

# Sinjarite, a new mineral from Iraq

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**SUMMARY.** A hygroscopic, soft, pink mineral was discovered in Sinjar town, west of Mosul city. Wet chemical and X-ray diffraction analyses proved that the mineral has a composition of calcium chloride dihydrate  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , which has not been known in nature before. It is therefore a new mineral, and is named sinjarite after its locality.

CALCIUM chloride hexahydrate has been found occurring naturally in Victoria Land, Antarctica, and named antarcticite (Torii and Ossaka, 1975), and Hausmann (1813) described a hydrated calcium chloride occurring on gypsum from the boracite deposits of Lüneburg, Germany, but it was not analysed.

Anhydrous calcium chloride is largely used as a drying agent; it absorbs water and changes to the dihydrate  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , which is very hygroscopic and changes quickly to the hexahydrate. The latter melts at about  $30^\circ\text{C}$  and hence is only found in cold regions like Antarctica. A monohydrate and two tetrahydrates are known but have not been found in nature.

**Geological setting.** The general succession of rocks in Sinjar area is given in Table I. The major structure consists of Sinjar Anticline. This is an asymmetrical, double-plunging anticline, trending in an almost E-W direction and forming Jebel Sinjar which extends into Syria (fig. 1). The highest point is about 1462 m above sea level; the rocks are of the Sinjar Limestone Formation. The

southern limb of the Sinjar anticline has a gentle dip between  $10-20^\circ$  SE, whereas the northern limb has a steeper dip between  $40-80^\circ$  (for detailed geology and structure of the Sinjar area see Youash and Naoum, 1970; Maala, 1977).

Sinjar town lies at the foot of the southern limb in the eastern part of Sinjar anticline. It has largely been built on the dip-slope of the Jeribe Formation. The sample studied was found in a braided wadi filling, about 150 m in width, cutting across the Serikagni Formation (Tamar-Agha, 1979, personal communication). The wadi is a dip valley, running

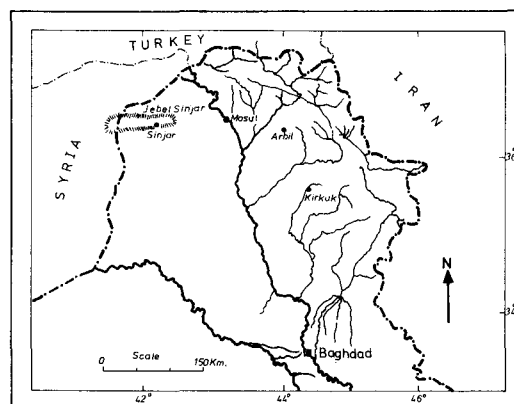


FIG. 1. Sample location.

TABLE I. General succession at Sinjar

Formation	Age	General lithology
Jeribe	Middle Miocene	Thinly bedded detrital limestone, chalky limestone, dolomitic limestone and marl
Dhiban anhydrite	Lower Miocene	Mainly gypsum
Serikagni	Lower Miocene	Limestone, marly limestone and marl
Jaddala	Eocene	Shale, marly limestone and limestone
Sinjar limestone	Palaeocene to Lower Eocene	Hard massive limestone
Shiranish	Upper Cretaceous	Marl and marly limestone

roughly in a N-S direction and sloping towards the south. It is dry for most parts of the year. Ephemeral streams, however, may form after torrential rains during wet seasons.

**Chemistry and physical properties.** Qualitative analysis on a PW 1450/10 automatic sequential X-ray fluorescence spectrometer indicated the presence of major Ca and Cl and minor or trace amounts of Na, K, Sr, Mg, and Fe; the scanning charts show no sulphur peaks, and the absence of  $\text{SO}_4^{2-}$  was confirmed by addition of  $\text{BaCl}_2$  to a solution of the mineral. Quantitative analysis, see Table II.

TABLE II. Chemical data for sinjarite

	A	B
Ca	25.84*	27.26
Cl	46.64†	48.24
H <sub>2</sub> O	26.55‡	24.50
Na	0.85§	—
Total	99.88	100.00
K	226 ppm§	—
Mg	5	—
Sr	141	—
Fe	9¶	—

A. Sinjarite, Sinjar, Iraq. B. Theory for  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ .

\* Mean of three gravimetric analyses.

† Mean of four gravimetric analyses.

‡ Mean of nineteen determinations of ignition loss at  $T$  150 to 400 °C.

§ Mean of five flame-photometer determinations.

|| Mean of five atomic-absorption determinations.

¶ Mean of five U.V. spectrophotometric determinations.

The mineral is granular (massive), pale pink with a white streak and vitreous to resinous lustre; hardness (Mohs)  $1\frac{1}{2}$ . Elongated prismatic crystals are very common, and give parallel extinction, length fast; some crystals had a rhombic shape. Cleavage prismatic, well developed.  $n$  1.54, M.P. 172 °C, sp.gr. 1.66 (weighing in air and  $\text{CCl}_4$ ), solubility at 20 °C 117 g in 100 g water ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  melts in its water of crystallization at about 175 °C; solubility at 20 °C 130 g in 100 g water).

The chemistry and physical data agree well with the synthetic hydrate  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , not hitherto known in nature, and the name sinjarite (Si-njārait) is proposed for the mineral, from the locality. The mineral and name have been approved by the I.M.A. Commission on New Minerals and Mineral Names. Type material is deposited at the Museum of Natural History, University of Mosul.

The X-ray diffraction analyses were first performed on a polished mounted slice of the sample using a PW 1130 diffractometer with Cu X-ray tube and Ni filter.

The X-ray diffraction pattern obtained showed some similarity to the published X-ray diffraction pattern of antarcticite ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ), which did

TABLE III. X-ray powder data for sinjarite, compared with JCPDS card 1-0989 ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ )

Sinjarite			$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (JCPDS)	
$d\text{\AA}$	I	I/I <sub>0</sub>	$d\text{\AA}$	I/I <sub>0</sub>
6.09	38.5	86.5	6.1	40
5.92	12.5	28.1	—	—
4.62	16.0	36	—	—
4.35	11.5	25.8	4.34	50
4.25	8.5	19.1	—	—
3.59	12	27	—	—
3.30	11.5	25.8	—	—
3.19	11	24.7	—	—
3.15	14.5	32.6	—	—
3.06	29.5	66.3	3.06	70
3.04	44	98.9	—	—
3.00	12.5	28.1	—	—
2.96	31.5	70.8	—	—
2.82	44.5	100	2.83	100
2.73	31.5	70.8	2.69	16
2.58	8	18	—	—
2.54	6	13.5	—	—
2.50	12	27	2.52	20
2.45	6	13.5	—	—
2.41	13	29.2	—	—
2.39	22	49.4	—	—
2.36	22.5	50.6	2.36	20
2.33	6.5	14.6	—	—
2.31	14	31.5	—	—
2.25	13	29.2	2.26	16
2.23	15	33.7	—	—
2.22	20	44.9	—	—
2.16	13	29.2	2.16	24
2.12	15.5	34.8	2.12	60
2.10	11.5	25.8	—	—
2.08	7.5	16.9	—	—
2.04	15.5	34.8	—	—
2.02	14	31.5	2.01	8
2.00	12	27		
1.89	4.5	10.1	—	—
1.86	5.5	12.4	1.87	20
1.78	7	15.7	1.78	12
1.76	7	15.7	—	—
1.70	5.1	11.5	1.71	12
1.67	9.7	21.8	1.67	16
1.63	6	13.5	1.62	4
1.52	32.2	72.4	1.52	4
1.51	16.5	37.1	—	—
1.48	6.5	14.6	1.48	16

not agree with the chemical composition of the investigated sample of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  obtained from chemical analyses. It was thought that the sample slice had absorbed water during the preparation and analysis.

A cavity slide was filled with fresh powder of the sample and introduced into the sample holder of the diffractometer. The X-ray diffraction pattern obtained in this way was different from the first and showed similarity to the published X-ray diffraction pattern of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (Table III).

The  $d$  values of the four most intense lines of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  agreed very well with measured diffractogram of the investigated sample. The determined relative intensities however were different from the published values. The difference could be due to the use of Cu-K $\alpha$  radiation in the present investigation, whereas the published data were obtained using Mo-K $\alpha$  radiation. Moreover, the measured diffractogram showed additional peaks of appreciable intensities, some very intense. Such lines were thought to reflect possible hydration phases of the original sample.

*Discussion and origin.* From the chemical and X-ray diffraction analyses it is evident that the sample examined consists largely of calcium chloride dihydrate  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , sinjarite, 87.6% with minor amounts of antarcticite  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  (10.1%) as hydration product and sodium Na (0.85%) either substituting for calcium or in the form of halite NaCl. There are traces of Sr substituting for Ca, traces of K and Mg as chlorides, and traces of Fe as impurities.

Calcium is a major constituent of most, if not all, the formations in the area, mainly in the form of carbonates or sulphates. It is therefore expected to be present in relatively high concentrations in groundwaters. Analysis of a water sample (No. 1/1677) from a hand-dug well through Quaternary (Recent) sediments in Sinjar town gives a relatively high chlorine content of 362 ppm compared with an average of 40 ppm for Sinjar area as a whole; the

calcium content is 108 ppm which is about an average for the area (Maala, 1977).

For calcium chloride to be precipitated rather than NaCl from a saturated solution containing  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{Cl}^-$  ions, its concentration must be 3.5 times that of NaCl. (The solubility of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  is taken to be 3.5 times that of NaCl.) Both Ca and Na cations, however, need not be present in large amounts to be precipitated, since their solubilities have been considerably reduced due to the presence of the chlorine common ion.

It may be assumed that the mineral sinjarite has been precipitated within recent sediments from the slow evaporation of groundwater saturated with Ca and Cl ions.

The mineral is ephemeral, it quickly dissolves away by ground or percolating surface waters during wet seasons. Alternatively, and because of its hygroscopic nature, it may change to the hexahydrate  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , which melts at 30 °C and will not survive hot seasons.

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