.8–87.1 °C (average of 85.4 °C), whereas one cumulate halite from 415.6 m, core K3 has the widest range of 95.2–119.5 °C, (average of 107.4 °C) (Table 2). Dissolution temperatures are reproducible between 0.1 °C and 10.2 °C (average of 1.8 °C) (Table 2). These results indicate that cumulates and chevrons crystallized at variable temperatures in warm brines.

Table 2. Dissolution temperature data from sylvite and carnallite daughter crystals in fluid inclusions, Cretaceous halites from the Maha Sarakham Formation. σ : standard deviation. For some halite crystals, reproduced temperature values are shown in parentheses.

Sample	Crystal	T (°C)	Average (°C)	σ
K1 86.7 m	Cumulate	45.7, 46.4, 46.5, 46.8, 47.3, 47.5, 47.8, 49.2, 49.8, 50.6, 51.5, 51.9, 53.3, 54.1, 54.7	49.5	3.0
	Cumulate	65.4, 66.5, 66.9, 69.2, 69.5, 70.3, 70.5, 71.8, 72.8, 74.1, 74.8, 81.2, 82.5, 84.3	72.8	6.0
	Cumulate	71.4, 71.6, 72.1, 72.2, 72.3, 72.4, 72.7, 73.4, 73.6, 73.8, 73.9, 74.1, 74.4, 74.5, 74.8, 75.3, 76.1, 79.5, 79.8	74.1	2.3
	Chevron	74.8(79.4), 76.1(74.8), 76.3(74.1), 76.8(76.2), 77.5 (75.5), 77.9(77.6), 78.2(78.4), 78.6(79.3), 79.1(82.6), 79.3(78.9), 81.2(80.8), 86.7(78.3), 86.8(86.1), 88.2(78), 89.2(82.8), 89.6(84.5)	81.0	5.2
K3 415.6 m	Cumulate	62.1, 62.3, 62.5, 63.6, 68.5, 68.5, 68.7, 71.2, 72.1, 72.4, 73.4, 75.3, 75.3, 75.4, 76.3, 77.5, 78.4, 78.9, 79.1, 79.4, 79.6	72.4	6.0
	Cumulate	95.2, 102.1, 103.6, 104.6, 104.6, 105.4, 106.1, 106.6, 106.8, 107.2, 107.9, 108.8, 110.7, 111.1, 111.9, 112.8, 114.2, 116.1, 119.5	107.4	6.3
	Cumulate	96.6, 98.8, 103.7, 104.1, 104.3, 105.2, 105.5, 106.2, 106.5, 107, 107.4, 108.5, 109.2, 112.9, 113.8, 115, 115.5, 115.9, 116, 117.2, 118.3, 119.7	109.4	6.4
RS2.10 89 m	Cumulate	74.3, 77.2, 79.8, 80.4, 80.5, 81.3, 81.7, 82.4, 82.8, 85.2, 87.1	81.2	3.5
	Cumulate	80.7, 84.5, 86.9, 88.4, 88.5, 90.4, 90.5, 90.6, 91.4, 91.5, 91.5, 91.6, 92.3, 92.3, 92.4, 92.6, 92.7, 93.2, 97.1, 101.6, 104.8	91.7	5
	Cumulate	98.6, 98.9, 100.5, 102.7, 104.4, 106.5, 107.5, 109.5, 112.6, 113.1, 113.5, 115.1, 115.3	107.6	6.1
RS2.6 154 m	Cumulate	55.5(57.4), 56.4(54.2), 56.5(57.4), 56.7(56.5), 56.8(57.3), 57.3(56.9), 57.4(55.1), 57.5(58.4), 57.6(54.1), 58.3(60.2), 58.3(56.5), 58.3(59.1), 58.4(56.3), 58.7(59.2), 58.7(58.3), 59.4(57.7), 63.2(58.9)	57.9	1.8
	Cumulate	70.1, 70.5, 71.2, 71.3, 73.4, 73.5, 73.6, 74.6, 75.4, 75.8, 75.8, 76.3, 78.4, 79.2, 80.2, 81.1, 81.7	75.4	3.7
	Chevron	83.2, 85.3, 85.4, 87.4, 87.6, 87.6, 88.2, 88.3, 88.3, 88.4, 88.5, 88.6, 88.9, 89.3, 89.6, 89.9	87.8	1.7
	Chevron	115.2, 115.4, 115.7, 115.8, 116.2, 116.2, 116.4, 116.8, 116.8, 117.6, 118.3, 118.5, 118.6, 118.7, 119.2, 119.2	117.2	1.4
K79 145 m	Cumulate	77.6(78.2), 77.9(76.7), 78.2(78.9), 78.3(77.9), 78.5(78.8), 78.5(78.3), 78.6(79.4), 78.6(79.6), 79.1(78.1), 79.3(79.4), 79.4(76.4), 79.6(79.3), 80.1(79.4), 82.2(82.7)	80.0	1.1
	Chevron	83.8, 84.1, 84.2, 85.2, 85.2, 85.2, 85.7, 85.9, 86.4, 87.1	85.4	1.0
	Chevron	94.3, 95.2, 95.3, 95.8, 95.9, 96, 96.1, 96.2, 96.3, 96.5, 96.7, 96.8, 97, 97.1, 97.6, 98	96.3	1.0

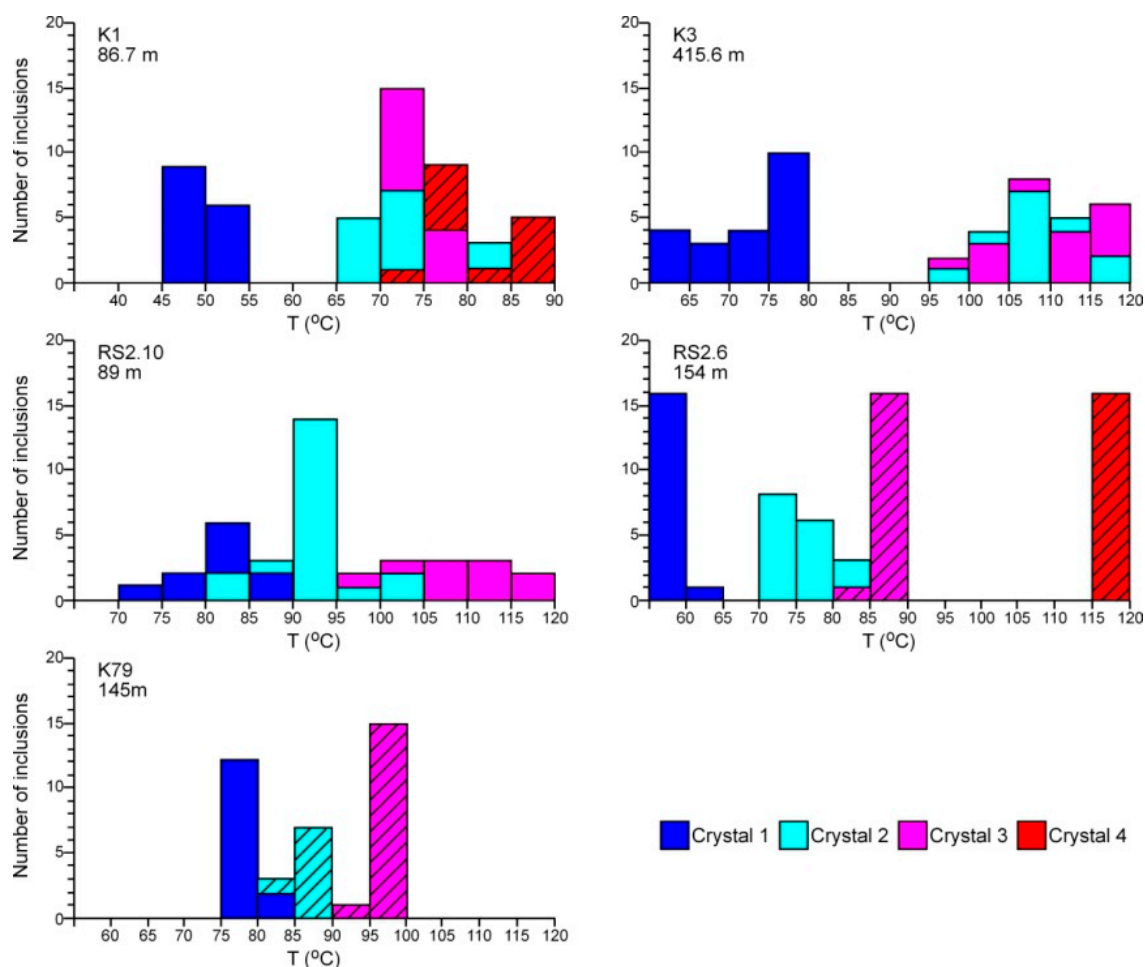


Figure 5. Dissolution temperatures of sylvite and carnallite daughter crystals in 277 primary fluid inclusions in halite from the Maha Sarakham Formation. Colors represent different halite crystals. Diagonal lines are fluid inclusions from chevron halite crystals; all others are cumulate halites.

Most single halite crystals exhibit narrow ranges of dissolution temperature, but within a halite layer, dissolution temperatures of daughter crystals from different halite crystals may vary widely (Figure 5). For example, dissolution temperatures of daughter crystals in fluid inclusions in halite from core K1, 86.7 m vary from 45.7 °C to 89.6 °C. Halite crystals from core RS2.6, 154 m, have daughter-crystal dissolution temperatures that range from 55.5 °C to 119.2 °C (Table 2). These daughter-crystal dissolution temperatures in halite crystals from the same layer indicate that halite precipitated from brines with variable and surprisingly high temperatures.

Of significance is that dissolution temperatures of daughter crystals in chevron halite are higher than cumulate halite (Figure 5). Chevron halite crystallized from warmer bottom brines, whereas cumulates nucleated and grew in the brine column at lower temperatures (Figure 5).

4. Discussion

4.1. Validity of Fluid-Inclusion Data

4.1.1. Primary versus Recrystallized Halite

Diagenetic recrystallization of halite could produce daughter crystals in fluid inclusions that dissolve at the relatively high temperatures achieved during burial. Previous studies demonstrate that daughter crystals of sylvite and carnallite in fluid inclusions from recrystallized halites dissolve at high

temperatures [17,20,21] (Table 1). Primary fluid inclusions in recrystallized halite are commonly large (hundreds of microns), isolated, and irregularly shaped, and the host halites do not retain primary depositional textures and fabrics. This contrasts sharply with the primary fluid inclusions from the bedded chevron and cumulate halite reported here from the Maha Sarakham Formation. We conclude that the halites analyzed from the Maha Sarakham Formation are not recrystallized; fluid inclusions were trapped during subaqueous crystallization at the surface. High dissolution temperatures of daughter crystals recorded from primary halite cannot be attributed to burial recrystallization in the presence of warm brines.

4.1.2. Stretching, Necking, or Leakage of Fluid Inclusions

The potential for permanent deformation and other changes has been a concern when analyzing fluid inclusions in halite [3,4,37,38]. Fluid inclusions in halite may undergo stretching, necking down, and leakage, all of which could affect fluid-inclusion microthermometry. Stretching of fluid inclusions, which is the permanent volume increase produced by overheating above the homogenization temperature, may occur during burial or even during sample preparation. Such stretching produces anomalously high homogenization temperatures in liquid + vapor fluid inclusions [1,38]. Dissolution temperatures of daughter crystals, however, are not affected by stretching because they depend on the mass and chemical composition of the brine trapped in fluid inclusions, not the volume of the inclusion cavity. Laboratory stretching of inclusions from two halite crystals from the Maha Sarakham Formation was undertaken by heating to 150 °C. Subsequent cooling caused renucleation of sylvite daughter crystals and vapor bubbles, the latter indicating fluid-inclusion volumes had increased. The dissolution temperatures of daughter crystals in these fluid inclusions were not substantially changed, which demonstrates that stretching is not a factor for liquid + daughter crystal microthermometry.

Necking down of fluid inclusions can occur when the crystal walls of fluid inclusions change shape to minimize their surface free energy. Necking down can affect the size, shape and number of fluid inclusions [1]. Consider, for example, a fluid inclusion in halite that contained a sylvite daughter crystal and then necked down to form two fluid inclusions, one with the sylvite daughter crystal and one without. In this case, the fluid inclusion with the daughter crystal would yield an anomalously high dissolution temperature, whereas in the other inclusion, the daughter crystal would dissolve at a lower temperature than that at which the halite crystal originally precipitated. The narrow range of daughter crystal dissolution temperatures from individual fluid inclusion bands indicates that necking down was not significant in the halite from the Maha Sarakham Formation (Table 2 and Figure 5).

Leakage of brine from inclusions will produce anomalously high dissolution temperatures if it occurred after the nucleation of daughter crystals [13]. However, all the fluid inclusions first examined at room temperature from the Maha Sarakham Formation halites contained two phases, liquid + daughter crystal and no vapor, implying they have not leaked [1,3,38].

4.2. Supporting Evidence for Extremely High Temperatures: Hematite (Fe_2O_3)

Potash evaporites and associated halites are commonly red, purple, or pink in color due to incorporation of tiny, micron-size crystals of hematite and goethite ($\alpha\text{-FeO}\cdot\text{OH}$). Early workers thought that hematite incorporated in carnallite formed by unmixing and oxidation of ferrous iron from solid solution in carnallite [39,40]. Alternatively, the preferential orientation of hematite plates and goethite fibers in the (001) direction in carnallite from the Devonian Prairie Evaporite showed that iron oxide and carnallite could grow epitaxially and contemporaneously from surface brines [39–41]. Early diagenetic sylvite and carnallite cements in halite beds from the Permian Salado Formation have zoned dark hematite-rich bands at crystal rims and progressively lighter colored, hematite-poor bands in the cores of crystals, which suggests co-precipitation of hematite and potash cements by cooling of warm K-rich brines in the void spaces of halite crystal frameworks [13].

Laboratory experiments using ferric chloride media [42,43] and sulfate solutions [44] showed that hematite can directly precipitate from ferric solutions and that its solubility increased with temperature.

In the presence of Fe_2O_3 seed crystals, hematite and akaganeite ($\beta\text{-FeO}\cdot\text{OH}$) precipitated in FeCl_3 media at temperatures as low as 60°C . Akaganeite can transform to hematite and goethite above 70°C via dissolution-reprecipitation in alkaline media [42]. Even in the absence of Fe_2O_3 seeding, prolonged reaction periods favor the precipitation of the thermodynamically stable hematite over akaganeite, and, at $>100^\circ\text{C}$, only hematite is evident after 100 h of reaction [42,43].

Microcrystalline hematite occurs in primary halite and carnallite of the Maha Sarakham Formation (Figure 6a,b). X-ray diffraction and SEM analysis on insoluble residues from red crystals of halite confirm that these crystals are hematite. Aeolian atmospheric aerosols can load Fe-rich particles to the open ocean via long range transport [45]. Hematite crystals observed in primary halite and carnallite of the Maha Sarakham Formation, however, are not dust particles because they occur as oriented hexagonal plates parallel to halite crystal growth faces (Figure 6). This indicates co-precipitation of iron oxide with halite or carnallite at brine temperatures $>60^\circ\text{C}$ and possibly as high as 100°C rather than oxidation of ferrous iron from solid solution during diagenesis [39,40,42,43]. In addition, hematite crystals derived from iron oxide dust would occur as randomly oriented particles incorporated within halite or carnallite or at their crystal boundaries, which is not observed. However, during halite and carnallite precipitation, soluble Fe^{2+} in shallow marine brines can be oxidized to Fe_2O_3 at low temperatures, leading to co-precipitation of hematite and halite or carnallite.

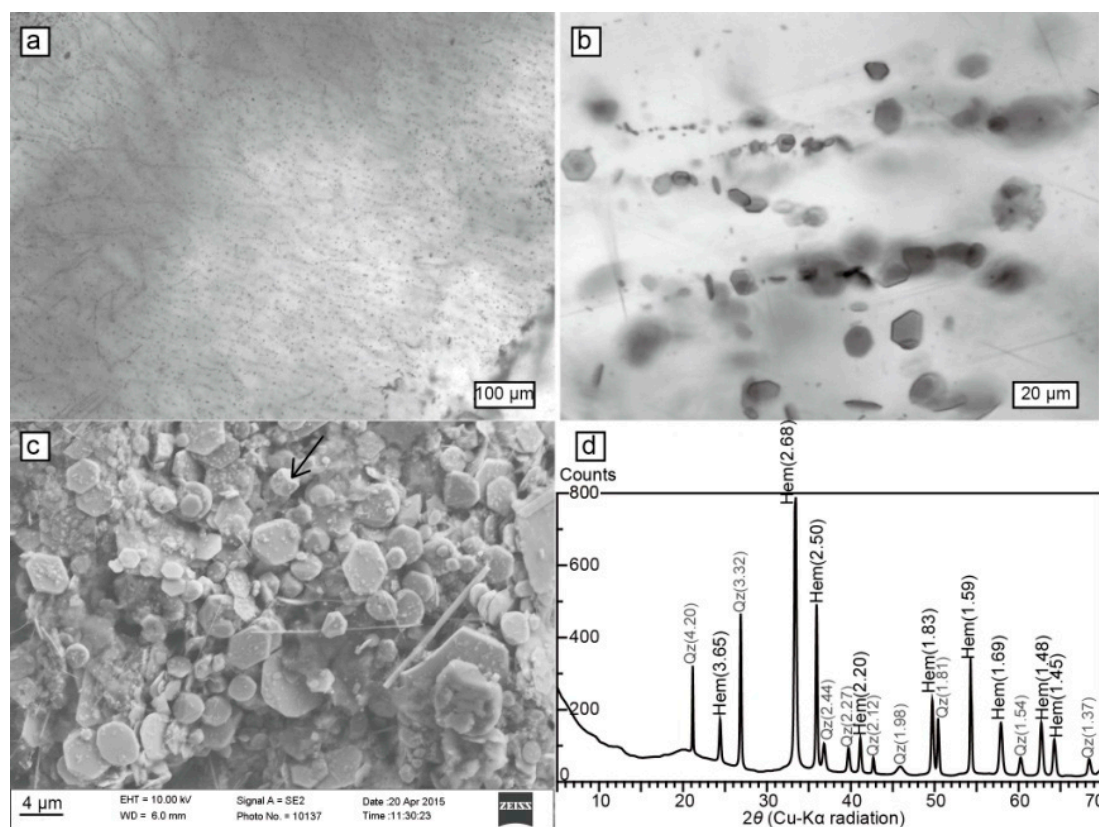


Figure 6. Photomicrographs and X-ray diffraction (XRD) analysis of hematite crystals from core RS2.6, 154 m. (a) Microcrystalline hematite incorporated within halite; (b) hematite crystals are 1–10 μm hexagonal plates; (c) scanning electron microscopy (SEM) image of the hematite crystals. All the hexagonal plates are hematite; crystals with trigonal pattern (arrow) are quartz; (d) XRD result of insoluble residue following dissolution of halite in water. Numbers in the parentheses are d-spacings in Å of Qz: quartz and Hem: hematite.

4.3. Explanation of the High Dissolution Temperatures of Daughter Crystals in Fluid Inclusions

4.3.1. Cretaceous Climate?

High dissolution temperatures (average of 85.6 °C) of daughter crystals in fluid inclusions from halites of the Cretaceous Maha Sarakham Formation are interpreted to reflect true brine temperatures during precipitation. How could these high paleobrine temperatures occur in a Cretaceous marginal sea? Although the Cretaceous was a time of hothouse climate, elevated atmospheric CO₂, warm surface and deep ocean waters, and high sea levels, air temperatures this high are unlikely. Polar climates with mean annual air temperatures above 14 °C are inferred from Late Cretaceous vertebrates from the Canadian Arctic [46], and warm polar oceans are suggested by Mid to Late Cretaceous Arctic Ocean sea surface temperatures of 15–20 °C [47]. $\delta^{18}\text{O}$ values of Cretaceous rudist bivalves from paleolatitudes between 8° and 31° N indicate maximum sea surface temperatures of 35 °C to 37 °C [48]. Land-sea configuration and enhanced poleward oceanic heat transport contributed to Cretaceous warmth.

However, there is no evidence to support the extreme Cretaceous air temperatures that would be needed to explain the daughter crystal dissolution data (Table 2). Furthermore, dissolution temperatures of daughter crystals in halite from icehouse evaporites, such as the Carboniferous and Permian (Table 1), are as high as those from the hothouse halites of the Maha Sarakham Formation, suggesting that these high brine temperatures are not produced from hot climates.

4.3.2. Hydrothermal Activity?

Another possibility for the anomalously high fluid-inclusion temperatures is halite crystallization from upwelling hydrothermal brines. In active rift and strike-slip systems, hydrothermal brines could be driven upward by density instabilities of thermal origin or by topographic gradients and leak to the surface in closed basins. Several lines of evidence support the hydrothermal model. The mineral precipitation sequence of halite–sylvite–carnallite–tachyhydrite in the Maha Sarakham Formation indicates that the Cretaceous parent waters were enriched in Ca²⁺ and depleted in Na⁺, Mg²⁺, and SO₄^{2−}, typical of hydrothermal CaCl₂ brines [49,50]. In addition, hydrothermal brines may carry high concentrations of trace elements, for example, Fe, Mn, Cu, Pb, Zn, and Ba [49,50]. Such brines may provide the Fe for the hematite in the Maha Sarakham Formation (Figure 6).

A hydrothermal brine origin, however, is not required to produce evaporites with the halite–sylvite–carnallite–tachyhydrite sequence of the Maha Sarakham Formation. Cretaceous seawater, estimated from primary fluid inclusions in marine halite from Brazil, Congo, and the Maha Sarakham Formation, was enriched in Ca²⁺, and depleted in SO₄^{2−}, Na⁺, and Mg²⁺ compared to modern seawater [31]. Hydrothermal brines are not needed to produce these unusual evaporites; the halite–sylvite–carnallite–tachyhydrite mineral sequence could form during evaporation of normal Cretaceous seawater. In addition, the Khorat Plateau is situated in the tectonically stable Indo-China Block where there is no evidence for Cretaceous volcanism and faulting (Figure 1). Significant Cretaceous hydrothermal activity associated with evaporites has not been reported for the Khorat Plateau [28]. Finally, hydrothermal activity is an unlikely explanation for other halites with high dissolution temperatures of daughter crystals, for example, the Permian Zechstein Basin of Poland and Salado Formation of New Mexico (Table 1).

The heat supplied by hydrothermal activity could not easily heat a brine body in a marginal sea to over 80 °C (Table 1). For example, the Danakil depression of the Afar rift, Ethiopia, has intense hydrothermal activity related to magmatism [51]. Although hot springs, 100 °C or higher in temperature, and saturated with NaCl and FeCl₂-rich discharge at the surface, hypersaline lakes from which potash minerals precipitate are ~30 °C [51,52]. Normal Ca²⁺-rich Cretaceous seawater, widespread warm brines from which halite precipitated (Figures 1 and 5), the paucity of contemporaneous faulting and volcanism on the Khorat Plateau, and insufficient heat supplied by hydrothermal waters, suggest that hydrothermal activity is not a plausible explanation for the

anomalously high brine temperatures observed from the dissolution behavior of daughter crystals in halite from the Maha Sarakham Formation.

4.3.3. Solar-Heating Hypothesis: Solar Pond Effect?

The most likely explanation for the high dissolution temperatures of daughter crystals and high brine temperatures involves solar radiation and formation of a salinity-stratified (meromictic) brine body. Natural hot brines have been found in many continental lakes, shallow coastal lagoons and ponds [53–58]. Hot brines also occur naturally in solar ponds where solar radiation is collected and stored as thermal energy. The salinity gradients required for solar heated ponds may be produced by various mechanisms, such as a natural salt bottom flooded with fresh or brackish water where diffusion gives rise to a salt concentration gradient that suppresses convection. The first documented natural hot lake was Medve Lake, 42,000 m², in Transylvania, where lake water temperatures up to 70 °C were observed at a depth of ~1.3 m during the end of summer [53]. Temperature variation was attributed to the salinity gradient which could suppress convection and retain the solar heat at the lake bottom. Hot Lake, a shallow meromictic saline lake occupying 12,720 m², in Washington, USA, has bottom temperatures in excess of 50 °C during summer at a depth of 2 m [54]. In Antarctica, the solar pond effect was found at Lake Vanda (5.2 km²) with bottom temperatures as high as 25 °C at a depth of 60 m, when the ambient air temperature was −20 °C and the lake surface was covered with ice [55]. Solar heating has been reported from other meromictic lakes, such as Solar Lake (140 m × 50 m), Israel [56], a small coastal lagoon in Venezuela [57], the south basin of Great Salt Lake (49,000 km²), Utah [58], and Lake Bonney (3.2 km²), Antarctica [59].

Temperatures of natural meromictic lakes inspired scientists and engineers to design artificial salinity gradient solar ponds to collect and store solar energy for desalination, electricity production, and heating of buildings [60,61]. El Paso Solar Pond, with a surface area of 3000 m² and depth of 3.25 m, is a representative artificial pond. The highest documented temperature at the bottom of El Paso solar pond during 1991–1993 was 93 °C [62]. From 5–10 April 1999, after sufficient salt dissolved at the pond bottom, a salinity gradient was created rapidly. The temperature of the pond bottom increased at a rate of ~1 °C per day from the ambient temperature of 17.4 °C on 6 April to 85 °C on 10 June 1999. After only two months, a temperature gradient with a maximum temperature difference between the surface and bottom brine of >70 °C was established [62]. Maximum temperatures of >90 °C were documented from artificial ponds operated in Israel with MgCl₂ saturated brine at the bottom; experiments on a 1200 m² pond produced temperatures of 103 °C [60]. It is clear that solar heating can produce hot bottom brines capable of storing large amounts of solar energy.

The salinity gradient, i.e., density stratification, plays a critical role in heating and solar energy storage in meromictic lakes or solar ponds. Generally, an ideal salinity gradient is composed of three layers from top to bottom: the upper convective zone (UCZ), the non-convective zone (NCZ), and the lower convective or storage zone (LCZ) (Figure 7). The UCZ is the topmost homogeneous layer of low-salinity brine or fresh water. Below the UCZ, the NCZ has higher salinity and temperature than the UCZ; the NCZ provides insulation for the LCZ, which is the bottom layer with greatest salt concentration, saturated with respect to halite or other evaporites [60]. Convective currents in the NCZ are suppressed by increasing the density gradient downwards when water is heated from the bottom by absorbed solar radiation. If the concentration gradient is great enough, no convection occurs in this region and the energy absorbed in the bottom of the pond is stored in the LCZ [60]. This salinity-density structure may occur in waters with variable depths, but preferably <10 m because solar radiation is needed to penetrate the water column and heat the bottom. Typical solar-heated lake depths are 1.32 m in Medve Lake [53], 2 m in Hot Lake [54], 3.25 m in El Paso Solar Pond [62], and 7.5 m in Great Salt Lake [58].

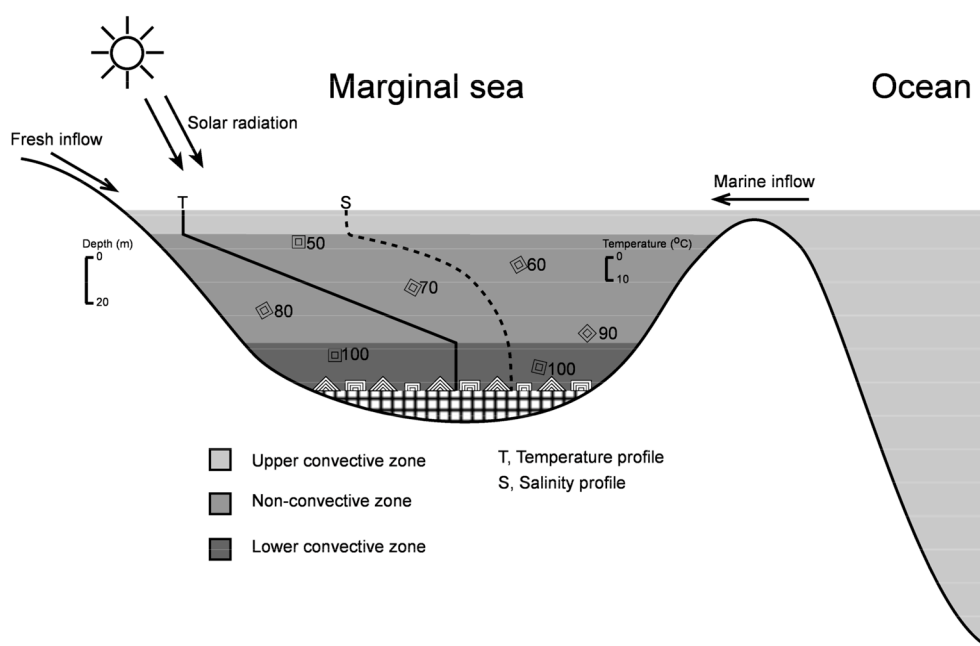


Figure 7. Cartoon illustrating the solar heating hypothesis in a salinity-stratified, marginal sea proposed in this paper to explain the anomalously high brine temperatures documented from dissolution temperatures of daughter crystals in fluid inclusions in Cretaceous halites. Crystals with numbers show nucleation/precipitation temperatures.

The evaporites of the Maha Sarakham Formation have been interpreted as marine in origin from sulfur isotopes in anhydrite, Br in halite, fluid-inclusion major-ion chemistries and regional geology [23,24,31]. We hypothesize that solar-radiation storage in a shallow, meromictic, marginal sea via solar heating is responsible for the high dissolution temperatures of sylvite and carnallite daughter crystals in fluid inclusions in halite. Support for this hypothesis includes: (1) the absence of dissolution features in primary halite, such as horizontal truncations and vertical dissolution pipes; (2) large temperature variations in halite beds, such as 49.5–81.0 °C at 86.7 m, core K1 and 57.9–117.2 °C at 154 m, core RS2.6 (Table 2); and (3) hematite microcrystals. Primary halites formed in non-stratified, shallow perennial brines less than 1 m deep are commonly characterized by dissolution truncations due to episodic flooding by freshwaters [33,63] or undersaturation when brine temperatures rise in the summer [36]. Well preserved chevron and cumulate textures without dissolution features in the Khorat halites (Figure 3) indicate that they were precipitated in density-stratified brines never in contact with fresh water and never undersaturated with halite during summer brine heating. Variable dissolution temperatures documented from different halite fragments in the same halite bed may be explained by the solar-heating hypothesis. If halite crystals nucleated at different depths in the NCZ and LCZ regions and then accumulated at the brine bottom, daughter crystals in the fluid inclusions from these halites would dissolve at distinct temperatures (Figure 7). Hot brines in the LCZ with temperatures over 80 °C could have high dissolved iron; hematite could precipitate from these bottom brines, leading to the red color in halites and associated potash minerals (Figure 5).

Solar heating can explain the high paleobrine temperatures in the Cretaceous Khorat Plateau. Dissolution temperatures of daughter crystals in fluid inclusions from bottom-growth chevron halites are higher than from cumulate halites (Figure 5), suggesting thermal stratification in the Khorat sea. Such a temperature structure supports the proposed solar-heating hypothesis. The salinity gradient could form and be maintained by continental or marine inflow, and seawater evaporation (Figure 7). In a restricted marginal sea, seawater becomes denser due to evaporation. Eventually seawater is isolated from the ocean via drawdown. Continental flooding or marine brackish water inflow, either from overflow above the barrier or from seawater seepage, may produce a thin low-salinity layer,

i.e., the UCZ (Figure 7). Large salinity gradients could develop as documented at the El Paso Solar Pond [62]. Subsequently, stable salinity gradients generate increasing temperatures toward the brine bottom. In the solar heating model proposed for the Khorat Plateau, halite crystals precipitated from brines at different depths and temperatures (Figure 7). Cumulate halites nucleated in a water column with increasing temperatures downward, whereas bottom-growth chevron halites grew at the brine bottom at the highest temperatures. Deposition of cumulate halites and bottom-growth chevron halites occurred simultaneously at the brine bottom.

Several issues must be considered with the solar heating hypothesis. Wind generated waves, especially in a large sea, will mix the upper layer, destroy density stratification, and homogenize the water column. In addition, solar absorption in the LCZ will be reduced if visible light is prevented from reaching the bottom of the water column. Thus salinity-density stratification is limited to shallow brine bodies whose depth depends on water transparency.

5. Summary and Conclusions

Anomalously high brine temperatures (average 85.6 °C) obtained from microthermometric analyses of daughter crystals in primary fluid inclusions in Cretaceous halites from the Maha Sarakham Formation corroborate the high dissolution temperatures reported from other studies (Table 1). Petrographic observations show that the Maha Sarakham halites are primary precipitates from surface brines and are not recrystallized. Fluid inclusions have not undergone stretching, leaking, or necking down, which could affect the dissolution temperatures of daughter crystals. Dissolution temperatures reflect true crystal growth temperatures, i.e., paleobrine temperatures. The occurrence of microcrystalline hematite within halite shows that iron oxide and halite precipitated simultaneously from warm brines in excess of 60 °C.

Although the Cretaceous had a hothouse climate, average air temperatures of 85.6 °C are not realistic. Hydrothermal activity was not significant in the Khorat Plateau so this is an unlikely heat source for warming a large Cretaceous marginal sea. The “unusual” halite–sylvite–carnallite–tachyhydrite mineral assemblage does not require hydrothermal inflow [49] because Cretaceous seawater was enriched in Ca^{2+} and depleted in SO_4^{2-} [31]. The solar-heating hypothesis proposed here involves storage of solar energy in density-stratified marine brines. The strong salinity gradient created by freshwater or brackish inflow from continental or marine flooding into a shallow, restricted marginal marine basin could suppress convection and store heat at the brine bottom, leading to extremely high brine temperatures. Halite crystals precipitated at various temperatures due to the brine stratification and the complicated thermal structure of the marginal marine basin.

Salinity-stratified brines are common in shallow natural meromictic lakes, lagoons, and ponds, and in artificially built ponds that utilize solar energy. If salinity stratification and solar heating of brines occurred in the Khorat Basin, the high temperatures recovered from microthermometric analysis of fluid inclusions in halite may reflect the brine temperatures at which halite precipitated but not extreme air temperatures in a hothouse world [7].

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