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.. In that old potter's shop I stood alone with the clay
opulation round in rows. ...

Leendert van der Plas
Jan van Doesburg

HEAVY MINERALS AND FELDSPARS IN POTSHERDS

Introduction

Potsherds from numerous excavations generally contain
feldspars and heavy minerals, either in the pottery-body or in
the temper or in both. Some sherds are rich in these minerals,
others poor. The mineralogical composition of such fragments
may provide information about the nature of the body and of
the temper. It can provide information about the origin of the
body; whether the material has been found locally or at some
distance from the settlement; whether the material or the ware
has been imported.

Both feldspars and heavy minerals can be studied in thin
sections of potsherds with the help of a petrographic
microscope. Generally, the amount of heavy minerals and even
of feldspars in a thin section is not large enough to allow a
quantitative analysis. Therefore, it is useful to concentrate
these minerals and to study them with specific methods.

The disintegration of sherds

In order to concentrate both feldspars and heavy minerals
from sherds, the sherd must be disintegrated in such a way
that the individual mineral grains are not broken but only
separated from the ceramic matrix. Here, a variety of problems
may be encountered. Ceramic products from various periods,
regions, and cultures not only differ in the nature of the raw
material, but also in the treatment of the clay before
shaping, in the various ways in which the products are formed
and in the firing techniques used. The disintegration of

earthenware, fired below 1000 °C, is generally rather easy. The disintegration of stoneware or soft porcelain is difficult if not impossible due to the presence of glass in the body. Another, rather difficult material is the body of true terra sigillata, because of the careful preparation of the calcium-rich unfired body through a cleaning process causing a dense well sintered sherd even at low firing temperatures.

Disintegration of ceramic bodies for concentration of minerals is performed in a number of ways. The material may be carefully ground to a size of not less than 5 mm. The resulting granules are treated with concentrated nitric acid in order to solve the ceramic matrix, material smaller than 0.01 mm, and free the grains of sand size minerals. Another rather useful method, especially for porous materials, is water saturation (24 hours in boiling water) followed by repeated freezing in liquid nitrogen and boiling in water.

In the case of a study of Neolithic sherds from Hinheim (Bakels 1978; Westrate 1978; van der Plas 1986), acid treatment was used to concentrate feldspars. About 10 g of sherd is carefully ground and stirred for 15 minutes in 75 ml concentrated nitric acid (ca. 14.4 N). The acid is removed and the sample washed with distilled water until the supernatant liquid is colourless and clear. If the sample still holds fragments, the procedure is repeated. This first step removes a large amount of the matrix of the sherd as well as part of the iron oxides. Magnetite, Fe_3O_4, a result of firing in a reduced atmosphere is rather resistant and still present after this first phase. Therefore, it is worthwhile to establish its presence now; a beaker, with the sample is put on a magnetic stirrer with a small amount of water; magnetite is seen to move with the stirring magnet.

After this first treatment, the sample is freed of remaining iron oxide by treating it with a sodium dithionite solution. Formulas are among others given in van der Plas (1966: 259), or Begheijn (1980: 43). This procedure is

repeated once in order to remove all the oxide. The sample is washed and brought in a beaker and a 0.5 N solution of sodium hydroxide is added untill the surface of the liquid is 50 mm above the bottom. The liquid and the mineral residue are thoroughly stirred and the suspension left to settle for four hours at 20 °C. The supernatant liquid is siphoned off and the procedure repeated a few times, leaving a residue free of particles smaller than 2_m.

The sample thus prepared is used for a concentration of feldspars of heavy minerals for further study.

The concentration of heavy minerals

The preparation of heavy mineral concentrates as well as the production of heavy mineral slides for study with a petrographic microscope is a well known procedure described in handbooks on sedimentary petrology, such as Krumbein and Pettijohn (1938) or Milner (1962). A few remarks on the special nature of heavy mineral concentrates of ceramic sherds suffice.

Heavy mineral concentrates of coarse ware are not too different from heavy mineral concentrates of sandy clays. The samples derived from fine-grained ceramics such as most early Neolithic pottery, made of loess or loess loam, tend to be very fine grained, with grains not larger than 100 _m. Consequently, minerals that are generally of a small size are more frequent than those normally encountered in the average heavy mineral slide of a sandy sediment. Such typical minerals are a.o., zircon and garnet. Therefore, the possible number of different species is smaller than normal, and the possibility to distinguish between different provenances is smaller also.

Heavy mineral concentrates of pottery are generally small, i.e., the number of grains in 10 g of sherd material is restricted. Therefore, the analyst has to work carefully in order to retrieve a sample large enough for counting. Samples from ceramic material of the Oss-Ussen excavation for instance

(van den Broeke in preparation) sometimes hold less than 150 grains.

Finally, the method used for disintegration of the sherds may have removed a number of interesting heavy minerals. For instance, acid disintegration will solve apatite; some of the iron oxides and some of the carbonates are solved by using strong acids. The analyst has to be aware of these aspects of the various disintegration and cleaning methods he is using in sample preparation.

The concentration of feldspars

For the concentration of feldspars two different methods have been developed (van der Plas 1966). The first method is based on the density differences of alkali feldspars and plagioclases. This method is only efficient if the sample is rather feldspar rich. Moreover, the amount of sample has to be at least 0.1 g. It has one advantage over the second method "flotation" in that it is 100 % selective.

In a flotation cell minerals in suspension can be separated on the basis of differences in wettability of their surfaces. The selectivity of the process is enhanced through various additives. Presently, froth flotation of feldspar sands is one of the important industrial methods for the production of both quartz sand and feldspar for the ceramic- and the glass industry (Edelstein 1987). The method is not selective within the group of feldspar minerals but only separates feldspars from quartz and mica. Moreover, the method is not selective in an absolute sense but produces a concentrate, a "float" enriched in feldspars with respect to the residue, the "tailing". The restricted selectivity is not an important drawback because the X-ray diffraction analysis of the enriched float enables a sufficient characterization of the feldspar fraction of a sample for most investigations. If, however, a quantitative differentiation of the feldspar fraction is needed, either a subsequent staining (van der Plas

1966) of the feldspar grains in the float is necessary or the much more laborious heavy liquid separation must be performed.

Flotation of feldspars

Flotation of feldspars in the laboratory is generally performed in a Hallimond tube (Fig. 1); with some practice it can also be done in a glass beaker with a small amount of liquid. Furthermore, the method is efficient only with grains
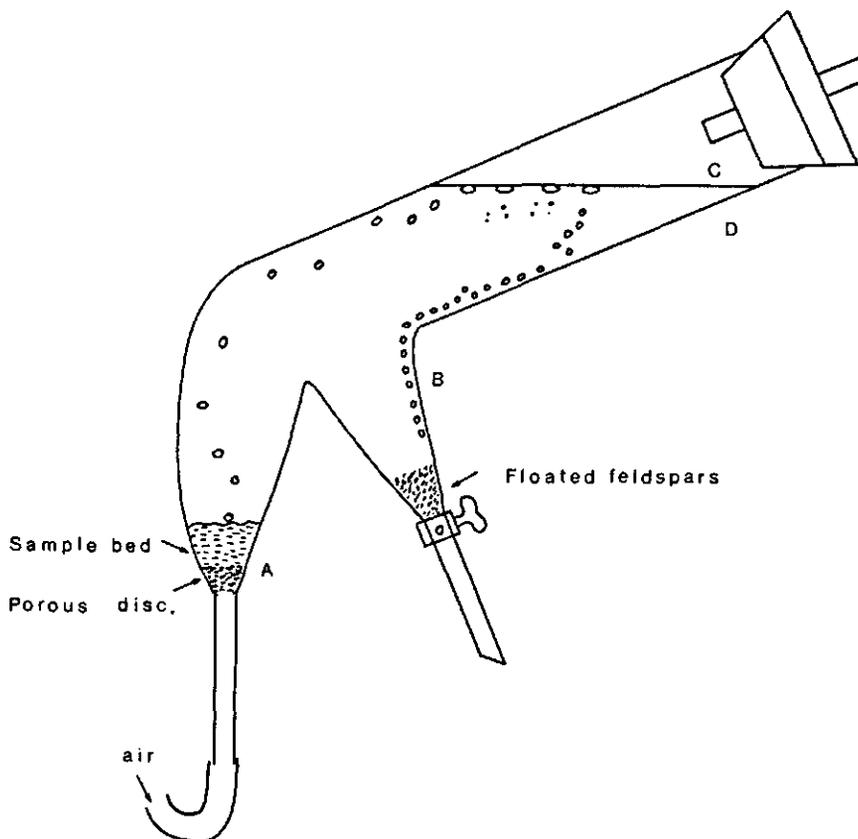

Fig. 1. Hallimond tube; the positions of the sample and the "float", the feldspar concentrate, is indicated.

larger than 50 _m. Therefore, the sample is passed over a sieve and the smaller grains are removed. The fraction > 50 _m is activated in a solution of HF at pH 2.3 for 15 minutes. The activated sample is than brought in a Hallimond tube (Fig. 1), connected to a container with either air or N_2 gas. The gasflow is preferably regulated with a needle valve. The Hallimond tube is filled with a solution of 6 mg/l dodecyl ammonium acetate (ARMAC C)[1] with an addition of a HF solution till pH 2.6 (3 or 4 drops of concentrated HF/ 100 cc) and a 1N HCL solution till pH 2.3. The pH values may be checked with indicator sticks. After conditioning for a few minutes the sample is floated for 2 minutes by opening the needle valve in order to allow a gentle gasflow through the sample bed. Both float (B in Fig. 1) and tailing (A in Fig. 1) are collected and used for subsequent X-ray diffraction. An example of such an X-ray analysis is given in Fig. 2.
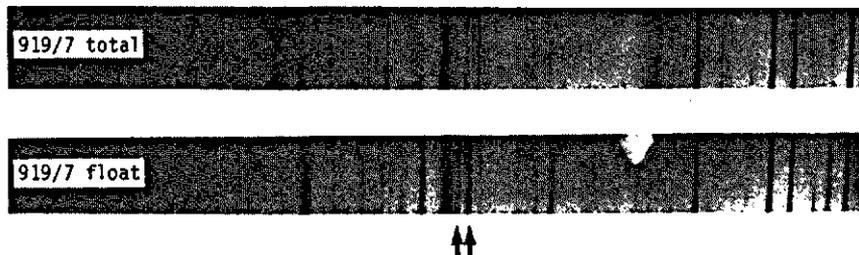

Fig. 2. X-ray patterns of the sandfraction of a Neolithic sherd (cf. van der Plas 1986), and of the feldspar concentrate, the "float" of this sandfraction.

The flotation method using a beaker is principally the same. The sample is immersed in the above flotation liquid in a glass beaker. The amount of liquid is approximately 10 mm above the bottom of a 250 ml beaker. After conditioning the liquid is gently swirled in such a way that part of the bottom is temporarily not covered by the liquid. Feldspar grains at

the contact of the liquid with the bottom have the opportunity to attach themselves at the surface of the liquid and to remain at the surface. In order to separate the float from the tailing the liquid with the floating feldspars is gently poured in a second beaker. Because the flotation method is not strictly quantitative, the technique with a beaker, if expertly performed, is hardly less efficient than the use of the Hallimond tube. Information on the technical background of flotation is reported in Gaudin (1957), Fuerstenau (1962) and van der Plas (1966).

Heavy liquid separation of feldspar

Heavy liquid separation of feldspars is similar to the heavy liquid separation of heavy minerals. Differences follow from the observation that the density differences of feldspars and quartz, the other important mineral in the sherds, are rather small. Heavy liquids generally have a somewhat larger viscosity than water, causing the grains to settle more slowly. Therefore, the shape of the funnels used for heavy minerals is unsuitable. Favejee (1965) developed a funnel with steep walls that has been used eversince (van der Plas 1966). Another aspect of the feldspar separation with heavy liquids is the careful preparation of the proper liquids. Again Favejee suggested to use liquids made by mixing bromoform and decalin[2], two liquids with rather similar vapour pressure over a wide temperature range; thus the careful prepared liquids do not change their proper density over time. Procedures as well as the preparation of the mixtures of density 2.59, and 2.67 in order to produce an alkalifeldspar fraction < 2.59, an > 2.59 albite + quartz fraction < 2.67 and a plagioclase fraction > 2.67 are given in Doeglas et al. (1965) and van der Plas (1966). In case small grains of size < 70 _m have to be treated one may consider using a centrifuge method instead of funnels. Still funnels, although less efficient with small grains, produce useful concentrates if

the analyst takes his time.

X-ray analysis of feldspars of pot fragments

Good X-ray patterns are obtained from powders with a grain size smaller than 10 _m; therefore, the finishing of the grinding of the feldspar concentrates is done by hand in an agate mortar. Powder thus obtained can be used both in a diffractometer or with a Guinier camera. Notwithstanding recent developments in diffractometer techniques, identification of feldspars as well as the study of structural aspects of feldspars is to a large extent still done with the Guinier camera and photographic recording. Especially, the problem of small amounts of sample is easily overcome with a Guinier camera.

X-ray patterns of feldspar concentrates as well as those of ground sherds show next to feldspar lines the lines of the omnipresent quartz and of mica (Fig. 3). Furthermore, the feldspar lines may belong to various mineral species. The
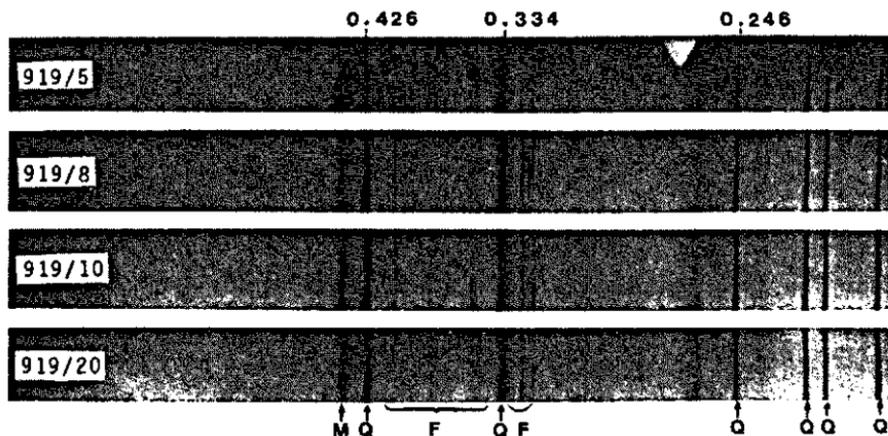

Fig. 3. X-ray patterns of the sandfraction of four Neolithic sherds (cf. van der Plas 1986). Both quartz and feldspar lines are marked.

group of feldspar minerals is rather rich in chemical
varieties as well as in structurally different feldspars from
volcanic rocks and from gneisses and granites (van der Plas
1966; Smith 1974). Finally, some alkali feldspars are
submicroscopic lamellar aggregates of two chemically different
species, microcline and sodic plagioclase, called perthites.
Although, this situation seems rather complex, it offers an
excellent possibility for the characterization of sets of
sherds, either showing e.g., volcanic feldspars, or feldspars
from metamorphic rocks or perthites or basic plagioclase.

For a routine analysis of a large set of sherds a simple
identification method is prefered. Using only a few relatively
strong lines of the X-ray powder pattern of feldspars it is
generally possible to identify the various kinds of
feldspar(s) present. The most conspicuous and strongest
feldspar lines have d-values between 0.425 and 0.180 nm. An
important feldspar line is the (201) diffraction line,
enabling the discrimination between potassium feldspar and
plagioclase. Pure potassium feldspar has a (201) line at ca.
0.424 nm, all plagioclases have at least 0.403 nm (Fig. 4).

In case the amount of feldspar in the sherd is not too
small, the feldspar lines are strong enough for the
determination of the chemical nature of the potassium
feldspars. Potassium feldspars are hardly ever pure $KAlSi_3O_8$.
Generally, there is an admixture of sodium and even some
calcium in the chemical composistion. Orville (1967) and
Whright (1968) published data on the chemical composition of
feldspars. A regression line with correlation coefficient
0.997 derived from these data can be used to estimate the
chemical composition. The percentage potassium feldspar, the
Or %, is given in the following formula:

$$Or\ \% = 4823.2 * d_{201} - 1944.9$$

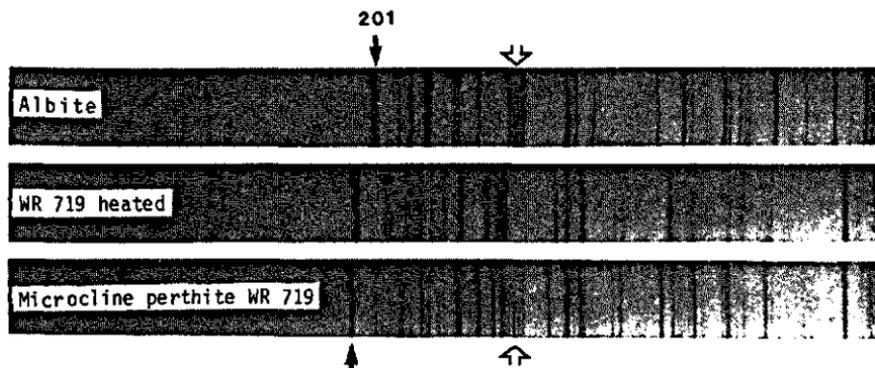If perthites, unmixed alkali feldspars are present, two

Fig. 4. The (201) diffraction lines of an albite and a
potassium feldspar, a microcline, are shown. The
middle pattern is the result of heating the microcline
perthite.

d(201) lines close to each other are seen, one at
approximately 0.424 nm, the other at 0.403 nm. The relative
amount of both the plagioclase and the potassium feldspar
share of the perthite can be estimated after heating the
sample for a few hours at 1000 °C (Fig. 4), and measuring the
position of the only one line that results from this heat
treatment in the way just described. In Fig. 5, an X-ray
photograph of a sample is shown before and after heating.

It goes without saying that the above perthite
determination in potsherds is only possible if the pots have
been fired for a rather short time at not too elevated
temperatures.

Other well established methods for the identification of
feldspars (Smith 1974; van der Plas 1966), are only possible
in those cases where samples are available that are rather
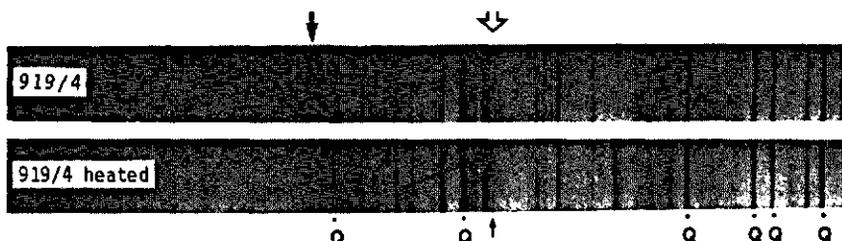rich in feldspars. Such methods are less efficient with
sherds.

Fig. 5. The result of heating the sandfraction of a Neolithic
        sherd. The presence of perthite is indicated by the
        result.

Conclusions

The foregoing considerations and examples show that both
feldspars and heavy minerals of potsherds can be studied with
rather simple methods. Both the preparation of the mineral
concentrates with heavy liquids or with flotation do not ask
for elaborate laboratory equipment. The study of these
concentrates with a petrographic microscope, an instrument
that has to be present in an archaeological laboratory for the
study of thin sections of sherds and of artifacts of stone, is
not unlike the study of these thin sections with polarized
light. Because, during such analyses, the nature of sand size
minerals has to be determined also. Moreover, the skills of
optical mineralogy are presently taught to a number of
archaeological students.

The X-ray identification of the mineralogical composition
of ground sherds as well as of mineral separates from these
sherds is a somewhat more advanced technique. It needs an
X-ray generator of a simple type, a Guinier camera and a dark
room for the developing of the X-ray films. In addition, the
X-ray room has to satisfy current safety regulations. If,
however, the archaeologists can have some cooperation of a
chemical or mineralogical laboratory willing to simply accept
his finely ground powder samples and simply produce the films

only, the measuring of the line positions and line intensities
and the determination of the minerals present can even be done
in the library.

Dedication

The authors want to dedicate this contribution to the study
of ceramic objects of archaeological interest to Professor
Dr. Henk Franken, who has been a lonely pioneer in the study
of the production methods of pottery during his very active
life. He emphasized the presence of traces of the potters'
shaping methods on the pots. He tried to reconstruct the
tradition of making pots in various cultures. He admired the
potters skill, his knowledge of the use of proper clays for
vessels with varying purposes and his knowledge of the
technology of shaping, drying, finishing and firing. He asked
the advise of studio potters on matters of technological
interest and was among the first to employ such a studio
potter in his laboratory. We wish him many more years with
potters and pots.

Notes

1. A product of the Armour Industrial Chemical Cy, Chicago,
   products made by other chemical industries may have a
   comparable composition.
2. Decalin or decahydronaphtalene, $C_{10}H_{18}$, is a liquid with a
   density between 0.9 and 0.87 because of a mixture of (cis)
   and (trans) forms.

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