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Did the Late Miocene (Messinian) gypsum form from evaporated marine brines during the salinity crisis?

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This document describes the methods (microthermometry and computer modeling) and shows tabulated data of the fluid inclusion measurements (Table DR1) and their frequency (Tm_{ice}, Fig. DR1).

Sampling and methodology

Messinian gypsum crystals were taken from freshly blasted, unweathered quarry faces. Modern gypsum was collected from the upper portion of the domal crystal structures, in order to compare the salinity obtained from inclusions with chemical analyses of the contemporaneous pond seawater.

A total of 27 millimeter-sized fragments of gypsum were obtained by cleaving each crystal along the (010) plane with a razor blade. Microthermometric observations were done following the methods of Attia et al. (1995) (see following paragraph; Figure DR1 and Table DR1). Salinities (expressed as weight % NaCl equivalent) of the Messinian and modern fluid inclusions were calculated from the final melting temperatures of ice (Bodnar, 1993) and hydrohalite (Sterner et al., 1988), respectively.

Evaporated seawater from the Conti Vecchi solarworks was sampled in spring 2012 from the same ponds from which gypsum was collected. Major ion chemistry of brines was determined by Ion Chromatography (IC) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Table 1).

Computer modeling was performed using EQL/EVP, a FORTRAN 90 program that simulates evaporation of aqueous solutions (Risacher and Clement, 2001). The major ion composition (expressed in molalities) of seawater during stepwise evaporation, and the sequence of precipitated salts, were calculated at 25 ºC assuming a hydrologically open system.

Fluid inclusion microthermometry

Microthermometric observations were done using a calibrated Linkam THMSG600 heating–freezing stage attached to an Olympus polarizing microscope equipped with a 100x objective. Inclusions were quickly frozen to –90°C and heated up to +30°C at a rate of 30°C/min. The volume increase upon freezing led to permanent stretching of inclusions and formation of a vapor bubble that remained during later freezing-melting runs. Such vapor bubbles formed by stretching eliminates metastable behavior during phase changes (Roedder, 1984; Attia et al.,1995). This procedure permanently deforms or "stretches" inclusions but it does not change the composition of the aqueous phase, and thus will not influence melting behavior when frozen. Fluid inclusions were then cooled again to –70°C and slowly heated at 1-2°C per minute and at 0.3°C per minute close to the melting temperatures. For 20 inclusions the final melting temperature of ice was reproduced twice, with negligible error (±0.2°C).

Sample name	Locality	First melting temperature (°C)	Final melting temperature of ice (°C)	Salinity* (Wt % NaCl equivalent)	Salinity† (ppt seawater)
Messinian gypsum					
BG1-1b-1	Banengo	–40	–0.6	1.1	11.1
			–0.3	0.5	5.5
			–0.5	0.9	9.3
			–0.4	0.7	7.4
			–0.5	0.9	9.3
BG1-1b-3	Banengo	–40	–1.0	1.7	18.5
			–0.9	1.6	16.6
			–0.5	0.9	9.3
			–0.6	1.1	11.1
			–0.6	1.1	11.1
BG1-1b-4	Banengo	–40	–1.0	1.7	18.5
			–1.5	2.6	27.7
			–0.6	1.1	11.1
			–0.4	0.7	7.4
			–0.8	1.4	14.9
			–1.2	2.1	22.1
			–0.7	1.2	12.9
BG1-2-f	Banengo	–40	–0.6	1.1	11.1
BG1-2-g	Banengo	–35	–0.2	0.4	3.6
BG1-2-h	Banengo		–0.8	1.4	14.8

			–1.6	2.7	29.6
			–0.5	0.9	9.3
BG1-2-i	Banengo	–35	–0.2	0.4	3.6
			–0.2	0.4	3.6
BG4-1-a	Banengo	–33	–0.5	0.9	9.3
			–0.3	0.5	5.5
			–0.2	0.4	3.6
			–0.2	0.4	3.6
BG4-1-b	Banengo	–35	–0.3	0.5	5.5
			–0.7	1.2	12.9
			–0.2	0.4	3.6
BG4-1-d	Banengo	–40	–0.9	1.6	16.6
			–0.2	0.4	3.6
			–0.2	0.4	3.6
BG4-3-a	Banengo	–38	–0.3	0.5	5.5
BG4-3-b	Banengo		–0.5	0.9	9.3
BG4-3-c	Banengo		–0.8	1.4	14.8
GcucI-1-c1	Moncucco	–36	–0.4	0.7	7.4
			–1.5	2.6	27.7
			–0.4	0.7	7.4
GcucI-1-c2	Moncucco	–33	–0.2	0.4	3.6
			–0.2	0.4	3.6
			–0.4	0.7	7.4
		–37	–0.9	1.6	16.6
GcucI-1-f1	Moncucco	–35	–1.2	2.1	22.1
			–2.2	3.7	41.4
			–0.4	0.7	7.4
GcucII-1-b2	Moncucco		–0.6	1.1	11.1
GcucII-1-b3	Moncucco		–0.3	0.5	5.5
			–0.6	1.1	11.1
			–0.3	0.5	5.5
			–0.4	0.7	7.4
GcucII-1-d2	Moncucco	–35	–0.8	1.4	14.8
			–0.4	0.7	7.4
			–1.1	1.9	20.3
			–0.2	0.4	3.6
GcucII-1-e	Moncucco		–1.7	2.9	31.5
			–0.5	0.9	9.3
			–1.1	1.9	20.3
			–0.6	1.1	11.1
			–2.3	3.9	43.3
GcucII-3-a	Moncucco	–35	–0.2	0.4	3.6
			–1.6	2.7	9.3
			–2.2	3.7	41.2
			–1.1	1.9	20.3
GcucII-3-b	Moncucco	–37	–0.8	1.4	14.8
			–4.9	7.7	111.7
			–2.4	4.0	45.3
			–4.1	6.6	86.4
			–3.0	5.0	58.3
			–1.3	2.2	24.0
			–0.5	0.9	9.3
GcucII-3-c	Moncucco	-34	–1.0	1.7	18.5
			–2.5	4.2	47.4
			–2.1	3.6	39.2
			–0.5	0.9	9.3
			–1.4	2.4	25.9
GcucII-3-e1	Moncucco		–1.0	1.7	18.5
			–1.3	2.2	24.0
			–1.4	2.4	25.9
			–1.4	2.4	25.9
			–1.5	2.6	27.7
			–0.9	1.6	16.6
GcucII-3-h2	Moncucco		–1.2	2.1	22.1
			–1.2	2.1	22.1
			–2.7	4.5	51.6
			–0.6	1.1	11.1
GcucII-3-h3	Moncucco		–3.3	5.4	66.4

Note: *Salinities calculated from the final melting temperatures of ice using the equation of Bodnar (1993).
† Salinities calculated from the $NaCl_{eq}$ values using the equation of Goldstein and Reynolds (1994).

Table DR1. Messinian fluid inclusion data

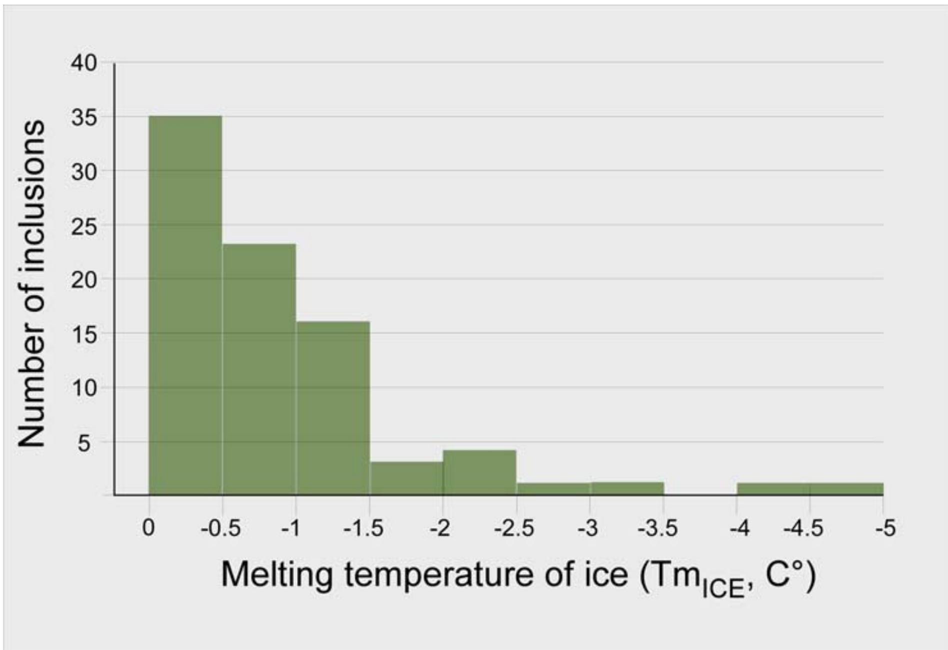

Figure DR1. Melting temperature of ice measured in Messinian gypsum fluid inclusions.

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