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Climate of the Past Discussions

Interactive comment on "Thenardite after mirabilite deposits as a cool climate indicator in the geological record: lower Miocene of Central Spain" *by* M. J. Herrero et al.

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This paper describes a series of 30 sediment samples collected in a salt formation of Central Spain. These samples have been collected directly in the underground mine or in cores from drill holes. Their mineralogical composition has been determined by X-ray diffraction, optical microscopy and SEM analysis. The composition of fluid inclusions has been determined by low temperature SEM. The authors describe and discuss the transformation of sodium sulfate decahydrate (mirabilite) into anhydrous sodium sulfate (thernardite). They attribute this postdepositionnal transformation to a diagenetic process that took place at the same time as a climate change 18.4 Ma ago. This climate

change is attested by the presence of particular mammal assemblages at other places in Spain (but not in the studied deposit) that are characteristic of a cool and arid climate. The paper is well organized and well written (although it may benefit from careful editing for the English language and for inadequate wording). The geological setting of the studied site, the sampling protocol and the observation techniques are adequately described. Most of the paper discusses the formation of mirabilite and thenardite and the conditions for the mirabilite-thenardite transition. I found the paper interesting and deserving publication, but I think it should be reorganized in order to avoid redundant discussions of the mode of formation of minerals. This point is not compulsory. In the introduction, I may be wrong, but the use of calling all salt formations evaporites is not adequate. The authors themselves describe mechanisms of salt formation that do not call for evaporation. They also recall (l. 25) that "a few of these deposits are not really evaporites". To me the first sentence (l. 18) should read "salt formations are natural deposits that have . . .". Then in line 20 ". . .most salt deposits are formed by evaporation under arid environmental conditions. . .". This may look petty, but it orients the discussion of salt formation, an important point of the manuscript. In section 5.2 (page 3232), the authors distinguish "two different pathways of salt formation": evaporative concentration and frigid concentration. They describe these two main mechanisms in detail in this section. The authors nevertheless distinguish two mechanisms in the frigid concentration pathway, namely cooling and freezing. I think these mechanisms can be described in a different way. Starting from a given aqueous solution (what the authors call the "mother brine"), that is undersaturated with respect to a given mineral, formation of this mineral can be achieved in three ways (and not two): 1) removal of the solvent (water) at more or less constant temperature by evaporation, 2) removal of water at constant salinity by freezing, 3) change in temperature at constant salinity (or total concentration). The first two mechanisms increase the concentration of all the dissolved species at the same time leading to a so-called brine (a high salinity solution). The third one relates to the change in mineral solubility with temperature, that the authors describe in an awkward sentence in line 24 page 3226 ("sodium sulphate

minerals appear to be highly dependent on temperature range"). This third mechanism only modifies the concentration of the dissolved species constituent of the mineral. The second mechanism (freezing) compulsorily implies the third one (solubility change with T). Note that in general mineral solubility increases with temperature, but there are cases where it decreases (this is the case of Ca carbonates). Even worse the change in solubility with temperature is also related to the change in solution composition (all this is taken into account by the interplay between non-ideality and common ion effects). A mineral can see its solubility in pure water increasing with temperature, while it may behave in a totally different manner in highly concentrated solutions due to changes in the activity coefficient of the dissolved species. I have not read the Zheng et al (2000) paper but a classification of evaporitic minerals according to their temperature of formation can only be related to the environmental and geological conditions of the salt deposit and cannot be an intrinsic property of such minerals. As such their temperature of formation may change from one setting to another. The references on seawater evaporation are somewhat outdated. While the citation of Marion's work on seawater freezing is adequate, the authors should cite the papers of Harvie, Weare, Eugster and others who calculated the mineral sequences forming during the evaporation of seawater and who provided evaporation pathways ressembling and updating those mentioned in Fig. 4. May be these references are included in Orti's papers (not available to me). In the discussion of the formation of salt deposits (like any sediment in fact), there are two things to distinguish (as the authors indicate in page 3234 line 5 et seq.): how the deposit itself has formed and how it has evolved afterwards. I think the paper could benefit from a description of the way the salt deposit has formed, i.e. expand section 2 "Study site", as far as there is any extensive study of the genesis of this deposit. For example, was the original environment marine? What is the subsequent role of continental waters? Etc. Do we have any idea of the composition of what the authors call the "mother brine"? The authors do describe the formation of salt deposits in other parts of the world in section 5, but it is a general point of view. In this same section 2, the authors describe post-depositional reactions such as the

replacement of glauberite and anhydrite by gypsum. They also describe the recent hydration of thenardite into mirabilite due to the percolation of meteoric waters? What is "recent"? How extensive (in time and in space) can this be? Is there any impermeable layer that stopped the downward flow of water? Why does it stop? Is it still continuing? The mineralogical composition of the sediment is described in detail in section 4.1 ("results"). It is followed by the description of the fluid inclusion composition in section 4.2. There is a very important result in this section: the authors show that fluid inclusions in thenardite contain only Na and S (likely as sulfate), a very strong argument in support of the formation of thernardite after mirabilite. Indeed if thernardite had formed from the "mother brine" it would contain the whole suite of major elements of the "mother brine", including magnesium, potassium and chloride. The fact that the fluid inclusions contain only sodium and sulfur (as sulfate?) composing thernardite is indeed indicative of the fact that it has recrystallized from mirabilite likely through a process locally releasing the mirabilite hydration water. This is clearly explained in section 5.2.5. May be this should be highlighted in the abstract. Lines 8 to 16 page 3238 are a clear conclusion of this point. The authors then describe mammal assemblages described in the literature and characterizing a cool period contemporary of the transformation of the salt deposit, with changes that coincide with the mirabilite-thenardite transition. These fossils have not been found in the studied deposit, but at other locations in Spain. This points to a change in climate at the time of the formation of the salt deposit and of the mirabilite-thenardite transition. I am quite far from being a paleontologist so I will not comment this part which nevertheless seems convincing to me. One question may come to the reader's mind. The mirabilite-thenardite transition and the change in mammal assemblages may have occurred 18.4 Ma ago. 5.5 Ma ago the Messinian salinity crisis affected the whole Mediterranean basin. Is it likely that such a large climatic event affected deposits like the one the authors have studied? Or have things stay put there since the lower Miocene? Finally my opinion is that the results provided in this manuscript (mainly the description of the mirabilite-thenardite transition and the change in the mammal assemblages) are robust enough to indicate a climate change

in the lower Miocene of Central Spain. Therefore I suggest that the paper is published in Climate of the Past. The Editor may want the manuscript to be reorganized following the suggestions above.

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