

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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We would like to thanks Dr. Monnin for all his insightful comments that will help improving the manuscript. We will proceed to incorporate his suggestions in the revised version. Our detailed comments are:

1.- Referee Suggestion: 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

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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.

Authors: We do agree with this comment. This is one of the main points of this work: salts found in nature are not always evaporites. We will modify the text as proposed by the referee in order to avoid confusion.

2.- Referee Suggestion: 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

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manner in highly concentrated solutions due to changes in the activity coefficient of the dissolved species.

Authors: We find this point very important. When writing the submitted document we discussed at length the development of an explanation of the two mechanisms of salts precipitation in cool environments, but we finally discarded this option in order to keep the text as simple as possible, but we agree with the reviewer concerning the importance of this topic. Following his recommendation, we will include both of these mechanisms in the revised paper.

3.- Referee Suggestion: 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.

Authors: We fully agree with Dr. Monnin in this point, nevertheless we wanted to cite this reference because we find it interesting as it is the first attempt to classify evaporites by their temperatures of formation. Certainly, salts precipitation is a complex process and obviously temperatures are just one of the factors.

4.- Referee Suggestion: 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 resembling and updating those mentioned in Fig. 4. May be these references are included in Orti's papers (not available to me).

Authors: Dr. Monnin is right: Most of the relevant works about precipitation sequences from seawater evaporation appear referenced in Ortí (2010), including those of Harvie, Weare, Hardie, Eugster etc. We decided to include Ortí's paper because we consider his contribution is a complete review of both natural and laboratory salt precipitation

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sequences. In any case, we will complete the revised manuscript with additional key references dealing with the precipitation sequences produced as a result of seawater evaporation.

5.- Referee Suggestion: 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 génesis of this deposit. For example, was the original environment marine? What is the subsequent role of continental waters? Etc.

Authors: We are going to complete the facies description and environmental interpretations in the revised version as both reviewers have suggested. We consider that this way we will give detail information of the sedimentary system and environmental conditions where the salts were formed.

6.- Referee Suggestion: 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.

Authors: The precise composition of the mother brine from which sodium sulphate formed has been impossible to obtain as there is a diagenetic transformation of this mineral phase into thenardite. Ayllon-Quevedo et al. (2007), cited in the text, obtained the brine composition from the analysis of primary fluid inclusions of the gypsum deposits from the Intermediate Unit, higher up in the sequence, being a $\text{SO}_4\text{-Ca-(Na)-(Cl)}$ brine, with $\text{HCO}_3^- \ll \text{Ca}^{2+} + \text{Mg}^{2+}$. This brine composition is coherent with the recycling of Triassic and Cretaceous gypsum and halite deposits that crop out in the borders of the basin.

Interactive comment on Clim. Past Discuss., 10, 3223, 2014.

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