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Occurrence Regularities of Nitrogen Defects in the Ural Type Crystal Diamonds from Different Regions

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Abstract. The collection of the Ural, Anabar and Brazilian diamonds is studied by infrared spectrometry method. For the reconstruction of the thermal formation conditions of diamond crystals, V. Taylor's diagrams are made with the calculated isotherms. Graphs of the ratio of B1 and B2 defects are drawn. Conclusions about the thermal conditions of the Ural diamonds formation and their possible affinity to the specific and type of indigenous sources are made.

Introduction

The Ural type diamonds, combining rounded crystals of this mineral, which not typical plane shapes inherent in most diamonds from deposits of kimberlite-lamproite type, long ago got the attention with the specific morphological traits and high yield jewelry differences.

The most important characteristic of the Ural type diamond deposits is the lack of a reliable set of the indigenous sources of placers, despite the fact that many of them have developed for more than 100 years. A range of assumptions about the possible types of indigenous sources of these placers is rather great: from ancient completely eroded kimberlite bodies to the modern diamondiferous tuffisites. In the absence of reliable information of indigenous sources and the rarity of finds of minerals-satellites in these placers, the diamonds can be the most important sources of information about the genetic characteristics of potential indigenous sources. Therefore, studies based on the analysis of the crystal-chemical characteristics of this mineral can contribute to the understanding of the formation processes and question decision of possible indigenous sources of the Ural type diamonds.

One of the most important crystal-chemical diamond characteristics is the presence of structural impurities of nitrogen. To identify the concentration and location of nitrogen in diamond crystals has been successfully using the method of IR-spectroscopy. A great contribution to the development of spectroscopic study methods of diamond crystals was made by national (F. V. Kaminskii, E. V. Sobolev, Y. A. Klyuev) and international (S. R. Boyd, W. R. Taylor, G. S. Woods) scientists. A significant amount of research of diamond crystals using the methods of IR-spectroscopy is made by I. N. Bogush, E. A. Vasiliev, M. B. Kopchikov, O.V. Palazhchenko, V. A. Petrovsky, G. K. Khachatryan, Fernando A. T. P. Laiginhas and others, but the Ural type diamonds purposefully by these methods have been insufficiently studied. Therefore, the method of IR-spectroscopy was chosen as the primary in this study because it allows without destroying mineral individuals quantitatively and with a high enough productivity to determine the concentration of nitrogen in the diamond, his shapes in the form of A and B1 defects and, ultimately, to identify patterns of occurrence of nitrogen defects in diamond crystals. In the present work under the patterns of the nitrogen defects in diamond crystals refers to the quantitative determination of the nitrogen concentration in diamond, in various forms of its presence, zone identification of their placement within the crystals, the setting of statistical regularities of allocation of diamond crystals in their content of various nitrogen defects.

Conducted research based on extensive and representative collection of the Ural type diamonds from the different regions have allowed revealing regularities of occurrence of the nitrogen defects in the studied crystals and to give them the correct genetic interpretation. These results are the basis for a more balanced approach to the analysis of the possible genetic types of indigenous sources of placers of the Ural type diamonds, which will contribute the choice of optimal search methods or make a reasonable decision about inexpediency of identifying the indigenous sources as potential industrial fields.

The work purpose is to identify regularities of occurrence of nitrogen defects in the Ural type diamond crystals from the various regions and its genetic interpretation.

Research Techniques

The study is based on materials obtained in the course of studying collections of diamonds of Mining Museum, Department of Mineralogy of St. Petersburg University, Komi Research center of Ural branch of RAS, the research materials of the Ural diamonds collection of All-Russian scientific research geological Institute and information from published sources. On the basis of the spectroscopy laboratory of the St. Petersburg Mining University has been studied the collections of the Ural diamond crystals - 173 pcs., Anabaro-Olenek interfluves - 164 pcs., Brazil - 179 pcs.

The determination of the type and content of nitrogen defects in diamond crystals was carried out by infrared spectroscopy using a FTIR Vertex 70 with IR-microscope Hyperion 1000. The photo luminescence spectra were recorded on a modular Fluorolog 3 spectrofluorimeter by Horiba – Jobin Ivon, equipped with Olympus microscope. Study with the method of optical spectroscopy was carried out on two-beam spectrophotometer UV-2550PC Shimadzu. For processing the results of the analyses statistical methods (Microsoft Excel, Statistica 7.0) were used. Processing and interpretation of the spectra was carried out with "Spector Examination".

In diamond, the absorption in the range of 1500-3500 cm^{-1} can be used as an internal standard in the study of crystals of small sizes or irregular shapes for the purpose of calculating their thickness and considering the reflection [8]. Spectra of optical density have been normalized at its own two-phonon absorption. As internal standard has been used the absorption coefficients at frequencies of 1973 cm^{-1} and 2500 cm^{-1}, accordingly k_{1973}= 12.5 cm^{-1}, k_{2500} = 4.9 cm^{-1} [9]. It should be noted that the method of spectra normalization at the optical density in two-phonon absorption at the moment is common and does not require preliminary thickness measurement of the studied sample, which significantly reduces and simplifies the measurement procedure.

The concentration of nitrogen was calculated with the program of visual selection on the standard spectra absorption A, B1 and C (programmer Kovalchuk O. E.), according to the certain coefficients of proportionality [10, 11]. The relative errors of determination of A and B1 defects concentration do not exceed 10% [12], depending on the shape, thickness, presence of inclusions, surface quality of the sample.

Results

IR-spectroscopic studies have enabled the comparison of crystals of Ural, Brazil, Anabaro-Olenek interfluves on nitrogen content and degree of aggregation of nitrogen defects. Distribution analysis of diamond crystals for nitrogen content has shown that in the Ural collection is dominated by crystals with a nitrogen content of about 800 ppm in the absence of low-nitrogen (less than 500 ppm) diamonds, while the collection of Brazil is characterized by two maxima of this parameter in the range of 100 and 600 ppm. Anabaro-Olenek interfluves diamonds on concentration of nitrogen forming three maximum: 200 ppm, 800 ppm and 2600 ppm (Fig. 1a). Therefore, in contrast to the Ural, Brazilian fields contain a significant part of crystals with low nitrogen content; the Anabar crystals similar to the Brazilian by the presence of low-nitrogen diamonds, to the Ural – for a significant part of the diamonds with average (800 ppm) nitrogen content and specific by the presence of high nitrogen (2500-2600 ppm) diamonds.

Histograms of the crystal distribution in size of aggregation of nitrogen defects (Fig. 1b) show that among the Ural diamonds dominates the crystals with an average degree of nitrogen aggregation (50–60 %); for the Brazilian crystals the main maximum is close to the parameter for the Ural collection (about 40%); the Anabaro-Olenek interfluves diamonds give a bi-modal distribution with peak values of 40% and 80%. As a result, it can be noted that in size of aggregation of nitrogen defects, the crystals of each of the studied collections cover almost the entire possible ratio range of A and B1 defects, but the maximum statistical is formed by crystals with similar proportion of nitrogen in the shapes of A and B1 defects. It must be emphasized that among the Anabaro-Olenek interfluves diamonds and especially Brazil there are crystals with a significant predominance of B1-defects, which part in some crystals reaches up to 100% [7].

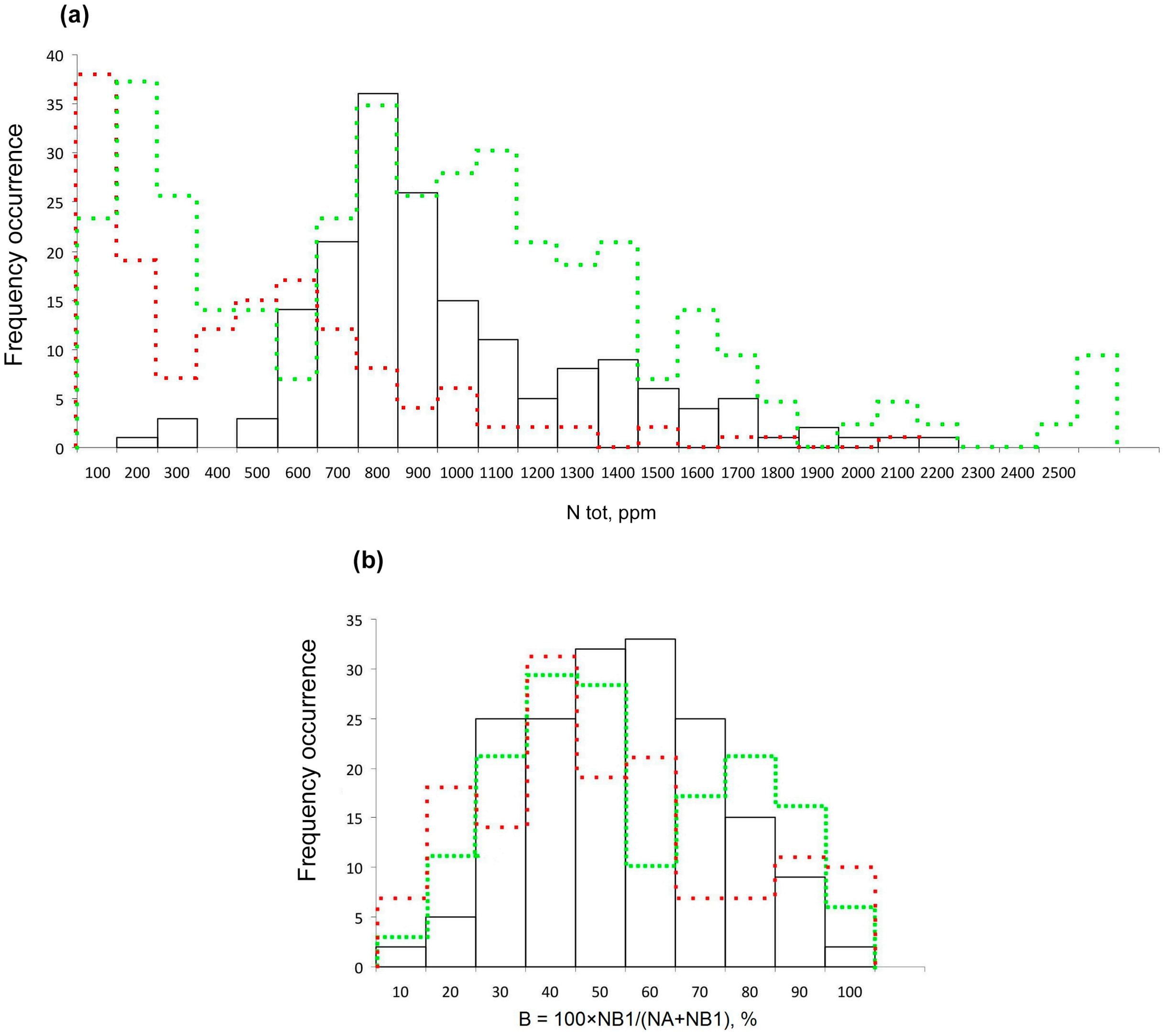

Fig. 1. Histograms of the Ural crystals distribution (black lines), Brazil (red specks), the Anabaro-Olenek interfluves (green specks) a) on the nitrogen content, b) on the degree of nitrogen defects aggregation

Information on features of the nitrogen defects distribution for the Ural type diamonds from the fields of Ural, Brazil and Anabaro-Olenek interfluves were compared with similar parameters for diamonds from the kimberlite-lamproite resources borrowed from published sources (Fig. 2). As it can be seen from the diagram, the field of the Ural type diamonds in all studied areas, as for the nitrogen content so the degree of aggregation, covers all known variants identified for indigenous diamond deposits of kimberlite-lamproite type.

Analysis of the thermal history of the diamonds, which refers to the temperature interval from the start of crystal growth to the completion of heat transformation of nitrogen defects in them, was conducted with Taylor diagram (Fig. 3) [3, 4]. Its analysis shows that the wide temperature range of the diamond formation (1070 – 1270 °C) is typical for Brazil crystals (Fig. 3b). The diamonds from placers of the Anabaro-Olenek interfluves have a range of temperatures of crystal formation is less (Fig. 3) than in the Brazilian crystals, and it ranges from 1070 – 1260 °C. The most compact on the Taylor diagram are points which reflect the ratio of nitrogen content and degree of nitrogen defects aggregation in the diamonds of the Ural (Fig. 3a). A narrower interval of temperatures 1080–1190 °C accords to them.

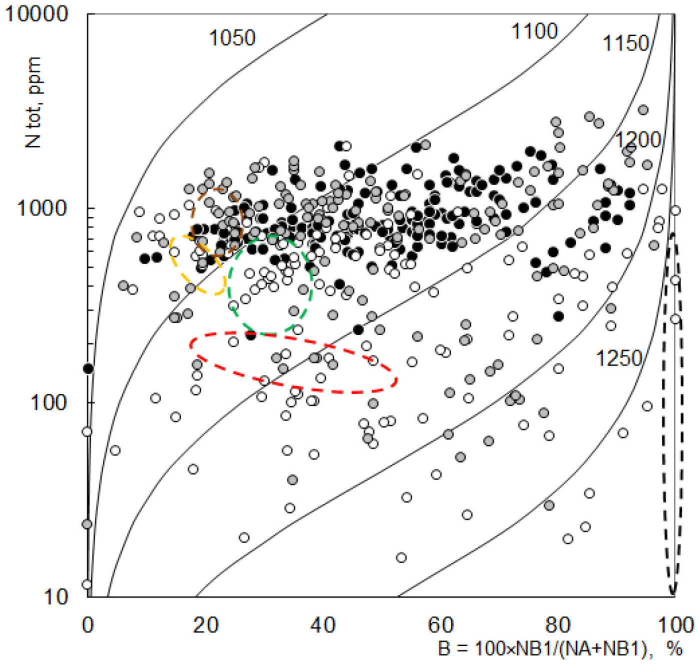

Fig. 2. A comparison of the results of determination of nitrogen content and degree of aggregation of nitrogen defects in the Ural type diamonds from different regions: ● – The Ural; ○ – Brazil; ◍ – the Anabaro-Olenek interfluves and indigenous fields: brown dotted line – Arkhangelsk diamondiferous province; yellow dotted line – Malo-Botuobinsky district; green dotted line – Daldyn-Alakit district, red dotted line – South Africa kimberlite sources [2]; black dotted line – kimberlite pipe Guina diamonds [1]

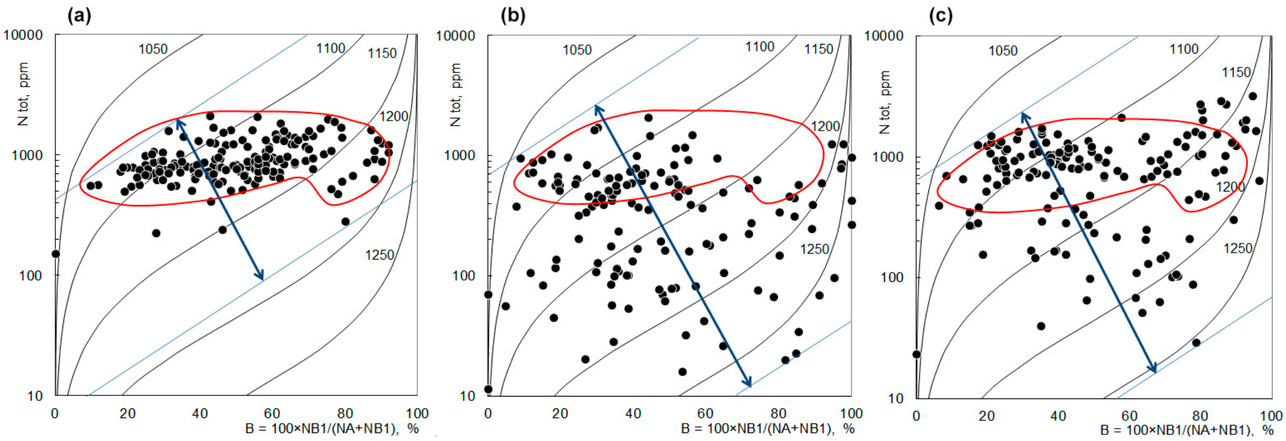

Fig. 3. The results of determination of nitrogen content and degree of aggregation of nitrogen defects on the Taylor diagram drawn for the Ural – (a), Brazilian (b) and Anabar (c) collections of diamonds. The red line is selected area for the main part of the Ural diamonds; the blue arrow – the interval of temperatures of diamond formation [5]

Higher temperature transformation of nitrogen defects in diamonds of the Anabaro-Olenek interfluves and Brazil emphasized by the presence of crystals containing only B1-defects, and the presence of diamonds in which there is a low content of B2-defects and correlation disorder between B1 and B2-defects (fig. 4), which is a sign of their destruction during high temperature annealing.

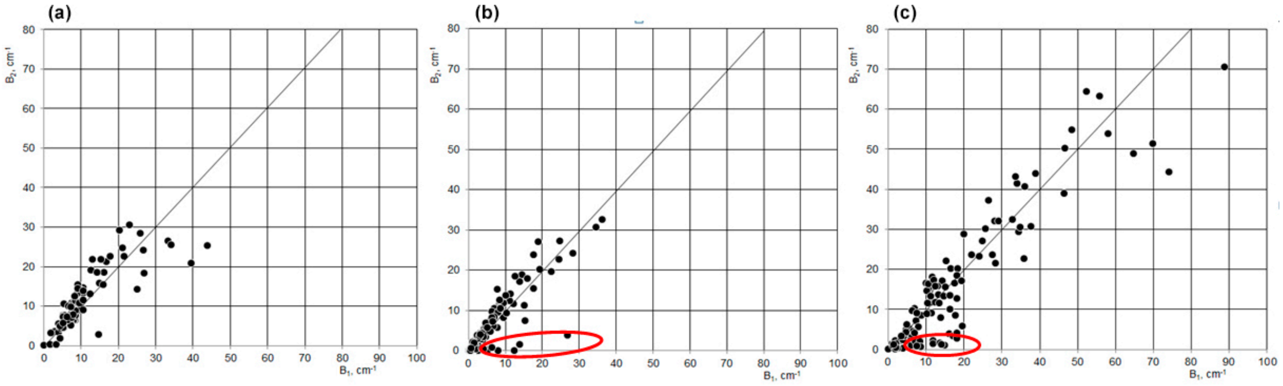

Fig. 4. The ratio of defects B1 and B2 in the diamonds of the a) Urals, b) Brazil and c) Anabaro-Olenek interfluves. In red highlighted region of violation of the correlation between the content of B1 and B2 defects

The result analysis allows concluding that the ratio of nitrogen in the form of A and B1 defects in the Ural type diamonds from deposits of Brazil, the western slope of the Ural and the Anabaro-Olenek interfluves covers the whole possible range for natural diamonds. One way of explanations for the discovered characteristics of allocation of diamond crystals of the Ural type from the placers of Brazil, the Ural and the Anabaro-Olenek interfluves on nitrogen content and degree of nitrogen defects aggregation may be a plurality of sources feeding these placers, which can be indigenous objects of kimberlite-lamproite type. In this case, you must assume collective inflow to the placers of crystals from indigenous objects in which diamonds differ significantly in nitrogen content and degree of nitrogen defects aggregation. However, the probability of finding in each specific and limited area of the placer zone the entire spectrum of kimberlite-lamproite bodies, which can provide typically for analyzed diamond placers, a broad range of content and degree of nitrogen defects aggregation is very small. Therefore, we cannot exclude the presence of specific and have not yet identified type of indigenous sources, which diamonds have a very wide range of content and degree of nitrogen defects aggregation.

Recently, the discovery of diamondiferous tuffs, developed on large areas in the North of the Siberian platform [6] and similar formations in the area Guina (Brazil), as well as tuffaceous material in the Ural objects that are currently associated with tuffisites, and may be associated with tuffs or tuffites, gives a basis for predicting is not yet known type of indigenous source, which is characterized by the areal development of diamond-bearing tuffaceous formations.

Conclusions

Research conducted through the study of representative collections of the Ural type diamonds from the placer fields of the Ural, Brazil and Anabaro-Olenek interfluves, allowed revealing new regularities of occurrence of nitrogen defects in diamond crystals of this type and give them a geological-genetic interpretation.

The main results are:

1. The Ural type diamonds have a wide range of content nitrogen in the form of A and B1 defects, but diamonds from fields of the western slope of the Ural are characterized by a predominance of crystals with high (over 500 ppm - 96% samples) nitrogen content.
2. The Ural type diamonds have a wide temperature range of formation, which refers to the entire thermal history of a crystal from the beginning of their growth until the completion of transformation of the nitrogen defects, with the temperature range typical for Brazil crystals, and the smallest for crystals of the Ural placers.

3. Among the diamonds of Brazil and the Anabaro-Olenek interfluves were identified the crystals with signs of lasting high-temperature annealing, leading to the collapse of the B2-defects that do not exist in the collection of diamonds from the Ural.
4. For diamonds of all studied regions typical a wide range of the ratio of nitrogen impurities in the form of A and B1 defects, overlapping and extending beyond the range of values of this parameter set for the diamond crystals from indigenous fields of kimberlite-lamproite type. This feature of diamond crystals of the Ural type of different regions suggests a plurality of types of the indigenous sources of placers or the presence of a previously unknown type of placer forming indigenous objects. Recently, the discovery of diamondiferous tuffs, developed on large areas in the North of the Siberian platform [6] and similar formations in the area Guina (Brazil), as well as tuffaceous material in the Ural objects that are currently associated with tuffisites, and may be associated with tuffs or tuffites, gives a basis for predicting is not yet known type of indigenous source. At the moment widespread areal of diamondiferous tuffs of Brazil and the north-eastern part of Siberian platform have not yet found an acceptable explanation and their further study could shed light on the processes of their formation.

References

[1] V. A. Petrovsky, E. A. Vasil'ev, V. P. Lyutoev, V. I. Silaev, A. V. Kozlov, A. E. Sukharev, M. Martins, Characteristics of spectroscopy of the Brazilian diamonds, Mineralogical magazine. 1 (2011) 63-71.

[2] F. V. Kaminski, Superdeep diamonds from the Juina area, MatoGrossu, Contrib. Mineral. Petrol. 140 (2001) p. 734.

[3] W. R. Taylor, J. J. Gurney, H. J. Milledge, Nitrogen aggregation character thermal history and stable isotope composition of some xenolith-derived diamonds from Roberts Victor and Finch, 6th Internat. Kimberlite Conf., ext. abstr, 1995, pp. 620-622.

[4] W. R. Taylor, Nitrogen-defect aggregation characteristics of some Australasian diamonds: time-temperature constraints on the source regions of pipe and alluvial diamonds / W. R. Taylor, A. L. Jaques, M. Ridd // Am. Mineral. – 1990. – V. 75. – pp. 1290-1310.

[5] E. A. Vasiliev, A. V. Kozlov, Y. V. Nefedov, V. A. Petrovsky, A comparative analysis of Anabar, Brazil and the Urals diamonds by method of infrared spectroscopy, The notes of the Mining Institute, T 200 (2013), 167-171.

[6] S. A. Grakhanov, V. I., Shatalov, V. A. Shtyrov, V. R. Kychkin, A. M. Suleymanov, Diamond placers of Russia, Novosibirsk: Publishing house Geo, 2007.

[7] Y. V. Nefedov, E. A. Vasiliev, A. V. Kozlov, V. A. Petrovskij, Structural features of Uralian, Anabar and Brazilian diamonds detected by FTIR, Scientific reports on resource issues, 2013, V. 1., pp. 29-35.

[8] G. B. Bokii, G. N. Bezrukov, Y. A. Klyuev and others, Natural and synthetic diamonds, Moscow, Pub. House Nauka, 1986.

[9] Y. A. Klyuev, The Intensity of stripes in the IR spectrum of absorption of natural diamonds, Diamonds. No. 6 (1971) pp. 9-12.

[10] S. R. Boyd, I. Kiflawi, G. S. Woods, Infrared absorption by the B nitrogen aggregate in diamond, Phil. Mag. B. V. 72 (1995) 351-361.

[11] S. R. Boyd, I. Kiflawi, G. S. Woods, The relationship between infrared absorption and the A defect concentration in diamond, Phil. Mag. B. V.69 (1994) 1149-1153.

[12] G.K. Khachatryan, An improved method of estimating concentrations of nitrogen in diamond and its application, Geological aspects of the mineral resource base of "ALROSA". Modern state and prospects of solution (2003) 319-322.