Formation of clay minerals and enrichment of chemical elements to anomalous levels during weathering of alkaline rocks and carbonatites

E. HASLINGER[a], F. OTTNER[b] and H. FRÖSCHL[c]

[a] Geological Survey of Austria, Department of Geochemistry, Neulinggasse 38, A-1030 Vienna, Austria, edith.haslinger@geologie.ac.at

[b] University of Natural Resources and Applied Life Sciences, Institute of Applied Geology, Peter-Jordan-Strasse 70, A-1190 Vienna, Austria, franz.ottner@boku.ac.at

[c] Austrian Research Centres Seibersdorf, Department of Analytical Chemistry, A-2444 Seibersdorf, Austria, heinz.froeschl@arcs.ac.at

Introduction

The research area is Alnö Island, which is located to the northeast of the town Sundsvall, Sweden (Fig.1). In this area, the main type of rock is migmatitic gneiss. In the northern part of the island, there is a special geological phenomenon - an intrusion of carbonatites and alkaline rocks, which took place at around 546 Ma BP. Carbonatites are defined as igneous carbonate rocks with more than 50 % modal carbonate minerals. The term 'alkaline rock' refers to rocks containing feldspathoidal minerals or rocks not necessarily containing a feldspathoid but with low SiO_2 and high alkali contents. Alkaline rocks and carbonatites often show anomalously high contents of trace (such as Nb, Ba, Th, U) as well as rare earth elements (REE). Alkaline rocks are very rare geological phenomena comprising only 1 % of the igneous rocks. Up to now, carbonatites and related rocks have been investigated petrologically or from an economic point of view with respect to their anomalous trace and rare earth element content. The examination of carbonatites and alkaline rocks from a soil scientific view point seems to have been neglected so far. The aim of this project to examine the differences in soil development, mineralogical, clay mineralogical and geochemical composition of soil

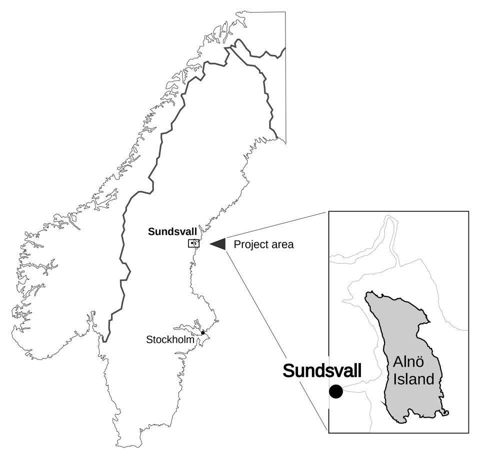


Fig. 1: Geographical position of the research area

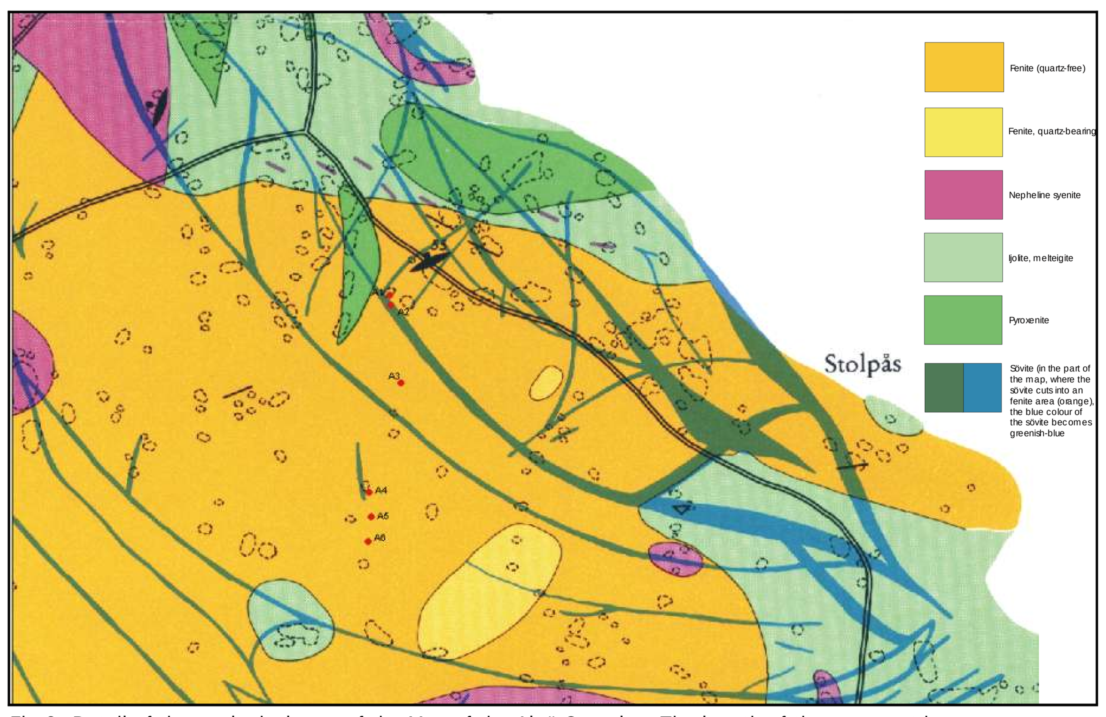


Fig.2: Detail of the geological map of the Map of the Alnö Complex. The length of the transsect is about 500 m. The red dots indicate the position of the six sampled soil profiles.

Methods

The six sampled profiles were chosen along a transect in a forest SSW of the village Pottäng on Alnö Island (Fig. 2). In this transect, it was very obvious from the assemblage of the vegetation, where the parent material is alkaline rocks or carbonatites and where the parent material is migmatitic gneiss. The geological map from this area is not very precise. Most of the soil profiles were supposed to have developed in a fenite area. But during the field work it became obvious, that the vegetation reflects the parent material better than the geological map. While excavating the six soil profiles we found that profiles A1, A3 and A6 developed on alkaline/carbonatitic material and profiles A2, A4 and A5 on migmatitic gneiss.

The samples were taken from the genetic horizons of the soil profiles. Afterwards, their mineralogical and geochemical composition as well as pedogenetic parameters were analysed in the laboratory by means of X-ray diffractometry, analysis of chemical and physical soil parameters, FT-infrared spectroscopy, light microscopy, scanning electron microscopy, microanalysis, thermal analysis, ICP-MS and X-ray fluorescence.

Results

The clay mineral assemblage of all the profiles is dominated by secondary chlorite and illite with various amounts of smectite, vermiculite and mixed layer minerals. However, profile A6 is an exception concerning the clay mineral assemblage. The clay fraction of this soil profile consists nearly entirely of trioctahedral smectite and illite. In the lowermost horizon, considerable amounts of corrensite can be found. The trioctahedral smectite derives from the weathering of phlogopite, which is a main constituent of the parent material of profile A6.

To show the differences between the clay mineralogical assemblage of a soil profile on migmatitic gneiss compared to a soil profile developed on carbonatite, the diffractograms and thermal analyses of single horizons of profiles A4 (gneiss) and A6 (carbonatite) are shown in Fig. 3 - 8.

The geochemical results showed that the rocks, fine soil (< 2 mm) and clay mineral fractions are enriched in the following elements: Ti, Fe, Mn, Ca, P, Ba, F, Nb, S, Sr, Th, U, Zn and Zr as well as REE in the rocks. Some rocks or fine soil fractions additionally showed high amounts of: Cl, Co, Cr, Cu, Ni, V and Y. In some profiles the contents of some trace elements, especially Ba, F, Nb and Zr, was higher in the fine soil and clay mineral fractions than in the parent rock. This is most likely due to the enrichment of Ba-, F-, Nb- or Zr-bearing minerals in these fractions during weathering. These minerals - such as barite, pyrochlore and zircon could only be detected with scanning electron microscopy and had diameters between 1 and 100 µm. The levels of these elements reach anomalously high contents for soils, e.g. Ba up to 10000 ppm or Nb up to 1000 ppm in the fine soil and 3300 ppm (Ba) and 500 ppm (Nb) in the clay fraction, respectively.

The weathering of minerals with subsequent enrichment in the fine soil and clay fraction is shown in Fig. 9 to 11. Fig. 9 shows a picture of a Cr-spinel which was found in the host rock of profile A6 alnöite (an ultramafic alkaline rock). As can be seen in the SEM-picture of the Cr-spinel the spinel is very weathered. The rim of the spinel is depleted in Cr. During weathering, Cr was released, which leads to the high Cr-values in the this soil profile. Fig. 10 and Fig 11 show correlations of Cr with SiO_2 in the fine soil (Fig. 10) and in the clay fraction (Fig. 11). They show, that there are two outliers: the uppermost and the third horizon of profile A6. The Cr

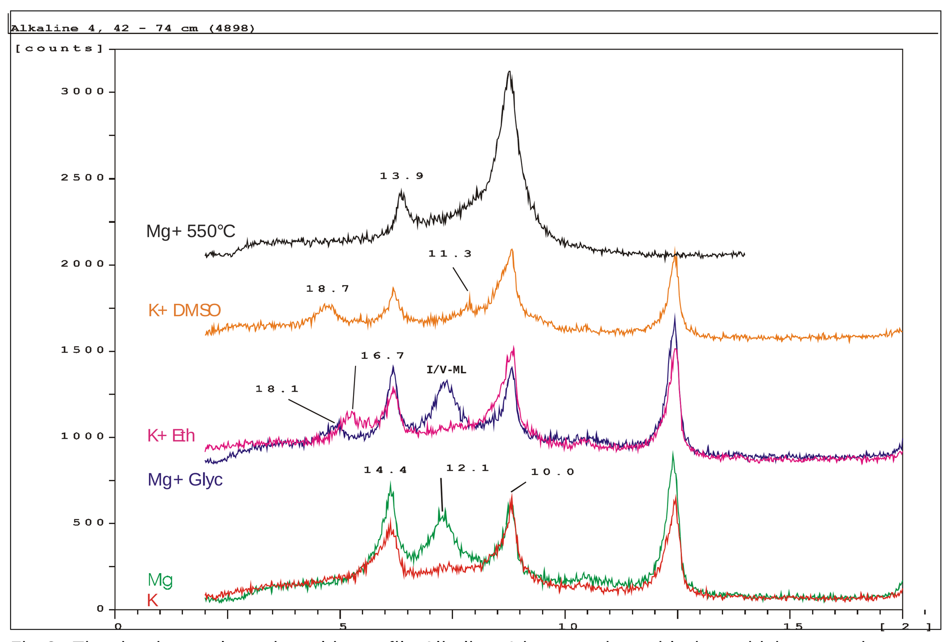


Fig.3: The dominant clay mineral in profile Alkaline 4 is secondary chlorite, which occurs in medium amounts in the upper three horizons. In the lowermost horizon (BwC2, 42 74 cm) the amount of secondary chlorite decreases. In the uppermost horizon, smectite 18,7 Å, K+DMSO) has already been dissolved and transformed to secondary chlorite. The smectite content then increases to low amounts in the rest of the profile. Primary chlorite (13,9 Å, Mg+550°C) occurs throughout the profile in low amounts and shows no dynamics. Kaolinite (11,3 Å, K+DMSO) can only be found in the first two horizons. The illite (10,0 Å, Mg) content is low, but increases in the lower most horizon. Noticeable is the occurrence of medium amounts of a mixed layer in the lowermost horizon (BwC2, 42 74 cm) only. Since the 002-reflection of this mixed layer contracts with K-saturation, it must be an Illite/Vermiculite (I/V) mixed layer.

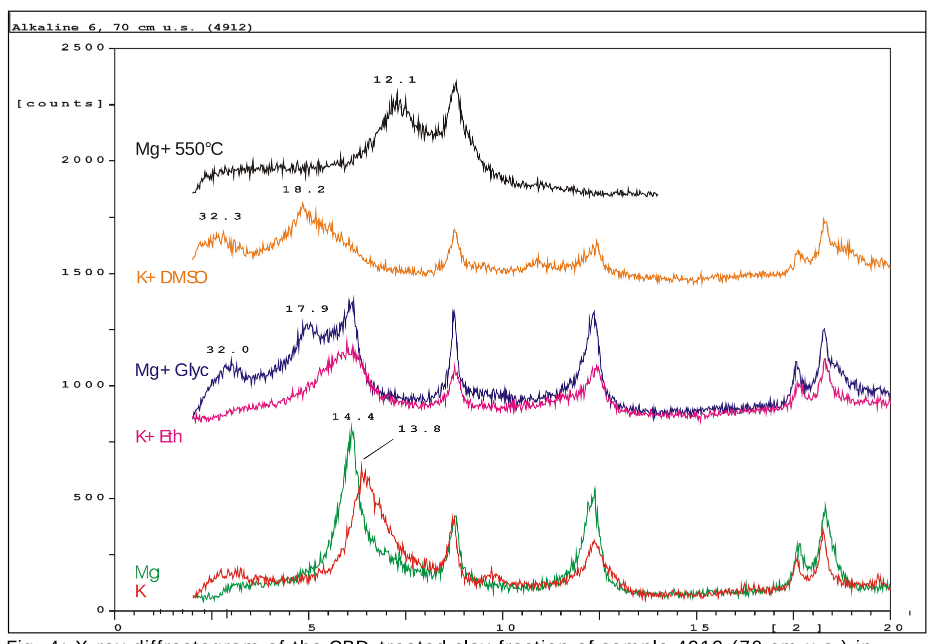


Fig. 4: X-ray diffractogram of the CBD-treated clay fraction of sample 4912 (70 cm u.s.) in profile A6. The corrensite consists of a chlorite and a smectite component, as it expands to about 32 Å upon glycerol and DMSO-saturation (14 Å from the chlorite and 18 Å from the smectite). With vermiculite present (instead of smectite), the ML would collapse to 24 Å (14 Å from the chlorite and 10 Å from the vermiculite) upon K+DMSO saturation.

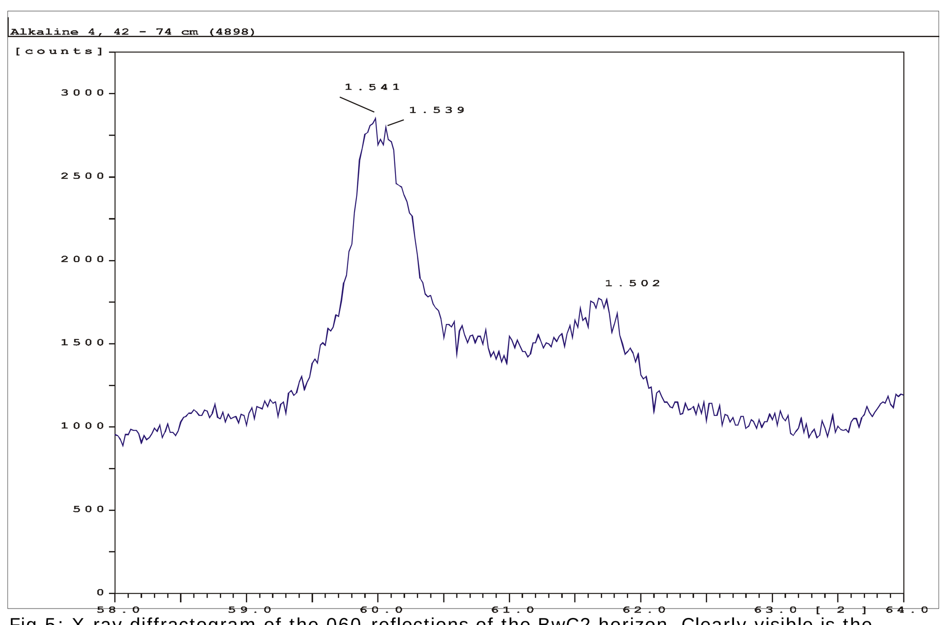


Fig.5: X-ray diffractogram of the 060-reflections of the BwC2 horizon. Clearly visible is the predominance of trioctahedral secondary chlorite, smectite and illite (1,541 and 1,539 Å) compared to the dioctahedral kaolinite (1,502 Å).

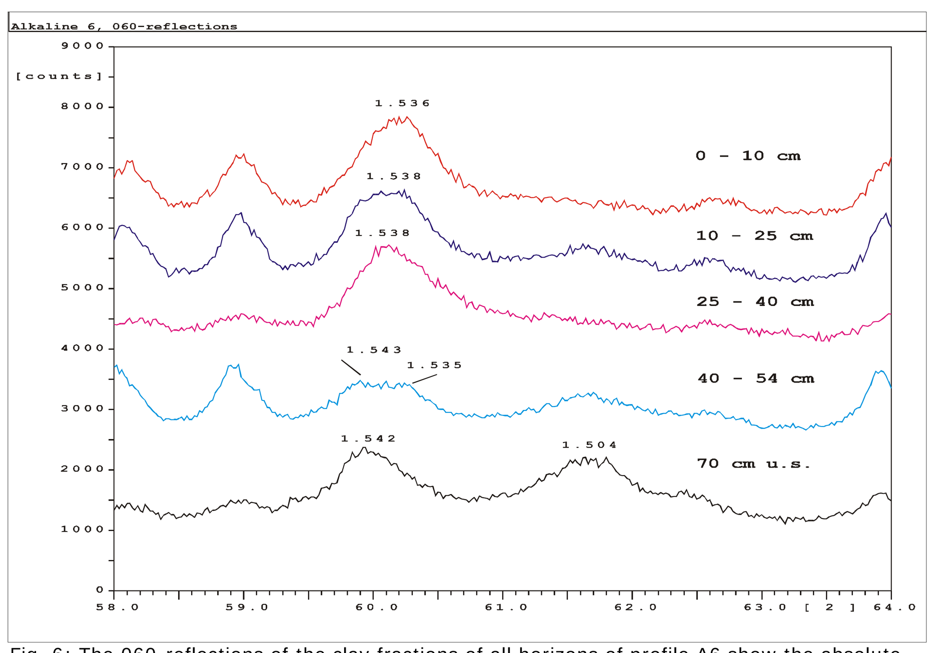


Fig. 6: The 060-reflections of the clay fractions of all horizons of profile A6 show the absolute predominance of trioctahedral smectite and illite, whereas the position of the trioctahedral positions shift a little bit from 1,536 from the uppermost horizon to 1,542 Å in the lowermost horizon. Weak dioctahedral reflections are present in the second (10 25 cm) and fourth (40 54 cm) horizon at 1,504 Å. In the lowermost horizon (70 cm u.s.), the dioctahedral reflection at 1,504 Å is stronger. This reflection is most likely due to a dioctahedral chlorite in the corrensite. The occurrence of the dioctahedral reflection in these three horizons is in accordance with the presence of corrensite.

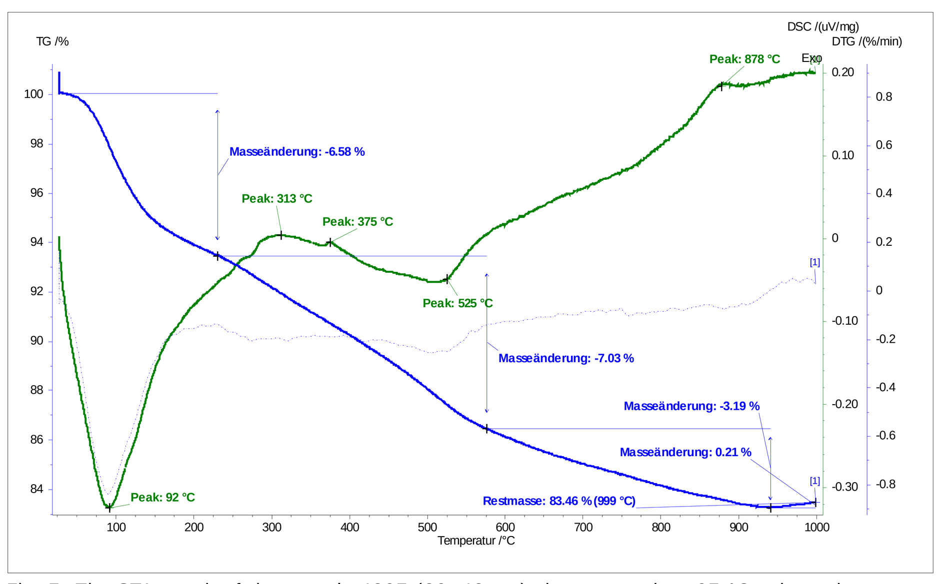


Fig. 7: The STA-graph of the sample 4897 (20 42 cm) shows a peak at 97 °C, where the interlayer water is removed from swellable minerals, like smectite in this sample. Furthermore peaks of organic matter occur at 313 and 375 °C occur. The peak at 878 °C indicates

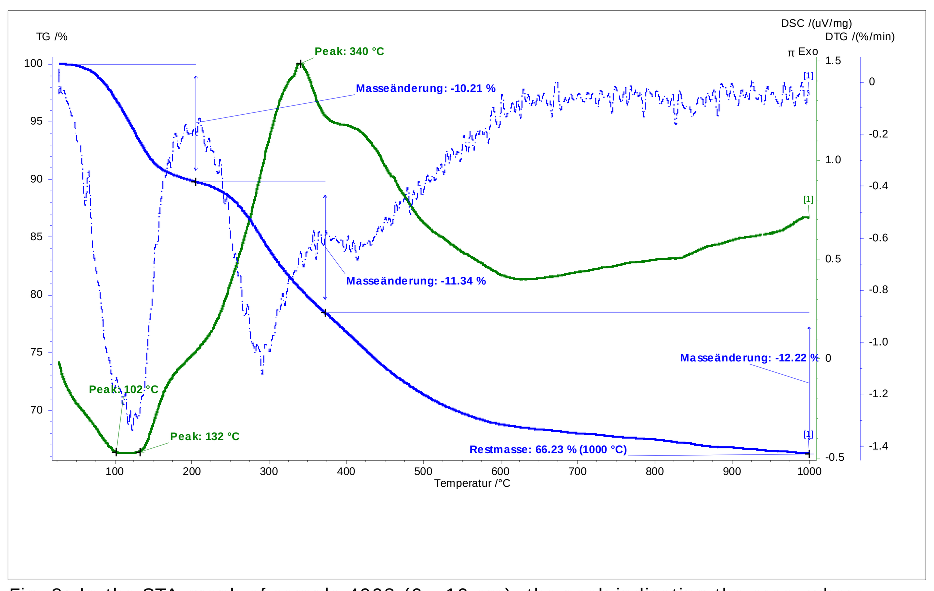


Fig. 8: In the STA-graph of sample 4908 (0 - 10 cm), the peak indicating the area, where swellable minerals like smectite lose their interlayer water, is very broad with peaks at 102 and 132 °C. When comparing with the STA-graphs of the other five soil profiles, the broadness of this peak is quite untypical for CBD-treated samples. This might have something to do with the trioctahedral nature of the smectite. Furthermore, the content in organic matter is rather high, which is shown by the peak at 340 °C and particularly by the very high LOI of 33,77 %.

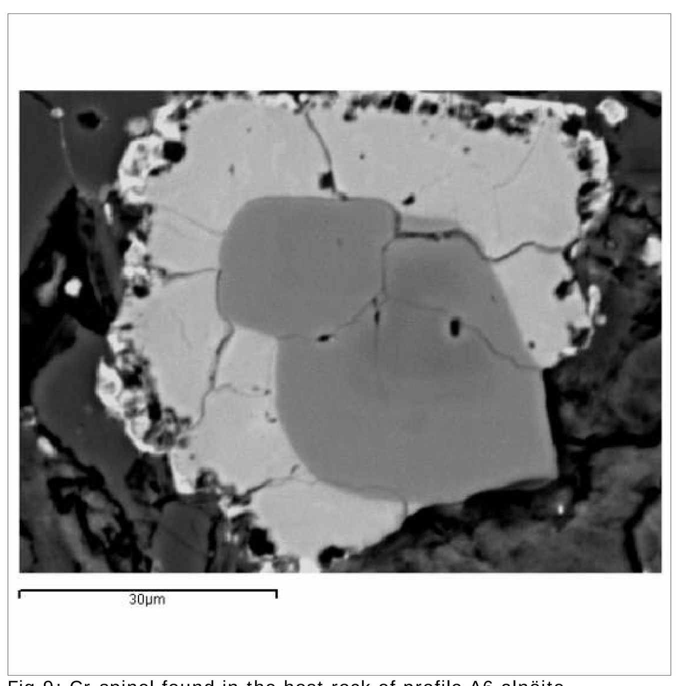
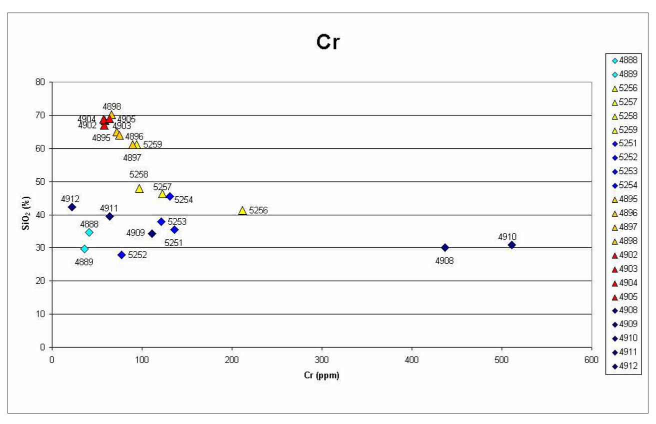


Fig.9: Cr-spinel found in the host rock of profile A6 alnöite (ultramafic alkaline rock). The rim of the mineral is Cr-depleted. The Cr was subsequently enriched in the fine soil and clay fraction during weathering.



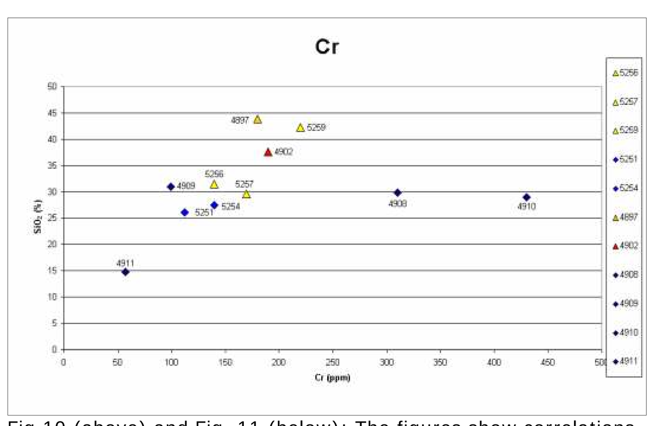


Fig.10 (above) and Fig. 11 (below): The figures show correlations of Cr against SiO_2 in the fine soil (Fig. 10) and in the clay fraction (Fig. 11) of profile A6. Clearly visible is that samples 4908 and 4910 which correspond to the uppermost (0 - 10 cm, Ah) and the third (25 - 40 cm, BwC2) horizon of this profile. The enrichment is due to the weathering of Cr-spinel, which can be found in the host rock of this profile.

Discussion

The results of this study show that rare chemical elements, such as Nb, Ta, Ba, Sr, Cr, REE etc. are enriched in the fine soil and clay fraction to anomalous levels during weathering of carbonatitic and alkaline rocks. This gives an important insight in the weathering behaviour of these rare rock types. Furthermore, as these rocks are of economical interest, this study could serve as precursor for further studies of the weathering of alkaline and carbonatitic rocks. The anomalous contents of rare chemical elements in the soil could be used as chemical signatures to find occurrences of these rocks.