



Comments on “Boron and lithium isotopic signatures of nanometer-sized smectite-rich mixed layers of bentonite beds from Campos Basin (Brazil)” by N. Clauer, L. B. Williams, and I. T. Uysal

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To investigate the initial stages of illitization in marine bentonites, fine-clay subfractions of Santonian bentonite samples from the Campos Basin, offshore Brazil, were examined by X-ray diffraction, K-Ar, and Rb-Sr methods (Clauer et al., 2020) and by chemical and isotopic analyses of B and Li (Clauer et al., 2022). Only three subfractions of fine clay from each of two bentonite samples were available for the latter study, so the results were characterized as preliminary information “thought to be of help for future studies” (Clauer et al., 2022, p. 73). A few substantial differences in boron content and isotopic composition among the six subfractions were found, but there was little variability in lithium content and isotopic composition. In the absence of information about B and Li in the bulk bentonites and their host rocks, and because of the presence of some detrital illite in one of the samples (sample A1, Clauer et al., 2020), these B and Li analyses add little toward understanding the character of the fluid environments in which the original volcanic ash was transformed into the now-present smectite-rich interstratified illite-smectite (I-S). Nevertheless, in a rather long discussion of the results, Clauer et al. (2022) addressed many possibilities that could account for their observations, but they drew no clear conclusions about

the origin of the illite beyond those drawn earlier by Clauer et al. (2020).

Critical evaluation of Clauer et al.’s (2022) isotopic study of B and Li is hindered by mistakes in the presentation of results and by inconsistencies between the text and the tabulated data (Online Resource 1). Most of these mistakes are of little consequence because they are not difficult to recognize and because no useful inferences were drawn from them. A few such mistakes in the Conclusions section are of more concern because misinformation there might be unrecognized and repeated by others.

More serious than the simple mistakes and inconsistencies are some assertions that are not supported by the results. Clauer et al. (2022, p. 75) initially recognized that, for each of the two bentonite samples, $\delta^7\text{Li}$ did not vary beyond analytical uncertainty among the three size fractions studied. Yet, in the second half of the final paragraph of the Discussion, variations in $\delta^7\text{Li}$ are described and discussed as if there were no analytical uncertainty in the values. Consider the final sentence, about supposed variations in $\delta^7\text{Li}$ among the three fine-clay subfractions of sample B1:

The zigzagging variation in the $\delta^7\text{Li}$ of the three B1 fractions with the lower value for the intermediate fraction is probably due to the dominant volcanic original reference in the coarser fraction combined with a variable impact of external pore fluids during further crystallization of the fine crystals. (p. 81)

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If a measured quantity varies only within the range of its analytical uncertainty, asserting probable causes for those variations is unwarranted.

Consideration of analytical uncertainty is also essential to recognize another misinterpretation of results:

The $\delta^{11}\text{B}$ remains almost constant in the A1 fractions relative to a continuously increasing K content with size, strongly suggesting that the illite content in the smectite-type interlayers is related to crystal size. This constant $\delta^{11}\text{B}$ relative to an increasing K content indicates that the fluids had to remain identical in composition and at an almost constant temperature during illite growth; the K increase following the overall crystal growth. (p. 80)

The constancy of $\delta^{11}\text{B}$ in the A1 subfractions does not require that temperature was almost constant during illite growth. The values of $\delta^{11}\text{B}$ for the illite in the A1 subfractions are not known. The authigenic-illite content of the subfractions is <10% (Clauer et al., 2022, Table 1), so temperature-dependent variation among subfractions in $\delta^{11}\text{B}$ of the authigenic illite would not likely have caused variation in the subfraction $\delta^{11}\text{B}$ values beyond the analytical uncertainty, which was $\pm 1\%$ at the 95% confidence level according to the typical precision for $\delta^{11}\text{B}$ shown in Table 2 of Clauer et al. (2022). Specifically, not more than a 3% difference in $\delta^{11}\text{B}$ (Williams et al., 2013, Fig. 8A) between the first- and last-formed authigenic illite would be expected if the illitization temperature range was from 60°C to 95°C and fluid $\delta^{11}\text{B}$ did not change. Corresponding differences in $\delta^{11}\text{B}$ among subfractions would have been far less than 3%, however, because authigenic illite was diluted by much more-abundant smectite and because authigenic illite in the several fine-clay subfractions would have differed in average crystallization temperature by much less than 35°C.

There is reason to expect that tetrahedral boron is somewhat more abundant in illitic layers of I-S than in smectitic layers, but no reason to expect that such enrichment would be sufficient to have caused a $\delta^{11}\text{B}$ difference of more than 1% among the A1 subfractions. Consider a few quantitative examples for hypothetical bentonite size fractions having 10% illite in I-S. Let each subfraction contain 20% by mass of illite fundamental particles 2 nm thick (Nadeau, 1999, Fig. 3), and let the rest be smectite particles 1 nm thick. Consider the

smectite particles to be uniform in $\delta^{11}\text{B}$ and the illite particles to have $\delta^{11}\text{B}$ dependent only on their crystallization temperature. If the B content of the illite particles were twice that of the smectite particles, the maximum difference in $\delta^{11}\text{B}$ between two size fractions would be only 1%. To reach that maximum would require that all the illite particles in one size fraction crystallized at 60°C and all in the other fraction crystallized at 95°C—a constraint that would not be realized in a natural system. If the illite particles were distributed as they might be in a natural system, so that, for example, the average crystallization temperatures of illite particles in two size fractions differ by 20°C instead of by 35°C, the illite particles would need to be enriched in B by a factor greater than 5 to cause the difference in $\delta^{11}\text{B}$ between two size fractions to be greater than 1%.

No information is available for sample A1 about the enrichment of B in authigenic illite relative to smectite, nor is there information about the distribution of early formed and late formed authigenic illite among the fine-clay subfractions. Without such information, there is no basis to assert that illite in that sample grew at an almost constant temperature.

Similar concerns apply to the discussion of the constancy of $\delta^7\text{Li}$ in the A1 subfractions:

The $\delta^7\text{Li}$ of the three A1 fractions averages $+9.6 \pm 1.6\%$ ($n=9$) with a content of $112 \pm 15 \mu\text{g/g}$. Both values are statistically within analytical uncertainty, suggesting again that the illite layers of the smectite-rich size separates formed in equilibrium with a chemically stable fluid, the initial crystals forming with a minimal change in the burial temperature. (p. 80)

Constancy of $\delta^7\text{Li}$ among subfractions is less informative about illite growth than is constancy of $\delta^{11}\text{B}$, because temperature-dependent isotopic fractionation is somewhat less for Li than for B (Williams et al., 2013, Fig. 8B), because the analytical uncertainty for $\delta^7\text{Li}$ is about twice that for $\delta^{11}\text{B}$ (according to the typical 2σ precision for $\delta^7\text{Li}$ shown in Table 2 of Clauer et al., 2022), and because there is no expectation of enrichment of structural Li in illite relative to smectite. The Li isotopic compositions of the A1 subfractions surely were determined largely by the Li in the smectite; they tell nothing useful about the conditions under which the illite layers formed.

Failure to recognize that the measured boron isotopic compositions are not those of illite may be responsible for some assertions in the abstract that are not supported by results: “The $\delta^{11}\text{B}$ of the few illitic tetrahedral sites from one of the samples remains quite constant, ...”; “In the second sample, the $\delta^{11}\text{B}$ of the illite layers from the two coarser fractions is indicative of an early volcanic origin, while the smaller size fraction also interacted with sedimentary fluids.”; “In turn, the information of the B and Li isotopic compositions and contents from studied mixed layers suggests a various origin for the few illite layers of the smectite-rich I-S that contain more B than the smectite layers that host more Li.” In recognition that the isotopic analyses do not tell the isotopic compositions of B and Li in the few illite layers of the studied bentonites, the message for future investigators should be that to use isotopic studies of B and Li to find conditions of initial illitization of smectite in marine bentonites would be a very demanding task.

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Declarations

Conflicts of interest The author declares that he has no conflict of interest.

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