spectrum (below) of the product obtained after 16 days of ageing. That the reaction is still not complete is indicated by the broad band around 22° 2θ on the X-ray trace, (CuKα radiation). This appears to be the first time that the crystallization of kaolinite is realized at such a low temperature from an amorphous material and in an almost neutral solution. It is thought that the transformation occurs through an undetectable "zeolitic" phase, which readily forms at high pH and facilitates the subsequent crystallization into kaolinite under neutral conditions. The direct transformation from the gel into a clay mineral using an acid solution or water is not feasible as it has been shown (De Kimpe, 1967) that under these conditions, the final products are pseudo-boehmite and an amorphous alumino-silicate with a different composition.

Further experiments are in progress to investigate in more detail this reaction, and a complete report will be given later.

Part of this study has been performed at the Laboratoire de Physico–Chimie Minérale, University of Louvain, Belgium, where the author was working as an assistant under the Ministère de l'Education Nationale.

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Boron contamination from platinum crucibles*

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INTRODUCTION

THE PAST few decades have seen the accumulation of a voluminous literature dealing with boron concentration in rock and soil materials. These numerous studies, which have been both experimental and empirical in nature, have been largely concerned with the role of boron as a nutrient in soils and the role of boron as a paleosalinity index in argillaceous sediments. The literature of the past few years suggests that the number of laboratories making such investigations continues to increase. While the analytical techniques used in these investigations vary considerably, colorimetric methods employing sample fusion in platinum crucibles appear to be quite common.

While platinum is widely recognized as a nearly ideal "inert" metal for various types of reaction vessels, it is known to be slightly soluble in extreme acid and alkaline environments. Thus, it is to be expected that trace quantities of impurities can be freed from the metal during alkaline fusion. However, to discover that enough boron can be leached from a new platinum crucible during sample fusion to make even semi-quantitative analysis for trace quantities of the element impossible, may be somewhat surprising. That such contamination is possible was recently discovered in our laboratory.

A few years ago, with the purchase of new platinum crucibles for boron analysis of rock samples, a contamination was observed which appeared to have come from the platinum (A. A. Levinson, unpublished report). Recently, when additional new crucibles were purchased, it was decided to make a deliberate effort to determine the nature and amount of such contamination. The results of that study are presented here in the hope that it may alert other analysts using fusion techniques of a possible source of analytical error.

Since our analytical method requires fusion of 1 g Na_2CO_3 with 20–50 mg of sample, this study involved blank fusion of that amount of Na_2CO_3 in the new crucibles. Six of the new crucibles were chosen randomly from the set and the melt from each analyzed for boron after various fusions. Melts from two old, reliable crucibles were used for control blanks with each analysis.

RESULTS

The amount of boron leached from each of the six crucibles during various fusions is shown in Table 1. During the first fusion, all the crucibles yielded more boron than can be accurately measured by our method (maximum about 10 μg). Comparison with prepared standards indicated 20–30 μg B was present in each melt. All the crucibles showed an order of magnitude decrease in the amount of boron leached during the second and successive fusions.

The data of Table 1 are more meaningful when it is noted that, for the sample size used in our analysis (20–50 mg), 1 μg B leached from the platinum would represent a 20–50 ppm error in analysis. Such error

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Table 1. Boron leached from platinum crucibles during various fusions

Fusion No.	μg boron leached from crucible no. MB1	MB4	MB8	MB16	MB20	MB23
1	20–30	20–30	20–30	20–30	20–30	20–30
2	1·74	1·15	1·58	1·54	0·25	1·62
3	0·98	1·00	0·75	0·78	0·68	0·53
4	0·43	0·25	0·67	0·45	0·30	0·25
5	0·68	0·65	0·88	0·53	0·43	0·48
6	0·49	0·42	0·26	0·10	0·15	0·16
7	0·25	0·26	0·26	0·07	0·07	0·06
8	0·20	0·26	0·12	0·00	0·00	0·02
12	0·23	0·10	0·05	0·01	0·00	0·00
15	0·37	0·30	0·42	0·00	0·00	0·12
17	0·65	0·52	0·48	0·00	0·00	0·18
18	0·20	0·27	0·12	0·00	0·00	0·00
25	0·34	0·51	0·42	—	—	—
30	0·28	0·34	0·28	—	—	—
31	0·72	0·68	0·66	—	—	—
37	0·10	0·00	0·00	—	—	—
39	0·32	0·00	0·00	—	—	—
40	0·02	0·00	0·00	—	—	—
41	0·79	—	—	—	—	—
42	0·42	—	—	—	—	—
43	0·01	—	—	—	—	—
45	0·00	—	—	—	—	—
46	0·01	—	—	—	—	—
49	0·00	—	—	—	—	—
51	0·00	—	—	—	—	—
52	0·00	—	—	—	—	—
53	0·00	—	—	—	—	—

should be reduced to less than 1 ppm. Thus, 0·02 μg B leached from the platinum is considered a maximum if the crucible is to be used for analytical work.

It is noted from Table 1 that the amount of boron leached from the platinum during a single fusion decreases irregularly with successive fusions. These irregularities probably reflect variations in time and temperature of fusion as these two variables were not rigidly controlled. It is also apparent that all the crucibles do not yield boron in the same manner. Thus, crucibles MB16 and MB20 were essentially stripped of available boron after eight fusions, whereas it required 43 fusions to extract all available boron from crucible MB1. (One other crucible from the new set required 60 fusions.)

DISCUSSION

Nature of leaching

According to Matthey Bishop, Inc., who manufactured the subject crucibles, their routinely-prepared platinum crucibles typically contain about 5–25 ppm B (personal communication). Jackson (1958, p. 275) indicates that platinum is soluble in molten Na_2CO_3 to the extent of about 0·5–1·0 mg Pt per fusion. Taking the maximum values, an assumption of homogeneous dissolution would predict that about 0·025 μg B would be released during a single fusion. Comparison of this value with Table 1 shows that the dissolution is far from homogeneous and that the boron is removed in strong preference to the platinum. For the first fusion, boron is preferentially leached by a factor of about 1000 and after several fusions, it is still preferentially removed from some crucibles by a factor of about 10–20.

The analytical data show that the subject crucibles fall into two groups – those from which the available boron was leached rather quickly (approximately 10 fusions required), represented by crucibles MB16, MB20, and MB23; and those which required over 30 fusions to remove the available boron, represented by crucibles MB1, MB4, and MB8. The data of Table 1 are rather typical of all the crucibles tested as they divided about evenly into the two groups. Figure 1 is a plot of total boron leached as a function of the number of fusions for crucibles MB1 and MB16, representative of these two groups. As analyses were not made following some fusions, some of the individual contributions represent interpolations.

Leached boron from crucible MB16 is seen to approach rapidly a limit of about 28·5 μg B (more or less depending on the exact value for fusion 1). Leached boron from crucible MB1 behaves in a similar manner for the first few fusions before becoming an essentially linear function of fusion number. Finally, after some 43 fusions, crucible MB1 also approaches a limit of approximately 41 μg B.

Possible location of boron in platinum

The above data suggest that the boron being leached is held in two types of sites in the platinum. One type of boron is rather loosely bound, is quickly removed in above 1000-fold preference to the platinum, and is found in all the crucibles tested. The other boron is more strongly bound, is removed in about 10- to 20-fold preference to the platinum, and is present in only those crucibles which are highly contaminated.

If it is assumed that the boron atom is sufficiently different from the platinum atom that substitution of boron for platinum in the structure is not a quantitatively important means by which the boron is held, then the contamination becomes a matter of occupation of the interstices between platinum atoms. Metallic platinum is reported to have a face-centered cubic structure; a geometry which is produced by a closest-packed arrangement of platinum atoms. In such an arrangement, it can be easily shown that there are two (and only two) distinctly different types of interstices – "octahedral voids", each of which is surrounded by six platinum atoms, and "tetrahedral voids", each of which is surrounded by four platinum atoms. In the platinum structure, there exist the same number of octahedral interstices as platinum atoms and twice that number of tetrahedral interstices. Each octahedral void is slightly less than twice the size of each tetrahedral void.

Although the data are not of the type to allow computations regarding reaction mechanics, it is suggested that the difference in ease of removal of boron from the platinum may reflect occupation of these two types of interstitial sites. It might be expected that small amounts of boron would preferentially occupy the larger, but less

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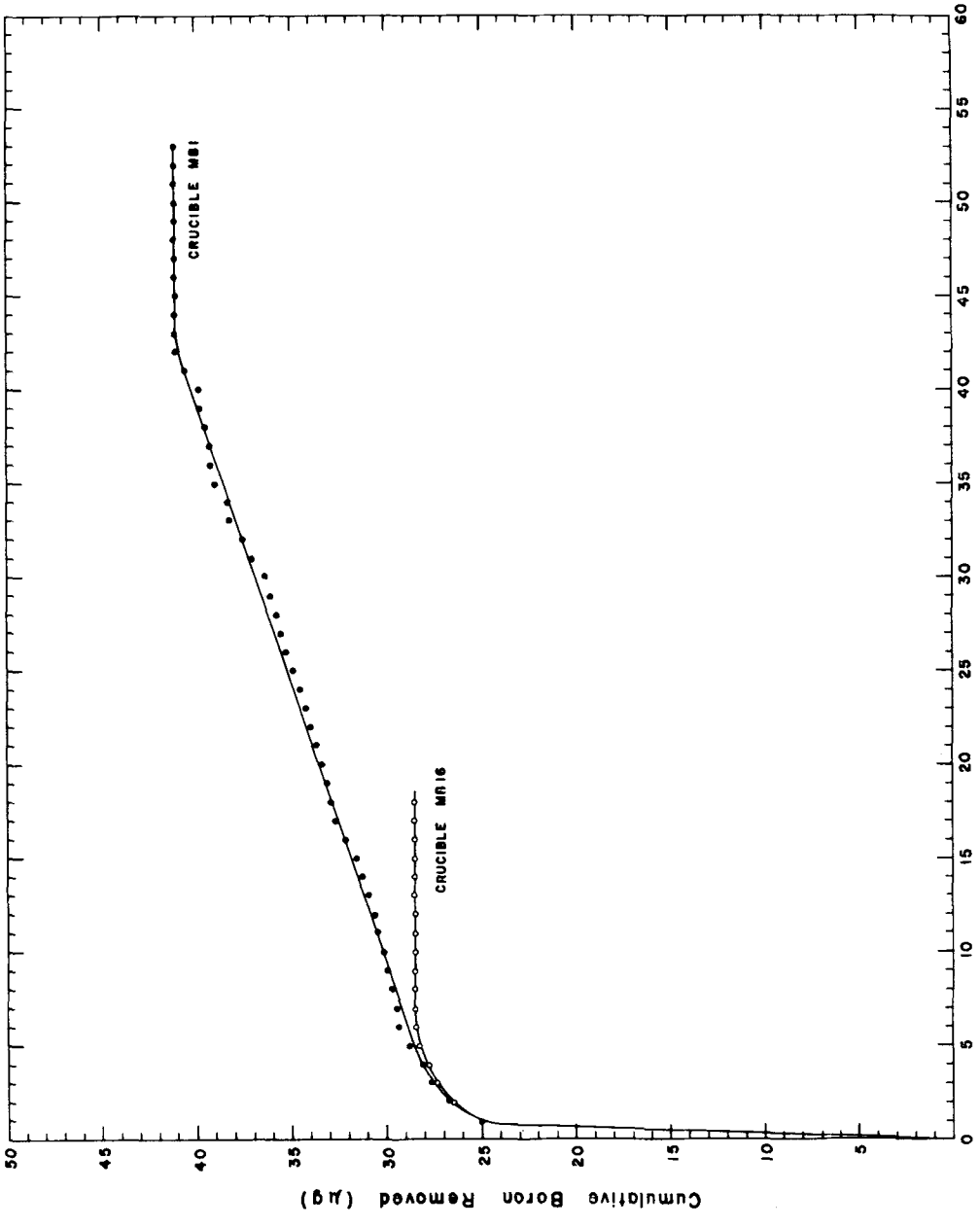


Fig. 1. Boron removal from two new platinum crucibles during fusion of Na_2CO_3.

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numerous, octahedral sites. However, with the presence of greater concentration of impurity boron, progressively more of the tetrahedral sites would also come to be filled. It would also follow that the octahedral boron would be more weakly bonded and hence more readily leached than the tetrahedral boron.

CONCLUSIONS

From the data presented here, it is seen that boron contamination from new platinum crucibles can be a major problem. It has also been shown that the amount of time required to render routinely-prepared platinum crucibles usable for boron analysis by successive alkaline fusions is excessive. Thus, the only effective solution to the problem seems to be to insist on delivery of boron-free crucibles. Communications from the principal U.S. manufacturers of platinum crucibles indicate that, while their routinely-prepared platinum crucibles contain small amounts of boron impurity, they are willing to supply "boron free" crucibles from spectroscopically-analyzed platinum for an additional fee. The detection limit for such analysis is about 2 ppm B.

In light of the approximately thousand-fold preference for leaching boron from platinum, even 2 ppm B or less may still present a problem in early fusions. Thus, it is also recommended that all crucibles to be used for alkaline fusion in boron analysis be thoroughly checked for contamination arising from leaching during the fusion.

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Recommendations for reporting thermal analysis data*

BECAUSE thermal analysis involves dynamic techniques, it is essential that all pertinent experimental detail accompany the actual experimental records to allow their critical assessment. This was emphasized by Newkirk and Simons (1963) who offered some suggestions for the information required with curves obtained by thermogravimetry (TG). Publication of data obtained by other dynamic thermal methods, particularly differential thermal analysis (DTA), requires equal but occasionally different detail, and this note is intended to present comprehensive recommendations regarding both DTA and TG.

In 1965 the First International Conference on Thermal Analysis (ICTA) established a Committee on Standardization charged with the task of studying how and where standardization might further the value of these methods. One area of concern was with the uniform reporting of data, in view of the profound lack of essential experimental information occurring in much of the thermal analysis literature. The following recommendations are now put forward by the Committee on Standardization, in the hope that authors, editors, and referees will be guided to give their readers full but concise detail. The actual format for communicating these details, of course, will depend upon a combination of the author's preference, the purpose for which the experiments are reported, and the policy of the particular publishing medium.

To accompany each DTA or TG record, the following information should be reported:

1. Identification of all substances (sample, reference, diluent) by a definitive name, an empirical formula, or equivalent compositional data.

2. A statement of the source of all substances, details of their histories, pre-treatments, and chemical purities, so far as these are known.

3. Measurement of the average rate of linear temperature change over the temperature range involving the phenomena of interest.

4. Identification of the sample atmosphere by pressure, composition, and purity; whether the atmosphere is static, self-generated, or dynamic through or over the sample. Where applicable the ambient atmospheric pressure and humidity should be specified. If the pressure is other than atmospheric, full details of the method of control should be given.

5. A statement of the dimensions, geometry, and materials of the sample holder; the method of loading the sample where applicable.

6. Identification of the abscissa scale in terms of time or of temperature at a specified location. Time or temperature should be plotted to increase from left to right.

7. A statement of the methods used to identify intermediates or final products.

8. Faithful reproduction of all original records.

9. Wherever possible, each thermal effect should be identified and supplementary supporting evidence stated.

In the reporting of TG data, the following additional details are also necessary:

10. Identification of the thermobalance, including the location of the temperature-measuring thermocouple.

11. A statement of the sample weight and weight scale for the ordinate. Weight loss should be plotted as a downward trend and deviations from this practice should be clearly marked. Additional scales (e.g., fractional decomposition, molecular composition) may be used for the ordinate where desired.

12. If derivative thermogravimetry is employed, the

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