CALCIUM-MAGNESIUM AND POTASSIUM-MAGNESIUM RELATIONS IN LOESS SOILS OF LIMBURG

CALCIUM-MAGNESIUM EN KALIUM-MAGNESIUM VERHOUDINGEN IN LÖSSGRONDEN IN LIMBURG

by/*door*

H. W. van der Marel[1]) and/en J. M. M. van den Broek[2])

1. INTRODUCTION

Loess in Limburg is considered to be formed mainly ca. 50.000 to 12.500 years ago during the Würm glacial period. Transported by the than prevailing northern and northwestern winds it sedimented at decreasing velocities. But also behind obstacles such as dense vegetation, hills etc. (Andersen et al. 1960).

The deposition of the loess occurred in at least three important stages separated by an arrest of sedimentation. In these periods the interstadial and interglacial climates were favourable for a slight weathering of the top layers. A weakly developed tundra soil was formed. This can for instance in some places be observed in deep excavations made in this sediment.

On plains and plateau-like parts the thickness of the loess may be 10 to 20 meters. On hilly grounds it is on an average of not over 3 to 5 meters.

Recent soil formation affected the loess to a depth of some meters, causing decalcification, changes in colour, eluviation and some weathering. Originally the loess sediment is, like all other fine aeolian products, rich in carbonates (here calcite, $CaCO_3$, and dolomite, $CaMg(CO_3)_2$). In Limburg it amounts to ca. 12–15% of the original unweathered material.

Another common component in aeolian products is mica, a mineral which like calcite partly belongs to the „lighter group" of soil minerals (sp. w. feldspar = 2.63—2.74, quartz = 2.66, calcite = 2.71—2.72, dolomite = 2.8—2.9., muscovite = 2.76—3.0, biotite = 2.79—3.16. The „heavy" minerals have higher specific weights: e.g. amphibole = 3—3.3, augite = 3.2—3.6, hypersthene = 3.3—3.5, zircon = 4.5—4.7, ilmenite = 4.5—5.0, magnetite = 5.1—5.2).

Because of their platy morphology the micas are more easily transported by air or water than rounded particles of the same specific weight. In the Limburg loess the mica consists mainly of biotite.

Furthermore it contains muscovite and chlorite, but in negligible amounts as compared to calcite and dolomite. The former moreover is very resistant in contrast to biotite – see for weathering sequence of minerals the detailed article on this subject by Jackson and Sherman (1953).

In the following calcium/magnesium and potassium/magnesium relations are given for the loess soils of Limburg being a result of the decomposition of the carbonates and of biotite and some muscovite.

[1]) Soil Chemist, Netherlands Soil Survey Institute.
[2]) Pedologist of the Netherlands Soil Survey Institute (Province of Limburg).
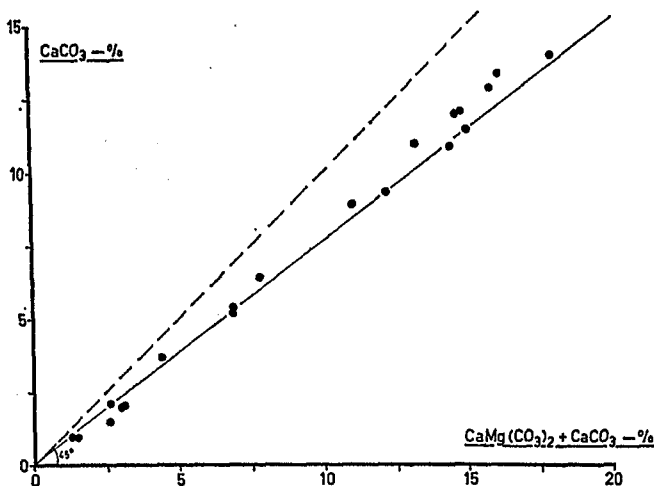
2. EXPERIMENTAL

A. CALCIUM-MAGNESIUM.

Method of analysis

Total carbonates (calcite + dolomite) were determined by the Scheibler method with 10% HCl.

Calcite was determined in the same way but by using acetic acid as recommended by Bruin (1936) and Wolfe and Bartlett (1958).

Acid soluble CaO and MgO were determined by extracting the soil with 25% HCl for 1 hour at about 100°C.

Results

Figure 1 gives the CaCO$_3$ and CaCO$_3$ + CaMg(CO$_3$)$_2$ contents of loessial soils. Through the several points a line is drawn representing the average relation between calcite and calcite + dolomite. On 100 parts of calcite 31 parts of dolomite are found.

As dolomite contains 30.4% CaO and 21.9% MgO, an average CaO/MgO ratio of 100: 10.4 can be calculated for calcite /calcite + dolomite proportion present in the loess soil.

The points designating the lower contents of carbonates however have a larger MgO/CaO ratio than the above mentioned. For the points designating the higher contents this ratio is somewhat smaller. Apparently the contents of the less soluble dolomite is increased relative to calcite when leaching proceeds.

Figure 2 gives for the same loessial soils the CaO and MgO contents, which are dissolved by extracting the soil with 25% HCl. In this table a line is drawn through the points with the higher contents of CaO and MgO. It yields a CaO/MgO ratio of 100: 11.7.

This higher CaO/MgO ratio compared with that found from the calcite and the calcite + dolomite determinations in 10% HCl has apparently its cause in the dissolving of some fine dolomite in the 10% acetic acid; see for this particle size effect with dolomite – Skinner et al (1959).
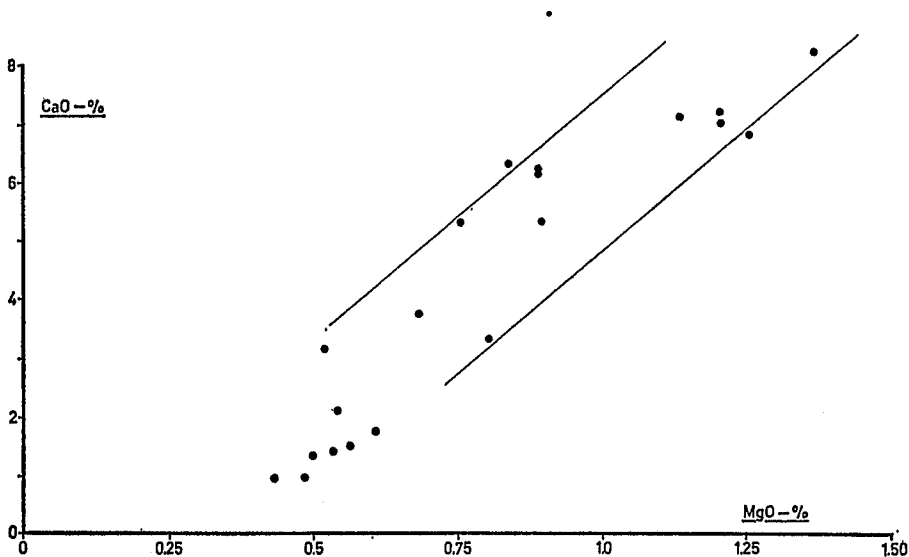
Fig. 2
CaO and MgO in % dissolved by extracting with 25% HCl for 1 hour at 100 °C. Loess Limburg (calcareous soils).
Opgelost CaO en MgO in % bij extractie met 25% HCl bij 100°C gedurende 1 uur. Löss Limburg (kalkhoudende gronden).

Calcite is only slightly soluble in water = ca. 15 mg $CaCO_3$ per liter of pure water at 25°C. Dolomite is even far less soluble than calcite.

$MgCO_3$ however is about 35 × more soluble as calcite; solubility product at 25°C : $CaCO_3 = 0.39.10^{-8}$, $MgCO_3 = 13.8.10^{-8}$ – Kurris (1930), $CaCO_3 = 0.48.10^{-8}$– Olsen and Watanabe (1959). Table 2 also shows that there is an increase of the MgO content relative to CaO and therefore when the weathering proceeds there is an increase of the dolomite percentage in the loess relative to calcite.

Solubility of carbonates depends on temperature, CO_2 pressure and the concentration of other irons. The rate of dissolving depends moreover on the form in which the carbonates occur in the soil. After Brooks et al (1950) $CaCO_3.6H_2O$ is two to three times as much soluble as calcite. The excistense of unstable, more soluble forms of calcite (mono- and hexahydrates) is clearly demonstrated by the analysis of Olsen and Watanabe (1959).

Besides the common dolomite another form should also exist e.q. protodolomite or disordered dolomite – Graf and Goldsmith (1956).

Solubility of calcite is governed by the following relation:

$$K = \frac{\gamma^c_{Ca++} \, P_{CO_2}}{(\gamma^c_{H+})^2}$$

in which γ = activity coefficient
c = concentration (moles/ltr)
P_{CO_2} = partial pressure of carbon dioxyde in atmospheres

Bjerrum and Gjaldbaek (1919) found from their experiments for $-\log K = 5.02$. This figure was also found in the experiments of Patscheke and Diestel

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(1951) which were carried out at 18 °C. Only in case of high Ca^{++} concentrations and high CO_2 partial pressures a higher value than 5.02 gives less discrepance between calculated and experimental data. Olsen and Watanabe (1959) found for —log K = 4.91 at 25 °C. As a contrast to calcite, experiments about the solubility of dolomite have only been few up till now. The reason is that the very low concentrations of Ca and Mg in a solution containing both, increase the difficulties in their quantitative determination. After the observations of Hissink (1935) and Maschhaupt (1950, 1952) concerning alluvial, marine soils in the Netherlands, about 1% $CaCO_3$ is washed out from the subsoil (0–20 or 0–25) in the course of 50 and 25 years respectively. After Edelman and de Smet (1951), 1% $CaCO_3$ in 65 to 90 years should be a better figure for the real leaching effect of carbonates in the marine subsoils of the Netherlands. Lüttmer (1952) found for marsh soils in Germany a loss of 1% over a period of 100 years. Tovborg-Jensen (1952) analysed the loss of differently limed plots on an acid soil in Denmark during a period of 13 years. The leaching of $CaCO_3$ was found to increase with increasing amounts of $CaCO_3$ applied. For the most heavily limed plot that had received 32 tons $CaCO_3$/ha, a loss of 1% $CaCO_3$ can be calculated over a period of 20 years for a layer of 0 to 20 cm.

To a depth of $2\frac{1}{2}$ to 3 metres the Limburg loess of youngest date lost its original carbonates maximal 14 to 15% completely. This happened during 25.000 to 12.500 years – Andersen et al (1960) – a lapse of time in which the last deposition can be considered to have taken place. From this a loss can be calculated of 1% total carbonates for a layer of 20 to 25 cm over a period of 160 to 110 years.

This figure is much higher than was found by the before mentioned authorss Therefore the weathering was probably less intens.

However, loess has a calcite/dolomite ratio of 1.33, whereas the marine soils in the Netherlands have only 1.15 to 1.20. The large losses of calcium carbonate in the liming experiments of Tovborg-Jensen may be ascribed to the sandy and acid properties of the experimental field concerned. And besides that also to the use of ground calcite which contains a large amount of very fine particles as a result of the grinding process. Calcite and dolomite in the Dutch marine soils and in the loess are mainly found in the 16–60 mu and 16–80 mu particle size fraction – Van der Marel (1950a).

B. POTASSIUM-MAGNESIUM

Method of analysis

Acid-soluble K_2O and MgO: determined by extracting the soil with 25% HCl for 1 hour at 100 °C.

Results

Figure 3 gives the ~~CaO~~ K_2O and MgO contents of loess soils of Limburg. But some from France and Germany are also noted. Only samples were analysed that have lost their carbonates, as dolomite is a common mineral of unweathered loess.

There exists a relation between K_2O and MgO with a ratio of about 2.70. Apperently this relation is caused by the gold coloured, weathered biotite found in these loess soils and which contains in its fresh and unweathered state a K_2O : MgO ratio which may vary from 0.6 to 1.5.
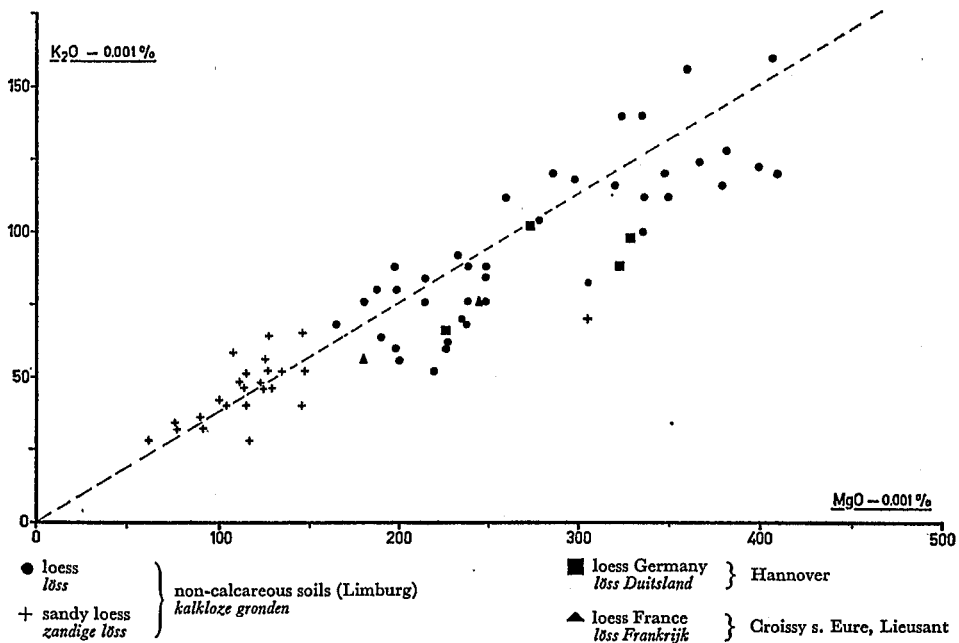
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Fig. 3.
K$_2$O and MgO (in 0.001%) dissolved by extraction with 25% HCl for 1 hour at 100 °C.
Opgelost K$_2$O en MgO (in 0.001%) bij extractie met 25% HCl bij 100 °C gedurende 1 uur.

The large spreading of the several points around the average K$_2$O/MgO ratio of 2.27 originates from the differences in granulometric composition. For instance heavy textured soils will contain more potassium and magnesium in adsorbed (exchangeable) state than the lighter ones.

The first stage in the weathering of biotite is a loss of K$^+$ but a gain of (H$_3$O)$^+$.

The mineral formed is called hydrous biotite. When weathering proceeds intermediate minerals between hydrous biotite and vermiculite are formed; the colour than changes from dark brown to goldlike. The latter contains H$_2$O, Mg^{++} and (H$_3$O)$^+$ between the layers. Vermiculite is poor in K. At last kaolinite is formed. All these stages can be followed by X-ray analysis. For instance the interlaying of (H$_3$O)$^+$ and the loss of K$^+$ manifests itself by a broadening of the 10Å reflection and the intermediate stages between vermiculite and biotite by reflections ranging from 14Å to 10Å respectively. These intermediates are called hydrobiotite. At last when the biotite particles are thoroughly weathered and than have a ragged appearance with holes in them, a strong 7Å reflection of kaolinite in the X-ray spectrum is generated. Compared with other K bearing minerals, such as muscovite, K-veldspar and leucite, biotite is easily weathering. After Mortland et al (1956) plant roots can break down biotite to vermiculite. Therefore biotite is of great interest to agriculture.

Especially under wet and hot conditions as occur in the tropics it proved to be a valuable K and Mg source for crops – van der Marel (1947). But also in soils formed under moderate climates it should be taken into consideration by the evaluation of the results obtained by extracting the soils with
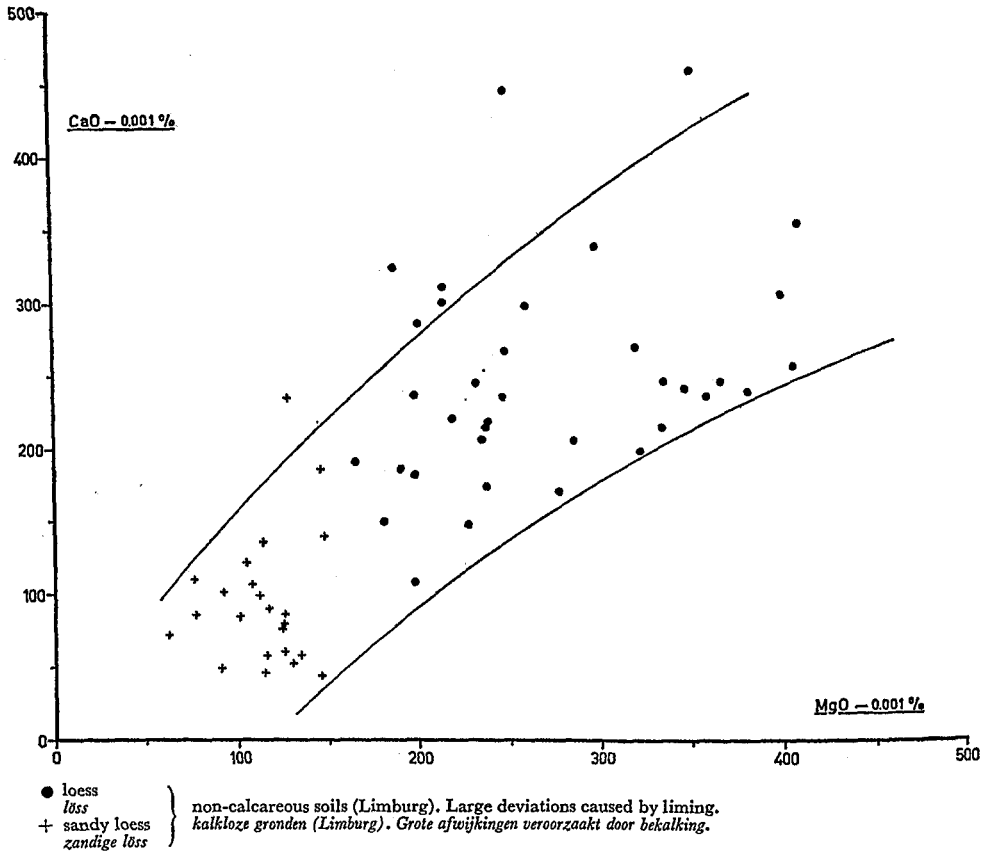
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CaO — 0.001 %

MgO — 0.001 %

● loess
    löss   } non-calcareous soils (Limburg). Large deviations caused by liming.
+ sandy loess   } kalkloze gronden (Limburg). Grote afwijkingen veroorzaakt door bekalking.
    zandige löss

Fig. 4.
CaO and MgO (in 0.001%) dissolved by extraction with 25% HCl for 1 hour at 100 °C.
The large deviations are caused by liming.
Opgelost CaO en MgO (in 0.001%) na extractie met 25% HCl bij 100°C gedurende 1 uur.

weak acids as used in „rapid" soil tests – Van der Marel, 1950b, Schroeder, 1955.

Figures 3 and 4 show that there is in the loess a predominance of magnesium over potassium plus calcium. Though however the most easiest weathering minerals as biotite, calcite, and to some extend also dolomite, contain more calcium and potassium than magnesium.

This phenomenon of the relative accumulation of Mg is caused by its more covalent (therefore less ionogen) nature as compared with K and Ca.

The extend to which an atom forms covalent bonds depends on its tendency to lose electrons and its affinity to acquire them.

Pauling (1944) introduced for this characteristic the term electronegativity For Mg a value was calculated of 1.2 e.V., for Ca = 1.0 e.V. and for -K = 0.8 e.V. – see also Haissinsky (1946). Thus the K atom is the easiest ionised in solutions and therefore it is also the more readily leached into the subsoil. As a contrast Mg is to a lesser extend ionised and therefore it will accumulate relative to Ca and K during the weathering process.

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3. SAMENVATTING

Limburgse loess bevat op 100 delen calciet ($CaCO_3$), ongeveer 31 delen dolomiet ($CaMg(CO_3)_2$). De oplosbaarheid van dolomiet is belangrijk lager dan die van calciet. Limburgse löss verliest ongeveer 1 % calciet per 160–110 jaren, gerekend tot een diepte van 20–25 cm.

Limburgse loess bevat ook biotiet. Evenals van calciet en dolomiet wordt ook de verwering van biotiet besproken. Het element, dat het gemakkelijkst kan worden uitgespoeld bleek Kalium te zijn, gevolgd door Calcium en Magnesium. Deze volgorde wordt veroorzaakt door verschillen in covalente aard. Gedurende de verwering van de loess neemt Magnesium daardoor, relatief gezien, toe (vergeleken met Calcium en Kalium), hoewel de mineralen (biotiet + calciet + dolomiet) die deze atomen leveren, meer Kalium en Calcium bevatten dan Magnesium.

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