

# SPECTROSCOPIC STUDIES ON DEMANTOID GARNETS. IS IT POSSIBLE TO ASSIGN ORIGINS BASED ON SCIENTIFIC EVIDENCE?

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## Introduction:

Demantoid garnets belong to the family of Ugrandites, more exactly they are Andradites with the general formula  $\text{Ca}_3\text{Fe}_2[\text{SiO}_4]_3$ . As their luster and dispersion are comparable to that of diamond (thus the name demantoid, meaning diamond-like), combined with a pleasing green to yellowish green color they are sought after gemstones and highly valued by connoisseurs. Gem material can be found in Namibia, Madagascar, Italy, Canada, Iran, Pakistan but most famed are the stones from Russia.

Demantoid is probably the only gemstones which has an increased value when a certain type of inclusion is present - the so called horse tails, a bunch of byssolith fibers typically emerging from a chromite crystal. This feature can be present at several localities and if so limits the identification of origin to Russia, Canada or Italy, but it is not always present.

It is the purpose of this research to determine if a scientific approach based on spectroscopy is capable of determining the origin of demntoid gemstones when no typical inclusions are present.

## The task:

The Russian Ural region and the area of Tubussis in Namibia are the most prolific mining areas today so it is utmost interest to be able to distinguish stones from these localities.

We have tested specimens from all possible locations and set up an analytical database using mainly Laser Ablation - icp Mass Spectrometry (LA-icp-MS) to determine various trace elements and set up a map. Then two parcels demantoids of different color and from unknown locality were purchased and analyzed similarly to assign their origin.

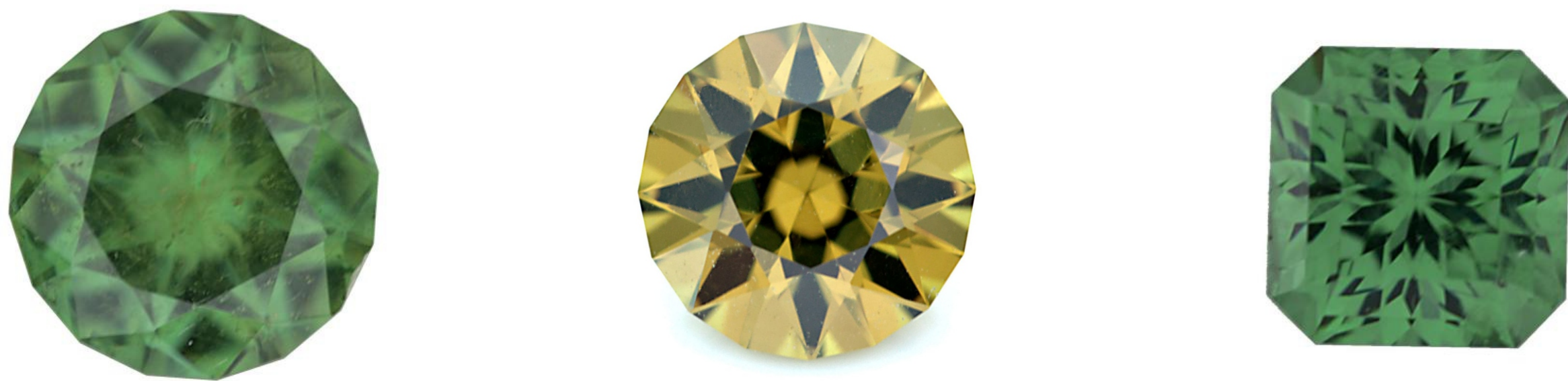


Fig. 1. Demantoid reference samples from Tubussis, Namibia showing different color shades (photos (c) www.csgemstones.com).

## Experimental:

Around 50 samples from various localities have been analyzed using LA-icp MS. For each sample 3 different spots were measured using a 100  $\mu\text{m}$  spot placed on the girdle of the gemstones or a flat spot on crystals and gem rough.

The trace elements Mg, Ti, V, Cr and Mn were measured and quantified, the main constituents Si, Ca and Fe were monitored but not used quantitatively as their concentrations are too high to give reliable results. Calibration was done with NIST 610, 612 and 614 glass standards.

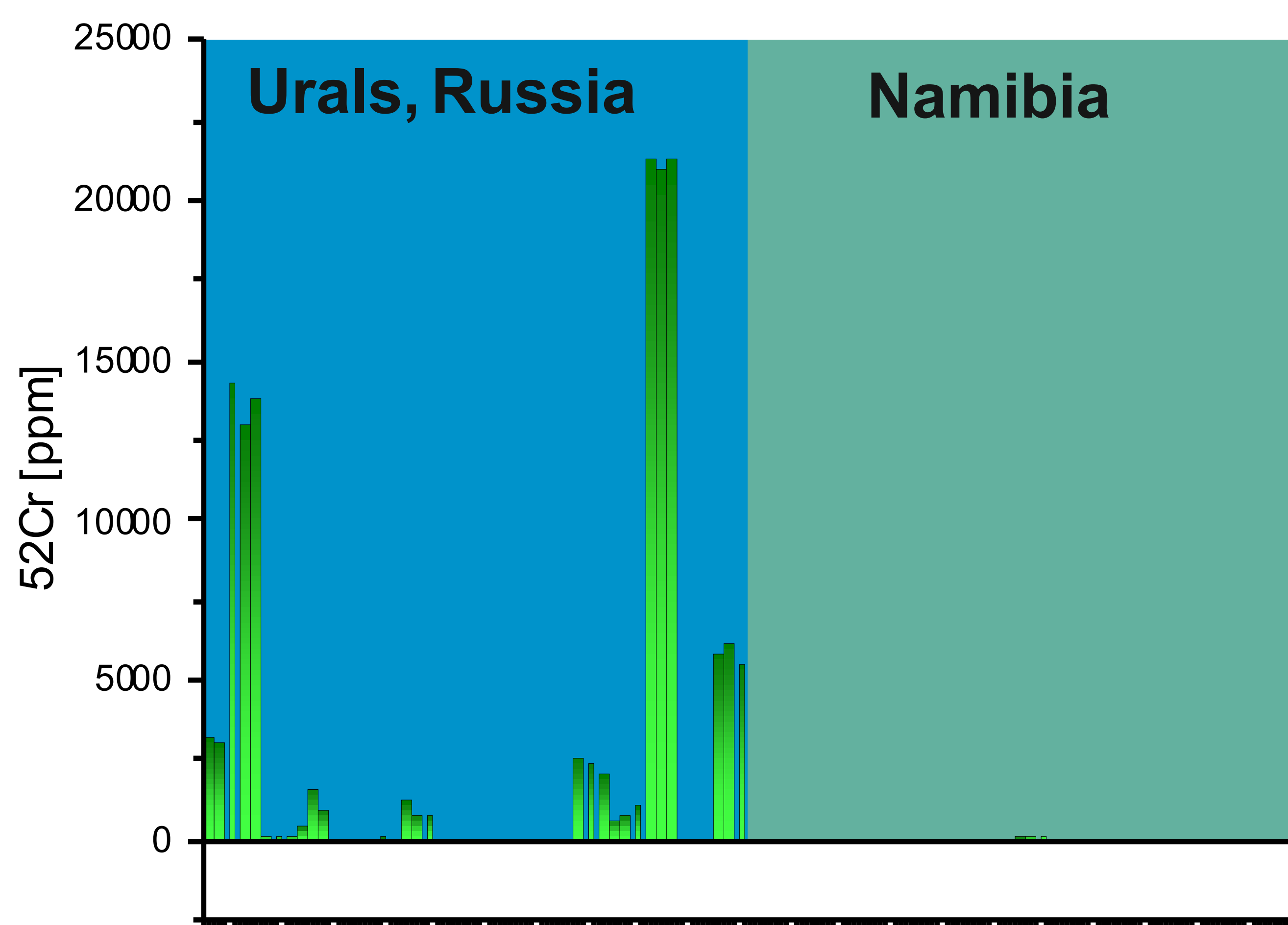


Fig. 2. Chromium concentration of the reference samples from the Urals, Russia (left) and Namibia (right).

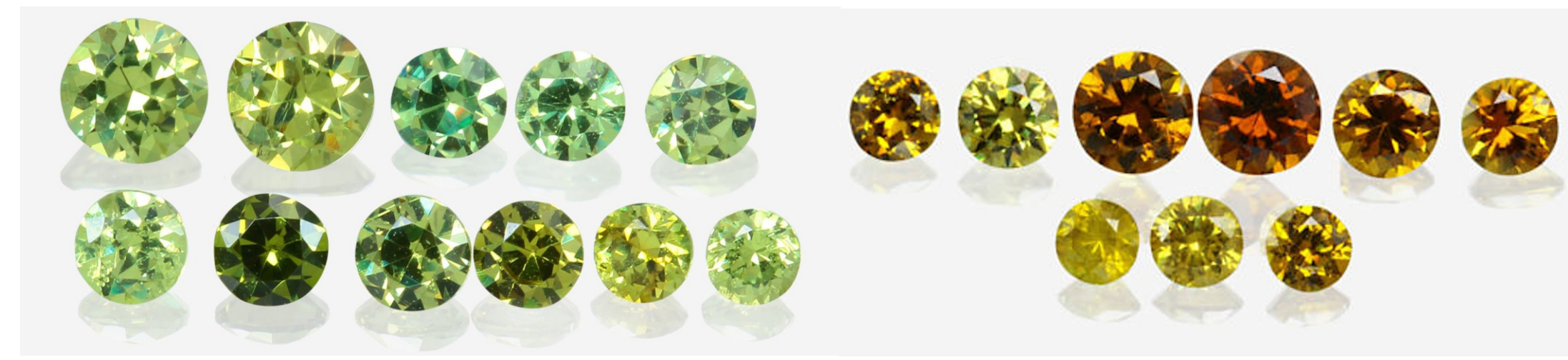


Fig. 3. Two demantoid parcels of different color and unknown origin were bought and could be identified as originating from Namibia.

## Results and Discussion:

A very indicative parameter is the chromium content. It is the chromophor that gives andradite garnets the typical green color which is coveted most. However, not all stones have chromium: Namibia and Madagascar typically has none, while Canada, Italy, Iran, Pakistan and Russia can have concentrations in the %-range. Fig. 2. shows the Cr-concentrations of Russian and Namibian stones; whilst in the first half concentrations of 0 ppm to 2% can be found, only one Namibian sample shows a significant amount of Cr (~100 ppm). Very high Cr values have also been found in Iran, Pakistan and some Canadian samples.

Another indicative element is titanium, which is very low (<10ppm) in Namibian stones, shows highest concentrations in Madagascar and Canada (>1500 ppm); Russian stones have between 0 and 1200 ppm.

Several statistical methods have been applied to best separate the dataset including principal component analysis, which gives best results in separating all possible localities. However, if the task is to separate Russian from Namibian material we have found out that using the chromium content and the ratio of manganese over titanium gives very good results. When both axes are plotted in a logarithmic scale a clear separation line can be drawn with very little overlap. In fact only one Russian sample (all three values) can be found in the „Namibian zone” and only two Namibian single values are in the „Russian zone” as can be seen in Figure 4.

When these settings are applied to the two parcels of unknown gemstones it becomes evident that they must have originated from Namibia.

In addition of LA-icp MS all samples were analyzed by FTIR and Raman spectroscopy. These techniques also show features that seem to be typical for certain locations, however, the space available here is limited and those data could not be incorporated so far.

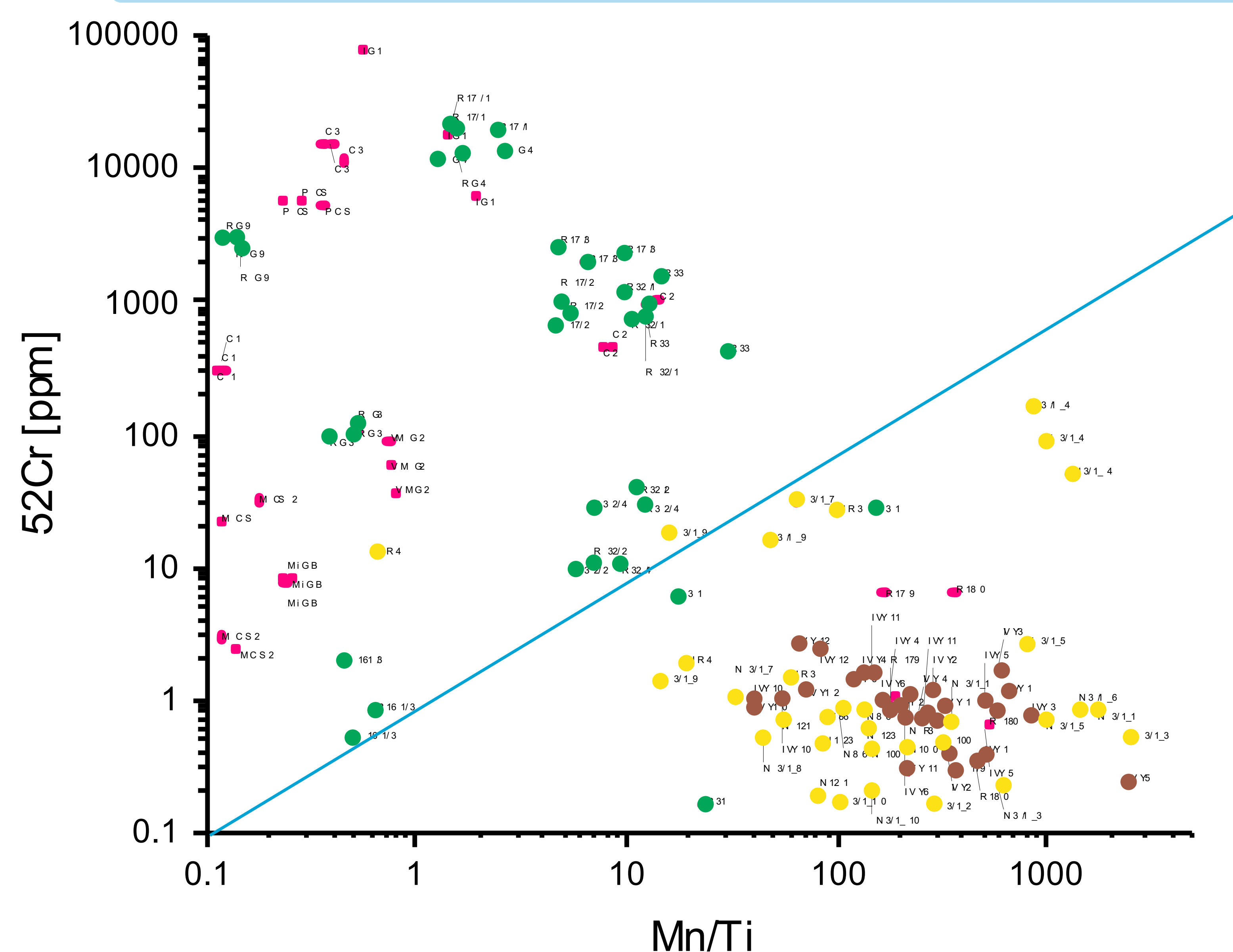


Fig. 4. Graphical separation based on trace elements. Green dots... Russia; yellow dots... Namibia; brown dots ... unknown samples.

## Acknowledgment:

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