

Application of gas chromatography to mineral chemistry: aluminium–silicon ordering in melilites

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SUMMARY. The mole fractions of the silicons present in melilites as monomeric (SiO_4) and dimeric (Si_2O_7) groups depends both upon the composition of the melilite and also upon the degree of Al–Si ordering. It is shown that the absolute numbers of monomeric and dimeric silicons in a 10 mg polycrystalline sample can be determined by a relatively rapid chromatographic method.

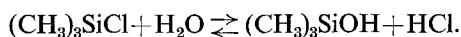
A statistical theory is developed to treat the data; this contains a variable k -parameter that describes the degree of ordering.

Experimental results are presented and interpreted for one natural and five synthetic melilites. The synthetic gehlenite-rich melilites are appreciably, but not completely disordered. The natural melilite is well ordered, but heating at 1050 °C introduces considerable disorder.

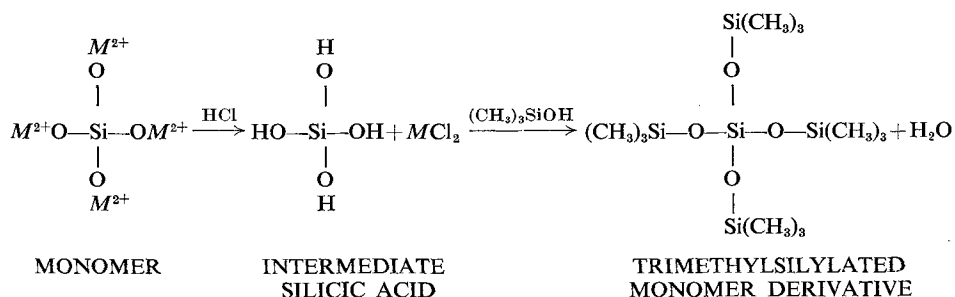
DIRECT information on the extent of Al–Si ordering, and hence on the degree of polymerization of the ‘silicate’ groups in a mineral structure is difficult to obtain. The great success of X-ray crystallographic techniques in determining the basic structures of minerals has tended to retard the application of other structure-sensitive techniques to mineralogical problems. It is true that these ancillary techniques often provide information only on some parts of the structure, but they are nevertheless useful either where a large number of specimens must be examined, or where the structural information provided by crystallography is less than complete. The melilites are an example where the crystal structure is known but where the finer details of the aluminium–silicon distributions still remain uncertain. In the present paper, a technique relatively new to mineralogy—gas chromatography—is applied to the problem of determining Al–Si distributions in melilites.

Lentz (1964) showed that it was possible to detect low-molecular-weight silicate anions using chromatography. The silicate anions were derived from silicate minerals having a known anion constitution, e.g. he used olivine as a source of SiO_4 groups, etc. These anions were dissolved out and rapidly converted to their trimethylsilyl (TMS) derivatives by reaction with trimethylsilyl chloride, $(\text{CH}_3)_3\text{SiCl}$. The trimethylsilyl derivatives are volatile molecular species that are readily detected using commercially available equipment. The first chromatograms were calibrated empirically but the calibration has now been placed on a more fundamental basis by Wu, Götz, Jamieson, and Masson (1970) who used high-resolution mass spectrometry directly to determine the molecular weight, and hence the degree of polymerization, of the

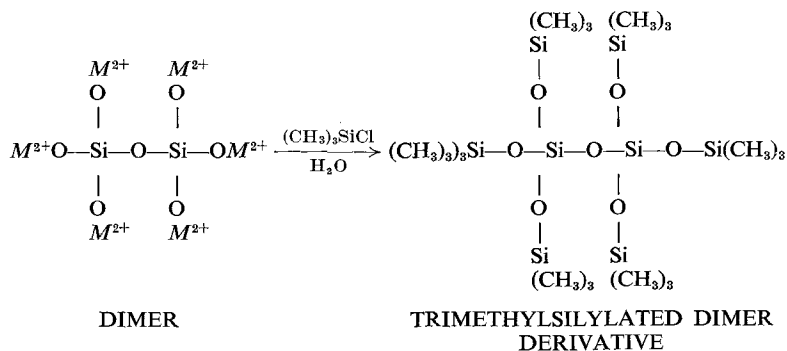
TMS derivatives that appear in chromatograms. Götze and Masson (1970, 1971) have examined the chemical reactions occurring during the process of converting silicate anions, originally present in a crystalline silicate, to their TMS derivatives. Water partially hydrolyses the trimethylsilyl chloride to trimethylsilanol



The HCl dissolves the metal cations (M^{2+}) while the trimethylsilanol reacts with the silicate units. It is possible that trimethylsilyl chloride may be the coupling agent. Thus the reaction with monomeric orthosilicate groups proceeds as follows:



The dimeric species forms from pyrosilicate groups as follows:



As the formation of the volatile derivatives is a stepwise process the specific conditions used for the extraction are often critical, both with respect to obtaining a satisfactory yield and also in order to minimize undesirable side reactions such as condensation or degradation of the intermediate silicic acids. Small variations in the water content of the reaction mixture may cause large changes in the reaction products: a large excess of water results in the rapid dehydration of trimethylsilanol to form hexamethyldisiloxane.

In the present study the capabilities of the chromatographic method have been extended by the addition of an integrator, so that the signal received from each TMS derivative can be integrated quantitatively, and also by using a calibration procedure that establishes the relationship between integrated counts and the number of silicons.

Experimental

Synthetic melilites. Gehlenite, åkermanite, and intermediate solid solutions at 25, 50, and 75 mole % gehlenite were prepared by prolonged sintering and repeated crushing of pure oxide and carbonate starting materials. These were reacted in platinum crucibles at *c.* 1300 °C until a homogeneous preparation was obtained as judged by optical and X-ray examination.

Natural melilite. Several melilites were examined; only one was satisfactory for present purposes. This melilite was from the University Collection, No. 6355; the locality is given as Tyrol (Austria). The melilite was readily separated from the main impurity, calcite, by hand-picking; any remaining calcite was dissolved in dilute acetic acid until optical and X-ray examination showed that the concentrate was free from impurity. A partial chemical analysis (Analyst, Mr. J. Marr) of a concentrate washed and dried at 110 °C gave, in wt %, $\text{SiO}_2 = 30.59$, $\text{Al}_2\text{O}_3 = 21.92$, $\text{CaO} = 37.68$, $\text{MgO} = 3.60$, $\text{Na}_2\text{O} = 1.83$, $\text{Fe}_2\text{O}_3 = 3.59$; total, 99.21 %. Recalculation to seven oxygens gives $(\text{Ca,Na})_{1.948}(\text{Mg,Al,Fe})_{0.971}(\text{Al,Si})_{2.011}\text{O}_7$.

Chromatographic analysis. The procedure used is essentially that described by Götz and Masson (1970). Much exploratory work had to be done in order to find the specific conditions for extraction that gave the best yields consistent with a minimum of side reactions. Åkermanite could readily be extracted without addition of water: addition of water to the extraction mixture did not change the yield, but increased the extent of side reaction. Completely extracted solutions were found to contain incompletely trimethylsilylated species. The reaction with TMS could be completed by an additional treatment with Amberlyst 15, a strong cation exchange resin, in the presence of excess hexamethyldisiloxane (HMD). Because the Amberlyst treatment is hindered by the presence of a large excess of trimethylsilyl chloride, this was first removed by hydrolysis before treatment with the resin. The addition of water at this stage did not increase the extent of side reaction.

Gehlenite is less reactive than åkermanite so that some water, added during the solution stage, is essential to obtain a satisfactory yield. The added water did not, however, alter significantly either the ratios of monomer to dimer TMS derivatives or the extent of side reactions. The intermediate solid solutions were treated as for åkermanite, although the yield declined as the Al content increased. The specific conditions chosen for extraction were, therefore, as follows:

Åkermanite and melilite solid solutions. 9 ml. of HMD and 0.8 ml of isopropanol were mixed with a weighed amount (*c.* 10 mg) of crystalline powder ground to pass 200 mesh. To these were added 2 ml of trimethylsilyl chloride and the resulting mixture stirred for 15 to 20 hr in a tightly stoppered glass bottle. Water (9 ml) was added and the mixture stirred for a further 30 minutes to hydrolyze the excess trimethylsilyl chloride. The organic layer was pipetted off and its trimethylsilylation completed by adding Amberlyst 15 and stirring it in a stoppered bottle for a further 15 to 20 hr.

Gehlenite. HMD (9 ml), 0.8 ml of isopropanol, and 0.2 ml of H₂O were added to a weighed amount (c. 10 mg) of gehlenite, ground to pass 200 mesh. To these were added 2 ml of trimethylsilyl chloride. The mixture was stirred, treated with Amberlyst 15, and again stirred as was done for åkermanite, except that no more water was added.

The chromatograph was calibrated as follows: Pure TMS derivatives were isolated by chromatographic separation. For example, in calibrating the instrument for monomer, any extract containing SiO₄ groups can be used because the TMS monomer derivative can be cleanly separated from other molecular weight fractions. The pure monomer effluent was collected in glass capillaries. The collection process was repeated, if necessary, until a yield of 100 to 1000 µg had been obtained. This was weighed to ±1 µg, dissolved in an inert solvent, such as HMD, and the solution made up to a known weight.

The procedure must be repeated for each molecular weight derivative. Experience shows that the monomer TMS derivative is the most difficult to collect and weigh accurately as it is rather volatile at ambient temperatures. It is best collected at 0 °C or less. Aliquots of these standard solutions were injected to calibrate the detector and integrator response. The response was found to vary linearly with concentration over several decades of concentration. Chromatograms were obtained using a standard Hewlett-Packard chromatograph, Model 5750G, equipped with a flame-ionization detector. The column was stainless steel, 1/8 inch internal diam. 12 ft long, packed with methyl silicone gum rubber, SE-30, 3 % on Chromosorb WAWDMCS, 80 to 100 mesh. The carrier gas was nitrogen dried by passage over a molecular sieve.

Results

The extraction efficiency may be measured by the percentage of total silicon in the weighed sample that was recovered at the detector. This efficiency was variable but, in general, the poorest yields were obtained from gehlenite and the gehlenite-rich solid solutions. Yields ranged from 95 to 98 % at the åkermanite composition to 25 to 75 % at gehlenite. Despite the variable yields from gehlenite-rich compositions, the relative proportions of the different molecular weight derivatives remained constant. Some of the silicon recovered, usually 2 to 4 % of the yield, was present as the trimeric ($n = 3$) and tetrameric ($n = 4$) species. These are believed to arise from side reactions leading to polymerization, which occur during extraction. In all samples, however, between 92 and 97 % of the silicon recovered occurred as TMS derivatives with $n = 1$ or $n = 2$. Results for derivatives having $n = 1$, $n = 2$ are shown separately in fig. 1: the sum of $n = 3$ and 4 is also shown. These are plotted as a function of the melilite composition. The only correction that has been applied to the data is to normalize the total silicon recovered for each sample to 100 %. Provided the extraction procedure is followed exactly, duplicate runs are usually reproducible to ±2 %.

The natural melilite (no. 6355) also contains sodium; therefore, rather than show the results obtained on fig. 1, they are given separately: SiO₄⁴⁻ 75.5 %, Si₂O₇⁶⁻ 22.3 %, Si₃ and Si₄ species 2.2 %; after heating at 1050 °C, SiO₄⁴⁻ 62.6 %, Si₂O₇⁶⁻ 33.3 %, Si₃ and Si₄ species 4.1 %.

Discussion

The crystal structure of melilite is well known: recent refinements by Smith (1953) and Louisnathan (1971) may be mentioned. These were done on natural melilites, which contained some alkali. It seemed that the most probable distribution of cations in the alkali-free end members would be: Åkermanite, T_1 Mg, T_2 Si, Si; gehlenite, T_1 Al, T_2 , Al, Si.

The notation used by Smith suffices for present purposes. He distinguished two sets of tetrahedral sites: the geometrically roomier set were designated T_1 , the smaller, T_2 . There are twice as many T_2 sites as T_1 sites. It seemed probable that the roomier T_1 set would be preferentially occupied by either Mg or Al rather than by Si although, given the similarity in X-ray scattering power of Mg, Al, and Si, this could not be proven.

The chromatographic results obtained for åkermanite are readily explained using this picture, which would predict that all the silicon should be present in T_2 sites: these occur in pairs in the structure and give rise to the 'Si₂O₇' groups. The consequences of distributing any silicon on T_1 sites is rapidly to increase the quantities of monomer and also, of derivatives having $n \geq 3$. It is true that a small amount of monomer and also of derivatives having $n \geq 3$ were found, but these are not thought to be significant. The derivatives with $n \geq 3$ are believed to arise from competing degradation and polymerization side reactions that occur during the preparative stages. While the choice of experimental conditions can minimize the extent of these reactions, they cannot be entirely eliminated given the present state of the art. For example, the yield of dimer that is obtained from hemimorphite—known to contain all silicon as the dimeric species—is usually about 92 to 96 % of the silicon. It is therefore concluded that the present results for synthetic åkermanite are entirely consistent with placing all silicon in T_2 sites.

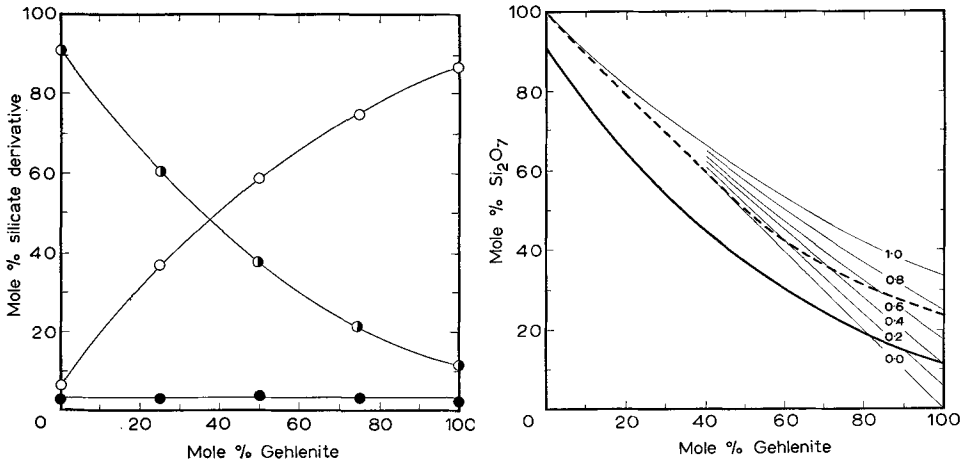
The results for gehlenite and the intermediate solid solutions require somewhat more explanation. For gehlenite, the proportion of dimer is significantly greater than zero, but is less than would be expected from a random distribution. The yields expected from a random distribution of Al and Si on T_2 sites may be calculated as follows: If both T_2 sites in a pair are occupied by Si, this would yield a dimer in the chromatogram. However, in gehlenite we have equal numbers of Al and Si in T_2 sites and both (AlSi)O₇ and Al₂O₇ groups might occur. An (AlSi)O₇ group is detected in the chromatogram as the monomer derivative. Now, if T_2 sites are occupied randomly, the expected distribution would yield 0.25 mole fraction Si₂O₇, 0.50 (AlSi)O₇, and 0.25 Al₂O₇. In fact, the mole fraction of Si₂O₇ found for synthetic gehlenite is much less. Placing some Si in T_1 sites—a possibility that is not absolutely excluded by the crystal structure determinations—would produce less dimer, but would also lead to an increased abundance¹ of derivatives having $n \geq 3$. We will return, therefore, to developing a model that explains the observations but in which silicons are distribu-

¹ This is best appreciated by examining a model of the melilite structure in which the T_1 and T_2 sites are linked into infinite tetrahedrally-coordinated sheets, which are isolated from each other by the Ca-O layers. Within a tetrahedral sheet, placing silicons in both T_1 and T_2 sites must inevitably lead to formation of units having $n > 2$. A trimer might form, for example, by placing the silicons thus: Si _{T_1} -Si _{T_2} -Si _{T_2} , etc.

ted only on T_2 sites. The model must be suitable to explain the data not only for gehlenite, but also for the alkali-free melilites generally.

Distribution of Al and Si on the T_2 sites. Let N_{Al} represent the mole fraction of T_2 sites occupied by Al and N_{Si} the mole fraction of T_2 sites occupied by Si. It follows that $N_{Si} = 1 - N_{Al}$. The fraction of Al_2O_7 groups, $N_{Al_2O_7}$, is equal to $N_{Al}^2 k_{Al}$ where k is an empirical coefficient.

It can readily be seen that for a random distribution, $k = 1.0$. If an Al, placed on a T_2 site, facilitates incorporation of an Al on the other T_2 site in numbers greater than



FIGS. 1 and 2: FIG. 1 (left). Results of chromatographic analyses of five synthetic melilites. Percentage yields of the monomer are shown by open circles, of the dimer by half-shaded circles and of trimer plus tetramer by shaded circles. FIG. 2 (right). Comparison between observed and calculated yields of the dimeric (Si_2O_7) species from synthetic melilites. The experimental results are shown by a heavy unbroken line before correction and by a heavy broken line after correction. Calculated yields for different values of k , a parameter reflecting the Al-Si ordering on T_2 sites, are shown by light unbroken lines. Numerical values for k are shown at intervals of 0.2.

chance, $k > 1.0$. This is physically unlikely, however, in view of the aluminium avoidance 'rule' which would tend to produce values of k which are numerically less than 1.0; indeed if the 'rule' is strictly obeyed, $k = 0.0$.

All Al on T_2 sites that is not present as Al_2O_7 groups must be present as $(AlSi)O_7$ or $(SiAl)O_7$; the two are indistinguishable and will be written as $(Al,Si)O_7$. One such group is formed for each remaining Al atom.

Therefore, the mole fraction of $N_{(Al,Si)O_7}$ is given by: $N_{(Al,Si)O_7} = 2N_{Al} - 2(N_{Al}^2 k_{Al})$. Recalling that the mole fraction of silicon, N_{Si} , is given by $(1 - N_{Al})$ and that some of the Si is used in forming $(Al,Si)O_7$ groups, the mole fraction of Si_2O_7 groups must be given by the expression: $N_{Si_2O_7} = (1 - N_{Al}) - (N_{Al} - N_{Al}^2 k_{Al})$. $N_{(Al,Si)O_7}$ and $N_{Si_2O_7}$ are determined experimentally, and therefore k may be evaluated. Fig. 2 also shows the dimer content of melilites calculated for selected values of k ranging from 0.0 to 1.0. The best estimate of the systematic error in the experimental values of the dimer contents of synthetic melilites suggest that they are too low by c. 9% at the åkermanite

end to *c.* 14 to 15 % at the gehlenite end. The 'experimental' curve in fig. 2 has therefore been adjusted upwards relative to its position in fig. 1. Even so, its curvature is markedly different than for any of the curves calculated for a constant *k* values.

The curvature of the experimental data can be explained by assuming that *k* is not constant, but that it is close to zero for åkermanite and rises steadily at higher gehlenite contents reaching a value of $k \approx 0.7$ at gehlenite itself.

The observed distributions of Al and Si can be described in terms of a single parameter, *k*, but the physical significance of the changing values may be interpreted in terms of a thermodynamic model.

In a system containing Al:Si in the ratio $a:(1-a)$, let the proportion of atom pairs that are Al,Al be *p*. Let energy change associated with the conversion of two like pairs to two unlike pairs: $(\text{Al,Al}) + (\text{Si,Si}) \longrightarrow (2\text{Al,Si})$ be ϵ . Then:

$$\ln p(1-2a+p)/(a-p)^2 = -\epsilon/KT,$$

where *T* = temperature (°K), and *K* = Boltzman's constant.

If we let $K = \exp(-\epsilon/KT)$, we obtain a quadratic in *p*:

$$p^2(1-K) + p[1+2a(K-1)] - Ka^2 = 0.$$

A value of $K = 0.45$ provides a good fit to the values obtained for synthetic gehlenite ($a = 0.50$, $p = 0.20$). However, the appearance of the chromatogram calculated assuming a constant value of *K* for the synthetic solid solutions does not provide a good fit to the experimental data. The curves of constant *K* are extremely similar in shape and disposition to those shown in fig. 2 for *k*, the descriptive parameter. The curve for $K = 0.45$ closely resembles that calculated for $k = 0.70$, etc. At this stage it suffices to describe the ordering by *k*, but as additional knowledge accumulates about the temperature dependence of *k*, a thermodynamic treatment would be more appropriate.

The reason why *K* (or *k*) changes with the composition of the solid solution may be explained qualitatively: the mean size of a T_2 site is less in åkermanite than in gehlenite. As the solid solutions increase in gehlenite content, some Al must enter T_2 sites. However, aluminiums initially avoid pairing in adjacent corner-shared T_2 sites. This initial trend, if extrapolated to gehlenite, would lead to an 'ordered' gehlenite; that is, one containing only T_2 pairs with $\text{Al}_{1,0}\text{Si}_{1,0}$ ($k = 0$). However, as Al enters T_2 sites, the mean size of the T_2 sites increases and the steric factor which initially inhibits formation of Al_2O_7 dimers becomes progressively less important. The synthetic gehlenite itself still contains only about 70 % of the Si_2O_7 content that would be expected on a random basis. This is interpreted as arising from the residual Al-Al repulsion which, in turn, lowers the Si_2O_7 content.

The *K* factor might also be expected to be temperature dependent. This would leave unchanged the Si-Al distribution in åkermanite but would produce changes especially in the gehlenite-rich solid solutions. The synthetic melilites were prepared at *c.* 1300 °C and consequently, are believed to reflect an Al-Si distribution characteristic of that temperature. All the synthetic samples gave identical (± 2 %) chromatographic yields after annealing 35 days at 800 °C.

Nevertheless, significant and apparently irreversible changes are produced by heating the natural melilite. There is, of course, some difficulty in comparing exactly the compositions of the soda-free synthetic specimens with that of the natural melilite. Its Al/Si ratio has been used to fix its composition, for comparative purposes, at 60 gehlenite–40 åkermanite. Before heating its dimer content is much lower than would be found for a synthetic melilite at 60 % gehlenite. After heating at 1050 °C for 16 hr the dimer content has increased markedly and has become comparable with that which would be expected from a synthetic melilite at the 60 % gehlenite composition. It is suggested that the unheated natural melilite has $K \approx k \approx 0.0$: that is, the aluminium avoidance rule controls the distribution of Al and Si in T_2 sites by preventing formation of Al_2O_7 groups in T_2 sites. After heating, however, the distribution has been partially randomized so that it is comparable with the synthetics. The natural melilite was otherwise apparently unaffected by the heating: its optical appearance and X-ray powder pattern were unchanged.

Additional remarks. The authors would welcome suitable melilite for analysis. Approximately 50 mg, either polycrystalline or single crystal, are required. The sample should have been analysed and be free from other contaminating silicates; some non-silicate impurity, e.g. spinel, calcite is tolerable. 'Low temperature' melilites relatively rich in gehlenite would be likely to show the greatest variations in Al–Si order and hence be the most interesting to examine. Given suitable samples, it should be possible to prove if a gehlenite having an ordered T_2 distribution exists.

Acknowledgements. These studies were financed by a grant from The Science Research Council. We are also indebted to E. J. W. Whittaker for his suggestions and especially for formulating the thermodynamic relations discussed in the text.

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[Manuscript received 23 February 1973]